

CY8151 - CHEMISTRY COMPLETE NOTES

DEPARTMENT OF SCIENCE AND HUMANITIES

SYLLABUS

CY8151 ENGINEERING CHEMISTRY

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UNIT- I WATER AND ITS TREATMENT 9

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.

UNIT- II SURFACE CHEMISTRY AND CATALYSIS 9

Adsorption: Types of adsorption – adsorption of gases on solids – adsorption of solute from solutions – adsorption isotherms – Freundlich's adsorption isotherm – Langmuir's adsorption isotherm – contact theory – kinetics of surface reactions, unimolecular reactions, Langmuir - applications of adsorption on pollution abatement. **Catalysis:** Catalyst – types of catalysis – criteria – autocatalysis – catalytic poisoning and catalytic promoters - acid base catalysis – applications (catalytic convertor) – enzyme catalysis– Michaelis– Menten equation.

UNIT- III ALLOYS AND PHASE RULE 9

Alloys: Introduction- Definition- properties of alloys- significance of alloying, functions and effect of alloying elements- Nichrome and stainless steel (18/8) – heat treatment of steel. **Phase rule:** Introduction, definition of terms with examples, one component system -water system – reduced phase rule - thermal analysis and cooling curves - two component systems - lead-silver system - Pattinson process.

UNIT- IV FUELS AND COMBUSTION 9

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).

UNIT- V ENERGY SOURCES AND STORAGE DEVICES

9

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 super capacitors: Types of batteries – primary battery (dry cell) secondary battery (lead acid battery, lithium-ion-battery) fuel cells – H₂-O₂ fuel cell.

TOTAL: 45 PERIODS

TEXT BOOKS:

1. S. S. Dara and S. S. Umare, “A Textbook of Engineering Chemistry”, S. Chand & Company LTD, New Delhi, 2015
2. P. C. Jain and Monika Jain, “Engineering Chemistry” Dhanpat Rai Publishing Company (P) LTD, New Delhi, 2015
3. S. Vairam, P. Kalyani and Suba Ramesh, “Engineering Chemistry”, Wiley India PVT, LTD, New Delhi, 2013.

REFERENCES:

1. Friedrich Emich, “Engineering Chemistry”, Scientific International PVT, LTD, New Delhi, 2014.
2. Prasanta Rath, “Engineering Chemistry”, Cengage Learning India PVT, LTD, Delhi, 2015.
3. Shikha Agarwal, “Engineering Chemistry-Fundamentals and Applications”, Cambridge University Press, Delhi, 2015.



M.I.E.T. ENGINEERING COLLEGE

(Approved by AICTE and Affiliated to Anna University Chennai)

TRICHY – PUDUKKOTTAI ROAD, TIRUCHIRAPPALLI – 620 007

DEPARTMENT OF SCIENCE AND HUMANITIES

SUBJECT CODE : **CY8151**

YEAR : **I**

SUBJECT NAME : **ENGINEERING CHEMISTRY**

SEM : **1**

Course Objectives

1. To make the students conversant with boiler feed water requirements, related problems and water treatment techniques
2. To develop an understanding of the basic concepts of phase rule and its applications to single and two component systems and appreciate the purpose and significance of alloys
3. Preparation, properties and applications of engineering materials
4. Types of fuels, calorific value calculations, manufacture of solid, liquid and gaseous fuels.
5. Principles and generation of energy in batteries, nuclear reactors, solar cells, wind mills and fuel cells

Course Outcomes

1. Understand the main knowledge and processes for drinking water and the design for basic treatment processes
2. Relate basic knowledge of surface science and catalysis
3. Illustrate the phase transition of one component and two component systems and the types of alloys and their applications in industries
4. Knowledge of methods to determine the calorific values of fuels, perform flue gas analysis and combustion analysis
5. Analyse and identify alternative energy storage devices
6. Applying the knowledge to perform gas analysis & combustion analysis in engineering fields

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HOD

Approved by

PRINCIPAL

UNIT I – WATER TECHNOLOGY

1.1 INTRODUCTION

Water is the most important compound essential for the survival of all living organisms. About 80% of the earth's surface is covered by water. Besides being a supporter of life, water plays a unique role in industries. Water is used in the power generation industry for the production of the electric current through steam generation. It is also used as a coolant in nuclear power plants and chemicals plants. Water is widely used in other fields such as production of steel, atomic energy, textiles, irrigation, etc.

The process of removing of all types of impurities from water and making it fit for domestic or industrial purposes is called water technology or water treatment.

SOURCES OF WATER

The main sources of water are

- Surface water
- Underground water
- Sea water

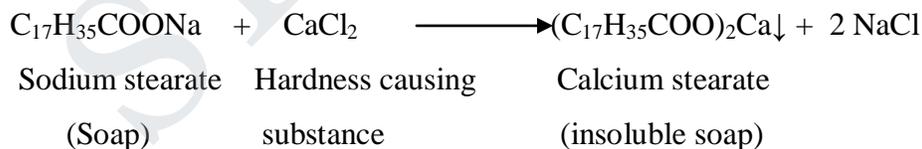
1.2 HARDNESS OF WATER

- **Hardness** is the characteristic property of water which “prevents **the lathering of soap**”.
- This is due to the presence of certain salts of calcium, magnesium and other heavy metals dissolved in water.

How to detect hardness?

When a sample of water is treated with soap solution, if it does not produce lather, but forms a white scum or precipitate, the water contains hardness.

This is due to the formation of insoluble soaps of calcium and magnesium.



TYPES OF WATER

On the basis of hardness, water can be classified into two types:

- Hard Water and Soft Water

HARD WATER

Water which does not produce lather easily with soap solution, but forms a white precipitate, is called **hard water**.

SOFT WATER

Water which lathers easily with soap solution, is called **soft water**.

It does not contain dissolved calcium and magnesium salts.

1.2.1 TYPES OF HARDNESS

- Hardness is classified into **two** types based on dissolved salts present in water. They are:
 - Temporary Hardness (or) Carbonate Hardness (CH)
 - Permanent Hardness (or) Non-Carbonate Hardness (NCH)

TEMPORARY HARDNESS

Temporary Hardness is due to the presence of dissolved bicarbonates of calcium and magnesium. Thus the salts responsible for temporary hardness are $\text{Ca}(\text{HCO}_3)_2$ and $\text{Mg}(\text{HCO}_3)_2$.

Temporary hardness is otherwise known as **Carbonate Hardness** (or) **Alkaline Hardness**.

Temporary Hardness can be removed by following two processes:

- Boiling of water
- Adding lime to the water

Boiling of water



Adding lime to the water



Lime

The above two processes convert the bicarbonates into insoluble carbonates and hydroxides, these are removed by filtering.

PERMANENT HARDNESS

Permanent hardness is due to the presence of dissolved chlorides and sulphates of calcium and magnesium. The salts responsible for permanent hardness are CaCl_2 , MgCl_2 , CaSO_4 and MgSO_4 .

Permanent hardness cannot be removed by boiling.

It can be removed by the following two processes:

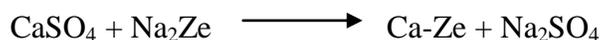
- Lime – soda process
- Zeolite process

Lime-soda process:



(Soda)

Zeolite process:



Sodium Zeolite

Permanent Hardness is otherwise known as **Non-Carbonate Hardness** (NCH) (or) **Non – alkaline Hardness**.

TOTAL HARDNESS

Total hardness = Temporary Hardness + Permanent Hardness

1.3.2 EXPRESSION OF HARDNESS INTERMS OF EQUIVALENTS OF CaCO₃

The concentrations of hardness producing salts are usually expressed in terms of an equivalent amount of CaCO₃. CaCO₃ is chosen as a standard because,

- (i) Its molecular weight (100) and equivalent weight (50) is a whole number, so the calculations in water analysis can be simplified.
- (ii) It is the most insoluble salt that can be precipitated in water treatment.

If the concentration of hardness producing salt is x mgs/lit, then

Amount equivalent to CaCO₃ = $x \times 100 / \text{Molecular weight of hardness producing salt}$

(or) i.e.,

Amount equivalent to CaCO₃ = $\text{Amount of hardness producing salt} \times \text{Molecular weight of CaCO}_3 / \text{Molecular weight of hardness producing salt}$

(or)

Amount equivalent to CaCO₃ = $\text{Amount of hardness producing salt} \times \text{Equivalent weight of CaCO}_3 / \text{Equivalent weight of hardness producing salt}$

1.3.3 UNITS OF HARDNESS**i. PARTS PER MILLION (PPM)**

It is defined as the number of parts of CaCO₃ equivalent hardness per 10⁶ parts of water.

ii. MILLIGRAMS PER LITRE (MG/LIT)

It is defined as the number of milligrams of CaCO₃ equivalent hardness per 1 litre of water.

iii. CLARKE'S DEGREE (°Cl)

It is defined as the number of parts of CaCO₃ equivalent hardness per 70,000 parts of water.

iv. FRENCH DEGREE (°FR)

It is defined as the number of parts of CaCO₃ equivalent hardness per 10⁵ parts of water.

Relationship between various units $1 \text{ ppm} = 1 \text{ mg/lit} = 0.1^\circ \text{ Fr} = 0.07^\circ \text{ Cl}$

1.3.4 PROBLEMS BASED ON HARDNESS**Problem 1**

A sample of water contains 120 mgs of MgSO₄ per litre. Calculate the hardness interms of CaCO₃ equivalents.

Solution**Given:**

The amount of MgSO₄ = 120 mgs/lit

Amount equivalent to CaCO_3 = The amount of hardness producing salt $\times 100$ / Molecular weight of hardness producing salt

We know that, the molecular weight of $\text{MgSO}_4 = 120$

$$\begin{aligned} \therefore \text{Amount equivalent to } \text{CaCO}_3 &= 120 \times 100 / 120 \\ &= 100 \text{ mgs/lit.} \end{aligned}$$

Problem 2

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:

$$\text{The amount of } \text{Ca}^{2+} \text{ ions} = 50 \text{ mgs/lit}$$

We know that,

$$\text{The molecular weight of calcium} = 40$$

$$\begin{aligned} \therefore \text{Amount equivalent to } \text{CaCO}_3 &= 50 \times 100 / 40 \\ &= 125 \text{ mgs/lit} \end{aligned}$$

Problem 3

A water sample contains 204 mgs of CaSO_4 and 73 mgs of $\text{Mg}(\text{HCO}_3)_2$ per litre. What is the total hardness in terms of CaCO_3 equivalent?

Solution

Name of the hardness producing salt	Amount in mgs/lit	Molecular weight	Amounts equivalent to CaCO_3
CaSO_4	204	136	$204 \times 100 / 136 = 150$ mgs/lit
$\text{Mg}(\text{HCO}_3)_2$	73	146	$73 \times 100 / 146 = 50$ mgs/lit

Temporary hardness = $\text{Mg}(\text{HCO}_3)_2 = 50$ mgs/lit

Permanent hardness = $\text{CaSO}_4 = 150$ mgs/lit

Total hardness = $\text{Mg}(\text{HCO}_3)_2 + \text{CaSO}_4 = 50 + 150 = 200$ mgs/lit

Problem 4

Calculate the carbonate and non-carbonate hardness of a sample of water containing the dissolved salts as given below in mgs/lit. $\text{Mg}(\text{HCO}_3)_2 = 7.3$; $\text{Ca}(\text{HCO}_3)_2 = 40.5$; $\text{CaSO}_4 = 13.6$; $\text{MgCl}_2 = 21.75$ and $\text{NaCl} = 50$.

Solution

Name of the hardness producing salt	Amount in mgs/lit	Molecular weight	Amounts equivalent to CaCO ₃
Mg(HCO ₃) ₂	7.3	146	7.3x100/146=5 mgs/lit
Ca(HCO ₃) ₂	40.5	162	40.5X100/162=25 mgs/lit
CaSO ₄	13.6	136	13.6X100/136=10 mgs/lit
MgCl ₂	21.75	95	21.75X100/95=22.9 mgs/lit
NaCl	50	NaCl does not contribute any hardness to water hence it is ignored	

$$\begin{aligned} \text{Carbonate hardness} &= \text{Mg(HCO}_3)_2 + \text{Ca(HCO}_3)_2 \\ &= 5 + 25 = 30 \text{ mgs/lit} \end{aligned}$$

$$\begin{aligned} \text{Non-carbonate hardness} &= \text{CaSO}_4 + \text{MgCl}_2 \\ &= 10 + 22.9 = 32.9 \text{ mgs/lit} \end{aligned}$$

$$\begin{aligned} \text{Total hardness} &= \text{Carbonate hardness} + \text{Non-carbonate hardness} \\ &= 30 + 32.9 = 62.9 \text{ mgs/lit} \end{aligned}$$

Problem 5

A sample of water contains the following dissolved salts in mgs/lit Mg(HCO₃)₂ =73;CaCl₂=111;Ca(HCO₃)₂=81 and MgSO₄=40. Calculate the temporary and permanent hardness of the water (At. Wts of Ca, Mg, O, C, Cl, S, H are 40,24,16,12,35.5,32,1)

Solution

Name of the hardness producing salt	Amount in mgs/lit	Molecular weight	Amounts equivalent to CaCO ₃
Mg(HCO ₃) ₂	73	146	73x100/146=50 mgs/lit
CaCl ₂	111	111	111X100/111=100 mgs/lit

Standard hard water

1 gm of pure CaCO_3 is dissolved in minimum quantity of HCl and then made upto 1000 ml using distilled water.

\therefore 1 ml of standard hard water \equiv 1 mg of CaCO_3 equivalent hardness.

EBT indicator

0.5 gms of EBT is dissolved in 100 ml of alcohol.

Buffer solution

67.5 gms of NH_4Cl and 570 ml of NH_3 are dissolved and the solution is made upto 1000 ml using distilled water.

Experimental procedure**Standardisation of EDTA**

Pipette out 50 ml of standard hard water into a clean conical flask. Add 10 ml of buffer solution and 4-5 drops of EBT indicator and titrate it against EDTA solution taken in the burette. The end point is the change of colour from wine red to steel blue.

Let the volume of EDTA consumed be V_1 ml

Estimation of total hardness of water sample

Pipette out 50 ml of the given hard water sample into a clean conical flask and titrate it against EDTA as before.

Let the volume of EDTA consumed be V_2 ml

Estimation of permanent hardness of water sample

Take 100 ml of the same hard water sample in a 250 ml beaker. Boil it for 15 minutes. During boiling temporary hardness gets removed. Cool and filter the solution and make upto 100 ml in a standard flask by adding distilled water.

Pipette out 50 ml of the made up solution into a clean conical flask and titrate it against EDTA as before.

Let the volume of EDTA consumed be V_3 ml.

Calculations**Standardisation of EDTA**

1 ml of Std. hard water = 1 mg of CaCO_3
 50 ml of Std. hard water = 50 mgs of CaCO_3
 50 ml of Std. hard water consumes = V_1 ml of EDTA
 \therefore V_1 ml of EDTA \equiv 50 mgs of CaCO_3 equivalent hardness
 (or)

1 ml of EDTA \equiv $50/V_1$ mgs of CaCO_3 equivalent hardness

Estimation of total hardness of water sample

50 ml of the given hard water sample consumes = V_2 ml of EDTA
 $= V_2 \times 50/V_1$ mgs of CaCO_3 equivalent hardness
 [\therefore 1 ml of EDTA = $50/V_1$ mgs of CaCO_3]

\therefore 1000 ml of the given hard water sample = $V_2 \times 50/V_1 \times 1000/50$
 $= 1000 \times V_2/V_1$ mgs of CaCO_3 equivalent hardness
 \therefore Total hardness = $1000 \times V_2/V_1$ ppm

Estimation of permanent hardness of water sample

50 ml of the same hard water sample after boiling, filtering, etc., consumes = V₃ ml of EDTA
 = V₃ × 50/V₁ mgs of CaCO₃ equivalent hardness

∴ 1000 ml of the given hard water sample = V₃ × 50/V₁ × 1000/50

= 1000 × V₃/V₁ mgs of CaCO₃ equivalent hardness

∴ Permanent hardness = 1000 × V₃/V₁ ppm

Temporary hardness

Temporary hardness = Total hardness – Permanent hardness
 = [1000 × V₂/V₁] – [1000 × V₃/V₁]

∴ Temporary hardness = 1000/V₁(V₂ – V₃) ppm

1.4.1 Problems based on EDTA method**Problem 1**

100 ml of a water sample requires 20 ml of EDTA solution for titration. 1 ml of EDTA solution is equivalent to 1.1 mgs of CaCO₃. Calculate hardness in ppm.

Solution

Given 1 ml of EDTA solution = 1.1 mgs of CaCO₃

∴ 20 ml of EDTA solution = 20 × 1.1 mgs of CaCO₃
 = 22 mgs of CaCO₃

100 ml of water sample requires = 20 ml of EDTA

= 22 mgs of CaCO₃

∴ 1000 ml of water sample = 22 × 1000/100 mgs of CaCO₃

Hardness = 220 mgs/lit or ppm.

Problem 2

100 ml of a sample of water requires 18 ml of an EDTA solution for titration. 22 ml of the same EDTA solution was required for the titration of 100 ml of standard hard water containing 1 gm CaCO₃ per litre. Calculate hardness of water sample in ppm.

Solution

Given 1 litre of std. hard water contains 1 gm of CaCO₃

i.e 1000 ml of std. hard water contains 1000 mgs of CaCO₃

∴ 1 ml of std. hard water = 1 mg of CaCO₃

22 ml of EDTA = 100 ml of std. hard water
 = 100 × 1 mg of CaCO₃

∴ 1 ml of EDTA = 100/22 mgs of CaCO₃

100 ml of sample of water = 18 ml of EDTA

= 18 × 100/22 mgs of CaCO₃

∴ for 1000 ml of sample of water = 18 × 100/22 × 1000/100

Hardness = 818.18 mgs/lit or ppm.

Problem 3

0.28 gm of CaCO₃ was dissolved in HCl and the solution was made upto one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of hard water sample required 33 ml of same EDTA solution on titration. 100 ml of this water, after boiling cooling and filtering required 10 ml of EDTA solution on titration. Calculate the temporary and permanent hardness of water.

Solution

$$\begin{aligned}
 \text{Given 1000 ml of std. hard water contains} &= 0.28 \text{ gm of CaCO}_3 \\
 \text{ie., 1000 ml of std. hard water contains} &= 0.28 \times 1000 \text{ mgs of CaCO}_3 \\
 &= 280 \text{ mgs of CaCO}_3 \\
 \therefore 1 \text{ ml of std. hard water} &= 0.28 \text{ mg of CaCO}_3 \\
 28 \text{ ml of EDTA} &= 100 \text{ ml of the std. hard water} \\
 &= 100 \times 0.28 \text{ mgs of CaCO}_3 \\
 &= 100 \times 0.28 \\
 &= 28 \\
 1 \text{ ml of EDTA} &= 1 \text{ mgs of CaCO}_3.
 \end{aligned}$$

Total hardness

$$\begin{aligned}
 100 \text{ ml of hard water} &= 33 \text{ ml of EDTA} \\
 &= 33 \times 1 \text{ mgs of CaCO}_3 \\
 &= 33 \text{ mgs of CaCO}_3
 \end{aligned}$$

$$\begin{aligned}
 \therefore 1000 \text{ ml of hard water} &= 33 \times 1000/100 \\
 \text{Total hardness} &= 330 \text{ mgs/lit (or) ppm.}
 \end{aligned}$$

Permanent hardness (NCH)

$$\begin{aligned}
 100 \text{ ml of the same water, after boiling, cooling and filtering required} &= 10 \text{ ml of EDTA} \\
 &= 10 \times 1 \text{ mgs of CaCO}_3 \\
 &= 10 \text{ mgs of CaCO}_3 \\
 \therefore 1000 \text{ ml of the water} &= 10 \times 1000/100 \text{ mgs of CaCO}_3 \\
 \text{Permanent hardness} &= 100 \text{ mgs/lit (or) ppm.}
 \end{aligned}$$

Temporary hardness (CH)

$$\begin{aligned}
 \text{Temporary hardness} &= \text{Total hardness} - \text{permanent hardness} \\
 &= 330 - 100 \\
 \text{Temporary hardness} &= 230 \text{ mgs/lit (or) ppm.}
 \end{aligned}$$

Problem 4

100 ml of a sample of water required 25.0 ml of 0.01 M EDTA for the titration using Eriochrome-Black-T indicator. Calculate the total hardness.

Solution

We know that,

$$\begin{aligned}
 1 \text{ ml of 0.01 M EDTA} &= 1 \text{ mg of CaCO}_3 \\
 25 \text{ ml of 0.01 M EDTA} &= 25 \text{ mgs of CaCO}_3 \\
 100 \text{ ml of sample of water required} &= 25.0 \text{ ml of 0.01 M EDTA} \\
 &= 25.0 \text{ mgs of CaCO}_3 \text{ equivalent} \\
 \therefore 1000 \text{ ml of water is equal to} &= 25.0 \times 1000/100 \text{ mgs of CaCO}_3 \text{ equivalent} \\
 \text{Total hardness} &= 250 \text{ mgs/lit or ppm.}
 \end{aligned}$$

Problem 5

Calculate permanent hardness from the following. 500 ml of a water sample is boiled for 1 hr. It is then cooled and filtered. The filtrate is made upto 500 ml again with distilled water. 50 ml of this solution requires 10 ml of N/50 EDTA with EBT-indicator and $\text{NH}_4\text{Cl} - \text{NH}_4\text{OH}$ buffer.

Solution

Given 50 ml of water sample after boiling, filtering requires 10 ml of N 50 EDTA

We know that 1 ml of N 50 EDTA \equiv 1 mg of CaCO₃ equivalent hardness

\therefore 10 ml of N 50 EDTA \equiv 10 mgs of CaCO₃

50 ml of the boiled water sample requires = 10 ml of N 50 EDTA

= 10 mgs of CaCO₃

\therefore 1000 ml of the water sample = $10 \times 1000 / 50$

Permanent hardness = 200 mgs/lit or ppm.

Problem 6

100 ml of a sample of water required 15.0 ml of 0.01 M EDTA for titration using Erio-chrome Black-T indicator. In another experiment, 100 ml of the same sample was boiled to remove the CH, the precipitate was removed and the cold solution required 8.0 ml of 0.01 M EDTA using Erio-chrome Black-T indicator. Calculate (i) the total hardness, (ii) permanent hardness or NCH, (iii) carbonate hardness CH, in terms of mg/lit of CaCO₃.

Solution

We know that 1 ml of 1 M EDTA \equiv 100 mgs of CaCO₃

1 ml of 0.01 M EDTA \equiv 1 mg of CaCO₃

Total Hardness

100 ml of a sample of water required = 15 ml of 0.01 M EDTA

= 15×1 mgs

= 15 mgs of CaCO₃

\therefore 1000 ml of sample of water is equivalent to = $15 \times 1000 / 100$ mgs of CaCO₃

= 150 mgs of CaCO₃ equivalent

Total hardness = 150 mgs/lit or ppm.

Permanent Hardness (NCH)

100 ml of the same water sample after boiling, filtering consumes = 8.0 ml of 0.01 M EDTA

= 8.0×1 mgs

= 8.0 mgs of CaCO₃

\therefore 1000 ml of sample of water is equal to = $8.0 \times 1000 / 100$ mgs

= 80 mgs of CaCO₃ equivalent

Permanent hardness of the water sample = 80 ppm.

Temporary Hardness (CH)

Temporary hardness = Total hardness – Permanent hardness

= $150 - 80 = 70$ ppm

Temporary hardness = 70 ppm.

Problem 7

100 ml of a water sample required 20 ml of 0.01 M EDTA for the titration with Eriochrome Black-T indicator 100 ml of the same water sample after boiling and filtering required 10 ml of 0.01 M EDTA. Calculate the total, carbonate and non carbonate hardness of the sample.

Solution

We know that 1 ml of 1 M EDTA \equiv 100 mgs of CaCO₃

1 ml of 0.01 M EDTA \equiv 1 mg of CaCO₃

Total Hardness 100 ml of a sample of water required = 20 ml of 0.01 M EDTA

= 20×1 mgs

= 20 mgs of CaCO₃

\therefore 1000 ml of sample of water is equivalent to = $20 \times 1000 / 100$ mgs of CaCO₃

$$= 200 \text{ mgs of CaCO}_3 \text{ equivalent}$$

$$\text{Total hardness} = 200 \text{ mgs/lit or ppm.}$$

Non-carbonate Hardness (NCH)

100 ml of the same water sample after boiling, filtering consumes = 10 ml of 0.01 M EDTA

$$= 10 \times 1 \text{ mgs}$$

$$= 10 \text{ mgs of CaCO}_3$$

$$\therefore 1000 \text{ ml of sample of water is equal to} = 10 \times 1000 \text{ mgs}$$

$$= 100 \text{ mgs of CaCO}_3 \text{ equivalent}$$

$$\text{Permanent hardness of the water sample} = 100 \text{ ppm.}$$

Carbonate Hardness (CH)

$$\text{Carbonate hardness} = \text{Total hardness} - \text{Non-carbonate hardness}$$

$$= 200 - 100$$

$$= 100 \text{ ppm}$$

$$\text{Carbonate hardness} = 100 \text{ ppm.}$$

Problem 8

In an estimation of hardness of water by EDTA titration, 250 ml of a sample of water required 15 ml of 0.025 M EDTA solution to get the end point. Calculate the hardness of water.

Solution

We know that 1 ml of 1 M EDTA \equiv 100 mgs of CaCO₃

1 ml of 0.01 M EDTA \equiv 1 mg of CaCO₃

\therefore 1 ml of 0.025 M EDTA \equiv 2.5 mgs of CaCO₃ equivalent

Total Hardness

$$250 \text{ ml of a sample of water required} = 15 \text{ ml of 0.025 M EDTA}$$

$$= 15 \times 2.5 \text{ mgs}$$

$$= 37.5 \text{ mgs of CaCO}_3 \text{ equivalent}$$

$$\therefore 1000 \text{ ml of a sample of water required} = 37.5 \times 1000 \text{ mgs}$$

$$= 150 \text{ mgs of CaCO}_3 \text{ equivalent}$$

$$\text{Total hardness} = 150 \text{ ppm.}$$

1.3 BOILER FEED WATER

- The water fed into the boiler for the production of steam is called boiler feed water.
- Boiler feed water should be free from dissolved salts, suspended impurities, silica, turbidity, oil, alkali and hardness producing substances.

1.3.1 BOILER TROUBLES (OR) BOILER PROBLEMS (OR) DISADVANTAGES OF USING HARD WATER IN BOILERS

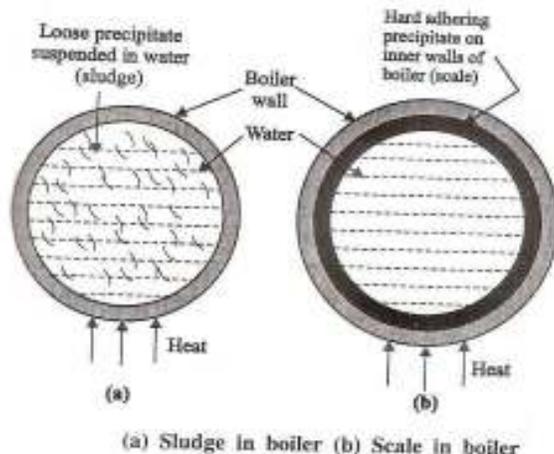
Presence of impurities in boiler feed water may lead to the following problems:

- Sludge and scale formation
- Priming and foaming (carry over)
- Caustic embrittlement
- Boiler corrosion

SLUDGE AND SCALE FORMATION IN BOILERS:

- When water is evaporated in boilers to produce steam continuously, concentration of the dissolved salts present in water increases progressively.

- When the concentration of the salts reaches their saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boilers.
- The least soluble one gets precipitated first.



SLUDGE:

- If the precipitate formed inside the boiler is soft, loose and slimy it is known as sludge.
- Sludges are formed by substances like $MgCO_3$, $MgCl_2$, $MgSO_4$ and $CaCl_2$.
- They have greater solubility in hot water than cold water.

DISADVANTAGES:

- Sludges are poor conductors of heat which results in wastage of fuel.
- Excess of sludge formation decreases the efficiency of boiler (i.e.) it disturbs the functioning of boiler.

PREVENTION:

- Sludge formation can be prevented by using softened water.
- It can be removed by “blow down operation”. It is a process of removing a portion of concentrated water frequently from the boiler during steam production.

SCALE:

- Scales are hard deposits formed by the evaporation of hard water in boilers.
- If the precipitate forms a hard and adherent coating on the inner walls of the boiler, it is known as scale.
- Scales are formed by substances like $Ca(HCO_3)_2$, $CaSO_4$ and $Mg(OH)_2$.

S.No.	Sludge	Scale
1	Sludge is a loose, slimy and non-adherent precipitate	Scale is a hard, adherent coating
2	The main sludge forming substances are $MgCO_3$, $MgCl_2$, $MgSO_4$ and $CaCl_2$ etc	The main scale forming substances are $Ca(HCO_3)_2$, $CaSO_4$, $Mg(OH)_2$

3	Disadvantages: Sludges are poor conductors of heat. Excess of sludge formation decreases the efficiency of boiler.	Disadvantages: Scales act as thermal insulators. It decreases the efficiency of boiler. Any crack developed on the scale, leads to explosion.
3	Prevention (i) Sludge formation can be prevented by using softened water. (ii) Sludges can also be removed by "blow-down operation".	Prevention (i) Scale formation can be prevented by dissolving using acids like HCl, H ₂ SO ₄ (ii) Scale formation can be removed by (a) External treatment. (b) Internal treatment.
	(iii) Blow-down operation is a process of removing a portion of concentrated water by fresh water frequently from the boiler during steam production.	(iii) They can also be removed by applying thermal shocks, scrapers, wire brush, etc

DISADVANTAGES:

- Scales decrease the efficiency of the boiler.
- Scales are poor conductor of heat. Therefore, it causes decrease in evaporative capacity of the boiler and increase in the fuel consumption.
- When the scale cracks, water suddenly comes in contact with the overhead boiler metal. This causes the formation of a large amount of steam suddenly. So, sudden high pressure is developed, which may even cause the explosion of the boiler. (Any crack developed on the scale leads to explosion.)

PREVENTION:

- Scale formation can be prevented by treating water in two ways:
 - External treatment
 - Internal treatment
- Scale formation can be prevented by dissolving it using acids like HCl and H₂SO₄.
- They can also be removed by applying thermal shocks, scrapers, wire brush, etc.

DISADVANTAGES OF SCALE FORMATION

1. WASTE OF FUELS

Scales have low thermal conductivity, so the heat transfer from boiler to inside water is not efficient. In order to provide steady supply of heat to water, overheating is done and this causes wastage of fuel. The wastage of fuel depends on the thickness and nature of the scale, which is shown in the table.

Thickness of scale(mm)	0.325	0.625	1.25	2.5	12
Wastage of fuel	10%	15%	50%	80%	150%

2. DECREASE IN EFFICIENCY

Scales sometimes deposit in the valves and condensers of the boiler and choke. This results in decrease efficiency of the boiler.

3. BOILER EXPLOSION

Sometimes due to overheating the thick scales may crack and causes sudden contact of high heated boiler material with water. This causes formation of a large amount of steam and high pressure is developed which may lead to explosion.

PREVENTION OF SCALE FORMATION

1. At the initial stage, scales can be removed using scraper, wire brush etc.
2. If scales are brittle, they can be removed by thermal shocks.
3. By using suitable chemicals like dil. acids, EDTA with which form suitable complexes.
4. If the scales are loosely adhering, they can be removed by frequent blow down operation.

1.3.2 REQUIREMENTS OF BOILER FEED WATER

Any natural source of water does not supply a perfectly suitable boiler feed water. The boiler feed water must have the following requirements.

TYPES	AMOUNT
Hardness	< 0.2 ppm.
Soda alkalinity	0.15-1.0 ppm
Caustic alkalinity	0.15-0.45 ppm
Excess soda ash	0.3-0.55 ppm
Dissolved gases like oxygen, carbon dioxide	0 ppm

S. NO	SPECIFICATIONS	DISADVANTAGES
1.	Boiler feed water should have zero hardness.	Scale and Sludge's will be produced, which prevents efficient heat transfer.
2.	It must be free from dissolved	It leads to boiler corrosion.

	gases like O ₂ , CO ₂ .	
3.	It should be free from dissolved salts and alkalinity.	Produces caustic embrittlement, which causes brittleness of boiler parts.
4.	It should be free from oil and turbidity.	Produces priming and foaming.
5.	It should be free from suspended impurities.	Produces wet steam.
6.	It should be free from total dissolved solids.	Produces priming, foaming and caustic embrittlement.

1.4 SOFTENING (OR) CONDITIONING METHODS

Water used for industrial purposes (for steam generation) should be free from dissolved gases and salts, hardness producing substances, suspended impurities, etc. The methods of removing hardness producing salts from water are known as **water softening** or **conditioning**.

Water Softening can be done by the following two methods:

- Internal conditioning (or) treatment
- External conditioning (or) treatment

1.5 EXTERNAL CONDITIONING

External conditioning method involves the removal of hardness causing salts from the water before feeding into the boiler.

External treatment can be done by:

- Demineralization or ion-exchange process
- Zeolite or Permutit process
- Lime soda process

1.5.1 DEMINERALISATION (OR) ION-EXCHANGE PROCESS

This process removes both cations and anions present in the water. The soft water produced by lime-soda and zeolite process, does not contain hardness causing ions Ca²⁺ and Mg²⁺, but it may contain other ions like Na⁺, K⁺, SO₄²⁻, Cl⁻, etc. On the other hand, demineralized water (D.M. water) does not contain both cations and anions. Thus, a soft water is not demineralized water whereas a demineralized water is soft water.

This process involves the use of ion-exchange resins for softening water.

Ion-exchange resins are insoluble, cross-linked, long chain organic polymers with micro-porous structure. The functional groups attached to the chains are responsible for the ion-exchanging properties.

There are two types of ion-exchange resins namely:

- ✓ Cation exchange resins and
- ✓ Anion exchange resins.

➤ **Cation Exchange Resins:**

- ❖ Resins capable of **exchanging the cations** from hard water are called cation exchange resins.
- ❖ It contains **acidic functional groups** like $-\text{COOH}$, $-\text{SO}_3\text{H}$ or H^+ , which can replace their H^+ ions with the cations of hard water.
- ❖ It can be represented as RH^+ (or) RH_2 .

Examples:

- Sulphonated coals
- Sulphonated polystyrene
- Phenol formaldehyde resin
- Commercial cation exchangers such as Amberlite and Dowex-50

➤ **Anion Exchange Resins:**

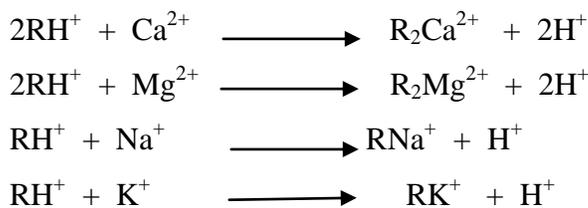
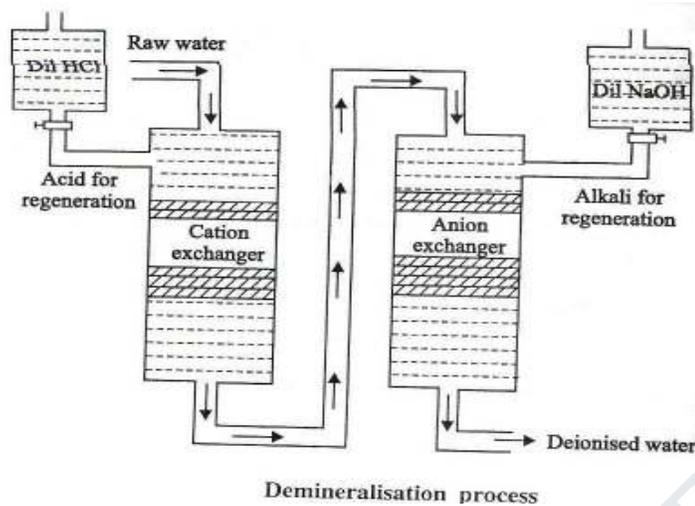
- ❖ Resins capable of **exchanging the anions** from hard water are called anion exchange resins.
- ❖ It contains **basic functional groups** like $-\text{NH}_2$, $-\text{NR}_3$ or OH^- , which can replace their OH^- ions with the cations of hard water.
- ❖ It can be represented as $\text{R}'\text{OH}^-$ (or) $\text{R}'(\text{OH})_2$.

Examples:

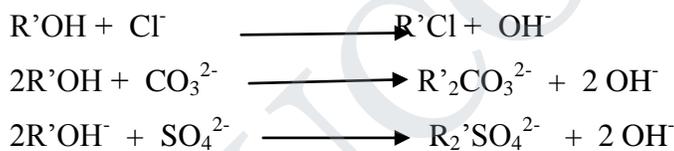
- Methyl ammonium hydroxy styrene
- Cross-linked quaternary ammonium salts.
- Urea formaldehyde resin
- Commercial cation exchangers such as Amberlite - 400 and Dowex-3

PROCESS OF DEMINERALISATION:

The hard water is passed first through cation exchange column (containing cation exchange resins, RH^+). All the cations such Ca^{2+} , Mg^{2+} , Na^+ , K^+ , etc. present in hard water are exchanged with H^+ ions of the cation exchange resin. That is, it removes all the cations from hard water and equivalent amount of H^+ ions are released from this column to water.



The water leaving the cation exchange column is now passed through anion exchange column (containing anion exchange resins, $R'OH$). All the anions such as Cl^- , SO_4^{2-} , HCO_3^- , etc. present in the water are exchanged with OH^- ions of anion exchange resins. So that all the anions are removed from water and equivalent amount of OH^- ions are released from this column to water.



H^+ and OH^- ions released from cation and anion exchange columns, combine to produce H_2O .



Thus, the water coming out of the anion exchange column is completely free from hardness causing cations and anions. This ion free water is known as **demineralized water** or **deionized water**.

REGENERATION:

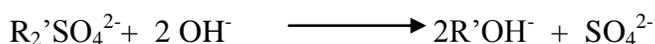
When all the H^+ and OH^- ions of the ion exchange columns are exhausted, the ion exchange resins have to be regenerated.

The exhausted cation exchange column is regenerated by passing dilute HCl or dilute H_2SO_4 through the column. The washing containing Ca^{2+} , Mg^{2+} , etc. is passed to sink.



Similarly the anion exchange column is regenerated by passing dilute NaOH through the column.

Then washing containing SO_4^{2-} , Cl^- , etc. is passed to sink.



The regenerated ion exchange resins are then used again.

ADVANTAGES OF ION-EXCHANGE PROCESS:

- This method produces soft water of very low residual hardness
- Highly acidic and alkaline water can be treated by this process.
- Regeneration of ion-exchange resin is possible.
- Maintenance cost is less.
- No sludge disposal problem arises.

DISADVANTAGES OF ION-EXCHANGE PROCESS:

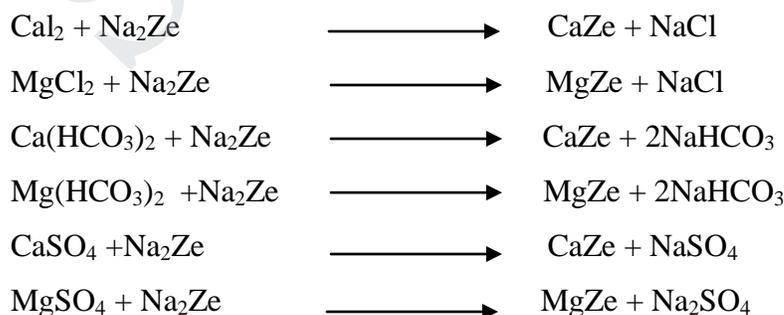
- Cost of the equipment is high.
- Highly turbid waters cannot be treated. Turbidity should be less than 10 ppm.
- Expensive chemicals are required.
- Water containing turbidity, Fe and Mn cannot be treated, because turbidity reduces the output as it blocks the pores and Fe and Mn form stable compound with the resin which cannot be regenerated.

1.6.1 ZEOLITE (OR) PERMUTIT PROCESS

- Zeolites are naturally occurring hydrated sodium aluminosilicate. Its general formula is $\text{Na}_2 \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ ($x=2-10$, $y=2-6$).
- Natural zeolite are green sand and non-porous. The synthetic form of zeolite is known as permutit, which is porous and possess gel like structure, hence it is generally used for water softening.
- Synthetic zeolite is represented by Na_2Ze are replaced by Ca^{2+} and Mg^{2+} ions present in the water.

PROCESS

When hard water is passed through a bed of sodium zeolite (Na_2Ze), kept in a cylinder (Fig. 1.1), it exchanges its sodium ion with Ca^{2+} and Mg^{2+} ions present in the hard water to form Ca^{2+} and Mg^{2+} zeolites. The various reactions taking place during softening process are



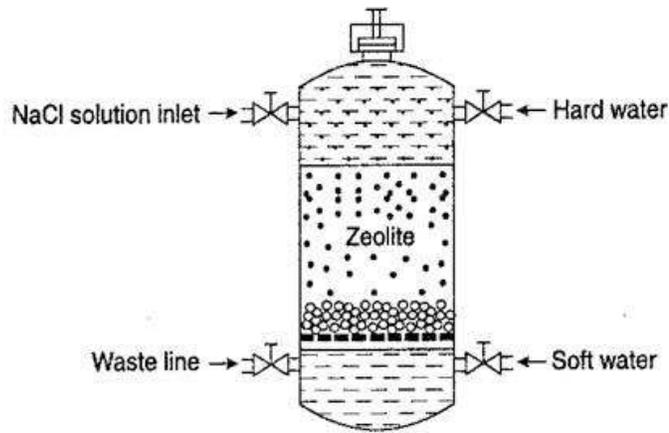
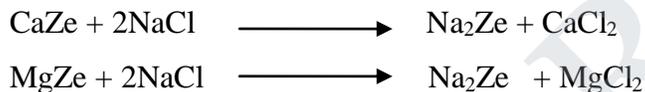


Fig.1.1 Zeolite process

The softened water is enriched with large amount of sodium salts, which do not cause any hardness, but cannot be used in boilers.

REGENERATION

After some time zeolite gets exhaust. The exhausted zeolite is again regenerated by treated with 10% solution of NaCl.



ADVANTAGES OF ZEOLITE PROCESS

- Water obtained by this process will have only hardness of 1-2 ppm.
- This method is cheap, because the regenerated zeolite can be used again.
- No sludge is formed during this process.
- The equipment used is compact and occupies a small space.
- It operation is easy.

DISADVANTAGES OF ZEOLITE PROCESS

- ▶ Turbidity water can't treated, because it blocked the porous of zeolite bed.
- ▶ Acidic water can't treated, because it decomposes the structure of zeolite.
- ▶ The softened water contains more dissolved sodium salts like NaHCO_3 , Na_2CO_3 , etc.
- ▶ When such water is boiled in boiler, CO_2 and NaOH is produced resulting in boiler corrosion and caustic embrittlement.
- ▶ Water containing Fe, Mn can't be treated, because regeneration is very difficult.
- ▶ This process can't be used for softening brackish water, because brackish water contains Na^+ ions.
- ▶ The ion exchange reaction will not occur.

Table 1.1 Differences between Zeolite and Demineralisation process

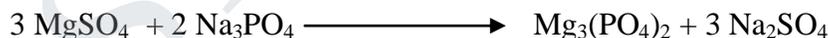
S.No.	ZEOLITE	DEMINERALISATION
1.	It exchanges only cations.	I exchange cations as well as anions
2.	Acidic water cannot be treated because acid decomposes the zeolite.	Acidic water can be treated.
3.	The treated water contains relatively large amount of dissolved salts, which leads to priming, foaming and caustic embrittlement in boilers.	The treated water does not contain any dissolved salts. Hence there is no priming and foaming.
4.	Water containing turbidity, Fe, Mn cannot be treated	Here also water containing turbidity, Fe, Mn cannot be treated.

1.7 INTERNAL CONDITIONING OR INTERNAL TREATMENT OR BOILER COMPOUNDS

This method involves the removal of scale forming substances and corrosive chemicals in water, which were not completely removed in the external treatment, by adding suitable chemicals directly inside the boiler. These chemicals are called **boiler compounds**.

i. PHOSPHATE CONDITIONING

Scale formation in high pressure boilers can be avoided by adding sodium phosphate. The added phosphate reacts with calcium and magnesium salts to produce soft sludges of calcium and magnesium phosphates.



Three types of phosphates are employed in phosphate conditioning. They are:

- ✓ Trisodium phosphate (Na_3PO_4)
- ✓ Disodium hydrogen phosphate (Na_2HPO_4)
- ✓ Sodium dihydrogen phosphate (NaH_2PO_4)

The optimum pH for the precipitation of $\text{Ca}_3(\text{PO}_4)_2$ is 9.5 to 10.5. The exact choice of the phosphate salt depends upon the alkalinity of boiler feed water.

- ✓ **Trisodium phosphate (Na_3PO_4)**

When the alkalinity of boiler feed water is low, it has to be raised to 9.5-10.5 for this highly alkaline phosphate is preferred. Na_3PO_4 is highly alkaline, used for strong acidic water.

✓ **Disodium hydrogen phosphate (Na₂HPO₄)**

When the alkalinity of boiler feed water is already sufficient for precipitation, Na₂HPO₄ is preferred. Na₂HPO₄ is weakly alkaline, used for weakly acidic water.

✓ **Sodium dihydrogen phosphate (NaH₂PO₄)**

When the alkalinity of boiler feed water is too high, acidic phosphate is preferred. It reduces the pH to the optimum range. NaH₂PO₄ is acidic, used for alkaline water.

ii. **CALGON CONDITIONING**

When calgon (Sodium hexa meta phosphate Na₂[Na₄(PO₃)₆]) is added to boiler water, it interacts with calcium ions forming a highly soluble complex and thus prevents the precipitation of sludge and scale forming salts.



The complex Na₂[Ca₂(PO₃)₆] is soluble in water and there is no problem of sludge disposal.

iii. **COLLOIDAL CONDITIONING**

Scale formation can be avoided by adding colloidal containing agents like kerosene, agar – agar, gelatin, etc., It is used in low pressure boilers. These colloidal substances get coated over the scale forming particles and converted them into non-adherent, loose precipitate called sludge, which can be removed by blow down operation.

iv. **SODIUM ALUMINATE CONDITIONING**

Sodium Aluminate (NaAl₂O₃) undergoes hydrolysis in boiler water to give gelatinous white precipitate of aluminium hydroxide and sodium hydroxide.



1.8 **DESALINATION OF BRACKISH WATER**

Water containing high concentration of dissolved salts or solids of peculiar salty or brackish taste is called **brackish water**. The sea water contains about 3.5% of dissolved salts. Before the removal of these salts, it is unfit for most of the domestic and industrial applications.

The process of removing common salt (sodium chloride) from the brackish or saline water is known as **Desalination** or **Desalting**.

Salinity of water is expressed in ppm or mg/L.

Based on the quantity of dissolved salts present, water is graded as:

✓ **FRESH WATER**

It contains less than 1000 ppm of dissolved salts.

✓ **BRACKISH WATER**

It contains above 1000 and below 35,000 ppm of dissolved salts.

✓ **SEA WATER**

It contains above 35,000 ppm of dissolved salts.

❑ Different methods of desalination are:

- ✓ **Distillation** – it involves separation of water from salts by evaporation followed by condensation.
- ✓ **Freezing** – it is based on the separation of pure water in the form of ice leaving the salt in the mother liquor when the saline water is cooled.
- ✓ **Electrodialysis** – It is the method of separation of ions from the salt water by passing electric current using a pair of electrodes and a pair of thin rigid plastic semipermeable membranes.
- ✓ **Reverse Osmosis**

The commonly used methods of desalination are Electro dialysis and Reverse Osmosis.

1.8.1 REVERSE OSMOSIS

When two solutions of different concentrations are separated by a semi-permeable membrane, solvent molecules flow from a region of lower concentration (dilute) to higher concentration side. This process is called **Osmosis**. The driving force in this phenomenon is called **Osmotic pressure**.

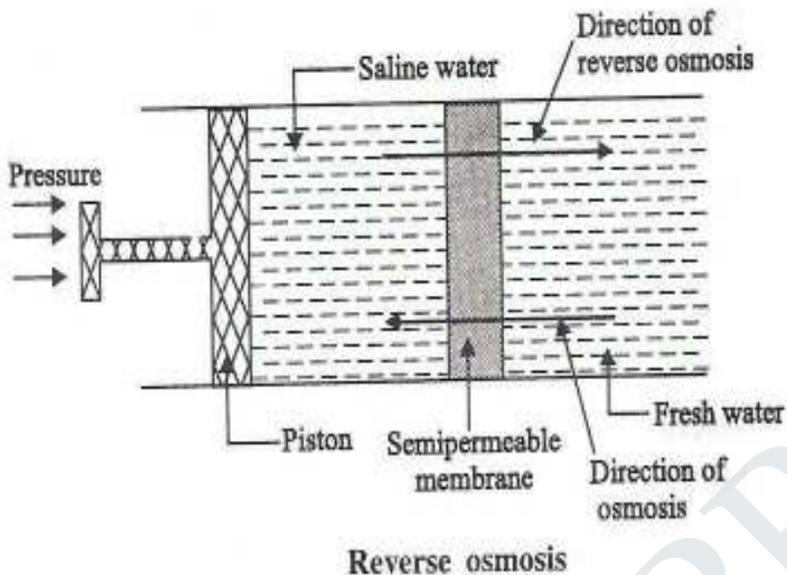
If a pressure higher than that of osmotic pressure is applied on the concentrated side, solvent flow reverses. That is the solvent molecules pass from concentrated side to dilute side through the membrane. This phenomenon is called **Reverse Osmosis**.

Using reverse osmosis, pure solvent (water) is separated from salt water. This membrane filtration is also called **Super Filtration** or **Hyper Filtration**.

The membranes consist of very thin film of cellulose acetate and cellulose butyrate. Polymers like polymethacrylate and polyamide of superior quality are also being used.

METHOD:

In this process, pressure of about 15 to 40 kgcm⁻² higher than that of osmotic pressure is applied to sea water so that pure water is forced to move through semi permeable membrane to pure water side. The membrane consists of very thin films of cellulose acetate.



ADVANTAGES:

- ✓ It removes ionic as well as non-ionic and colloidal impurities.
- ✓ Life time of the membrane is high (2 - 3 years) and it can be replaced within few minutes.
- ✓ Maintenance cost is less.
- ✓ Capital cost is low and operation is simple.

UNIT II – SURFACE CHEMISTRY AND CATALYSIS

2.1 IMPORTANT TERMS:

ADSORPTION :

It is a surface phenomenon. It is defined as ‘the accumulation of a substance at the surface of a solid’.

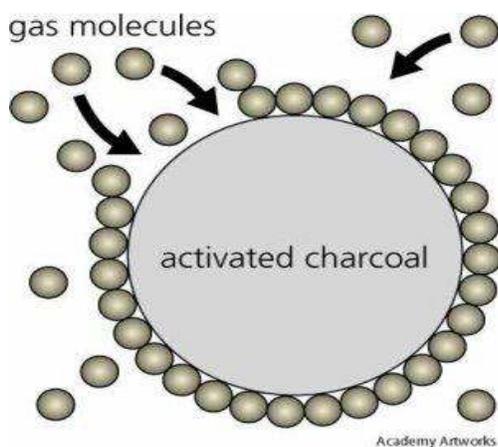


Fig 2.1 Illustration of adsorption

Examples:

- Activated charcoal adsorbs gases like CO_2 , SO_2 , Cl_2 etc.
- Pt or Ni metal kept in contact with a gas adsorbs the gas - Hydrogenation of oils.
- Animal charcoal, when added to acetic acid solution and shaken vigorously, adsorbs acetic acid.
- Molasses is decolourised by activated charcoal.

ABSORPTION:

It is a bulk phenomenon. It is defined as “process in which a substance is uniformly distributed throughout the body of the solid or liquid”.

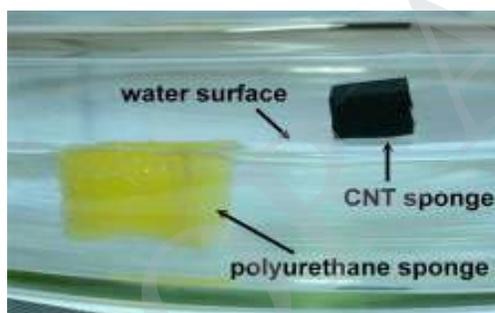


Fig 2.2 Illustration of absorption

Examples:

- If a chalk piece is dipped into a solution of coloured ink and kept for some time, the chalk piece absorbs the coloured substance.
- A sponge placed in water absorbs water into it.
- H_2 gas kept in contact with finely divided palladium metal is absorbed by Pd metal. This absorption of H_2 gas by Pd is known as occlusion.

ADSORBATE: The substance held on the surface of the solid is called adsorbate.

Example: Various gases (NH_3 , water vapour, CO_2 , etc)

Substances in solution (NaCl , dye, etc.)

ADSORBENT:

The substance on which adsorption occurs. (OR) The solid that takes up a gas or a solute from the solution is called adsorbent.

Example: Silica gel, charcoal, Pd, Pt, Ni, alumina gel, etc.

OCCLUSION: The adsorption of gas on a solid surface is called occlusion.

SORPTION: It is a process in which both adsorption and absorption takes place simultaneously.

EXAMPLES:

- In the adsorption of acetic acid by charcoal, “acetic acid is Adsorbate and the charcoal is Adsorbent ”
- In the adsorption of H_2 gas on platinum or nickel , “ H_2 gas is adsorbate and Pt or Ni is adsorbent”.

DESORPTION:

The removal of adsorbed substance from the surface is called desorption.

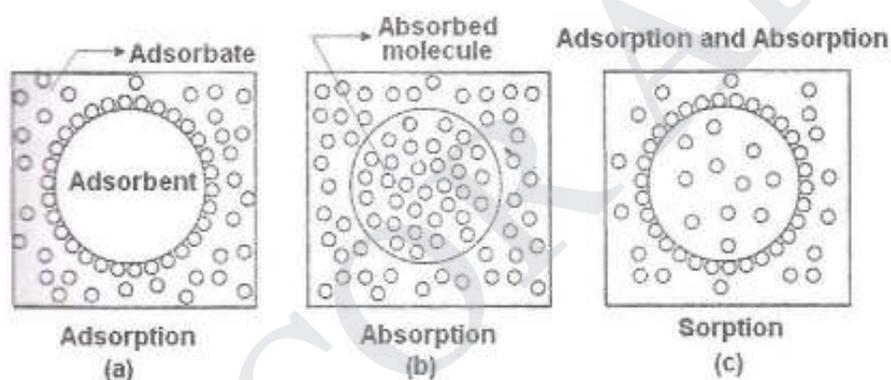


Fig 2.3 Illustration of adsorption, absorption and sorption

Examples of Adsorption and Absorption:

- ❖ When a sponge is put into water, the water enters into the whole body of sponge – it is an example of absorption.
- ❖ When a solution of methylene blue (dye-coloured substances) in water is stirred with solid carbon, the dye gets adsorbed by charcoal and thus decolourises the water – it is an example of adsorption.
- ❖ Ammonia is adsorbed on charcoal while it is absorbed by water.
- ❖ Water vapours are adsorbed on silica gel while they are adsorbed by anhydrous $CaCl_2$.
- ❖ NH_3 can undergo adsorption and absorption. When ammonia is passed through water in contact with charcoal. Water dissolves NH_3 (absorption) which is then adsorbed by charcoal crystals.

Exothermic nature of adsorption:

The amount of heat evolved when 1 mole of any gas is adsorbed on a solid adsorbent surface is called enthalpy or molar heat of adsorption”.

2.1.1 DIFFERENCES BETWEEN ADSORPTION AND ABSORPTION

S.No.	Adsorption	Absorption
1.	It is a surface phenomenon i.e. higher concentration of a liquid or gas molecules over the surface of a solid.	It is a bulk phenomenon i.e. accumulation of substrate on the surface of the solid, in which the substrate is uniformly distributed throughout the body of the solid substance.
2.	It is a fast process.	It is a slow process.
3.	Equilibrium is attained easily.	Equilibrium is attained slowly.
4.	It depends upon the surface area of the adsorbent. Adsorption is more rapid when the surface of adsorbent is more.	No such effect is observed.
5.	Example: Ammonia is adsorbed on charcoal.	Example: When a sponge is put into water, the liquid enters into the whole body of the sponge.

2.1.2 TYPES (OR) CLASSIFICATION OF ADSORPTION

Adsorption is classified into two types:

- Physical adsorption (or) Physisorption (or) Vander Waal's Adsorption
- Chemical adsorption (or) Chemisorption (or) Activated Adsorption

2.1.3 PHYSICAL ADSORPTION (OR) PHYSISORPTION

It is a process in which the adsorbed molecules are held to the surface of the adsorbent by weak physical or Vander Waal's forces.

(e.g) Adsorption of H_2 on charcoal

2.1.4 CHEMICAL ADSORPTION (OR) CHEMISORPTION

It is a process in which the adsorbed molecules are held to the surface of the adsorbent by strong chemical bonds.

(e.g) Adsorption of H_2 on Ni, adsorption of O_2 on tungsten

Example: Adsorption of H_2 on Ni

H_2 molecule is first adsorbed by Vander Waal's forces and then undergoes dissociation to hydrogen atoms. Then the H-atoms are chemisorbed on Ni.

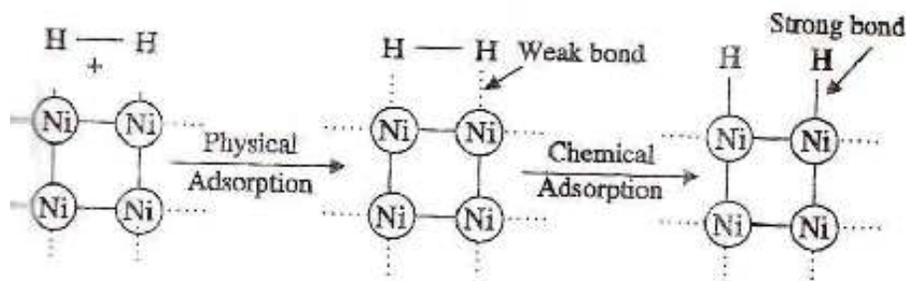


Fig 3.4 Adsorption of H₂ on Ni

2.1.5 DIFFERENCES BETWEEN PHYSISORPTION AND CHEMISORPTION

S.No.	Property	Physical adsorption	Chemical adsorption
1.	Nature of adsorption	Weak	Strong
2.	Enthalpy of adsorption	Low. (20-40 Kcal/mol)	High. (40 – 400 Kcal/mole)
3.	Reversibility of adsorption process	Reversible and occurs rapidly.	Irreversible and occurs slowly.
4.	Temperature at which adsorption is more pronounced	Low temperatures (below the b.pt of the adsorbate gas)	High temperatures (generally above the b.pt. of the adsorbate gas)
5.	Effect of change in temperature	Decreases with rise in temperature.	Increases with rise in temperature.
6.	Specificity of adsorption	Not specific. Generally takes place on all surfaces.	Highly specific. Takes place on specified surfaces only.
7.	Nature of adsorbate layers formed	Multilayered	Unilayered
8.	Effect of pressure on adsorption	Increases with rise in pressure of adsorbate gas and finally attains a limiting value.	Pressure of the adsorbate has a negligible effect.
9.	Energy of activation	Insignificant i.e. very low.	Significant i.e. relatively high.
10.	Dependence on the nature of the adsorbate & adsorbent	Depends on the adsorbate (gas) only. Easily liquefiable gases are more readily adsorbed.	Depends on the adsorbate as well as adsorbent. No correlation can be given.

11.	Ease of desorption	Easy since Vander Waals forces are involved.	Not easy since chemical forces are involved.
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2.2 CHARACTERISTICS OF ADSORPTION

- Adsorption is a highly selective process.
- It is a physical phenomenon accompanied by a chemical change.
- It depends on the nature of the adsorbent and adsorbate.
- It is always spontaneous.
- It is always accompanied by evolution of heat.
- The rate of adsorption depends on temperature, pressure and concentration.

2.3 ADSORPTION OF GASES ON SOLIDS

Most of the surface reactions takes place by chemisorption and solids adsorb gases to some measurable extent. The adsorption of gases on solid surfaces of finely divided metals like Fe, Ni, Pt, Pd, etc. depends on the following factors:

- Nature of gases
- Nature and surface area of adsorbents
- Enthalpy of adsorption
- Reversible character of adsorbed gases
- Effect of pressure and temperature
- Thickness of adsorbed layer of gas
- Activation of adsorbent

2.4 FACTORS INFLUENCING THE ADSORPTION OF GASES ON SOLIDS

➤ NATURE OF GASES:

Gas molecules with high polarity, which is soluble and easily liquefied, will be easily adsorbed. Easily liquefiable gases (HCl, NH₃, Cl₂, SO₂, etc.) are adsorbed more easily than the permanent gases (H₂, N₂, O₂, etc.).

Reasons:

They are having high critical temperature (i.e. the minimum temperature above which a gas cannot be liquefied) and greater Vander Waal's forces. The higher the critical temperature (T_c), the more easily the gas is liquefied and more readily it is adsorbed.

Example: Adsorption of various gases on 1 g of activated charcoal

Gases	SO ₂	NH ₃	CO ₂	CO	N ₂	H ₂
Critical temperature (T_c) (K)	403	406	304	134	126	33
Amount of gas adsorbed (mL)	380	180	48	9.3	8.0	4.5

➤ **NATURE OF THE ADSORBENT:**

Since adsorption is a surface phenomenon, it is evident that

Highly porous substances undergo adsorption to a greater extent because pores permit the diffusion of gases.

Example:

Activated charcoal at 24°C adsorbs 1.47gm of CCl₄ per gram of charcoal whereas before activation it would adsorb only 0.011gm of charcoal.

➤ **SURFACE AREA OF THE ADSORBENT :**

Adsorption involves concentration of a substance on the surface. Hence, the extent of adsorption depends on the surface area of the adsorbents.

Larger the surface area of the adsorbent, the greater is its adsorption capacity under the given conditions of temperature and pressure.

Example:

Finely divided metals like Ni, Pt, etc. and porous substances like charcoal, fuller's earth, silica gel, etc. provide large surface area and are excellent solid adsorbents.

➤ **EFFECT OF PRESSURE:**

According to Le-Chatlier's Principle, since dynamic equilibrium exists between the adsorbed gas and the gas in contact with the solid, the amount of gas adsorbed by a given solid is directly proportional to pressure.



(i.e.) increase of pressure increases the adsorption and decrease of pressure causes desorption (decreases the adsorption).

➤ **EFFECT OF TEMPERATURE:**

Physical adsorption: It occurs rapidly at lower temperature and decreases with increase of temperature.

Chemical adsorption: Initially it increases with increase of temperature to some extent and then decreases with temperature because chemisorption like an ordinary chemical change requires some activation energy.

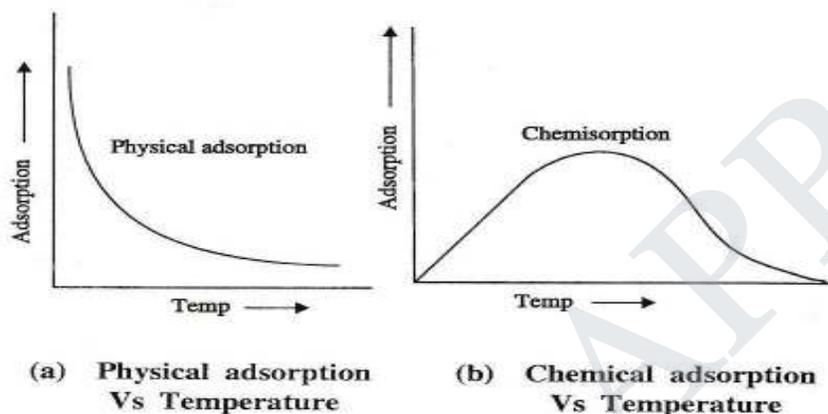


Fig 2.5

Example:

At 60 mm pressure, 1 gm of charcoal adsorbs about 10 cc of N_2 at $0^\circ C$, about 20 cc of N_2 at $-30^\circ C$ and about 45 cc of N_2 at $-80^\circ C$.

➤ **THICKNESS OF ADSORBED LAYER OF GAS:**

In physisorption, the adsorbed gases form a unimolecular thick layer at low pressure. But, above a certain pressure, multimolecular thick layer is formed.

In chemisorption, only a unimolecular thick layer is formed, since adsorbed gases combine directly with the adsorbent surface.

➤ **EFFECT OF ACTIVATION OF ADSORBENT:**

In order to increase the rate of adsorption, activation (i.e increasing the adsorbing power of the adsorbent) is necessary. Activation can be done by:

✓ **Creation of rough surface:**

- Mechanical rubbing of metallic or solid adsorbents.
- Subjecting to some chemical reactions on the solid adsorbent.

✓ **Increasing effective area of the surface:**

- By sub-dividing the solid adsorbents into finer particles.

- Strong heating of solid adsorbent in superheated steam opens the pores and thereby adsorption activity increases.

➤ **ENTHALPY OF ADSORPTION:**

Adsorption is always exothermic.

In **physical adsorption**, enthalpy of adsorption is about 5 kcal/mole due to weak Vander Waal's forces. Hence, such gases are adsorbed to a smaller extent on solid adsorbent.

In **chemical adsorption**, enthalpy of adsorption is about 100 kcal/mole due to relative formation of chemical bond between gas and the adsorbent. Hence, such gases are adsorbed to a larger extent on solid adsorbent.

➤ **REVERSIBLE CHARACTER OF ADSORPTION:**

Physical adsorption: It is a reversible process. The gas adsorbed on a solid can be removed (desorbed) under reverse conditions of temperature and pressure.



Chemical adsorption: It is an irreversible process, because surface compound is formed and desorption is quite difficult.

2.5 ADSORPTION OF SOLUTES FROM SOLUTIONS

A solution is made up of two basic components – solute and solvent.

When an adsorbent is dropped into a solution, either the solute or the solvent may become adsorbed. Adsorption of solvent is very rare. Adsorption of solutes from the solution follows two mechanisms.

- **An adsorbent adsorbs dissolved substances (solutes) from solutions.**

Example: Activated animal charcoal (i.e. charcoal from which pre-adsorbed gases have been removed completely)

- It adsorbs colouring matter present in sugar solutions thereby making the latter colourless.
- It adsorbs certain acids like acetic acid and oxalic acid present in water, thereby acid concentration in water decreases.
- It also adsorbs ammonia from the solution of ammonium hydroxide.
- It adsorbs Cl^- ions from NaCl or AgCl solution.

- **An adsorbent adsorbs certain substance from the solution in preference to other substances.**

Examples:

- **Charcoal:** It adsorbs non-electrolytes more readily than electrolytes from a solution.
- **Alumina:** It adsorbs electrolytes in preference to non-electrolytes.

2.6 FACTORS INFLUENCING ADSORPTION OF SOLUTES FROM SOLUTION

The amount of solute adsorbed by a solid from the solution depends on the following factors:

- **Surface area of the adsorbent:** If the surface area of the adsorbent is greater, the rate of adsorption is also greater.
- **Nature of the adsorbent:** Some adsorbents are specifically more effective in attracting certain substances to their surface than the other.
- **Nature of the solute adsorbed:** If the molecular weight of the solute is high, the extent of rate of adsorption is also high.
- **Effect of temperature and concentration:**

Adsorption of substances from the solution depends on temperature and concentration of the solution. An increase in temperature decreases the extent of adsorption and vice versa.

Freundlich adsorption isotherm is suitable to explain the effect of concentration.

When an adsorbent is dropped into a solution, either the solute or solvent may be adsorbed.

- ✓ If the solute is adsorbed by the adsorbent, it is known as **positive adsorption**.
- ✓ If the solvent is taken up by the adsorbent, it is known as **negative adsorption**.
- **NEGATIVE ADSORPTION:** Adsorption from a solution decreases with rise of temperature and decrease in concentration of the solution. This type of adsorption is known as negative adsorption.

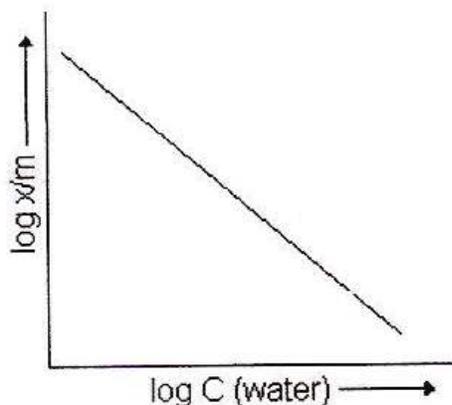


Fig 3.6 Negative Adsorption

Example: From the dilute solution of KCl, charcoal adsorbs water thereby the salt concentration is increased.

➤ **POSITIVE ADSORPTION:**

Adsorption from a solution increases with decrease of temperature and increases in concentration of the solution. This type of adsorption is known as positive adsorption.

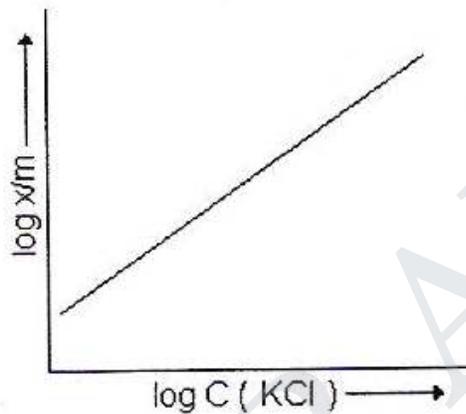


Fig 3.7 Positive Adsorption

Example: From the concentrated solution of KCl, charcoal adsorbs KCl rather than water thereby the salt concentration gets decreased.

2.6 ADSORPTION CURVES

The amount of gas molecules adsorbed on the surface of the adsorbent depends on pressure and temperature (i.e) the amount of gas adsorbed is a function of the T and P only.

If 'x' is the amount of gas adsorbed on mass 'm' of the adsorbent at pressure 'P' and temperature 'T', then it can be represented as

$$x/m = f(P, T) \dots\dots\dots (1)$$

This mathematical equation is called adsorption curve.

This equation (1) gives three types of adsorption curves under different conditions of P, T and x/m.

ADSORPTION ISOTHERM

If T is kept constant, then equation (1) becomes

$$x/m = f(P) \dots\dots\dots (2)$$

Equation (2) explains the variation of adsorption with P at constant T.

ADSORPTION ISOBAR

If P is kept constant, then equation (1) becomes

$$x/m = f(T) \dots\dots\dots (3)$$

Equation (3) explains the variation of adsorption with T at constant P.

ADSORPTION ISOSTERE

If the amount of adsorbed gas is kept constant, then

$$P = f(T) \dots\dots\dots (4)$$

Equation (4) explains the variation of P with T when x/m is kept constant.

2.7 ADSORPTION ISOTHERMS

The extent of adsorption (x/m) [where 'x' is the mass of the adsorbate and 'm' is the mass of the adsorbent] depends on pressure.

This can be understood by plotting a graph between x/m against P.

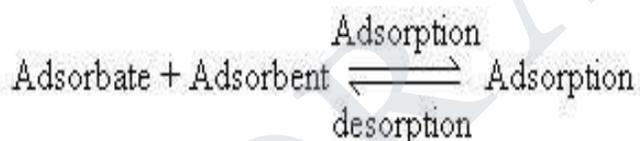
2.7.1 DEFINITION

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 at constant temperature".

2.7.2 BASIC ADSORPTION ISOTHERM

In the process of adsorption, adsorbate gets adsorbed on adsorbent.



According to Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved.

In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases.

Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favoured.

From the graph, it is clear that the extent of adsorption (x/m) increases with increasing pressure (P) and becomes maximum at P_s , called the saturation pressure.

At P_s , the rate of adsorption becomes equal to the rate of desorption i.e. dynamic equilibrium is reached and further increase of P does not alter this equilibrium.



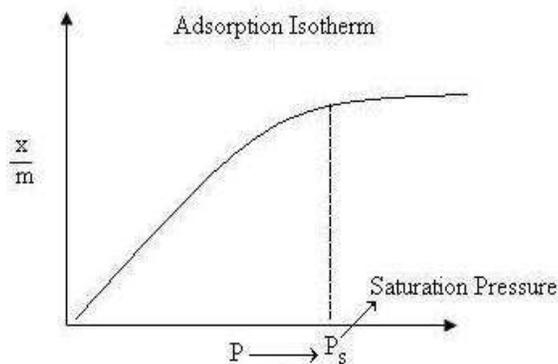


Fig 2.8 Basic Adsorption Isotherm

From the graph, we can predict that after saturation pressure P_s , adsorption does not occur anymore. This can be explained by the fact that there are limited numbers of vacancies on the surface of the adsorbent. At high pressure a stage is reached 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.

2.7.3 TYPES OF ADSORPTION ISOTHERMS

Adsorption isotherms are divided into five different types. A large number of adsorption isotherms of gases on a variety of adsorbents at different temperatures have been studied. In each type, the saturation pressure, where the maximum adsorption occurs, is indicated by ' P_s '.

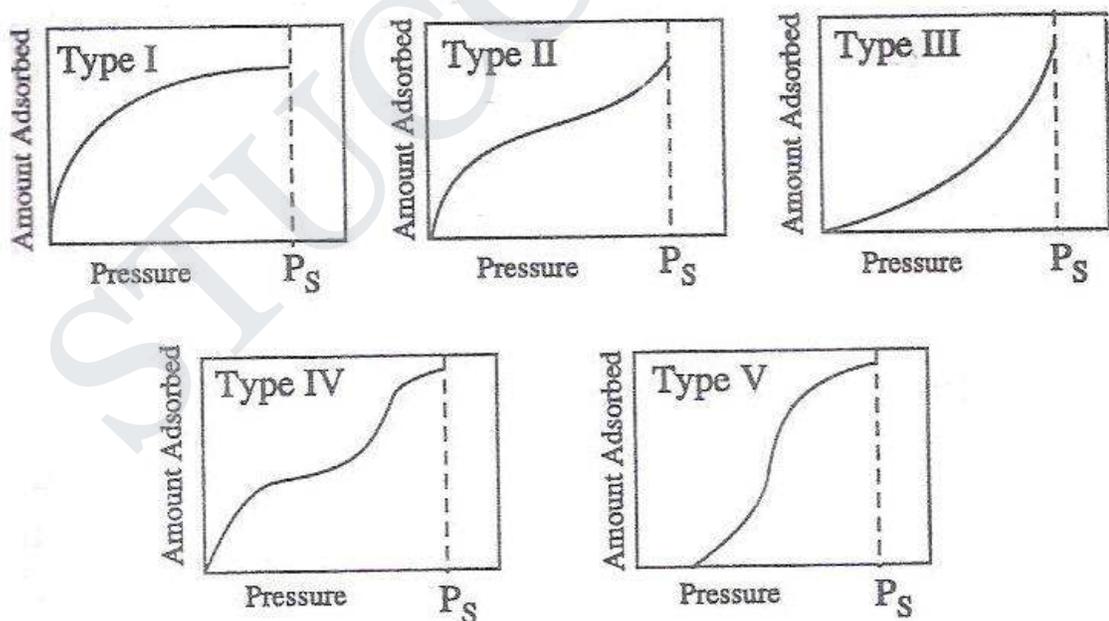
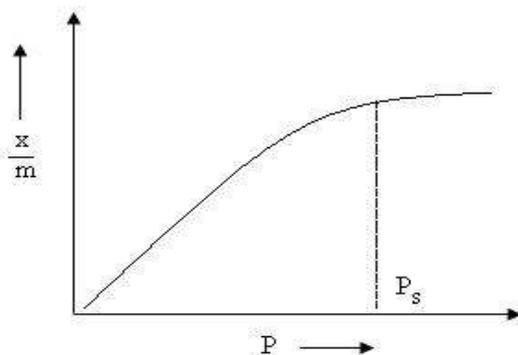


Fig 2.9 Different types of adsorption isotherms

TYPE I:

2.10 Type I

- The above graph depicts Monolayer adsorption.
- This graph can be easily explained using Langmuir Adsorption Isotherm.
- The amount of gas adsorbed approaches a limiting value ' P_s ', which is just enough to complete a monomolecular layer, even when the gas pressure is high. Further increase in pressure will not increase the amount of adsorption.

Examples: Adsorption of Nitrogen (N_2) or Hydrogen (H_2) on charcoal at temperature near to $-180^\circ C$.

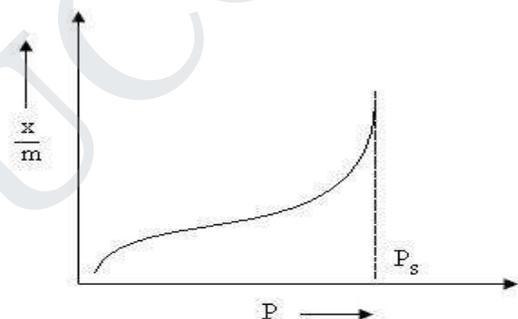
TYPE II:

Fig 3.11 Type II

- Type II Adsorption Isotherm shows large deviation from Langmuir adsorption model.
- The graph represents a case of multi-molecular layer physical adsorption on non-porous materials.
- It has been suggested that, the gas molecules adsorbed in the first layer may hold a second layer by weak Vander Waal's forces, which in turn, may hold a third layer and so on.
- The intermediate flat region in the isotherm corresponds to monolayer formation.

- So, this represents the transition of monomolecular layer to multimolecular layer.
- Thus the curve shows that, there is a transition point 'B' which represents the P at which the formation of monolayer is complete and that of multilayer is being started.

Examples: Nitrogen [N₂ (g)] adsorbed at -195⁰C on Iron (Fe) catalyst and Nitrogen [N₂ (g)] adsorbed at -195⁰C on silica gel.

TYPE III:

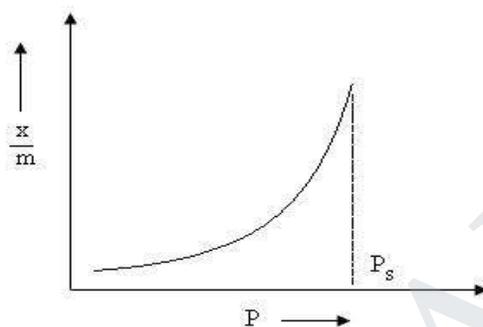


Fig 3.12 Type III

- Type III Adsorption Isotherm also shows large deviation from Langmuir model.
- This isotherm explains the formation of multilayer.
- Examples: Bromine (Br₂) at 79⁰C on silica gel or Iodine (I₂) at 79⁰C on silica gel.
- It represents a case of physical adsorption on porous materials.
- There is no flat portion in the curve which indicates that monolayer formation is missing.
- The curve represents that multilayer formation starts even before the completion of monolayer formation.

TYPE IV:

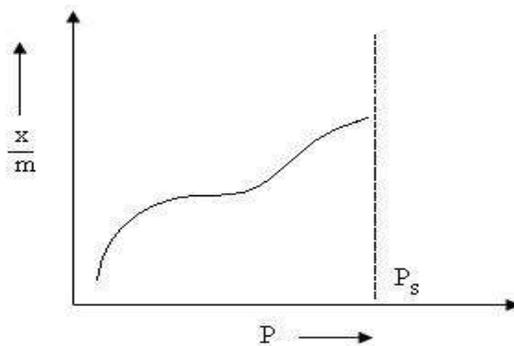


Fig 3.13 Type IV

- Adsorption isotherm represents a case of physical adsorption on porous materials accompanied by capillary condensation.
- Examples: Adsorption of Benzene on Iron Oxide (Fe_2O_3) at 50°C and adsorption of Benzene on silica gel at 50°C .
- At lower pressure region the graph is quite similar to Type II. This explains formation of monolayer followed by multilayer.
- The saturation level reaches at a pressure below the saturation vapour pressure.
- This can be explained on the basis of a possibility of gases getting condensed in the tiny capillary pores of adsorbent at the pressure even below the saturation pressure (P_s) of the gas.
- This is only due to the formation of multimolecular adsorption layers of the gas molecules but also due to condensation of some of the gas molecules within the capillary pores of the adsorbent. This is known as capillary condensation of the gas.

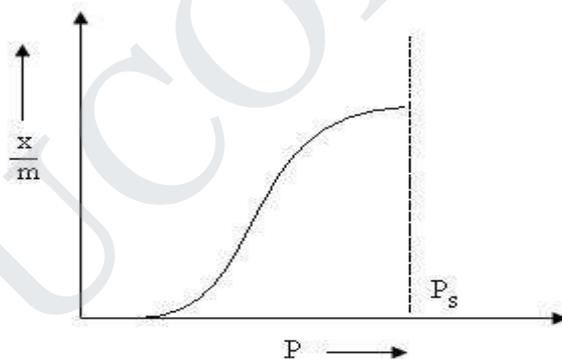
TYPE V:

Fig 2.14 Type V

- It also represents a case of physical adsorption on porous materials.
- It indicates that the formation of multi molecular layer starts at the beginning of adsorption.
- Example: Adsorption of Water vapours at 100°C on charcoal.
- Explanation of Type V graph is similar to Type IV.
- Type IV and V shows phenomenon of capillary condensation of gas.

2.8 FREUNDLICH'S ADSORPTION ISOTHERM

The amount of gas adsorbed for a given quantity of adsorbent (substrate) increases rapidly as pressure increases and the rate decreases as the surface covered is more and more.

The relationship between the magnitude of adsorption (x/m) and pressure (P) can be expressed mathematically by an empirical equation known as Freundlich adsorption isotherm.

$$\frac{x}{m} = KP^{1/n}$$

2.8.1 DERIVATION OF FREUNDLICH'S ADSORPTION ISOTHERM:

The equation for Freundlich's adsorption isotherm may be derived from the result obtained from the graph.

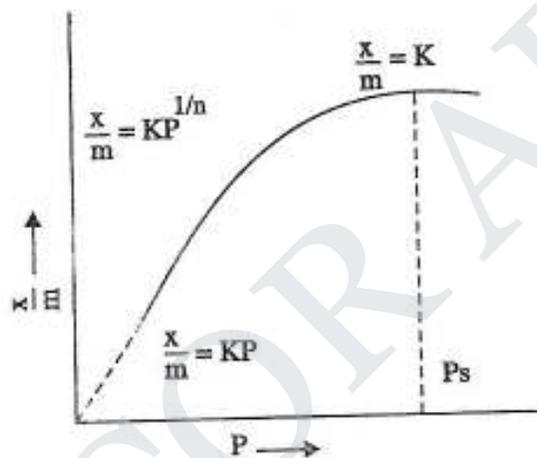


Fig 2.15 Adsorption isotherm

(i) At low pressure: Adsorption increases with pressure. The adsorption isotherm is almost a straight line indicating a direct relationship between the extent of adsorption and pressure.

$$x/m \propto P \quad (\text{OR}) \quad x/m = KP \quad \dots \dots (1)$$

(ii) At high pressure: The adsorption is almost constant. The adsorption isotherm is parallel to the X - axis indicating that the extent of adsorption is independent of the pressure.

$$x/m = \text{constant} \quad (\text{OR}) \quad x/m = K \quad \dots \dots (2)$$

(iii) At intermediate (normal) pressure : The extent of adsorption should be proportional to fractional power of pressure.

$$x/m \propto P^{1/n} \quad (\text{OR}) \quad x/m = KP^{1/n} \quad \dots \dots (3)$$

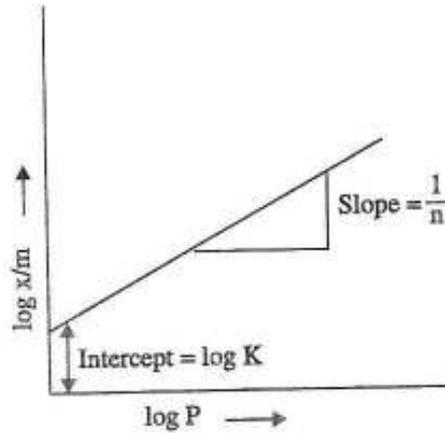
where 'n' is a whole number, whose values lies between 0 and 1.

Equation (3) is known as Freundlich's Adsorption isotherm.

Taking logarithm on both sides, equation (3) becomes

$$\log x/m = \log K + 1/n \log P$$

On plotting $\log x/m$ versus $\log P$, a straight line is obtained with a slope of $1/n$ and intercept $\log K$.



2.16 Freundlich adsorption isotherm

2.8.2 DISADVANTAGES (OR) LIMITATIONS OF FREUNDLICH'S ADSORPTION ISOTHERM

- Freundlich equation is purely empirical and has no theoretical basis.
- The equation is valid only upto a certain pressure and invalid at higher pressure.
- The constant K and n vary with T .
- It fails when the concentration of adsorbate is very high.

2.9 LANGMUIR'S ADSORPTION ISOTHERM

Irving Langmuir (1916) has shown that there is an equilibrium established between adsorption and desorption. He has derived an isotherm equation on the basis of the following assumptions.

- The adsorbed molecules form only a unimolecular layer on the solid adsorbent surface.
- The adsorbed molecules on the surface do not interact with each other.
- The molecules of a gas are adsorbed only on vacant sites of adsorbent surface. Each site can hold only one molecular species of the adsorbate.
- The adsorption process consists of two opposing processes (i) condensation of the adsorbate molecules on the adsorbent surface (ii) desorption of molecules from the adsorbent surface.
- The adsorbed gas molecule behaves ideally in the vapour phase.

3.9.1 DERIVATION OF LANGMUIR ADSORPTION ISOTHERM

Consider an adsorbing surface of area 1 sq.cm on which the molecules of a gas are condensing and evaporating.

When the adsorption starts, the rate of adsorption or condensation is highest initially while the rate of desorption is very small. As the adsorption proceeds, the two rates gradually approach each other until a dynamic equilibrium is obtained when the rate of adsorption is equal to the rate of desorption.

If 'A' is gas molecule and 'M' is solid surface, then

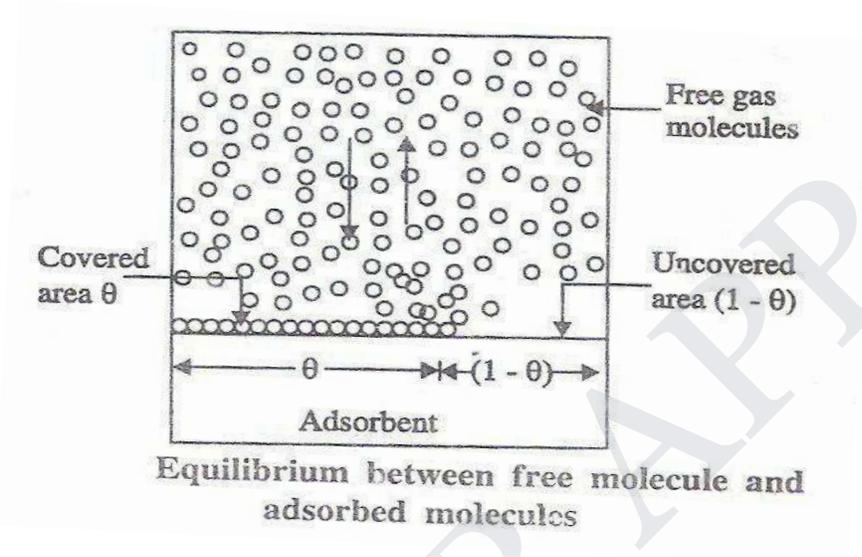
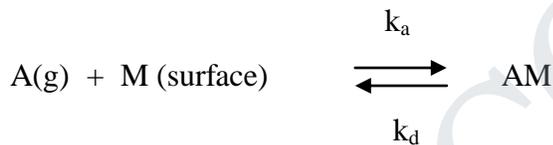


Fig 2.17



k_a = adsorption rate constant

k_d = desorption rate constant

Let,

Fraction of the total surface area covered by the adsorbed gas molecule = θ

If the total area is 1 sq.cm., then fraction of the remaining surface available for adsorption i.e.

uncovered area = $1 - \theta$

If P is the pressure of the gas, the rate of adsorption is proportional to the pressure and fraction of uncovered area ($1 - \theta$)

The rate of adsorption, $R_a = k_a (1 - \theta) P$

The rate at which gas molecules evaporate from the surface (desorption) will depend on the fraction of the surface covered by gas molecules (θ). Hence,

The rate of desorption, $R_d = k_d \theta$

At equilibrium,

$$R_a = R_d$$

$$k_a (1 - \theta) P = k_d \theta$$

$$kaP - \theta kaP = kd\theta$$

$$kaP = kd\theta + \theta kaP$$

$$kaP = \theta (kd + kaP)$$

$$\theta = \frac{kaP}{kd + kaP} \dots\dots\dots (1)$$

On dividing equation (1) by kd, we get

$$\theta = \frac{(ka / kd) P}{(kd / kd) + (ka / kd) P}$$

$$\theta = \frac{(ka / kd) P}{1 + (ka / kd) P} = \frac{KP}{1 + KP} \dots\dots\dots (2)$$

Where, ka / kd = K, is adsorption co-efficient

But, the amount of gas adsorbed per unit mass of the adsorbent, 'x' is proportional to the fraction of the surface covered, θ

$$x \propto \theta \text{ (OR) } x = K' \theta \dots\dots\dots (3)$$

From equation (2) and (3) we get,

$$x = \frac{K' K P}{1 + KP} \dots\dots\dots (4)$$

Where, K' = new constant

Equation (4) gives the relation between the amounts of gas adsorbed to the pressure of the gas at constant temperature which is called as Langmuir's Adsorption Isotherm.

Equation (4) can be re-written as

$$1 + KP = \frac{K'KP}{x}$$

Dividing both sides by K'K

$$\frac{1 + KP}{K'K} = \frac{K'KP}{K'K x}$$

$$\frac{1}{K'K} + \frac{KP}{K'K} = \frac{P}{x} \dots\dots\dots (5)$$

Equation (5) is similar to an equation for a straight line $y = mx + c$

$$\frac{P}{x} + \left[\frac{K}{K'K} \right] P = \frac{1}{K'K}$$

Thus, if the graph is plotted between P/x versus P , we should get a straight line with slope $K / K'K$ and intercept $1 / K'K$.

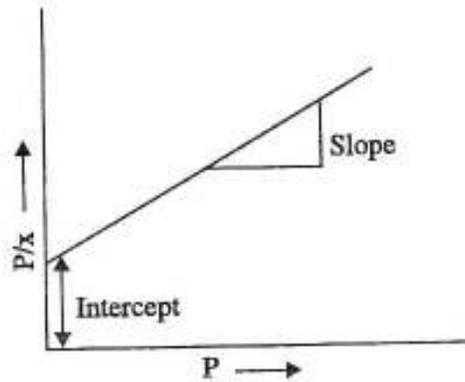


Fig 2.18 Plot of P / x Vs P

Case 1 : At low pressure, $(K / K'K) P$ term is negligible. (i.e.) $1 / K'K \gg (K / K'K) P$.

Hence equation (5) becomes

$$1 / K'K = P / x \quad (\text{OR}) \quad x = P K'K \dots\dots (6)$$

i.e. the amount of adsorption per unit mass of adsorbent is directly proportional to 'P' at low pressure.

Case 2 : At high pressure, $1 / K'K$ term is negligible. (i.e.) $(K / K'K) P \gg 1 / K'K$.

Hence equation (5) becomes

$$(K / K'K) P = P / x \quad (\text{OR}) \quad x = K' \quad (\text{OR}) \quad x = K' P^0 \dots\dots\dots (7)$$

i.e. at high pressure, the extent of adsorption at a given temperature is independent of pressure of the gas, because the surface becomes completely covered.

Case 3 : At normal pressure, equation (7) becomes

$$x = K' P^n \dots\dots\dots (8)$$

where 'n' lies between 0 and 1.

Equation (8) is Freundlich's adsorption isotherm.

2.9.2 Merit and Demerits:

Langmuir adsorption isotherm holds good at lower pressure but fails at high pressure.

3.10 APPLICATIONS OF ADSORPTION

(1) Activated charcoal is used in gas masks, which adsorbs poisonous gases (like CO) in coal mines and it is employed in both military and industrial purposes.

(2) Activated charcoal is used for removing colouring matter from solutions.

- (3) Silica gel and alumina gel are used as adsorbent for removing moisture and for controlling humidities of room.
- (4) Silica gel is used for drying air used in blast furnace.
- (5) Fuller's earth is used in large quantities for refining petroleum and vegetable oil by using Ni catalyst, which adsorbs unwanted materials.
- (6) Silica gel and alumina gel act as an adsorbent which is extensively used in cracking of heavy oil vapours to yield high quality petrol.
- (7) Arsenic poisoning from the body is removed by using colloidal ferric hydroxide, which adsorbs arsenic poison and retains it and can be removed from the body by vomiting.
- (8) Softening of hard water can be done based on the principle of adsorption using ion-exchange resins.
- (9) Sulphide ores (PbS, ZnS) are freed from silica and other earthy matter by froth flotation process. (Oil adsorbs sulphide ores only)
- (10) The phenomenon of adsorption is useful in heterogeneous catalysis, in which the molecules are adsorbed on the surface of solid catalyst and form activated complex. Then it decomposes to give product.
Example: Manufacture of SO_3 by contact process.
- (11) Mordants are used in dyeing industry, which adsorb the dye particles (colouring matter) without attaching to the fabrics.
- (12) Adsorption process is used in production of vacuum by using activated charcoal in Dewar's flask.
- (13) A layer of stearic acid is spread over water in lakes and reservoirs during summer as the adsorbed stearic acid on the surface of water reduces the loss of water by evaporation.

2.11 ROLE OF ADSORBENTS

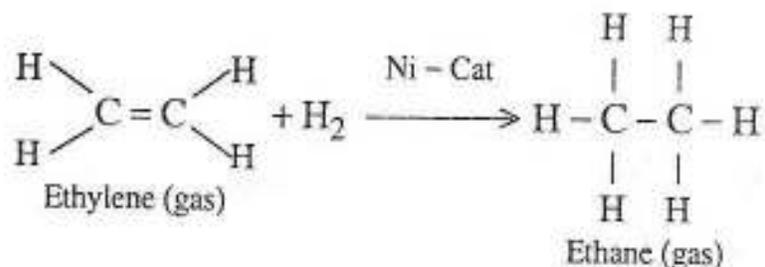
2.11.1 ROLE OF ADSORBENT IN CATALYSIS (OR) ADSORPTION (or) CONTACT THEORY

(1) In heterogeneous catalysis:

Adsorption or contact theory explains the mechanism of a reaction between two gases catalysed by a solid, heterogeneous catalyst. Here, the catalyst functions by adsorption of reactant molecules on

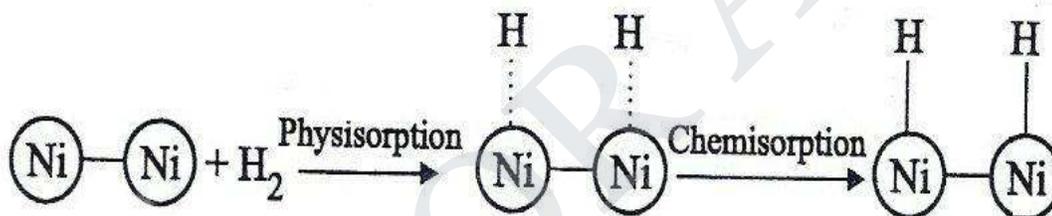
its surface forming an activated complex. This complex decomposes giving rise to the products which are readily desorbed.

Example: Hydrogenation of ethylene in the presence of finely divided nickel as catalyst.



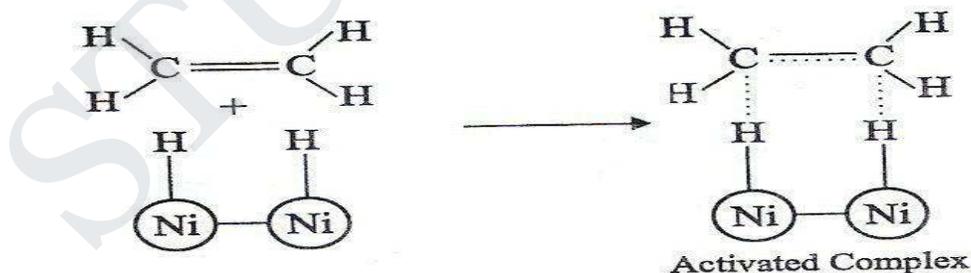
STEP 1: Adsorption of hydrogen gas on nickel

The surface of the solid catalyst has certain isolated active centers, due to unsaturation of valencies. The gaseous hydrogen molecules are adsorbed at the active centre of the nickel surface either by physisorption or by chemisorption. If the temperature is sufficiently high, the gases get chemisorbed on the surface.



STEP 2: Formation of activated complex

The activated hydrogen molecule reacts with ethylene gas to form an activated complex. This activated complex is unstable, which decomposes giving rise to the products that are readily desorbed.



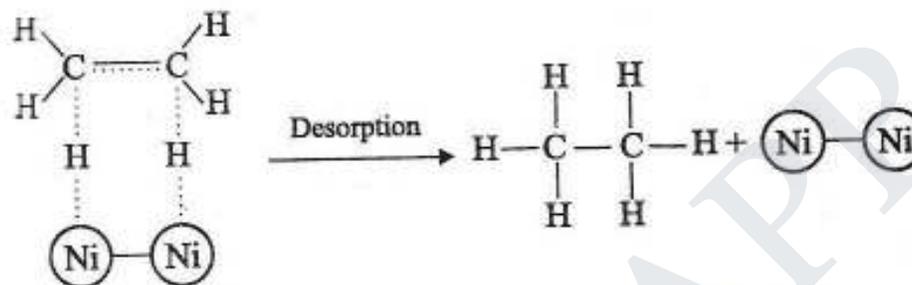
STEP3 : Decomposition of activated complex

The activated complex breaks to form the products. The separated particles of the products bound to the catalyst surface by partial chemical bonds.



STEP 4: Desorption of products

The Ni catalyst is desorbed from the surface and gives stable ethane gas.



(2) The catalyst is more efficient in finely divided state:

When the subdivision or fineness of the catalyst increases, the free surface area gets increased. Thereby free valencies (or) active centers, which are responsible for the adsorption of reactant molecules increases, consequently the activity of the catalyst are also increased.

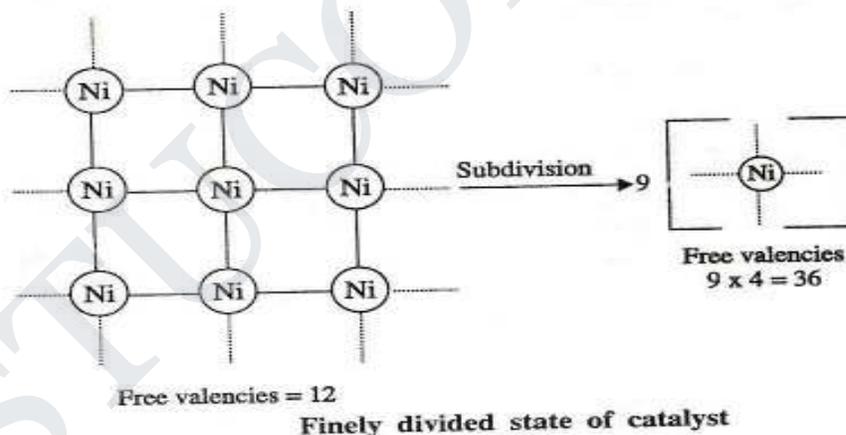


Fig 2.19

(3) Enhanced activity of a rough surfaced catalyst:

Rough surface of a catalyst possesses cracks, peaks, corners, etc., consequently the surface have larger number of active centre's, which increases the rate of adsorption.

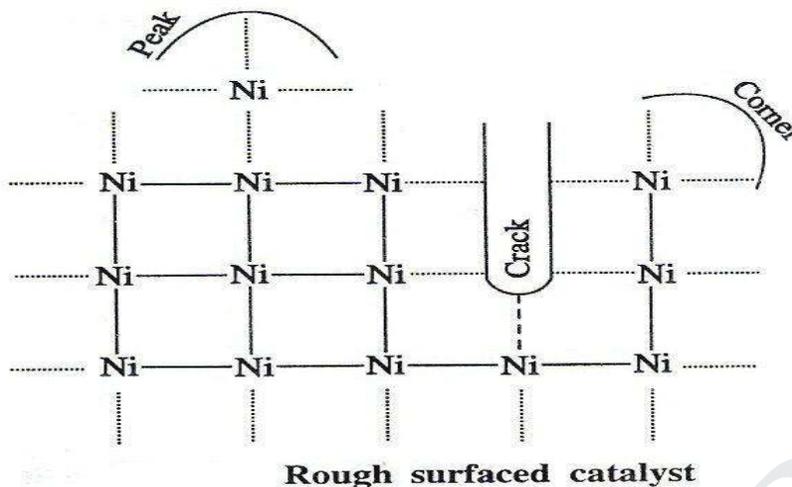


Fig 2.20

(4) Action of promoters:

Promoters are defined as, “the substances which increase the adsorption capacity or activity of a catalyst”. The action of promoter is explained as follows:

(i) Change of lattice spacing:

Promoters increase the spaces between the catalyst particles, so the adsorbed molecules are further weakened and cleaved. This makes the reaction to go fast.

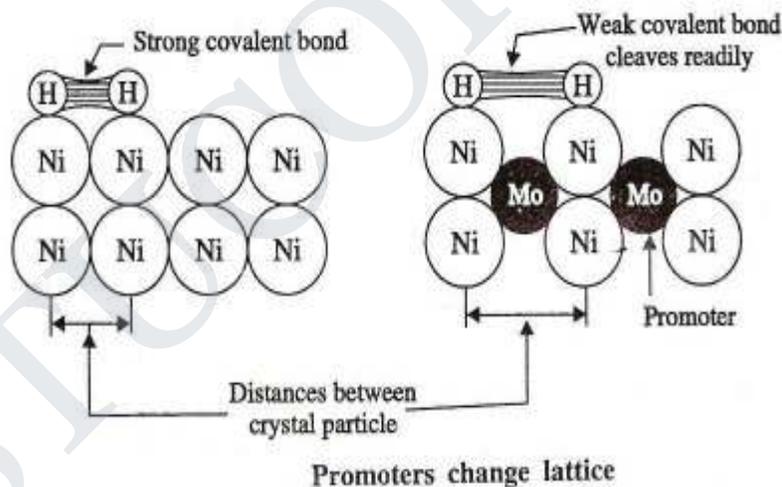


Fig 2.21

(ii) Increase of peaks and cracks:

Promoters increase the peaks and cracks on the catalyst surface. This increases the concentration of reactant molecules and hence the rate of the reaction.

(5) Action of catalytic poisons:

“A substance which destroys the activity of the catalyst to accelerate the reaction” is known as catalytic poisoning.

(e.g) The Pt catalyst used in the oxidation of H_2 is poisoned by CO.

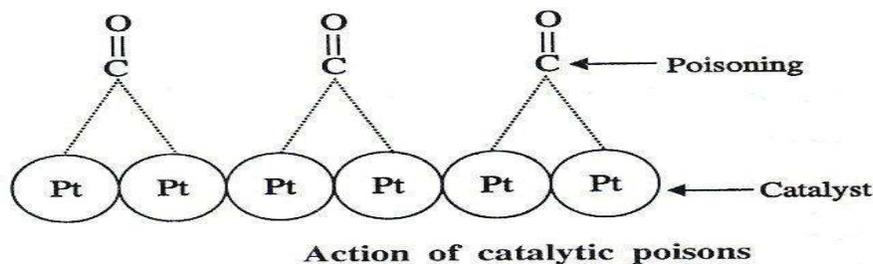


Fig 2.22

The number of free valencies (or) active centers of the catalyst is reduced by the preferential adsorption of the poisonous substances. So, the rate of reaction decreases.

(6) Specific action of catalyst:

The adsorption depends on the nature of both the adsorbent (catalyst) and the adsorbate (reactants). So, different catalyst cannot possess the same affinity for the same reactant. Hence, the action of the catalyst is also specific.

(e.g) Ethanol gives ethylene in the presence of hot Al_2O_3 , but with hot copper it gives acetaldehyde.

2.12 ACTIVATED CARBON IN POLLUTION ABATEMENT OF AIR AND WASTE WATER

Among the various adsorbents, in pollution abatement of air and waste water, activated carbon is the most commonly used adsorbent because it has a large surface area per unit weight (or) unit volume of solid.

2.12.1 Treatment of Polluted Water and Air

Polluted water and air can be treated by using the following two types of activated carbons.

- 1) Granular Activated Carbon (GAC)
- 2) Powdered Activated Carbon (PAC)

1. Using Granular Activated Carbon (GAC)

A fixed - bed activated-carbon contactors (column) is often used for contacting polluted water (or) air with GAC. It can be operated singly, in series (or) in parallel. Several types of fixed-bed activated - carbon contactors are used in the treatment of polluted water (or) air, of which the followings are important.

1. Down flow fixed-bed carbon contactors.
2. Upflow fixed-bed carbon contactors.

(a) Down flow fixed-bed Carbon Contactors

Down flow fixed-bed carbon contactors usually consist of two (or) three columns operated in series (or) in parallel as shown .

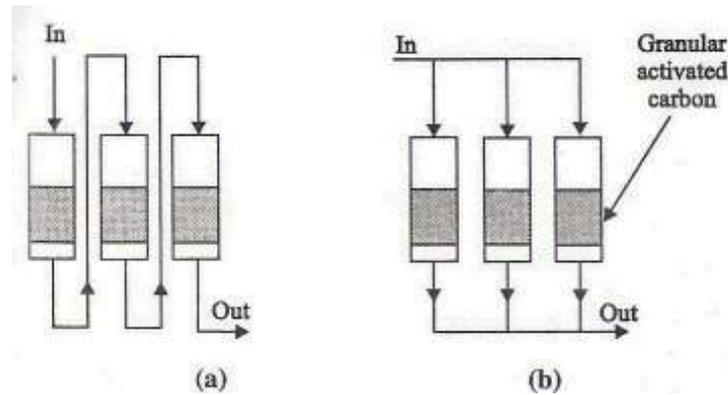


Fig. 2.26 (a) Down flow in series (b) Down flow in parallel

The water (or) air is applied to the top of the column and withdrawn at the bottom. The activated carbon is held in place with an under drain system at the bottom of the column. Provision for back washing and surface washing is usually necessary to limit the headless build up due to the removal of particulate material within the carbon column.

Advantages

Adsorption of organic materials and filtration of suspended solids are accompanied in a single step.

Disadvantages

- Down flow filters may require more washing because of the accumulation material on the surface of the contactor.
- Plugging of carbon pores may require premature removal of the carbon for regeneration thereby decreasing the useful life of the carbon.

(b) Up flow fixed-bed Carbon Contactors

In the upflow fixed-bed columns, the polluted water (or) air moves upward from the base of the column as shown.

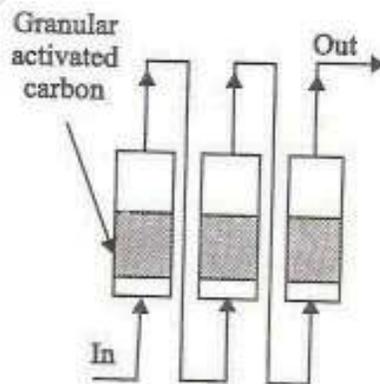


Fig 2.27 Upflow expanded in series

Advantages

As the carbon adsorbs organic materials, the apparent density of the carbon particles increases and encourages migration of the heavier or spent carbon downward.

Disadvantage

Upflow columns may have more carbon fines in the effluent than downflow columns, because upflow tends to expand, not compress, the carbon. Bed expansion allows the fines to escape through passage ways created by the expanded bed.

2. Using Powdered Activated Carbon (PAC)

In this method powdered activated carbon (PAC) is added directly into the effluent coming out from the various biological treatment processes.

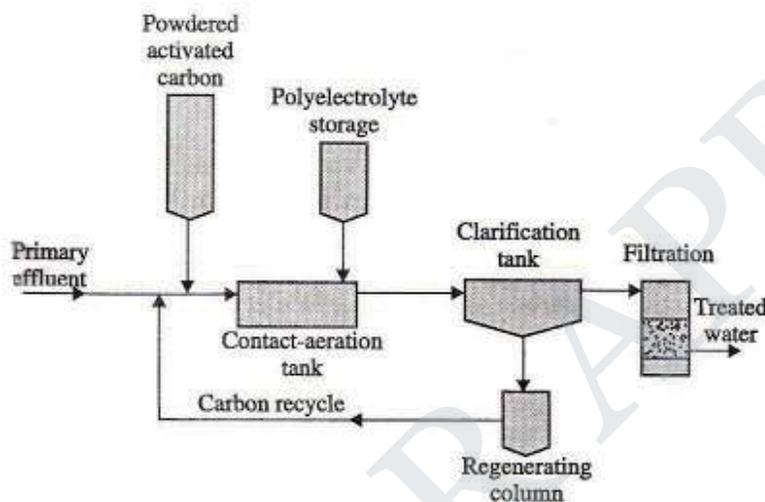


Fig. 2.28 Flow diagram of activated-sludge process

The effluent, coming out from the biological treatment plant, is mixed with PAC and a coagulant (polyelectrolyte) in a contact-aeration tank. After some time, the effluent is allowed to store in a clarification tank, where the carbon particles get settled at the bottom of the tank. Since the carbon particles are very fine, a coagulant such as polyelectrolyte is added to aid the removal of the carbon particles. The spent carbon is regenerated by passing it into the regenerating column and is used again for the process. Finally the water (effluent) is filtered by passing it through the filtration column.

2.12.2 General Applications of Adsorption

1. Inodour Control

Activated - carbon adsorbers are commonly used for odour control. Activated carbon has different rates of adsorption for different substances. It is effective in removing hydrogen sulfide. The removal of odours depends on the concentration of the hydrocarbons in the odorous gas. Hydrocarbons are adsorbed preferentially before the compounds like H_2S are removed.

2. As a Decolourant

Activated carbon, with its very great surface area and pore volume, removes colour from the solution.

3. InSolution Purification

Activated carbon is also used in cleaning sugar solution and for the removal of tastes from water supplies, vegetable and animal fats and oils, alcoholic beverages, chemicals and pharmaceuticals.

4. InGas Masks

The vapour - adsorbent type of activated carbon is used in gas masks, because of its ability to adsorb poisonous gases. It is now employed in both military and industrial gas masks.

5. Fuller's earth

It is used in large quantities for refining petroleum and vegetable oils, which absorb unwanted materials

6. Froth Flotation process

The sulphide ores are freed from silica and other earthy matter by froth flotation process.

7. Lake test for Al^{3+}

It is based on the adsorption of litmus colour by $Al(OH)_3$

8. Mordants

These are used in dyeing industry, which absorb the colouring matter without attaching the fabrics.

9. Measurement of surface area

Surface area of powders and rough surfaces can be measured using adsorption measurements.

10. Evaporation of water is minimized

Due to scarcity of water during summer a layer of stearic acid is spread over water lakes and reservoirs. The adsorbed stearic acid on the surface of water minimizes evaporation of water.

3.1 CATALYST

Definition

Catalyst is defined as a substance, which alters (increases or decreases) the rate of a chemical reaction without undergoing any change in amount and chemical composition at the end of the reaction.

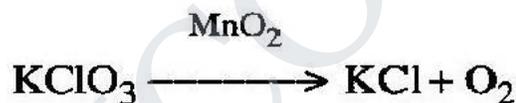
3.1.1 Types of catalysts

Positive catalyst

A catalyst, which enhances (increases) the rate of the chemical reaction is called a positive catalyst.

Example

MnO_2 in the decomposition of KClO_3 into KCl and O_2 .



Negative catalyst

A catalyst, which retards (decreases) the rate of the chemical reaction is called a negative catalyst (or) Inhibitors.

Example

Alcohol retards the oxidation of chloroform to poisonous phosgene.

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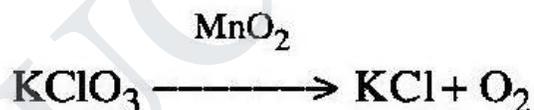
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A catalyst, which retards (decreases) the rate of the chemical reaction is called a negative catalyst (or) Inhibitors.

Example

Alcohol retards the oxidation of chloroform to poisonous phosgene.

3.2) CATALYSIS

Definition

The process of altering (increasing or decreasing) the rate of a chemical reaction with the help of a catalyst is known as catalysis.

3.2.1 Effect of a catalyst

A catalyst increases the rate of a reaction by lowering the energy barrier between the reactant and products. Otherwise we may say that, the catalyst provide another path for the reaction, that has lower energy of activation (E_a). Fig. 3.1 shows the new path, in presence of the catalyst.

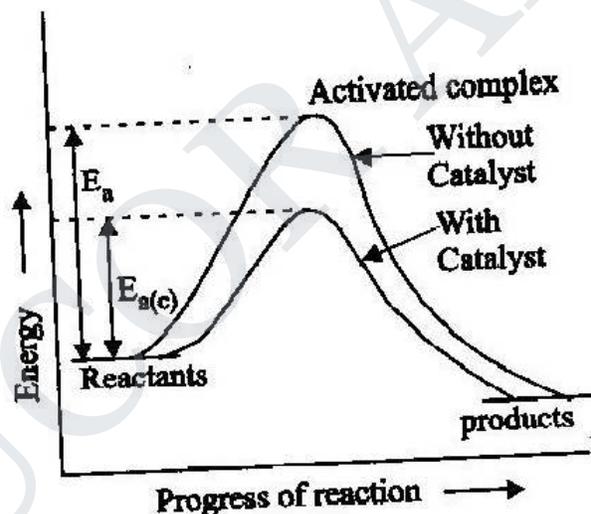


Fig. 3.1 Energy level diagram of a catalyst

3.3) CLASSIFICATION (or) TYPES OF CATALYSIS

Catalysis is classified into two types

1. Homogeneous catalysis
2. Heterogeneous catalysis

3.3.1 Homogeneous catalysis

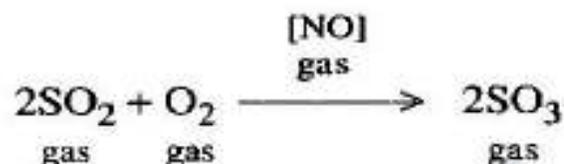
Homogeneous catalysis is the reaction in which the catalyst as well as the reacting substances are present in the

phase. That is if the reactants are solid (or) liquid (or) gas, the catalysts are also solid (or) liquid (or) gases respectively.

Examples

Homogeneous catalysis in gas phase

(i) Oxidation of SO_2 to SO_3 with nitric oxide (NO) as catalyst.

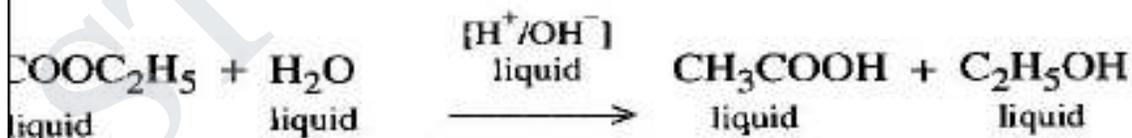


(ii) Decomposition of CH_3CHO with iodine (I_2) as catalyst.

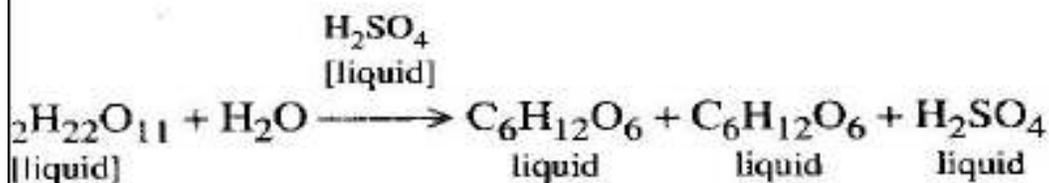


Homogeneous catalysis in liquid phase

(i) Hydrolysis of an ester in the presence of acid or base catalyst.



(ii) Hydrolysis of cane sugar in aqueous solution in presence of acid catalyst.



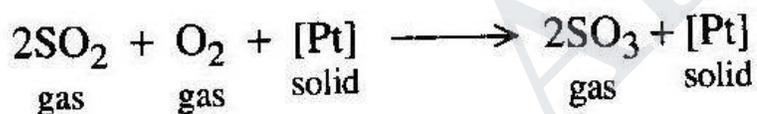
3.3.2 Heterogeneous catalysis

Heterogeneous catalysis is the reaction in which the catalyst as well as the reacting substances are present in the *different phases*.

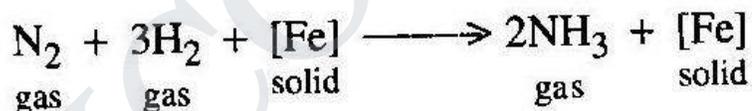
Examples

1. Heterogeneous catalysis with gaseous reactants

(a) Combination of SO_2 and O_2 in presence of finely divided Pt.

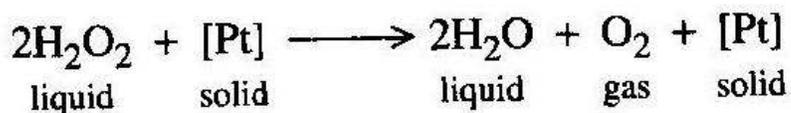


(b) Combination of N_2 and H_2 to form NH_3 in presence of finely divided Fe.



2. Heterogeneous catalysis with liquid reactants

Decomposition of aqueous H_2O_2 in presence of colloidal Pt.



3. Heterogeneous catalysis with solid reactants

Decomposition of KClO_3 in presence of solid MnO_2 .

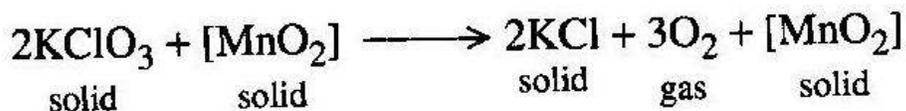


Table 3.1 Differences between Homogeneous catalysis and Heterogeneous catalysis

1.	Reactants, products and catalyst are present in only one phase i.e., either in liquid (or) gaseous phase.	Reactants, products and catalyst are present in different phases i.e., solid phase & liquid phase.
2.	Catalyst cannot be regenerated.	Catalyst can be regenerated and activated.
3.	Thermal stability of catalyst is low.	Thermal stability of the catalyst is high.
4.	Reactions are carried out at lower temperature and lower pressure.	Reactions are carried out at higher temperature and higher pressure.
5.	Temperature increases the rate of the reaction.	Temperature increases the rate of the reaction.
6.	Selectivity of the catalyst does not depend on the physical nature.	Selectivity of the catalyst depends on the physical nature.

3.4

CHARACTERISTICS (OR) CRITERIA OF CATALYSIS

The following characteristics are common to most of the catalytic reactions.

1. The catalyst remains unchanged in amount and chemical composition at the end of the reaction.

But the physical state, colour may undergo change.

Example

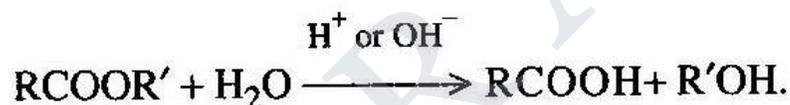
Granular MnO_2 , used as catalyst in the thermal decomposition of KClO_4 , will be converted to fine powder of MnO_2 .

2. Only small amount of the catalyst is required.

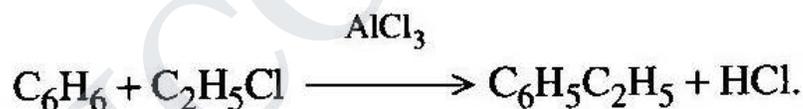
One mole of colloidal Pt in 10^8 litres, catalyze the decomposition of H_2O_2 .

But in some cases, the rate of the reaction is proportional to the concentration of catalyst.

(i) Acid and alkaline hydrolysis of an ester.



(ii) Friedel-Craft reaction

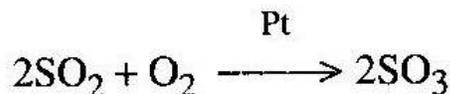


The catalyst AlCl_3 functions effectively, when its quantity is more than 30% of the quantity of benzene.

3. The catalyst does not alter the position of equilibrium in a reversible reaction.

Example

In the combination of SO_2 and O_2 platinised asbestos as a catalyst increases the rate of the reaction, but it does not increase the yield of SO_3 .

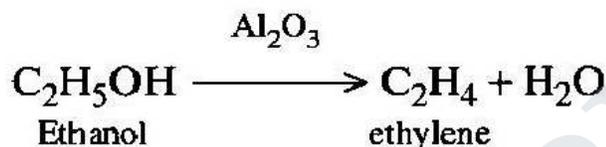


4. The catalyst is specific on its action.

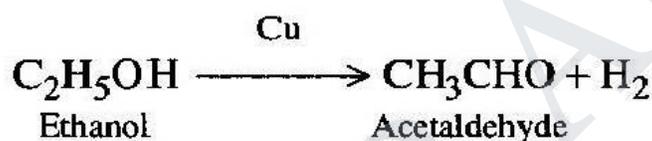
When a particular catalyst works for one reaction, it will not work for another reaction. Different catalysts, can bring about completely different reactions for the same substance.

Example

Ethanol gives ethylene, when passed over hot Al_2O_3 .



But the same ethanol with hot Cu gives CH_3CHO .



5. Generally catalyst cannot initiate a reaction.

In most cases a catalyst speed up the reaction already in progress and does not initiate the reaction.

6. A catalyst is more effective, when it is finely divided.

In heterogeneous catalysis, a finely divided solid catalyst is more effective than it is used in bulk.

Example

(i) Finely divided Ni is a better catalyst than lumps of solid Ni.

(ii) Colloidal Pt has greater catalytic activity than lumps of Pt.

7. Optimum temperature

A catalyst is most active at a particular temperature, called the optimum temperature.

8. A catalyst is poisoned by certain substances

9. The activity of a catalyst is enhanced by a promoters.

3.5**CATALYTIC POISONING AND CATALYTIC PROMOTERS****3.5.1 Catalytic poisoning**

Catalytic poisoning refers to the partial (or) total deactivation of a catalyst caused by exposure to a range of chemical compounds (or) substance.

Thus, substances which destroy the activity of the catalyst are known as catalytic poisons.

Poisoning process

Catalytic poisoning reaction involves compounds make bond chemically to the active surface sites of a catalyst. The process may have two effects.

- (i) The total number of catalytic sites (or) the fraction of the total surface area that has the capability of promoting reaction always decreases.
- (ii) The average distance that the reactant molecule must diffuse through the pore structure before undergoing reaction may increase.

Examples

- (i) The activity of iron catalyst is destroyed by the presence of H_2S or CO in the synthesis of ammonia by Haber's process.
- (ii) The platinum catalyst used in the oxidation of hydrogen is poisoned by CO .

Types of catalytic poisoning

1. Temporary poisoning

In this type of catalytic poisoning, the catalyst regains its activity when the substance, responsible for poisoning, is removed from reactants.

2. Permanent poisoning

In this type of catalytic poisoning the catalyst is poisoned permanently and cannot regain its activity even by removing the catalytic poison.

3.5.2 Catalytic promoters

The addition of a small amount of foreign substances increases the activity of the catalyst such substances are called catalytic promoters.

Functions of promoters

Promoters, when added to a catalyst as a minor component, improve one or more of the following properties of the catalyst.

1. Changes the crystal lattice spacing of catalyst

The promoter increases the spaces between the catalyst particles. This results in further weakening and cleaving of adsorbed reactant molecules. And hence rate of reaction further increases.

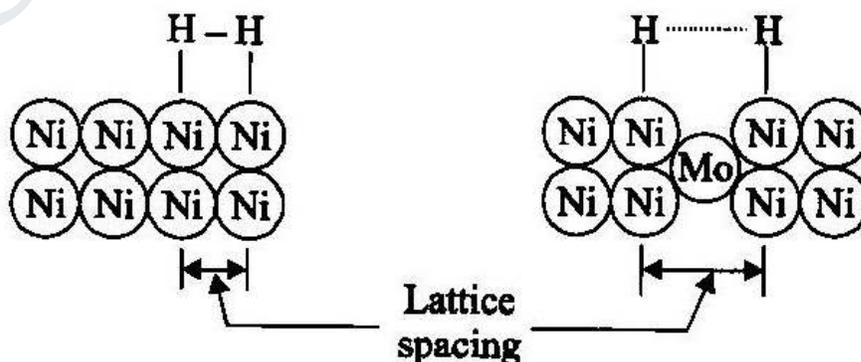


Fig. 3.2 Change in the lattice spacing of Ni catalyst

2. Increases the peaks and cracks on the catalyst

Promoters increases the peaks and cracks on the catalyst surface, where reactants can be adsorbed more easily. This increases the concentration of the reactant molecules and hence reaction speeds up.

3. Changes the pathway

A promoter changes the pathway of a reaction to enhance the rate of formation of the product.

Example

In manufacture of CH_3OH from the combination of CO and H_2 , the activity of the catalyst ZnO , is greatly enhanced by the presence of Cr .

3.6 AUTO CATALYSIS

3.6.1 Definition

When one of the products of a reaction itself acts as a catalyst for that reaction the catalyst is called auto-catalyst. This process (or) phenomenon is called auto-catalysis.

In autocatalysis the initial rate of the reaction increases as the catalytic product is formed (Fig 3.3) instead of decreasing steadily as in the case of ordinary catalytic reaction. The curve plotted between the rate of reaction (concentration of the product) and time shows a maximum rate when the reaction is complete.

The maximum rate at the time of completion of the reaction is due to the more catalyst (product) concentration. When the concentration of the catalyst is more, the rate of the reaction is maximum.

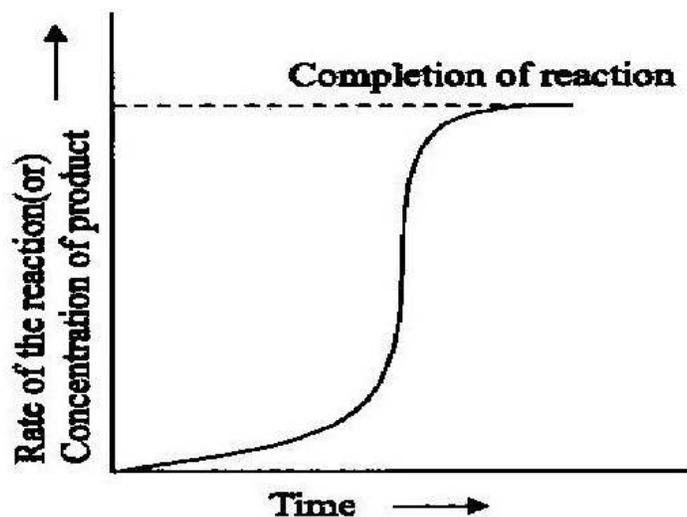


Fig. 3.3 Rate of auto-catalytic reaction

amples for Autocatalysis

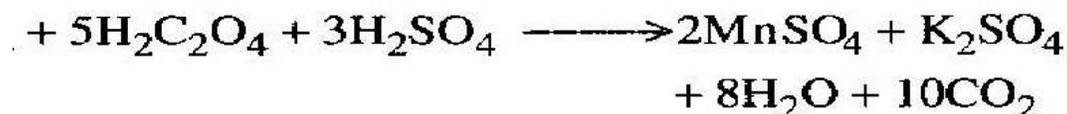
ysis of an Ester

Hydrolysis of ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5$) gives acetic acid (CH_3COOH) and ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$). Of these acetic acid acts as a catalyst for this reaction.



Titration of oxalic acid

Oxalic acid is titrated against KMnO_4 solution, in which the pink colour undergoes disappearance slowly, but after decolorisation takes place rapidly. This is due to the presence of Mn^{2+} ions (MnSO_4) during the titration.



Decomposition of Arsine

Free arsenic, produced by the decomposition of arsine (AsH_3), autocatalyses the reaction.

Example

H^+ , undissociated acids (CH_3COOH), cations of weak bases (NH_4^+) and water (H_3O^+).

Classification of acid catalysis**(a) Specifically proton catalysed**

If the reaction is catalysed only by H^+ (or H_3O^+) ions, but not Bronsted acids (Proton donors) the reaction is said to be specifically proton catalysed.

Example

Inversion of cane sugar, keto-enol tautomerism.

(b) General acid catalysis

If the reaction is catalysed by Bronsted acid, the reaction is said to be general acid catalysis.

2. Base catalysis

A reaction, which is catalysed not only by OH^- ions (base), but also all Bronsted bases (Proton acceptors) cause base catalysis.

Example

OH^- , undissociated bases (NH_4OH), anions of weak acids (CH_3COO^-) and water (H_2O).

Classification of Base catalysis

(a) Specifically base-catalysed: If the reaction is catalysed only by OH^- ions, the reaction is said to be specifically-base catalysed reactions.

(b) General base catalysis: If the reaction is catalysed by Bronsted base. The reaction is said to be general base catalysis.

The solvent water may act as a Bronsted acid or Bronsted base.

3.8 MECHANISM OF ACID-BASE CATALYSIS

Addition and removal of protons is the important part in the mechanism of acid-base catalysis.

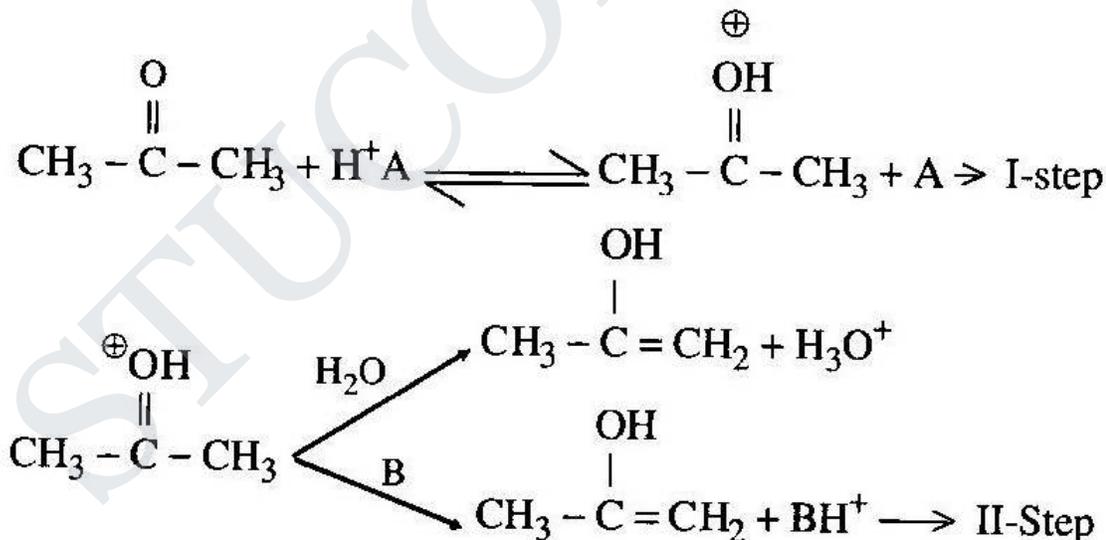
3.8.1 Acid catalysis

I-Step Involves addition of H^+ ions to the substrate forms intermediate complex.

II-Step Involves removal of proton from the intermediate complex using water (or) base.

Example

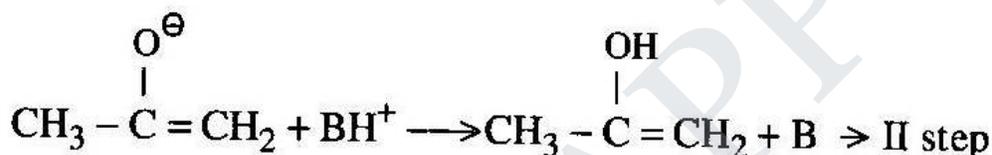
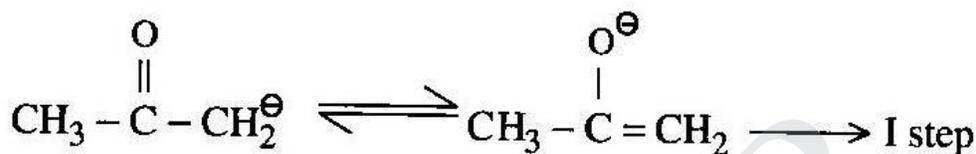
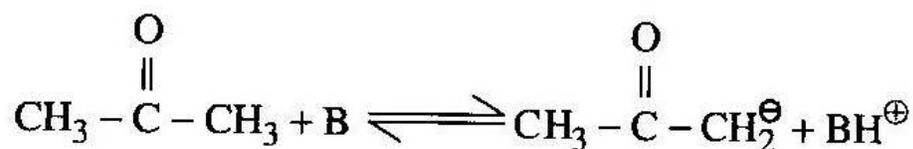
Keto-enol tautomerism of acetone



3.8.2 Base catalysis

I-Step Involves removal of H^+ ions from the reactant to form an intermediate complex.

II-Step Involves addition of proton to the intermediate complex.

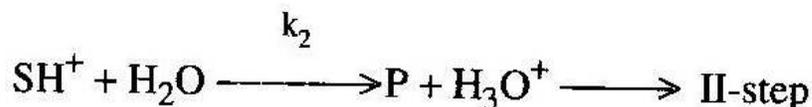
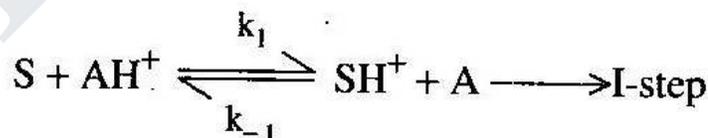
Example**3.9 KINETICS OF ACID-BASE CATALYSIS**

The kinetics of acid-base catalysis can be illustrated by considering the two types of mechanisms.

1. First mechanism

Assume that the I-step involves transfer of H^+ ions from an acid AH^+ to the substrate S.

Then the II-step involves the reaction of the acid form of the substrate with water to form the product P.



Applying steady state approximation to the intermediate $[\text{SH}^+]$

$$\frac{d[\text{SH}^+]}{dt} = 0 = k_1 [\text{S}] [\text{AH}^+] - k_{-1} [\text{A}] [\text{SH}^+] - k_2 [\text{SH}^+] \quad \dots (1)$$

Since the reactions are conducted with very dilute solutions, the concentration of H_2O remains almost constant. So the term $[H_2O]$ is not included in the above equation (1).

Solving for $[SH^+]$, the equation (1) becomes

$$k_1 [S] [AH^+] = k_{-1} [A] [SH^+] + k_2 [SH^+]$$

$$[SH^+] = \frac{k_1 [S] [AH^+]}{k_{-1} [A] + k_2} \quad \dots (2)$$

The rate of formation of product is given by

$$\frac{d[P]}{dt} = k_2 [SH^+] \quad \dots (3)$$

Substituting (2) in (3) we get

$$r = \frac{d[P]}{dt} = \frac{k_2 k_1 [S] [AH^+]}{k_{-1} [A] + k_2} \quad \dots (4)$$

Two important cases

It follows two important cases

Case (i) When $k_2 \gg k_{-1} [A]$, $k_{-1} [A]$ is negligible, so the above equation (4) becomes

$$r = \frac{k_2 k_1 [S] [AH^+]}{k_2}$$

$$r = k_1 [S] [AH^+] \quad \dots (5)$$

In this case the reaction is general acid catalysed.

Case (ii) When $k_{-1} [A] \gg k_2$, k_2 is negligible, the equation (4) becomes

$$r = \frac{k_2 k_1 [S] [AH^+]}{k_{-1} [A]} \quad \dots (6)$$

The ionisation constant of the acid AH^+ is



$$\therefore K = \frac{[H^+] [A]}{[AH^+]}$$

$$[A] = \frac{K [AH^+]}{[H^+]} \quad \dots (7)$$

Equation (7) is substituted in (6)

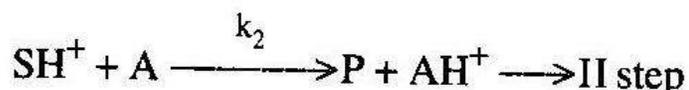
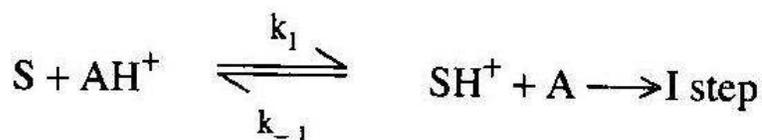
$$r = \frac{k_2 k_1 [S] [AH^+]}{k_{-1} \frac{K [AH^+]}{[H^+]}}$$

$$r = \frac{k_1 k_2 [S] [H^+]}{k_{-1} K} \quad \dots (8)$$

In this case the reaction is specifically hydrogen - ion catalyzed, because the equation contains $[H^+]$.

2. Second mechanism

Assume that in the II step, the acid form of the substrate reacts with a base A instead of the water to form product P.



Applying steady state approximation for $[SH^+]$, as before, we have

$$\frac{d[SH^+]}{dt} = 0 = k_1 [S] [AH^+] - k_{-1} [SH^+] [A] - k_2 [SH^+] [A] \quad \dots (1)$$

Solving for $[SH^+]$, the equation (1) becomes

$$[SH^+] = \frac{k_1 [S] [AH^+]}{(k_{-1} + k_2) [A]} \quad \dots (2)$$

\therefore The rate of formation of product is given by

$$r = \frac{d[P]}{dt} = k_2 [SH^+] [A] = \frac{k_1 k_2 [S] [AH^+]}{k_{-1} + k_2} \quad \dots (3)$$

$$r = \frac{k_1 k_2 [S] [AH^+]}{k_{-1} + k_2}$$

This reaction is general acid catalyzed.

3.10 APPLICATIONS OF CATALYSIS

3.10.1 General Applications

1. Catalysis impacts the environment by increasing the efficiency of industrial processes.
2. Many fine chemicals are prepared by using catalysts.
3. **Shape selective catalysis:** The reaction that depends on the pore structure of the catalyst and the size of the reactant and product molecules is called shape selective catalysis.
4. Zeolites are used as catalysts in petrochemical industries for cracking of hydrocarbons.
5. Petroleum refining uses lot of catalysts for alkylation, catalytic cracking, etc.,
6. Fuel cells depend on catalysts.

7. Hydrogenation of oil can be done by using nickel catalysts.
8. Catalytic heaters generate flameless heat from a supply fuel.
9. Green chemistry in catalysis.

3.10.2 Catalytic converter

A catalytic converter is a device used to reduce the emissions coming out from an IC engine. If enough oxygen is not available to oxidise the carbon fuel completely into carbon dioxide and water, toxic byproducts are produced. Catalytic converters are used in the exhaust systems to provide a site for the oxidation and reduction of toxic byproducts to less hazardous products like CO_2 , water vapour and nitrogen gas.

Construction

A catalytic converter is a simple device that uses basic redox reactions to reduce the pollutants coming out from the exhaust gas. Catalytic converter is composed of a metal housing with a ceramic honey comb like interior with insulating layers. This honey comb interior has thin wall channels that are coated with a wash coat of aluminium oxide. This coating

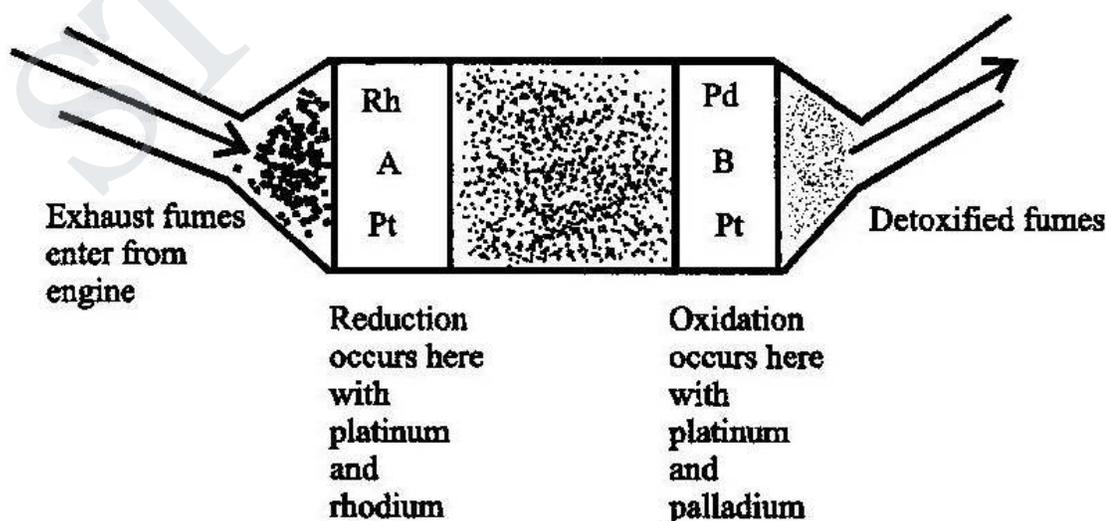


Fig. 3.4 Basic catalytic converter

is porous and contains precious metals such as platinum, rhodium and palladium.

Working

The exhaust fumes are first allowed to enter into the compartment A, where the redusable impurities are reduced. Then the remaining gases are allowed to pass through the compartment B, where all the oxidisable impurities are oxidised. Thus, the outgoing fumes contains no toxic by products.

Functions of catalytic converter

The followings are some important functions of the catalytic converter.

1. Reduction of nitrogen oxides into elemental nitrogen and oxygen.



2. Oxidation of CO into CO₂
3. Oxidation of hydrocarbons into CO₂ and H₂O

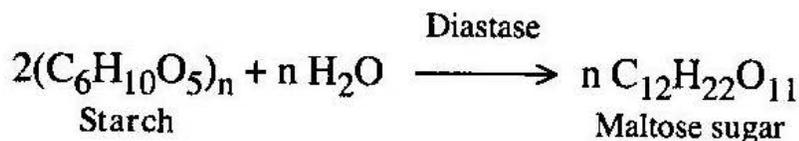
3.11 ENZYME CATALYSIS (OR) CATALYSIS BY BIOLOGICAL CATALYST

Enzymes (or) Biological catalyst are complex organic substances of high molecular weight proteins derived from living organisms. The catalysis brought about by enzymes are known as Enzyme catalysis. Each enzyme can catalyse a specific reaction.

3.11.1 Examples for Enzyme Catalysis

1. Conversion of Starch into Maltose

The enzyme diastase produced in the barley seeds converts starch into maltose sugar.

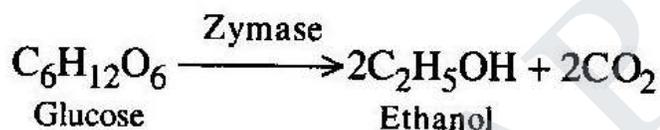


2. Inversion of Cane Sugar

The enzyme **invertase** present in yeast converts cane sugar into glucose and fructose.

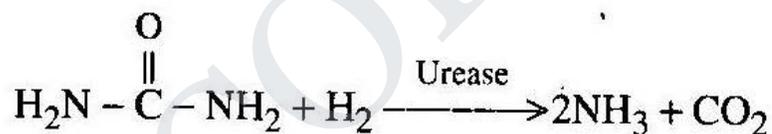
3. Conversion of Glucose into Ethanol

The enzyme **zymase** present in yeast converts glucose into ethanol.



4. Hydrolysis of Urea

The enzyme **urease** present in soyabean converts urea into ammonia.



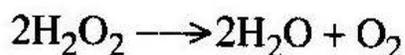
3.11.2 Characteristics of Enzyme Catalysis

1. Enzymes are Most Efficient Catalysts

Enzyme catalysed reactions proceed at high rates in comparison to those catalysed by inorganic substances. Like inorganic catalysts, enzymes also lowers the activation energy of a reaction.

Example

The activation energy of the decomposition of hydrogen peroxide.



Activation energy without catalyst = 18 k.cal/mole.

Activation energy with colloidal platinum = 11.7 k.cal/mole.

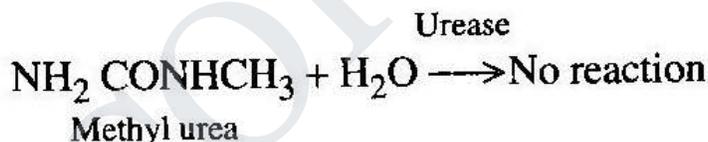
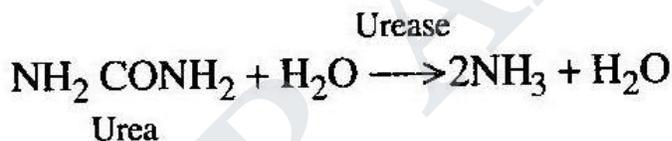
Activation energy with enzyme catalyst > 2 k.cal/mole.

2. Enzyme Catalysed Reactions are More Specific

An enzyme as a rule catalyses just only one reaction with a particular substance.

Example

An enzyme urease catalyses the hydrolysis of urea and no other amide, not even methyl urea.



3. The Rate of Enzyme Catalysed Reactions is Maximum at the Optimum Temperature

The rate of an enzyme catalysed reaction is increased with the rise of temperature only upto a certain temperature. Thereafter the enzyme is denatured and hence its catalytic activity is lost. Thus the temperature at which the reaction rate is maximum is called the optimum temperature.

Example

The optimum temperature of enzyme reactions occurring in human body is 37°C. At higher temperature, all physiological reactions will cease due to loss of activity of enzyme. This is one reason why high body temperature (fever) is very dangerous.

4. Rate of Enzyme Catalysed Reactions is Maximum at the Optimum pH

The rate of enzyme catalysed reaction passes through a maximum at a particular pH, known as the optimum pH. The rate decreases below and above the optimum pH.

Example

Many enzymes of the body function best at pH of about 7.4 (the pH of the blood and body fluids).

5. Catalytic Activity of the Enzymes is Enhanced by Activators (or) Co-enzymes

If activators (metal ions Na^+ , Mn^{2+} , Co^{2+} , Cu^{2+} , etc) or co-enzymes (a small nonprotein) are added to enzymes, they get weakly bonded to enzyme and promote their catalytic activity.

Example

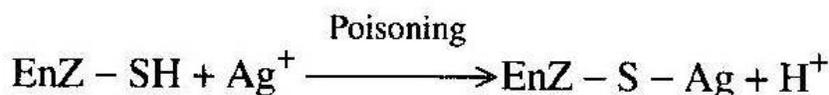
Addition of NaCl (Na^+) makes amylase catalytically very active.

6. Enzymes are Poisoned by Other Substance

The catalytic activity of an enzyme is reduced (inhibited) or completely destroyed (poisoned) by addition of other substances.

Example

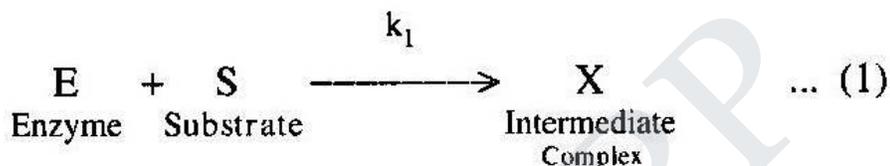
Heavy metal ions (Ag^+ , Hg^{2+}) react with the $-\text{SH}$ group of the enzyme and poison it.



3.12 MICHAELIS-MENTEN EQUATION (ENZYME KINETICS)

Michaelis and Menten proposed the following mechanism for enzyme-catalysed reaction.

Let enzyme E react with the substrate S. The first stage is the formation of an intermediate complex X.



The intermediate complex may either dissociate back into E and S (or) may give rise to the final product P. These two possibilities are represented by the following equations.



k_1, k_2, k_3 are rate constant for the respective reactions.

The rate of formation of the complex X is given by the following equation.

$$\begin{aligned} \frac{d[\text{X}]}{dt} &= k_1 [\text{E}] [\text{S}] - k_2 [\text{X}] - k_3 [\text{X}] \\ &= k_1 [\text{E}] [\text{S}] - (k_2 + k_3) [\text{X}] \quad \dots (4) \end{aligned}$$

where,

$[\text{E}], [\text{S}]$ and $[\text{X}] =$ Molar concentrations of the enzyme, substrate and the complex respectively.

The rate of formation of the product P is given by the following equation

$$\frac{d[P]}{dt} = k_3 [X] \quad \dots (5)$$

Since, $[E_0] = [E] + [X]$, the equation (4) may also be written as

$$\frac{d[X]}{dt} = k_1 \{ [E_0] - [X] \} [S] - (k_2 + k_3) [X]$$

$$\left[\because [E] = [E_0] - [X] \right] \quad \dots (6)$$

where,

$[E]$ = molar concentration of the unreacted enzyme

$[X]$ = concentration of the enzyme present in the complex

$[E_0]$ = total concentration of the enzyme

The intermediate complex is unstable, it decomposes instantaneously, so

$$\frac{d[X]}{dt} = 0 \quad \dots (7)$$

This state is termed as the stationary state.

At the stationary state, equation (6) may be written as

$$k_1 \{ [E_0] - [X] \} [S] = (k_2 + k_3) [X] \quad \dots (8)$$

$$k_1 [E_0] [S] - k_1 [X] [S] = (k_2 + k_3) [X]$$

$$k_1 [E_0] [S] = k_1 [X] [S] + (k_2 + k_3) [X]$$

$$k_1 [E_0] [S] = \{ k_1 [S] + (k_2 + k_3) \} [X]$$

$$\text{(or)} \quad [X] = \frac{k_1 [E_0] [S]}{k_1 [S] + k_2 + k_3} \quad \dots (9)$$

Dividing the equation (9) by $k_1 [S]$, it becomes

$$[X] = \frac{[E_0]}{1 + \frac{k_2 + k_3}{k_1 [S]}} \quad \dots (10)$$

Substituting this value of $[X]$ in equation (5), we get

$$\frac{d[P]}{dt} = \frac{k_3 [E_0]}{1 + \frac{k_2 + k_3}{k_1 [S]}} \quad \dots (11)$$

$$\frac{k_2 + k_3}{k_1} = K_m = \text{Michaelis constant}$$

$$\frac{d[P]}{dt} = \frac{k_3 [E_0]}{1 + K_m/[S]} \quad \dots (12)$$

$$\text{or } r = \frac{k_3 [E_0] [S]}{[S] + K_m}$$

This equation (12) is known as Michaelis-Menten equation. It follows two important cases.

Two important cases

Case (i) At lower concentration

When the concentration of substrate is less than K_m , it may be neglected in the denominator. i.e., $[S] \ll K_m$ then,

$$\frac{d[P]}{dt} = \frac{k_3 [E_0] [S]}{K_m} \quad \dots (13)$$

So the rate of the reaction is first order with respect to the substrate and enzyme.

Case (ii) At higher concentration

When the concentration of substrate is higher than K_m i.e., $[S] \gg K_m$, then

$$\frac{d[P]}{dt} = \frac{k_3 [E_0] [S]}{[S]}$$

$$\frac{d[P]}{dt} = k_3 [E_0] \quad \dots (14)$$

So the rate of the reactions is zero order with respect to substrate.

Effect of substrate concentration on the rate

From the above two cases it is clear that the reaction rate of an enzyme - catalysed reaction gets changed from first order to zero order with increase in the substrate concentration. This is because, each enzyme molecule has one or more "active sites" at which the substrate molecule must be bound in order that catalytic action may occur.

(i) *When the substrate concentration is low*, most of these active sites remain unoccupied at any time. As the substrate concentration is increased, the number of active sites which are occupied increases and hence the reaction rate gets increased.

(ii) *But, when the substrate concentration is high*, almost all the active sites get occupied at any time. At this stage, any further increase in the concentration of substrate will not increase in the formation of enzyme-substrate complex and the kinetics of the reaction passes over to zero order.

Significance of Michaelis-Menten equation

The Michaelis-Menten equation can be simplified by assuming that all the enzymes have reacted with the high substrate concentration. In such a case, the rate will be

maximum and no free enzyme will remain, so that $[E_0] = [X]$

∴ From equation (5) we have

$$\frac{d[P]}{dt} = v_{\max} = k_3 [E_0] \quad \dots (15)$$

where,

v_{\max} = maximum rate

The Michaelis-Menten equation (12) can now be written as

$$r = \frac{v_{\max} [S]}{K_m + [S]} \quad \left[\because v_{\max} = K_3 [E_0] \right]$$

If $K_m = [S]$, then

$$r = \frac{v_{\max} [S]}{[S] + [S]} = \frac{v_{\max} [S]}{2 [S]}$$

$$\text{(or) } r = 1/2 v_{\max} \quad \dots (16)$$

Thus, **Michaelis constant** is defined as, "equal to the concentration of substrate $[S]$ at which the rate of formation of product is half the maximum rate obtained at high concentration of the substrate $[S]$."

Determination of Michaelis-Menten constant (K_m)

Lineweaver-Burk equation (Reciprocal of Michaelis-Menten equation) is used to calculate Michaelis constant.

$$\frac{1}{r} = \frac{1}{v_{\max}} + \frac{K_m}{v_{\max} [S]}$$

A plot of $\frac{1}{r}$ Vs $\frac{1}{[S]}$ gives a straight line with intercept $\frac{1}{v_{\max}}$ and slope K_m/v_{\max} . Thus Michaelis-Menten's constant can be determined.

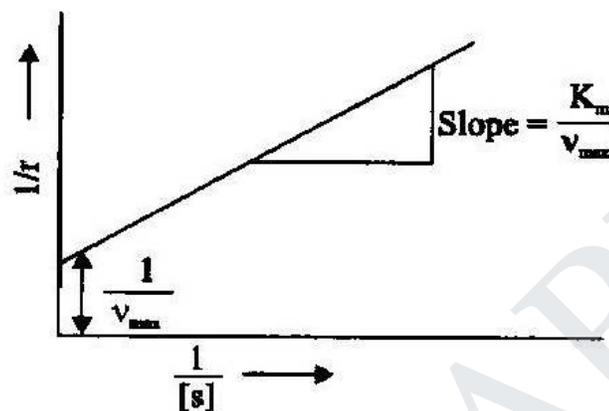


Fig. 3.5 A plot of $\frac{1}{r}$ Vs $\frac{1}{[S]}$

turn over number (k_3)

The constant k_3 present in the equation (13) is known as turnover number. It is defined as *“the number of molecules inverted into products in unit time by one molecule of enzyme”*.

3.13 FACTORS AFFECTING ENZYME CATALYSIS

pH

Many enzymes perform well in the neutral pH range and are denatured at either an extremely high or low pH.

Temperature

Generally, enzyme reactions tend to go faster with increasing temperature.

Salt concentration

If the salt concentration is very low, the charged amino acid chains of the enzyme molecules attract each other results in denaturation of enzyme.

On the other hand, if the salt concentration is very high, interaction of the charged groups will be blocked and the enzyme will precipitate.

Activators and Inhibitors

Many molecules may interact with an enzyme to increase the rate of reaction or to decrease the rate of the reaction. These molecules can regulate the enzyme action. Thus the rate of enzyme catalyzed reaction depends on the nature of activators and inhibitors.

UNIT III –ALLOYS AND PHASE RULE**3.1 INTRODUCTION**

Generally metals are insoluble in ordinary solvents like water, alcohol. A metal can dissolve in another metal in molten state forming a homogeneous liquid mixture. On cooling solidifies to a solid mixture called an alloy. Most of the metals can mix up in all proportions, e.g. tin and lead mix up in all proportions forming alloys. Alloys are formed not only by metals among themselves, but also by metal and non-metal. So, it is clear that an alloy contains at least one metal.

DEFINITION:

“Homogeneous solid solution of two or more different elements, one of which at least is essentially a metal”. Alloys containing Hg as a constituent element are called **amalgams**.

3.2 PROPERTIES OF ALLOYS

- Alloys are harder, less malleable and possess lower melting points than their component metals.
- Alloys possess low electrical conductivity.
- Alloys resist corrosion and the action of acids.

3.3 IMPORTANCE (OR) NEED (OR) PURPOSE OF MAKING ALLOYS

Generally pure metals possess some useful properties such as high melting point, high densities, malleability and ductility, good thermal and electrical conductivity. The properties of a given metal can be improved by alloying it with some other metal or non-metal.

(1) To increase the hardness of the metal

Generally pure metals are soft, but their alloys are hard.

Examples:

- (i) Gold and silver are soft metals; they are alloyed with copper to make them hard.
- (ii) Addition of 0.5% arsenic makes lead so hard and used for making bullets.
- (iii) Addition of 0.15-2% carbon to iron for getting steel, hardness is improved to it.

(2) To lower the melting points of the metal

Alloying makes the metal easily fusible.

Example:

Wood's metal (an alloy of lead, bismuth, tin and cadmium) melts at 60.5° C, which is far below the melting points of any of these constituent metals.

(3) To resist the corrosion of the metal

Metals, in pure form, are quite reactive and easily corroded by surrounding, thereby their life is reduced. If a metal is alloyed, it resists corrosion.

Example:

Pure iron gets rusted, but when it is alloyed with carbon or chromium (stainless steel), resists corrosion.

(4) To modify chemical activity of the metal

Chemical activity of the metal can be increased or decreased by alloying.

Example:

Sodium amalgam is less active than sodium, but aluminium amalgam is more active than aluminium.

(5) To modify the colour of the metal

The dull coloured metals are improved by alloying with metals.

Example:

Brass, an alloy of copper (red) and zinc (silver-white), is white in colour.

(6) To Get Good Casting of Metal

Some metals expand on solidification but are soft and brittle. The addition of other metals produce alloys which are hard, fusible and expand on solidification and thus give good casting.

Example:

An alloy of lead with 5% tin and 2% antimony is used for casting printing type, due to its good casting property.

3.4 FUNCTIONS (OR) EFFECT OF ALLOYING ELEMENTS

Addition of small amounts of certain metals, such as Ni, Cr, Mo, Mn, Si, V and Al imparts some special properties like hardness, tensile strength, resistance to corrosion and coefficient of expansion on steel. Such products are known as special steels or alloy steels. Some important alloying elements and their functions are given in Table below.

Element	Effect on properties	Uses of alloys
1. Nickel	(i) Fine grains are produced. (ii) Co-efficient of expansion decreases and corrosion resistance increases.	For making balance wheels.
2. Chromium	Tensile strength, depth hardening and resistance to corrosion are increased.	For making surgical instruments, cutlery, connecting rods, etc.
3. Manganese	(i) Hot shortness is removed. (ii) Resistance to abrasion is increased.	For making grinding wheels, steering spindles and rails.
4. Vanadium	(i) Reversible stresses are produced. (ii) Tensile strength and resistance to abrasion are increased.	For making axless, crank pins, heavy locomotive forgings, piston rods., etc.

5. Molybdenum	Cutting hardness at high temperature is increased, because phases are stabilized.	For making high speed tools.
6. Tungsten	(i) Grain structure is refined. (ii) Magnetic retentivity as well as cutting hardness are increased.	For making cutting tools, permanent magnets, etc.
7. Nickel and Chromium	Corrosion resistance and tensile strength are increased.	For making stainless steel.

3.4.1 HEAT TREATMENT OF ALLOYS (STEEL)

Heat treatment is defined as, “*the process of heating and cooling of solid steel article under carefully controlled conditions*”. During heat treatment certain physical properties are altered without altering its chemical composition.

Objectives (or) Purpose of Heat treatment:

Heat treatment causes

- (i) Improvement in magnetic and electrical properties.
- (ii) Refinement of grain structure.
- (iii) Removal of the imprisoned trapped gases.
- (iv) Removal of internal stresses.
- (v) Improves fatigue and corrosion resistance.

3.4.2 TYPES OF HEAT TREATMENT OF ALLOYS (STEEL)

1. Annealing
2. Hardening
3. Tempering
4. Normalizing
5. Carburizing
6. Nitriding

(1) ANNEALING

Annealing means softening. This is done by heating the metal to high temperature, followed by slow cooling in a furnace

Purpose of annealing:

- (i) It increases the machinability.
- (ii) It also removes the imprisoned gases.

Types of Annealing:

- (i) Low temperature annealing (or) process annealing.
- (ii) High temperature annealing (or) full annealing.

(i) Low temperature annealing (or) process annealing:

It involves in heating steel to a temperature below the lower critical temperature followed by slow cooling.

Purpose:

- (i) It improves machinability by relieving the internal stresses or internal strains.
- (ii) It increases ductility and shock - resistance.
- (iii) It reduces hardness.

(ii) High temperature annealing (or) full - annealing

It involves in heating steel to a temperature about 30 to 50° C above the higher critical temperature and holding it at that temperature for sufficient time to allow the internal changes to take place and then cooled to room temperature.

The approximate annealing temperatures of various grades of carbon steel are:

1. mild steel = 840 – 870° C
2. medium-carbon steel = 780 – 840° C
3. high-carbon steel = 760 – 780° C

Purpose:

- (i) It increases the ductility and machinability.
- (ii) It makes the steel softer, together with an appreciable increase in its toughness.

(2) HARDENING (OR) QUENCHING

It is the process of heating steel beyond the critical temperature and then suddenly cooling it either in oil or brine-water or some other fluid. Hardening increases the hardness of steel. The faster the rate of cooling harder will be the steel produced. Medium and high-carbon steels can be hardened, but low-carbon steels cannot be hardened.

Purpose:

- (i) It increases its resistance to wear, ability to cut other metals and strength, but steel becomes extra brittle.
- (ii) It increases abrasion-resistance, so that it can be used for making cutting tools.

(3) TEMPERING

It is the process of heating the already hardened steel to a temperature lower than its own hardening temperature and then cooling it slowly. In tempering, the temperature to which

hardened steel is re-heated is of great significance and controls the development of the final properties. Thus,

- for retaining strength and hardness, reheating temperature should not exceed 400°C.
- for developing better ductility and toughness, reheating temperature should be within 400 – 600° C.

Purpose:

- (i) It removes any stress and strains that might have developed during quenching.
- (ii) It reduces the brittleness and also some hardness but toughness and ductility are simultaneously increased.
- (iii) Cutting-tools like blades, cutters, tool-bites always require tempering.

(4) NORMALISING

It is the process of heating steel to a definite temperature (above its higher critical temperature) and allowing it to cool gradually in air. A normalised steel will not be as soft as an annealed job of the same material. Also normalising takes much lesser time than annealing process.

Purpose:

- (i) It recovers the homogeneity of the steel structure.
- (ii) It refines grains. It removes the internal stresses.
- (iii) It increases the toughness.
- (iv) Normalised steel is suitable for the use in engineering works.

(5) CARBURIZING

The mild steel article is taken in a cast iron box containing small pieces of charcoal (carbon material). It is then heated to about 900 to 950°C and allowed to keep it as such for sufficient time, so that the carbon is absorbed to required depth. The article is then allowed to cool slowly within the iron box itself. The outer skin of the article is converted into high-carbon steel containing about 0.8 to 1.2% carbon.

Purpose: To produce hard-wearing surface on steel article.

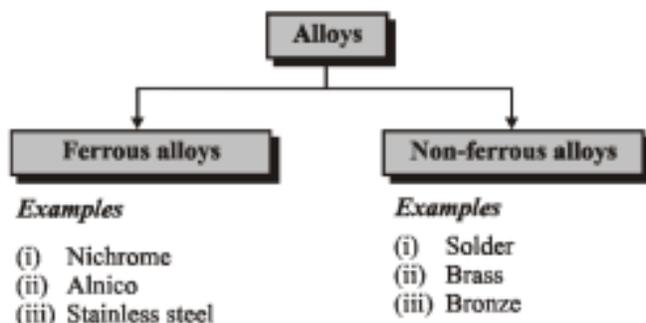
(6) NITRIDING

Nitriding is the process of heating the metal alloy in presence of ammonia at a temperature to about 550°C. The nitrogen (obtained by the dissociation of ammonia) combines with the surface of the alloy to form hard nitride.

Purpose: To get super-hard surface.

3.5 CLASSIFICATION (OR) TYPES OF ALLOYS

Based on the type of base metals, alloys are classified into two types:



3.6 FERROUS ALLOYS

Ferrous alloys are the type of steels in which the elements like Al, B, Cr, Co, Cu, Mn are present in sufficient quantities, in addition to carbon and iron, to improve the properties of steels.

3.6.1 PROPERTIES OF FERROUS ALLOYS

- (i) It possesses high yield point and high strength.
- (ii) It possesses sufficient formability, ductility and weld ability.
- (iii) They are sufficiently corrosion and abrasion resistant.
- (iv) Distortion and cracking are less.
- (v) High temperature strength is greater.

3.7 IMPORTANT FERROUS ALLOYS

3.7.1 NICHROME

Nichrome is an alloy of nickel and chromium. Its composition is:

Metal	Percentage
Nickel	60%
Chromium	12%
Iron	26%
Manganese	2%

PROPERTIES:

- (i) It shows good resistance to oxidation and heat.
- (ii) Steels containing 16 to 20% chromium with low carbon content (0.06 to 0.15%) possess oxidation resistance upto 900°C.
- (iii) Steel containing 18% nickel, with small amounts of chromium can withstand temperature above 900°C.
- (iv) It possesses high melting point.
- (v) It can withstand heat upto 1000 to 1100°C.

(vi) It possesses high electrical resistance.

USES:

- (i) It is widely used for making resistance coils, heating elements in stoves.
- (ii) It is also used in electric irons and other household electrical appliances.
- (iii) It is used in making parts of boilers, gas-turbines, aero-engine valves, retorts and annealing boxes.
- (iv) It is also used in making other machineries or equipments exposed to very high temperatures.

3.7.2 STAINLESS STEELS (OR) CORROSION RESISTANT STEELS

These are alloy steels containing chromium together with other elements such as nickel, molybdenum, etc. Chromium is effective if its content is 16% or more. The carbon content in stainless steel ranges from 0.3 to 1.5%.

Stainless steel resists corrosion by atmospheric gases and also by other chemicals. Protection against corrosion is mainly due to the formation of dense, non-porous, tough film of chromium oxide at the surface of metal. If this film cracks, it gets automatically healed-up by atmospheric oxygen.

TYPES OF STAINLESS STEEL:

- (1) Heat treatable stainless steels.
- (2) Non heat treatable stainless steels.

(a) HEAT TREATABLE STAINLESS STEEL:**COMPOSITION:**

These steels mainly contain upto 1.2% of carbon and less than 12-16% of chromium.

PROPERTIES:

Heat-treatable stainless steels are magnetic, tough and can be worked in cold condition.

USES:

- (i) They can be used upto 800°C.
- (ii) They are very good resistant towards weather and water.
- (iii) They are used in making surgical instruments, scissors, blades, etc.,

(b) NON-HEAT TREATABLE STAINLESS STEEL:

These steels possess less strength at high temperature. They are more resistant to corrosion.

TYPES OF NON-HEAT TREATABLE STAINLESS STEEL:

According to their composition, they are of two types

- (i) Magnetic type
- (ii) Non-Magnetic type

(I) MAGNETIC TYPE**COMPOSITION:**

It contains 12 - 22% of chromium and 0.35% of carbon.

PROPERTIES:

1. It can be rolled and machined by the use of specially designed tools.
2. It resists corrosion better than heat-treatable stainless steel.

USES:

It is used in making chemical equipment and automobile parts.

(II) NON-MAGNETIC TYPE**COMPOSITION:**

It contains 18 - 26% of chromium, 8 - 21% of nickel and 0.15% of carbon. Total percentage of Cr and Ni in such steel is more than 23%.

18/8 Stainless Steel

If it contains 18% Cr and 8% Ni, it is referred to as 18/8 stainless steel. It is the most widely used stainless steel.

PROPERTIES:

1. It exhibits maximum resistance to corrosion
2. Corrosion resistance of which can be further increased by adding a little quantity of molybdenum.

USES:

It is used in making household utensils, sinks, dental and surgical instruments.

3.8 INTRODUCTION

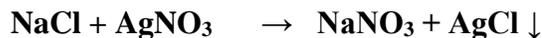
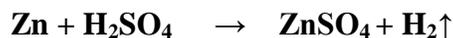
System is a part of the universe which is focused for chemical study.

Surroundings are the rest of the system.

Boundary is the real or imaginary surface that separates the system and surroundings.

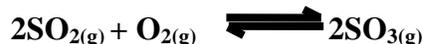
TYPES OF CHEMICAL REACTIONS:

IRREVERSIBLE REACTION: These types of reactions are represented by a single forward arrow.



REVERSIBLE REACTION: These types of reactions are represented by two arrows in opposite direction.

(a) Homogeneous reversible reaction:



(b) Heterogeneous reversible reaction:



- In reversible reaction when the rate of forward reaction becomes equal to the rate of backward reaction, the equilibrium state is reached.
- The equilibrium is said to be **homogeneous** when all the reactants and products are in the same states.
- The equilibrium is said to be **heterogeneous** when all the reactants and products are in the different states.
- The homogeneous reversible reactions can be studied using the law of mass action proposed by Guldberg and Waage in 1864.
- The behavior of heterogeneous reversible reactions can be studied by phase rule given by Willard Gibbs (1874).

3.8.2 INTRODUCTION TO PHASE RULE:

“Phase rule predicts quantitatively by means of a diagram the effect of pressure, temperature and concentration on the equilibrium existing between different phases of heterogeneous or poly-phase systems.”

GIBBS PHASE RULE

It states that “when the equilibrium between any number of phases is not influenced by gravity (or) electricity (or) magnetic forces but is influenced by pressure, temperature and concentration, then the number of degrees of freedom (F) of the system is related to the number of components (C) and number of phases by the phase rule equation

$$F = C - P + 2$$

Where,

P is the number of phases present in equilibrium

C is the number of components of the system

F is the number of degrees of freedom for the equilibrium and

2 represents the variables T & P.

3.8.3 EXPLANATION OF IMPORTANT TERMS INVOLVED IN PHASE RULE:

➤ PHASE(P)

Definition: “Any homogeneous physically distinct and mechanically separable part of a system which is separated from other parts of the system by definite boundaries”.

A phase is a form of matter that has same physical and chemical properties throughout.

❖ GASEOUS PHASE

A pure gas or a mixture of gases constitutes a single phase.

All gases are completely miscible and there is no boundary between one gas and the other i.e., all the gases are freely mixed with each other to form a homogeneous mixture.

Examples:

- A mixture of N₂, O₂, CO₂, and water vapour - single phase
- Pure O₂ gas – single phase
- Mixture of CO and N₂ – single phase

❖ LIQUID PHASE

The number of liquid phases depends on the number of liquids present and their miscibilities.

- If two or more liquids are completely miscible with each other, then they will form a one liquid phase.

Example: A solution of ethanol & water.

- A mixture of two immiscible liquids on standing forms two separate layers.

Example: A mixture of benzene & water.

❖ AQUEOUS SOLUTIONS

An aqueous solution of a solid substance in a solvent forms a single phase only.

Example: Sugar or NaCl solution

❖ SOLID PHASE

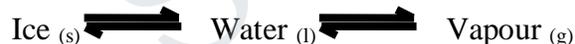
Each solid constitutes a separate phase.

Example 1:



Two solid phases, one gaseous phase- three phase system

Example 2:



❖ MIXTURE OF SOLIDS:

A phase must have throughout the same physical and chemical properties.

Ordinary sulphur occurs in nature as a mixture of rhombic and monoclinic sulphur. These allotropes of sulphur possess the same chemical species but differ in their physical properties.

Thus a **mixture of two allotropes is a two phase system**. If a substance exists in more than one crystalline form, each form is considered as a distinct phase.

➤ COMPONENT (C)

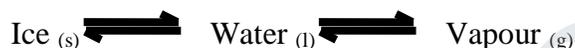
The number of components of a system at equilibrium is “the smallest number of independent variable chemical constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation”.

To understand the above definition and to use it for finding the number of components of a system:

- The chemical formula representing the composition of a phase is written on LHS.
- The rest of the chemical constituents existing independently in the system are represented by chemical formulas are placed on RHS.
- The quantities of constituents on RHS can be made minus or zero to get at the composition of the phase on LHS.
- For expressing the chemical composition of each phase in the system, positive, negative and zero values of the constituents may be used.

Example:

(1) **Water system** – three phases



The chemical composition of all the three phases is expressed in terms of one chemical individual H₂O, but it is in different physical form. Hence it is a **one** component system.

(2) **Sulphur system** - four phases namely rhombic, monoclinic, liquid and vapour.



The chemical composition of each phase can be expressed in terms of sulphur only.

Hence it is a **one** component system.

(3) **Mixture of gases:** A mixture of O₂ & N₂ constitutes a single phase but it is a two component system. Its composition can be expressed by two chemical substances O₂ and N₂.



The number of components of a gaseous mixture is given by the number of individual gases present.

(4) **Aqueous Solution:** A solution of NaCl in water is a single phase system. Its composition can be expressed in terms of two chemical individuals NaCl & H₂O.



An aqueous solution of any solute in a suitable solvent is a **two** component system.

(5) **Thermal Decomposition of CaCO₃:**



The system consists of **three phases**. It is a **two** component system.

Reason: The chemical composition of all the three phases can be expressed in terms of at least any two of the three independent variable constituents CaCO_3 , CaO and CO_2 in equilibrium.

When CaCO_3 & CaO are chosen as the two components, then the composition of three different phases can be represented as follows:

Phase	Components
CaCO_3	$= \text{CaCO}_3 + \text{OCaO}$
CaO	$= \text{OCaCO}_3 + \text{CaO}$
CO_2	$= \text{CaCO}_3 - \text{CaO}$



$$P = 3 \text{ and } C = 2$$

The chemical composition of each phase can be represented by CuSO_4 and H_2O . Hence it is a two component system.

(7) Dissociation of ammonium chloride:



$$P = 2 \text{ and } C = 1$$

The system has two phases. The composition of both the phases can be represented by the same chemical compound, NH_4Cl when NH_3 & HCl are present in the same proportion as they are present in the solid NH_4Cl .

Since the phase rule does not distinguish between a chemical compound (NH_4Cl) and its constituents ($\text{NH}_3 + \text{HCl}$) present in the same proportion in homogeneous mixture, this system is considered as one component system.

The composition of both the phases can be expressed in terms of the same chemical individual NH_4Cl .

Phase	Components
Solid	$= \text{NH}_4\text{Cl}$
Gaseous	$= x \text{NH}_3 + x \text{HCl} \text{ (or) } x \text{NH}_4\text{Cl}$

If the vapour phase of the system does not have the same composition as they are present in the solid, the system will be no longer one component. Suppose if we introduce excess of NH_3 or HCl it will become a two component system.

Phase	Components
$\text{NH}_4\text{Cl} (s)$	$= x \text{NH}_4\text{Cl} + 0 \text{HCl}$
Gaseous phase	$= x \text{NH}_4\text{Cl} + y \text{HCl}$
	$= x \text{NH}_3 + x \text{HCl} + y \text{HCl}$

(8) Na₂SO₄ – water system:

It is a two component system because the composition of each phase can be expressed in terms of Na₂SO₄ and H₂O.

Phase	Components
Na ₂ SO ₄	= Na ₂ SO ₄ + 0 H ₂ O
Na ₂ SO ₄ .7H ₂ O	= Na ₂ SO ₄ + 7 H ₂ O
Na ₂ SO ₄ .10 H ₂ O	= Na ₂ SO ₄ + 10 H ₂ O
H ₂ O (g)	= 0 Na ₂ SO ₄ + H ₂ O
Na ₂ SO ₄ (l)	= Na ₂ SO ₄ + x H ₂ O

(9) PCl₅(s) ⇌ PCl₃(l) + Cl₂(g)

$$P = 3 \text{ and } C = 2$$

Though there are three molecular species the number of components will be only two. This is because the number of moles or concentration of any two of the three species can be altered and the concentration of the third species will be automatically fixed. It is noted that if the temperature involved is very high all the constituents will be in the gaseous state and then there will be only one component.

➤ DEGREE OF FREEDOM (F)

Definition: “The minimum number of independent variable factors such as temperature, pressure and composition, which must be fixed in order to define the system completely”.

A system having 1, 2, 3 or 0 degrees of freedom is called univariant, bivariant, trivariant and non variant respectively.

Examples:

These three phases will be in equilibrium only at a particular temperature and pressure.

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



$$P = 2 \text{ and } C = 1, F = C - P + 2 = 1 - 2 + 2 = 1 \text{ (Univariant (or) Monovariant).}$$

(3) For a gaseous mixture of N₂ and H₂, we must state both the pressure and temperature.

$$P = 1 \text{ and } C = 2, F = C - P + 2 = 2 - 1 + 2 = 3 \text{ (Trivariant).}$$

(4) For pure gas, the degree of freedom is two.

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

3.9 MERITS OF PHASE RULE

- It is applicable to both physical and chemical equilibria.
- It does not take into account the nature or amount of the substances.

- It indicates that systems having the same number of degrees of freedom behave similarly.
- It helps in studying the behaviour of systems when subjected to changes in temperature, pressure and concentration.
- It predicts whether the number of phases would remain in equilibrium or not if some of the substances have been transformed to a new substance.
- It is applicable to macroscopic system, so it requires no information regarding molecular/micro-structure.
- It is a convenient method of classifying the equilibrium states in terms of phases, components and degrees of freedom.

3.10 LIMITATIONS OF PHASE RULE

- It is applicable only to heterogeneous systems in equilibrium.
- It concentrates mainly on the number of phases rather than their amounts.
- It takes into account only the P, T & C. The influence of other factors such as electrical, magnetic, gravitational forces, etc. is ignored.
- Solid and liquid phases must not be in finely divided state, otherwise deviations occur.
- It assumes that all the phases of the system must be present simultaneously under the same conditions of pressure and temperature.

3.11 PHASE DIAGRAM

Phase diagram is a graphical representation obtained by plotting one degree of freedom against another. A diagram which illustrates the conditions of equilibrium between various phases of a substance is called a **phase diagram**.

3.11.1 TYPES OF PHASE DIAGRAM

P-T DIAGRAM

If the pressure is plotted against temperature, the diagram is called P-T diagram.

P-T diagram is used to explain one component systems.

T- C DIAGRAM

If the temperature is plotted against composition, the diagram is called T-C diagram.

T-C diagram is used to explain two component systems.

3.11.2 USES OF PHASE DIAGRAM

- The phase diagrams are useful in understanding the properties of materials in the heterogeneous equilibrium system.
- It helps in proper understanding of the relative stability of equilibrium between phases.
- From the knowledge of the number of phases and components of the system, phase rule enables one to predict conditions under which a system can remain in equilibrium.

- They help in studying and controlling the various processes such as phase separation, solidification of metals and change of structure during heat treatment like annealing, quenching, tempering, etc.
- It is possible to predict from the phase diagrams whether a eutectic alloy or a solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.

3.12 APPLICATION OF PHASE RULE TO ONE COMPONENT WATER SYSTEM

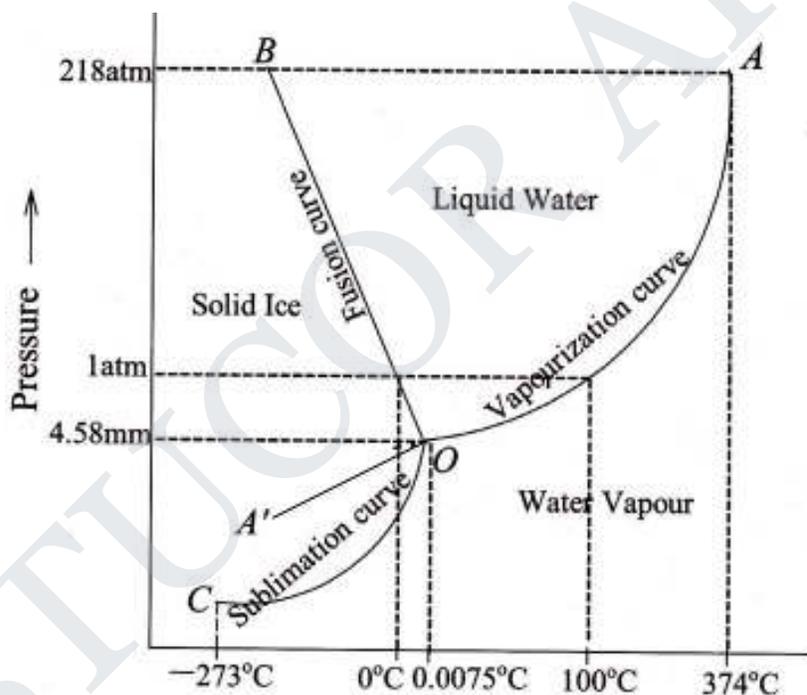
Water exists in three possible phases namely: solid, liquid and vapour. Hence, there can be three forms of equilibria.

Solid \rightleftharpoons Liquid

Liquid \rightleftharpoons Vapour

Solid \rightleftharpoons Vapour

Each of the above equilibrium involves two phases.



SALIENT FEATURES OF THE PHASE DIAGRAM:

- Curves or lines OA, OB, OC and OA'
- Areas AOB, BOC and AOC
- Triple point 'O'

(i) CURVE OA:

- The curve OA is called vapourisation curve.

- It represents the equilibrium between water and water vapour. At any point on the curve the following equilibrium will exist.



- The degree of freedom along the line OA is one, as predicted by the phase rule
 $F = C - P + 2; F = 1 - 2 + 2; F = 1$ (univariant)
- This equilibrium (i.e. line OA) will extend upto the critical temperature (374°C). Beyond the critical temperature the equilibrium will disappear and only water vapour will exist.

(ii) CURVE OB:

- The curve OB is called sublimation curve of ice.
- It represents the equilibrium between ice and water vapour. At any point on the curve the following equilibrium will exist.



- The degree of freedom along the line OB is one, as predicted by the phase rule
 $F = C - P + 2; F = 1 - 2 + 2; F = 1$ (univariant)
- This equilibrium (line OB) will extend upto the absolute zero (-273°C), where no vapour can be present and only ice will exist.

(iii) CURVE OC:

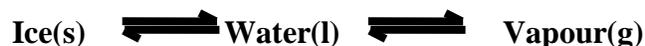
- The curve OC is called melting point curve of ice.
- It represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.



- The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.
- The degree of freedom along the line OC is one, as predicted by the phase rule
 $F = C - P + 2; F = 1 - 2 + 2; F = 1$ (univariant)

(iv) TRIPLE POINT 'O':

- The three curves OA, OB and OC meet at a point 'O', where three phases namely solid, liquid and vapour are simultaneously at equilibrium.
- This point is called triple point, at this point the following equilibrium will exist:



- The degree of freedom of the system is zero, as predicted by the phase rule
 $F = C - P + 2; F = 1 - 3 + 2; F = 0$ (nonvariant)
- Temperature and pressure corresponding to the triple point 'O' are 0.0075°C and 4.58 mm.

(v) CURVE OA' (METASTABLE EQUILIBRIUM):

- The curve OA' is called vapour pressure curve of the super-cool water or metastable equilibrium where the following equilibrium will exist.



- Sometimes water can be cooled below 0°C without the formation of ice, this water is called super-cooled water. Super cooled water is unstable and it can be converted into solid by “seeding” or by slight disturbance.

(vi) AREAS:

- Area AOC, BOC, AOB represents water, ice and vapour respectively. In order to define the system at any point in the areas, it is essential to specify both temperature and pressure.
- The degree of freedom of the system is two, as predicted by the phase rule

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

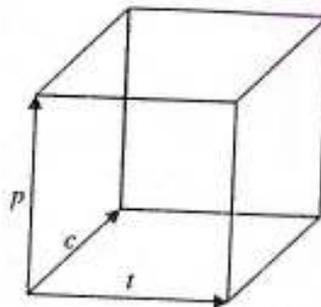
3.13 TWO COMPONENT ALLOY SYSTEM**3.13.1 Reduced Phase rule or Condensed phase rule**

For a two component system,

$$F = C - P + 2 = 2 - P + 2 = 4 - P$$

Since the minimum number of phases in any system is one, the maximum number of degrees of freedom in a two component system is three ($F = 4 - P = 4 - 1 = 3$).

This means that three variables must be specified in order to describe the system. Thus in such a system, in addition to P & T, the composition of one of the components has also to be given. For graphical representation of these variables, three coordinate axes at right angles to each other are required. Therefore the phase diagram obtained would be a three dimensional figure or a solid model, which cannot be represented on a paper.

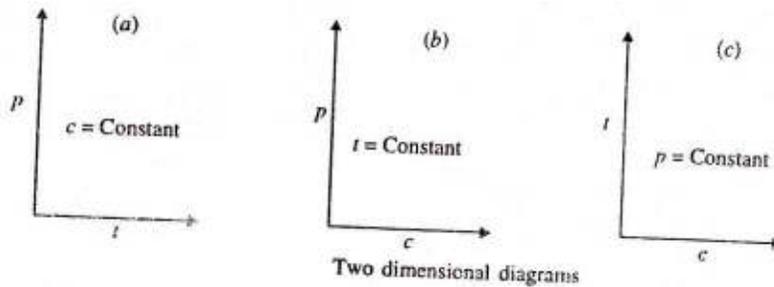


For the sake of having simple plane diagrams we generally consider any two variables for the graphic representation, assuming the third one being constant.

Based on this, the following three types of phase diagrams are possible.

- Pressure - Temperature diagram
- Pressure - Composition diagram

- Temperature – Composition diagram



But in most of the cases it is usually convenient to keep pressure constant at the atmospheric value and a T- C diagram is often used.

A diagram drawn for a constant value of temperature is called **isothermal**, while one obtained by keeping composition constant is called **isoplethal** diagram.

In case of systems consisting of only solid and liquid phases, small changes of pressures have very little effect on the systems. Such systems are called **condensed systems**.

Example: A solid - liquid equilibrium of an alloy system has practically no gaseous phase and the effect of pressure is negligible. Therefore, experiments are conducted under atmospheric pressure. Thus, the system in which only the solid and liquid phases are considered and the gas phase is ignored is called a condensed system. Since the pressure is kept constant, the degree of freedom reduces by one. Thus, the phase rule becomes

$$F' = C - P + 1$$

This equation is known as **reduced or condensed phase rule**. This reduced phase rule is applicable to solid-liquid two component condensed system. The phase diagram of such system consists of T- C graph.

3.13.2 CLASSIFICATION OF TWO COMPONENT SYSTEM

Based on the solubility and reactive ability, the two component systems are classified into three types.

- Simple eutectic formation
- (a) Formation of compound with congruent melting point
- (b) Formation of compound with incongruent melting point
- Solid solution formation

TYPE 1: SIMPLE EUTECTIC FORMATION

- Two solid substances can form a simple eutectic under the following conditions:
 - ✓ They must be completely miscible in the liquid state but immiscible in the solid state.
 - ✓ They should not react chemically with each other.
- Therefore, the eutectic has the same composition both in liquid and solid states.

- They do not form any compound and on solidification they give rise to an intimate mixture known as eutectic.
- Eutectic has a sharp melting point as the pure metals. Hence eutectic composition is a unique mixture of two solids, which has the lowest melting point.
- Examples: Lead-Silver system, Bismuth-Cadmium system

TYPE 2: The two components enter into the chemical combination giving rise to one or more stable compounds.

CLASS I: Formation of compounds with congruent melting point:

- When two solid substances combine in a definite proportion, they react to form a compound which is stable upto its melting point.
- At the melting point, it melts at constant temperature to give a liquid of the same composition as that of the solid compound.
- The compound formed which melts sharply at a constant temperature into a liquid, having the same composition as that of solid, is said to have a congruent melting point.
- Examples: Zn-Mg system; Sn-Mg system (Intermetallic compounds formed by the combination of metals). FeCl₃-H₂O (Formation of salt hydrates involving salt and water).

CLASS II: Formation of compounds with incongruent melting point:

- The compounds formed by the combination of two solid substances, does not remain stable up to the melting point.
- When such a compound is heated, instead of melting sharply, it starts decomposing before the melting point to give a new solid phase and a solution (liquid melt) with a composition different from that of the solid phase.
- Such a compound is said to undergo a transition and is said to have incongruent melting point.



- Examples: Na₂SO₄-H₂O system, Sodium-Potassium system, Gold-Antimony system.

TYPE 3: Formation of Solid Solution:

- When two substances, especially metals are completely miscible in both the solid and liquid states, they form solid solution.
- The condition for the formation of solid solution is the two metals should not differ in atomic radius by more than 15%.
- Example: Copper-Nickel system

In all the types, measurements are made at constant pressure. Therefore one of the independent variable gets fixed. This reduces the degree of freedom by one.

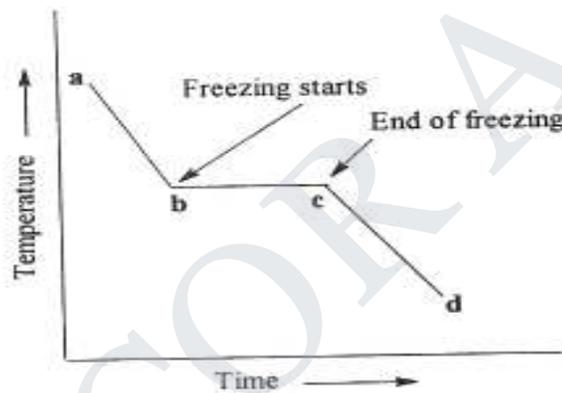
The reduced phase rule equation for two component system is written as:

$$F = C - P + 1 = 2 - P + 1 = 3 - P$$

3.13.3 EXPERIMENTAL METHOD OF CONSTRUCTION OF A SIMPLE EUTECTIC PHASE DIAGRAM BY THERMAL ANALYSIS (OR) COOLING CURVE METHOD

It involves the study of cooling curve of various compositions of two solids during solidification. In this method a mixture of two components A & B of known composition is heated to get a homogeneous liquid melt. The melt is then cooled at a slow rate with constant stirring. The cooling temperature is recorded at regular intervals till it completely solidifies. The same method is repeated for different compositions of alloy mixture ranging from 0 to 100%. The plots are known as cooling curves for a particular composition.

Example 1: Consider a pure solid substance in the fused state. Allow it to cool slowly. The temperature is noted at different time intervals. Then a graph is plotted between temperature and time.



Cooling curve of a pure metal

a : Represents the pure metal is in molten state.

ab: Along 'ab', the temperature of the melt decreases gradually with time.

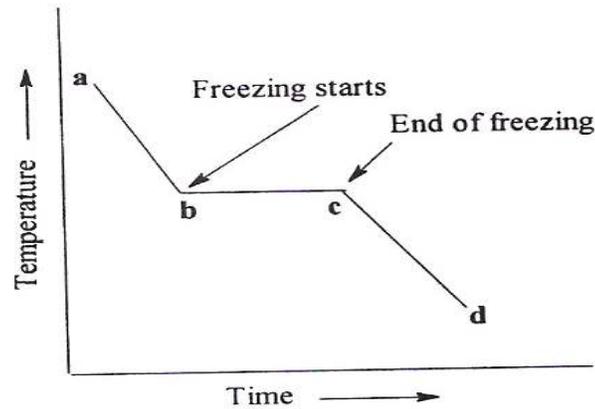
b : The point 'b' indicates the temperature at which the molten metal starts freezing at its surface.

bc: Along 'bc' the liquid melt and solid metal are in equilibrium. Further the temperature remains constant until the liquid melt is completely solidified because the liquid melt and solid metal have same composition.

c : Indicates the end of freezing.

cd: Along 'cd', the temperature of the solid metal again decreases with time.

Example 2: Consider a mixture of two solids A & B



Cooling curve of a mixture of two solids A & B

a : Represents a mixture of solid A and solid B in molten state.

ab : Along 'ab', the temperature of the mixture A & B decreases gradually with time.

b : The point 'b' indicates the temperature at which the freezing of base metal (either A or B depends upon their freezing point) starts from the liquid mixture.

bc : Along 'bc' the liquid melt and solid metal A (or solid metal B) are in equilibrium.

Further, the line 'bc' indicates the composition of molten mixture progressively changes due to continuous separation of solid A (or B) with time.

c : The point at which the liquid mixture (containing both A&B) starts freezing into solid A and solid B (eutectic mixture)

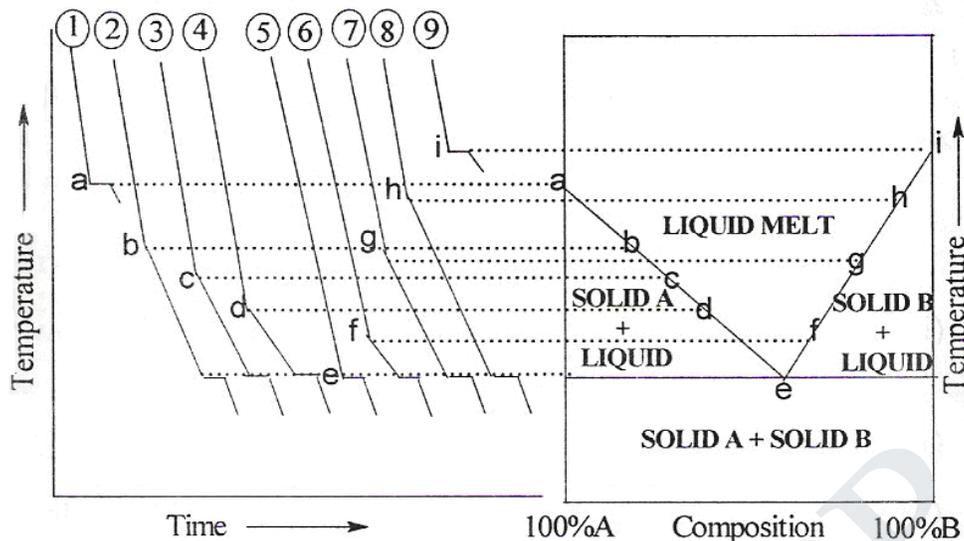
cd : Along 'cd', the liquid mixture and solid A & B are in equilibrium.

d : Indicates the end of freezing of eutectic mixture.

de : Along 'de', the temperature of the solid again decreases with time.

CONSTRUCTION OF SIMPLE EUTECTIC DIAGRAM

It is possible to construct a complete phase diagram for the two component system on the basis of large number of cooling curves of various compositions. Each curve corresponds to a definite composition of A and B. The first break or discontinuity in the graph (a, b, c, d, e, f, g, h, i) denotes phase transformation (freezing point of either A or B). The eutectic phase diagram is obtained by plotting various compositions of two substances (in X-axis) against the first break point (in Y-axis), which is nothing but characteristic temperature.



COOLING CURVES OF VARIOUS COMPOSITIONS OF TWO SOLIDS

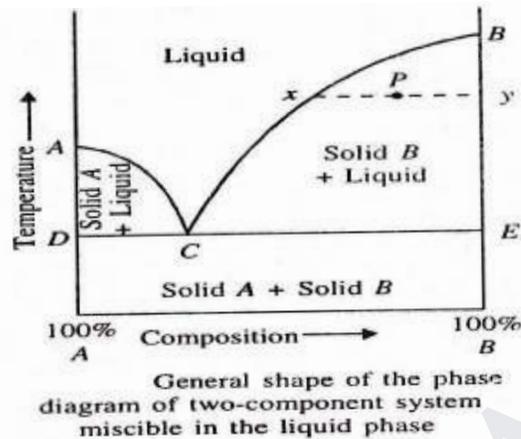
(1) Pure A	(6)	30%	A	+	70	%	B
(2) 80% A + 20 % B	(7)	20%	A	+	80	%	B
(3) 70% A + 30 % B	(8)	10%	A	+	90	%	B
(4) 60% A + 40 % B	(9)				Pure		B
(5) 40% A + 60 % B							

3.13.3 USES OF COOLING CURVES

- Melting point and Eutectic point can be noted from cooling curve.
- The behavior of the compound can be clearly understood from the cooling curve.
- Percentage purity of the compounds can be noted from the cooling curve.
- The composition corresponding to its freezing point yields the composition of the alloy.
- The procedure of thermal analysis can be used to derive the phase diagram of any two component system.

3.14 TWO COMPONENT PHASE DIAGRAM FOR A BINARY ALLOY SYSTEM

(OR) THE SIMPLE EUTECTIC



Salient Features of the phase diagram:

Curves: The eutectic phase diagram consists of two curves AC and BC. Along the curve, two phases (Solid \rightleftharpoons Liquid melt) are in equilibrium and hence the system is univariant ($F = 2 - 2 + 1 = 1$).

Point E (Eutectic point): The curve AC & BC intersect at C which is called Eutectic point. At the eutectic point three phases are in equilibrium.



Hence the system is non-variant ($F = 2 - 3 + 1 = 0$).

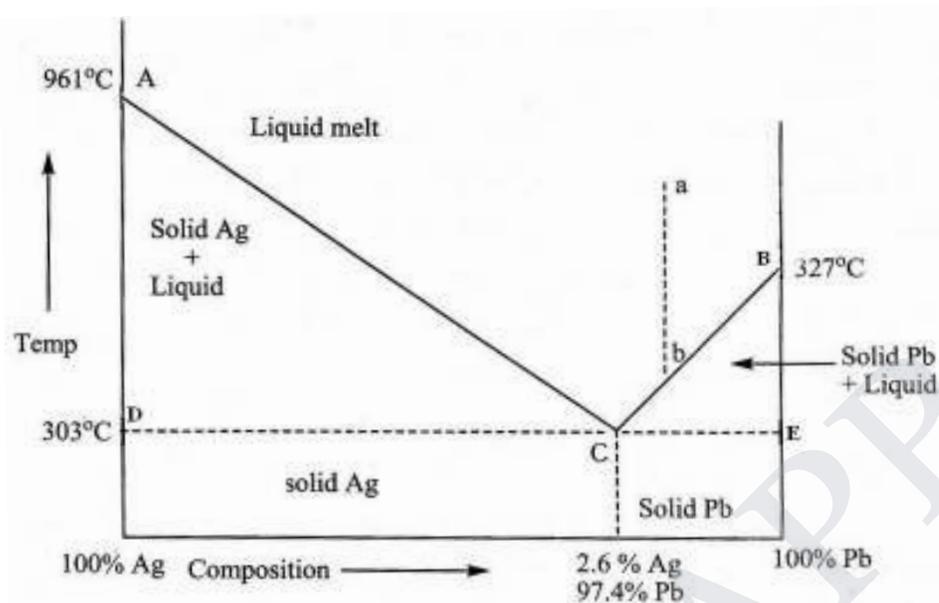
Areas: The eutectic phase diagram consists of four distinct areas

- (i) Above ACB has a single phase (molten A & B)
- (ii) Below AC (solid A + liquid melt)
- (iii) Below BC (solid B + liquid melt) and
- (iv) Below the point DCE (solid A + solid B)

3.14.1 LEAD SILVER SYSTEM (SIMPLE EUTECTIC BINARY ALLOY SYSTEM)

This system has two components and four phases. The phases are (i) solid silver (ii) solid lead (iii) solution of molten Ag & Pb and (iv) vapour. The boiling points of Ag & Pb being considerably high, the vapour phase is practically absent. Thus Pb/Ag is condensed system with three phases. In such a case, pressure can have no effect on the system. Therefore we need only two variables, namely temperature (T) and composition (C).

PHASE DIAGRAM OF LEAD-SILVER SYSTEM



SALIENT FEATURES OF THE PHASE DIAGRAM:

- Two lines (or) curves AC and BC
- Eutectic point 'C'
- Four areas : Area above ACB, below AC, below BC and below DCE

(i) Curve AC:

- 'A' represents the melting point of pure Ag (961°C).
- The curve AC is the freezing point curve of Ag.
- Addition of Pb lowers the melting point of Ag along the curve AC.
- Along AC, solid Ag and liquid melt (solution of Ag & Pb) are in equilibrium.
- Applying reduced phase rule, $F' = C - P + 1 = 2 - 2 + 1 = 1$. Hence the system is univariant along the curve AC.

(ii) Curve BC:

- 'B' represents the melting point of pure lead (327°C).
- The curve BC is the freezing point curve of Pb.
- Addition of Ag lowers the melting point of Pb along the curve BC.
- Along BC, the solid Pb and liquid melt (solution of Ag & Pb) are in equilibrium.
- Applying reduced phase rule, $F' = C - P + 1 = 2 - 2 + 1 = 1$. Hence the system is univariant along the curve BC.

(iii) Eutectic Point 'C':

- The curve AC and BC intersect at 'C' which is called eutectic point.

- Below the point 'C' both Pb & Ag exist in the solid state.
- At this point three phases (solid Ag, solid Pb and their liquid melt) are in equilibrium.
Solid Pb + Solid Ag \rightleftharpoons Liquid melt
- Applying reduced phase rule, $F' = C - P + 1 = 2 - 3 + 1 = 0$. Hence the system is nonvariant at point 'C'.
- Eutectic point is the lowest possible temperature (303°C) in the system that corresponds to fixed composition (97.4% Pb & 2.6 % Ag), below which a liquid phase cannot exist and above which the solid phases disappear.
- The temperature and composition corresponding to the eutectic point 'C' are called eutectic temperature and eutectic composition.
- A liquid mixture of two components – Ag & Pb, which has the lowest freezing point compared to all other liquid mixtures, is called eutectic mixture.

(iv) Areas:

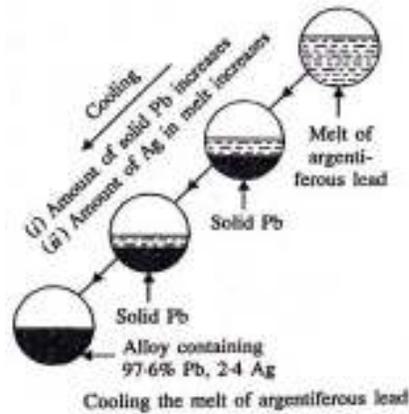
- The **area above ACB** represents a single phase (solution of molten Pb & Ag).
- Applying reduced phase rule, $F' = C - P + 1 = 2 - 1 + 1 = 2$. The system is bivariant.
- **Area below AC** represent the phases solid Ag + liquid melt, **area below BC** represents the phases solid Pb + liquid melt and **area below 'DCE'** represents solid Pb + solid Ag.
- All the three areas have two phases and hence the system is univariant.
($F' = C - P + 1 = 2 - 2 + 1 = 1$)

3.14.2 APPLICATION OF LEAD-SILVER SYSTEM

Pattinson's Process for the Desilverisation of Argentiferous Lead:

The process of recovery of silver from argentiferous lead is called as desilverisation. Argentiferous lead contain very small amount of silver (less than 0.1%). Desilverisation of lead is based on the formation of eutectic mixture.

Argentiferous lead is heated well above the melting point of pure lead (327°C) so that the system consists only of the liquid phase represented by the point 'a' in the phase diagram. When the liquid melt is allowed to cool gradually, the temperature of the melt falls along the dashed line 'ab'. As soon as the temperature corresponding to 'b' is reached, solid lead begins to separate and the solution would contain relatively larger amount of silver. On further cooling, more and more of lead is separated along BO. At 'O', a eutectic mixture consisting of 2.6% Ag and 97.4% Pb is obtained. The eutectic alloy is then treated for the recovery of silver profitably. The process of raising the relative proportion of Ag in the alloy is known as Pattinson's process.



3.14.3 APPLICATIONS OF EUTECTIC SYSTEM

- Suitable alloy composition can be predicted with the use of eutectic system.
- Eutectic systems are applicable for the composition of a metal in quantitative manner. (e.g) Desilverisation of argentiferous lead.
- Eutectic systems are used in preparing solders, used for joining two metal pieces together.
- Low melting alloys which are used in safety devices, fire-sprinklers and as 'fail safe' device in boilers can be prepared by suitable choice of metals.
- Right side consists of MgZn₂ and Mg system.

UNIT IV – FUELS AND COMBUSTION

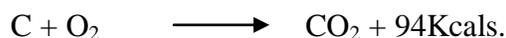
4.1 INTRODUCTION

Fuel is a combustible substance, containing carbon as the main constituent, which on proper burning gives large amount of heat which can be used economically for domestic and industrial purposes eg. Wood, charcoal, kerosene, diesel, petrol etc.

During combustion atoms present in the fuel such as carbon, hydrogen, etc. combine with oxygen with the simultaneous liberation of heat at a rapid rate. The products formed will have less energy or heat content than the reactants. It is this difference in energy or heat content that is released as energy or heat.



More heat energy content lesser heat energy content



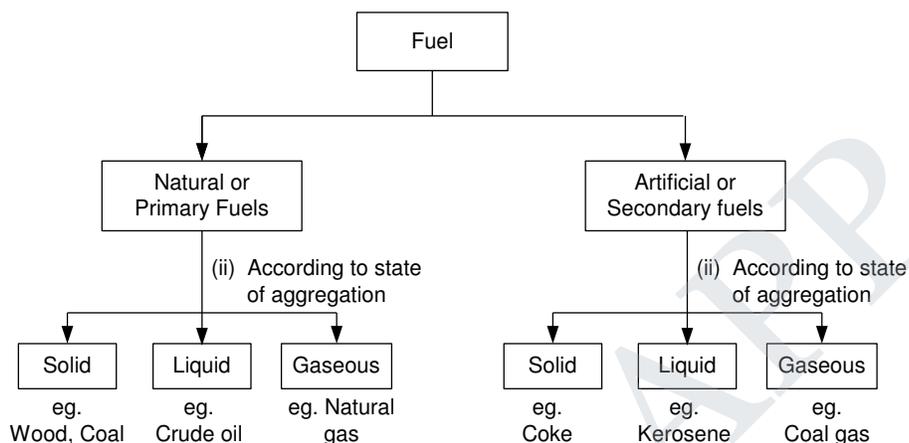
4.1.1 Classification of Fuels

Fossil fuels have been classified according to

- 1) Occurrence
- 2) State of aggregation

Classification based on occurrence

- 1) Natural or primary fuels which occur in nature as such eg. wood, peat, coal, petroleum, natural gas etc.
- 2) Artificial or secondary fuels are those which are prepared from the primary fuels eg. charcoal, coke, kerosene oil, diesel oil, petrol, coal gas, producer gas etc.



The second classification is based on the state of aggregation like

- a) Solid fuels
- b) Liquid fuels
- c) Gaseous fuels

4.1.2 Requirements of a good fuel

- 1) High calorific value
- 2) Moderate ignition temperature
- 3) Should not undergo combustion
- 4) Moderate velocity of combustion
- 5) Combustion should be easily controlled
- 6) Low moisture content
- 7) Low non-combustible matter content
- 8) Products of combustion should not burn
- 9) Should burn in air with efficiency without much smoke
- 10) Low cost
- 11) Easy to transport
- 12) Storage cost in bulk should be minimum

4.2 CALORIFIC VALUE

Calorific value is a measure of the efficiency of a fuel.

The calorific value of a fuel is defined as the total amount of heat liberated by the complete combustion of a unit mass of the fuel.

4.2.1 Unit of Heat Measurement

The quantity of heat can be measured by the following units:

1) Calorie:

Calorie is defined as the amount of heat required to raise the temperature of 1 gm of water through 1°C (15 to 16°C)

2) Kilocalorie:

Kilocalorie is defined as the quantity of heat required to raise the temperature of a kilogram of water through one degree centigrade.

$$1 \text{ kcal} = 1000 \text{ cal.}$$

3) British Thermal unit (B.Th.U)

British Thermal Unit is defined as the quantity of heat required to raise the temperature of one pound of water through one degree Fahrenheit (60-61°F)

$$1 \text{ B.Th.U} = 252 \text{ Cal} = 0.252 \text{ kcal}$$

$$\text{or } 1 \text{ kcal} = 3.968 \text{ B.Th.U.}$$

4) Centigrade heat unit (C.H.U.)

Centigrade heat unit is the quantity of heat required to raise the temperature of 1 pound of water through one degree centigrade.

$$\text{Thus } 1 \text{ kcal} = 3.968 \text{ B.Th.U} = 2.2 \text{ C.H.U.}$$

4.2.2 Units of Calorific Value

The calorific value is generally expressed in calorie / gram (cal/g) or kilocalorie/kg (kcal/kg) or British thermal unit/lb (B.Th.U. / lb) in case of solid or liquid fuels.

B.Th.U. / Cubic feet (B.Th.U/ft³).

4.2.3 Classification of calorific value

➤ Higher Calorific Value

➤ Lower Calorific Value

GROSS (OR) HIGH CALORIFIC VALUE AND NET (OR) LOWER CALORIFIC VALUE

When a fuel containing hydrogen is burnt, the hydrogen present in the fuel undergoes combustion and is converted into steam. If the products of combustion are cooled to room temperature, the steam gets condensed into water and latent heat is evolved. Hence in the calorific

value determination this latent heat of condensation of steam will also be included. This is hence referred to as higher calorific value or gross calorific value (GCV or HCV).

Gross calorific value (GCV) is hence defined as the total amount of heat produced when one unit of the fuel has been burnt completely and the products of combustion have been cooled to room temperature.

In actual use of a fuel the water vapour and moisture are not condensed and escape along with the combustion gases. Hence only a lesser amount of heat is available and this is called the lower or net calorific value.

Net or Lower calorific value(LCV) is “the net heat produced when unit mass/volume of the fuel is burnt completely and the products are permitted to escape”.

Theoretical calculation of calorific value

The calorific value of the fuel can be approximately computed if the percentages of the various elementary constituents such as C, H, O, S are available.

The higher calorific value of some of the chief combustible constituents of a fuel are as tabulated below:

Calorific value of fuel constituents:

Constituent	Hydrogen	Carbon	Sulphur
HCV (kcal/ Kg)	34500	8080	2240

The oxygen present in the fuel is assumed to be present in the combined form with hydrogen i.e. in the form of fixed hydrogen viz. H_2O .

Hence hydrogen available for combustion will be

= Total mass of hydrogen in fuel – Fixed Hydrogen

= Total mass of hydrogen in fuel – (1/8) mass of oxygen in the fuel

(since 8 parts of oxygen combine with one part of hydrogen to form water)

The quantity of hydrogen in combination with oxygen will not take part in the combustion reaction.

So the surplus hydrogen available for combustion is $H - O/8$

According to Dulong, the calorific value of a fuel is the sum of the calorific values of its constituent elements.

The calorific values of C, H and S are found to be 8080, 34500 and 2240 kcals when 1 kg of the fuel is burnt completely.

Dulong's formula for GCV is

$GCV = [8080 C + 34500 (H - O/8) + 2240 S]$ Kcals/Kg or cal / gm

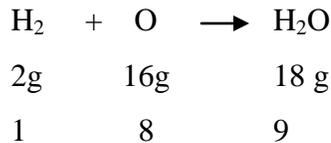
In Dulong's formula C, H, O and S represent the percentage of the corresponding elements.

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

Net calorific value or LCV = (Gross calorific value - Latent heat of condensation of vapour produced)

$$\text{LCV} = \text{GCV} - \text{mass of hydrogen per unit weight of the fuel burnt} \times 9 \times \text{Latent heat of steam}$$

[One part by weight of hydrogen produces nine parts by weight of water as follows.



Latent Heat of Steam is 587 cal/g]

$$\begin{aligned} \text{Thus NCV} &= \text{GCV} - \frac{9\text{H}}{100} \times 587 \\ &= \text{GCV} - 0.09 \times \text{H} \times 587 \end{aligned}$$

Where H = % of H₂ in the fuel

4.3 COAL

4.3.1 Coal and its varieties (or) coalification of wood (or) rank of coal (or) classification of coal by rank

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 rank of coal stands for its degree of maturity or degree of alteration or coalification from the parent material wood.

Wood → Peat → Lignite → Bituminous coal → Anthracite

moisture content H, O, N & S content, volatile matter

carbon content, calorific value and hardness →

The progressive transformation of wood to anthracite results in

- i) decrease in the moisture content
- ii) decrease in hydrogen, oxygen, nitrogen & sulphur contents
- iii) decrease in volatile matter content
- iv) increase in carbon content from 57% to 93%
- v) Increase in calorific value
- vi) Increase in hardness

4.3.2 Analysis of Coal

The quality of coal can be assessed by

- (a) Proximate analysis
- (b) Ultimate analysis

(a) PROXIMATE ANALYSIS

It involves determination of

(i) Moisture

• Significance

When coal is burnt the moisture in it will evaporate. This moisture will take away some of the liberated heat in the form of latent heat of evaporation. Therefore the presence of moisture will lower the effective calorific value of coal. Besides this the moisture will also quench the fire in the furnace.

Hence lesser the moisture content better will be the quality of coal as a fuel.

• Determination of moisture

About 1 gm of finely powdered air dried coal sample is weighed in a crucible. This is then placed in an air-oven maintained at 105°C – 110°C. After 1 hr the crucible is taken out, cooled in a desiccator and weighed. Loss in weight gives the moisture content.

$$\text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$

ii) Volatile Matter

• Significance

If the content of volatile matter is high it means a large part of the fuel will escape unburnt. Hence coal with higher volatile content is undesirable. Lesser the volatile matter better will be the rank of coal.

• Determination of volatile matter

The procedure for determination of moisture is repeated. The dried sample of coal left in the crucible is then covered with a lid and placed in an electric furnace maintained at 925°C ± 20°C. The crucible is taken out of the oven after 7 mts of heating. The crucible is cooled first in air, then inside a desiccator and weighed again. The loss in weight will give the volatile matter.

$$\text{Percentage of volatile matter} = \frac{\text{Loss in wt due to removal of volatile matter} \times 100}{\text{wt of coal sample taken}}$$

iii)Ash content**•Significance**

Ash is a useless, non-combustible matter and it reduces the calorific value of coal.

- a) It hinders the flow of air and heat thereby lowering the temperature.
- b) It forms clinkers (fused ash lumps) which will block the interspaces on the grate on which coal is being burnt. As a result it will block the air supply and the burning of the coal will become irregular
- c) It also increases transporting, handling and storage costs.
- d) It causes early wear of furnace walls
- e) Ash disposal becomes a problem

Hence lower the ash content the better the quality of coal.

•Determination of Ash content

The residual coal in the crucible, for finding the volatile matter is heated without lid in a muffle furnace at $700 \pm 50^\circ\text{C}$ for half an hour. The crucible is then taken out, cooled first in air, then in a desiccator and weighed.

Heating, cooling and weighing is repeated till a constant weight is obtained. The residue is ash.

$$\text{Percentage of ash} = \frac{\text{Wt. of ash left}}{\text{Wt. of coal taken}} \times 100$$

iv)Fixed Carbon**•Significance**

If the percentage of fixed carbon is high it means the percentage of volatile matter will be less.

The calorific value and the quality of coal will be greater if the percentage of fixed carbon is high.

Hence high percentage of fixed carbon is desirable.

It is the fixed carbon that burns in the solid state. Hence knowing percentage of fixed carbon helps in designing the furnace and the shape of the fire box.

•Determination of fixed carbon

Percentage of fixed carbon = $100 - \% \text{ of (moisture + volatile matter + ash)}$

Hence in proximate analysis we find the percentage of moisture, volatile matter, fixed carbon and ash in the coal.

Thus proximate analysis gives the approximate composition of the main constituents of coal.

These results will help in deciding the use of the coal for a particular industry.

(b) ULTIMATE ANALYSIS

By this method the weight percentage of carbon, hydrogen, nitrogen and sulphur of the pure coal free from moisture and inorganic constituents is found out. Hence it is an analysis of the elementary constituents of coal.

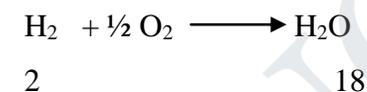
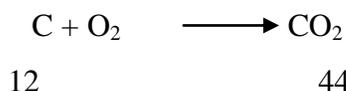
(i) Carbon and Hydrogen**•Significance**

Greater the percentage of carbon, greater will be the quality and calorific value of the coal. The higher percentage of carbon in coal will reduce the size of the combustion chamber required.

Greater the percentage of hydrogen better will be coal quality and calorific value. But hydrogen will be mostly associated with the volatile matter. When coal which contains more of hydrogen is heated it will combine with nitrogen present in the coal forming NH_3 . This NH_3 is recovered as $(\text{NH}_4)_2 \text{SO}_4$, a useful fertiliser.

•Determination of Carbon and Hydrogen

A known weight (wgm) of the coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and CaCl_2 tubes of known weights. The increase in weights of these are then determined.



$$\therefore \text{Percentage of carbon} = \frac{\text{Increase in wt of KOH tube}}{\text{wt. of the coal sample taken}} \times \frac{12 \times 100}{44}$$

$$\therefore \text{Percentage of hydrogen} = \frac{\text{Increase in wt of CaCl}_2 \text{ tube}}{\text{wt. of the coal sample taken}} \times \frac{2 \times 100}{18}$$

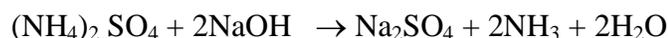
(ii) Nitrogen**•Significance**

Its presence in coal is undesirable as it has no calorific value. Good quality coal should have low nitrogen content. However when coal is carbonized its N_2 and H_2 combine thereby producing NH_3 which is recovered as $(NH_4)_2 SO_4$ a valuable fertilizer.

•Determination of Nitrogen in Coal

Nitrogen is estimated using the Kjeldahl's flask.

About Wgm of exactly weighed coal is heated with conc. H_2SO_4 along with K_2SO_4 (catalyst) in a long-necked flask (called kjeldahl's flask). When the solution becomes clear i.e. when all the nitrogen has been converted to ammonium sulphate it is heated with 50% NaOH.



The liberated ammonia is distilled over and absorbed in a known volume of standard H_2SO_4 (say xN). The volume of unused xN H_2SO_4 is then determined by back titrating against standard NaOH using phenolphthalein as the indicator. From this the volume of the acid neutralized by ammonia can be calculated.

Let,

Volume of xN $H_2SO_4 = A$ ml

Volume of unused xN $H_2SO_4 = B$ ml

Acid neutralized by ammonia = $(A - B)$ ml

1000 ml of 1N acid $\equiv 14$ gm of N_2 (or 17 gm of NH_3)

$$14 \times (A - B) \times xN$$

$$\therefore (A-B) \text{ ml of } xN \text{ acid} = \frac{14 \times (A - B) \times xN}{1000 \times 1} \text{ gm of } N_2$$

$$\therefore \% \text{ of } N_2 \text{ in coal} = \frac{14 \times (A - B) \times xN}{1000 \times W} \times 100$$

$$= \frac{14 \times \text{volume of acid used} \times \text{Normality}}{1000 \times W} \times 100$$

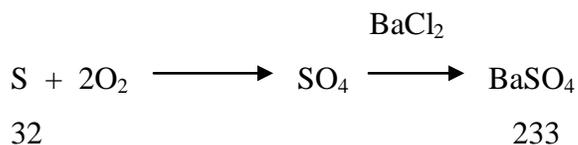
$$= \frac{1.4 \times \text{volume of acid used} \times \text{Normality}}{W}$$

(iii) Sulphur**•Significance**

Presence of sulphur increases calorific value of the coal. It however has undesirable side effects because its oxidation products like SO_2 , SO_3 etc. in presence of moisture can corrode the equipments and cause atmospheric pollution.

•Determination of Sulphur

When coal is burnt in the bomb calorimeter with oxygen, ash is obtained. This ash will contain sulphates from the sulphur present in the coal. This is extracted with diluted HCl. On treatment with BaCl_2 , barium sulphate will get precipitated. This is filtered, washed, dried and weighed. Let the weight of BaSO_4 obtained = x gm



233 gm of BaSO_4 contains 32 gm of sulphur

\therefore x gms of BaSO_4 will contain

$$= \frac{32 \times x}{233} \text{ gm of sulphur}$$

\therefore % of sulphur in coal

$$= \frac{32 \times x}{233 w} \times 100$$

Where w is the weight of the coal taken.

iv) Oxygen**•Significance**

When the oxygen content in the coal is high, the inherent moisture content will be high. It will have low calorific value and low coking power.

Further if oxygen content is there it will be in combination with hydrogen in coal and hence the hydrogen available for combustion will be lesser than otherwise.

Presence of oxygen will lower the quality of the coal.

•Determination of oxygen in coal

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

(v) Ash

Ash determination is done as in proximate analysis

4.4 METALLURGICAL COKE(CARBONISATION OF COAL)

Metallurgical coke is derived from the primary solid fuel coal. When coal is subjected to destructive distillation (heated in the absence of air) it leaves behind a white lustrous, porous mass which is called coke. This process is called carbonization viz preparation of coke from coal.

4.4.1 Types of Carbonization

(i) Low temperature carbonization

If carbonization is carried out in the temperature range of 500-700°C it is called low temperature carbonization. Low temperature carbonization produces high yield of 75-80% but the quality of coke produced will be of the lowest rank as it contains 5-15% volatile matter. Hence it is mostly used as a domestic fuel.

(ii) High temperature carbonization

If carbonization is carried out in the temperature range of 900-1200°C it is called high temperature carbonisation. High temperature carbonisation produces a yield of 65-75% but the volatile matter content will be low (1-3%). Coke produced by high temperature carbonisation is of right porosity and hardness which suits the requirement for metallurgical processes.

4.4.2 Prerequisites of coke used in Metallurgy

Good coke for metallurgy should possess the following requisites.

(i) **Porosity:** It should be porous, so that oxygen can easily come in contact with the carbon of the coke.

(ii) **Strength:** The coke should be hard and strong to withstand dropping abrasion as well as pressure of the over-burden (ore + fuel + flux) in the furnaces.

(iii) **Constituents:** Coke should have low ash, S and P contents to avoid these getting incorporated in the metal to be extracted.

(iv) **Size :** The size of the coke should be neither too big nor too small. If the size of the coke is too big, the uniformity of heating is never maintained. If the size is too small choking will result.

(v) **Cost :** Coke should be cheap and easily available near the site of the metallurgical plant so that the transportation cost is low.

vi) **Calorific value:** The calorific value of coke should be high.

vii) **Combustibility :** Coke should burn easily. This will depend on the nature of the coal, carbonization temperature and reaction temperature.

Coke is superior to coal as a metallurgical fuel, as coke is stronger and more porous, contains lesser amount of sulphur and less volatile matter than coal.

4.4.3 Manufacture of Metallurgical Coke(Otto-Hoffman's Method)

Coke for metallurgical purpose is obtained by Otto Hoffman's Process.

Otto Hoffman's Byproduct coke oven

Otto Hoffman devised the modern byproduct coke oven to

- i) Increase the thermal efficiency by saving on fuel used.
- ii) Recover various byproducts like coal gas, tar, ammonia, naphthalene, benzene, H_2S , etc.

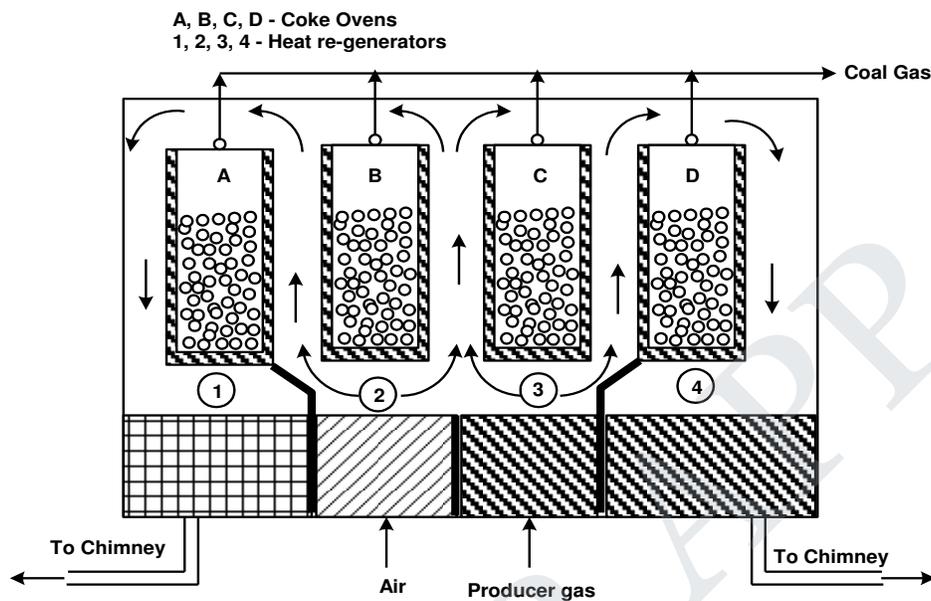


Fig. 4.1 Otto Hoffman's Byproduct coke oven

Heating is done externally on the basis of "regenerative system of heat economy" Here waste gas produced during carbonisation is used for heating the heat regenerators or checker-brick works.

The by-product coke oven consists of a number of narrow silica chambers each being about 10 to 12 m long, 3 to 4m high and 0.40 to 0.45 m wide. They are erected side by side with vertical flues in between them.

The ovens are charged by introducing finely crushed coal through the charging hole at the top and closed to restrict the entry of air.

Carbonisation is carried out at a temperature of $1200^{\circ}C$. Preheated air and producer gas will supply heat for carbonisation through the second and third heat regenerators. If the fuel has a low calorific value both air and fuel need to be preheated. If the fuel gas has a high calorific value preheating of air alone will be sufficient.

The flue gases produced during combustion, before escaping to the chimney will pass their sensible heat to the 1st and 4th regenerators until this brick-work has been raised to a temperature of about $1000^{\circ}C$. Now the flow of the heating gases will be reversed and the inlet gases will be passed through the 1st and 4th regenerators. The flue gases will now be made to pass through the 2nd and 3rd heat regenerators to heat them. This will now preheat the inlet gases when the flow is again

reversed. Thus the cycle will go on and the heating will be continued until all the volatile matter escapes. The carbonisation time is usually between 11 to 18 hours.

After the carbonisation is complete the red hot coke is removed and quenched by a water spray —**wet quenching** (or) placed in a chamber and cooled by passing inert gases from boilers like nitrogen—**dry quenching**. These heated inert gases can be circulated to boilers where they can generate steam.

Coke produced by dry quenching is cheaper, drier and will contain lesser dust than ‘wet quenched’ coke.

Recovery of Byproducts

The gas coming out from the oven during carbonisation is called “coke oven gas”. It contains coal gas, tar, ammonia, naphthalene, benzene, hydrogen sulphide etc.

i) Recovery of tar

Coke oven gas is passed first through a tower in which liquor ammonia is sprayed. Dust and tar will collect at the bottom of the tank, which is heated by steam coils to recover back the ammonia sprayed.

ii) Recovery of ammonia

When passed through a tower in which water is sprayed the ammonia gas will go into solution as ammonium hydroxide.

iii) Recovery of naphthalene

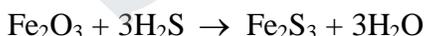
When passed through another tower in which water at very low temperature is sprayed naphthalene will condense.

iv) Recovery of benzene

When the gases are sprayed with petroleum, benzene and its homologues will be removed.

v) Recovery of hydrogen sulphide

When the gases are passed through a purifier packed with moist Fe_2O_3 , hydrogen sulphide will be retained.



When the conversion of all the Fe_2O_3 to Fe_2S_3 is complete the purifier will be exposed to the atmosphere to regenerate Fe_2O_3



4.5 PETROLEUM PROCESSING AND FRACTIONS

Petroleum is also referred to as crude oil. It is a naturally occurring dark greenish-brown viscous oil found deep under the earth's crust. Chemically it is composed of several hydrocarbons together with small amounts of organic compounds containing nitrogen, oxygen and sulphur.

The approximate composition of petroleum is 79.5 to 87.1% C ; 11.5 to 14.8% H, 0.1 to 3.5% S and 0.1 to 0.5% N + O

4.5.1 Classification of Petroleum

i) Paraffin-base type crude

They consist mainly of n-alkanes viz. saturated hydrocarbons from CH_4 to $\text{C}_{35}\text{H}_{72}$ together with a little of naphthalenes and aromatics.

The paraffins from $\text{C}_{18}\text{H}_{38}$ to $\text{C}_{35}\text{H}_{72}$ are semi-solids called waxes

ii) Naphthenic or Asphaltic base type crude

They contain aromatic and alicyclic hydrocarbons

iii) Mixed-base type crude

They contain both paraffinic and asphaltic hydrocarbons. They are generally rich in semi-solid waxes.

4.5.2 Refining of Petroleum or crude oil

The process of removing impurities and separating out the oil into various fractions having different boiling points is known as refining of petroleum. The plants set up for the purpose are called oil refineries.

Refining is carried out as follows:

(i) Separation of water: Cottrell's process: crude oil is a stable emulsion of oil and salt water.

Water is separated from the oil by Cottrell's process. In this process crude oil is allowed to flow between two highly charged electrodes. The colloidal water-droplets coalesce to form large drops, which separate out from the oil.

Modern methods to remove NaCl , MgCl_2 , etc. from the oil like electrical desalting are also resorted to.

(ii) Removal of harmful sulphur compounds: when oil is treated with copper oxide, copper sulphide will be formed. This solid can be removed by filtration.

(iii) Fractional distillation

The crude oil, thus purified, is then heated in an oil heater which is a furnace, where the temperature is maintained around 400°C . All volatile constituents, except asphalt or coke will vaporise. The hot vapours are then passed up a fractionating column.

The fractionating column is a tall cylindrical tower in which a number of horizontal stainless steel trays are located at short distances. Each tray is provided with a small chimney which is covered with a loose cap. The tower will be hotter at the bottom and comparatively cooler upwards. As the vapours move up in the tower they get cooler and cooler and fractional condensation will occur at different regions of the column. Higher boiling fractions will condense first while the lower boiling fractions will condense later. Low boiling fractions are purified and used. High boiling fractions which collect at the bottom can be subjected to “cracking” to get more useful lower boiling fractions.

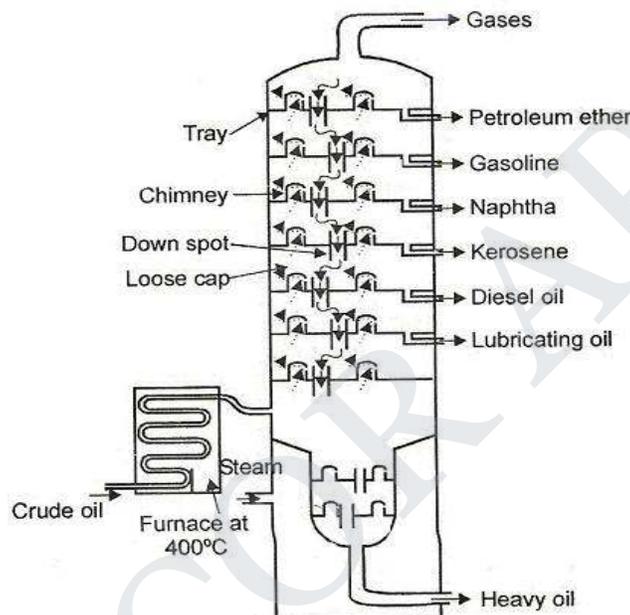


Table: Fractions obtained by distillation of crude oil

Name of fraction	Boiling range	Approx composition in terms of hydrocarbon containing atoms	Uses
1. Uncondensed gas	< 30°C	C ₁ – C ₄	Domestic Fuel – LPG
2. Petroleum ether	30-70°C	C ₅ – C ₇	Solvent for varnish and rubber
3. Gasoline or Petrol	40-120°C	C ₈ – C ₉	Motor fuel, as solvent and in dry cleaning
4. Naphtha or solvent spirit	120-180°C	C ₉ – C ₁₀	As solvent and in dry cleaning
5. Kerosene oil	180-250°C	C ₁₀ – C ₁₆	Domestic fuel, jet engine fuel

6. Diesel oil or fuel oil or gas oil	250-320°C	C ₁₀ - C ₁₈	Diesel engine fuel
7. Heavy oil	320-400°C	C ₁₇ -C ₃₀	To get gasoline by cracking process
This heavy oil on refractionation gives			
a) Lubricating oil			As lubricant
b) Petroleum jelly (vaseline)			As lubricant, in cosmetics and medicine
c) Grease			As lubricant, used in candles
d) Paraffin wax			Boot polishes, tarpolin cloth etc.
8. Residue Residue may be a) Asphalt (or) b) Petroleum coke	Above 400°C	C ₃₀ and above	a) For water proofing of roofs and in road making b) As fuel and in moulding arc light rods

Some of the important liquid fuels derived from petroleum are

a) Gasoline or Petrol

- Low boiling fraction of petroleum, highly volatile and inflammable.
- Obtained between 40-120°C
- Mixture of hydrocarbons ranging from C₅H₁₂ (pentane) to C₈H₁₈ (Octane).
- Calorific value is about 11250 kcal/kg
- Approximate composition is C=84%, H=15%, N+S+O=1%

Uses

- As a fuel for internal combustion engines of automobiles and aeroplanes.

b) Kerosene oil

- High boiling fraction of petroleum, does not vaporise easily.
- Obtained between 180-250°C
- Mixture of hydrocarbons ranging from C₁₀H₂₂ (decane) to C₁₆H₃₄ (hexadecane)
- Calorific value is 11100 kcal/kg
- Approximate composition is C=84%, H=16% with less than 0.1% S
- Specific gravity is 0.75-0.85

Use: As a domestic fuel in stoves, as jet engine fuel and for making oil gas.

c) Diesel oil

- Relatively high boiling fraction of petroleum
- Obtained between 250-320°C
- Mixture of hydrocarbons ranging from $C_{15}H_{22}$ to $C_{18}H_{38}$
- Calorific value is about 11000 kcal / kg

Uses :As a diesel engine fuel.

d) Fuel oil or heavy oils or Residual oils

The residue of petroleum after the lighter fraction is distilled off is called fuel oil.

- They are high molecular weight fraction of petroleum
- Obtained between 320-400°C
- Mixture of hydrocarbons ranging from $C_{17}H_{36}$ to $C_{58}H_{118}$
- Calorific value is of the order of 10000 kcal/kg
- Heaviest fraction

Uses :As fuel for ships, metallurgical furnaces.

On refractionation of the heavy oil the following fractions can be recovered.

Lubricating oil.

Composition ranges from $C_{17}H_{36}$ to $C_{20}H_{42}$

Used as a lubricating oil

Petroleum jelly

Used as a lubricant and in cosmetics and medicines.

Grease

Used as a lubricant in vehicle, machines, motors etc.

Paraffin Wax

Composition ranges from $C_{20}H_{42}$ to $C_{28}H_{58}$. Used for making candles, wax paper, boot polishes etc.

Asphalt or Bitumen

Used for making road and water-proofing roofs etc.**Petroleum coke**

used for moulding electrode rods for cells and as a fuel.

e)Naphtha or white spirit

- Distills off from Petroleum between 120-180°C
- Light, Colourless to straw-coloured liquid
- Mixture of hydrocarbons ranging from C_9H_{20} (nonane) to $C_{10}H_{22}$ (decane).

Uses:

- Mainly used as an industrial solvent
- Used in dry cleaning

- Used as varnish thinner
- Used for floor and furniture polishes

f) Aviation fuel / Aviation gasoline

Aviation gasoline is the gasoline which is used as fuel in aeroplanes. It can be produced or converted to from any gasoline by alkylation, isomerisation, polymerisation and reforming.

Aviation gasoline is made of higher percentage of isoparaffin and smaller percentage of naphthalenes and aromatics. Aviation gasoline has higher antiknock value, volatility and stability than any other gasoline.

It has an octane number of 100 or even more.

4.5.KNOCKING

Piston engines comprise of Spark Ignition (SI) and Compression Ignition (CI). The former runs on petrol while the latter operates on diesel.

4.5.1 SI Engine (Petrol engine)

A mixture of gasoline vapour and air forms the fuel in the internal combustion engine. A spark in the cylinder will initiate the combustion reaction. The flame should spread rapidly and smoothly through the gaseous mixture. The expanding gas will drive 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 the compression-stroke of the piston is known as compression ratio. The efficiency of an internal combustion engine will increase with the compression ratio. This will depend on the nature of the constituents present in the gasoline used.

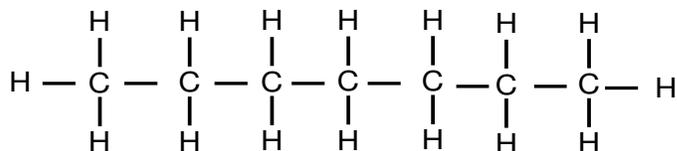
Due to the presence of certain constituents in the gasoline used the rate of oxidation will increase and become so great that the last portion of the fuel-air mixture will get ignited instantaneously. This will result in an explosive violence known as 'knocking', which will cause a drop in the efficiency.

The tendency of fuel constituents to knock will be straight chain paraffins > branched chain paraffins i.e. isoparaffins > olefins > cycloparaffins > aromatics.

So from above it follows that olefins have better anti-knock properties than the corresponding paraffins and so on.

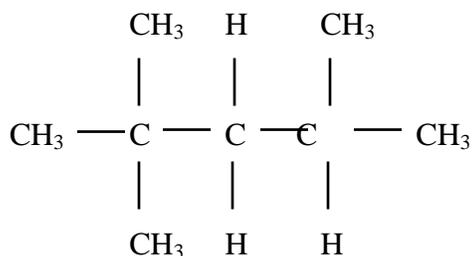
Octane rating

n-heptane, knocks very badly. Hence its anti-knock value has been arbitrarily fixed as zero.



n - heptane

Isooctane (2:2:4 – trimethyl pentane) gives very little knocking and its anti-knock value has been fixed as 100



(2:2:4 – trimethyl pentane)

Therefore octane number or rating of a gasoline or any other internal combustion engine fuel is the percentage of isooctane in a mixture of isooctane and n-heptane, which matches the fuel under test in knocking characteristics.

Hence if a petrol sample behaves like a mixture of 60% isooctane and 40% n-heptane, its octane number is taken as 60.

Improvement of anti-knock characteristics of a fuel.

Addition of extremely poisonous material such as tetraethyl lead $(\text{C}_2\text{H}_5)_4\text{Pb}$ (TEL) and diethyl telluride $(\text{C}_2\text{H}_5)_2\text{Te}$ will raise the octane number.

Petrol to which TEL is added is called leaded petrol.

Mechanism

TEL decomposes thermally to form ethyl free radicals. The process of knocking involves a free radical mechanism. The growth of the chain can be stopped if this is combined with the ethyl free radicals from TEL. However, TEL forms lead oxide which will deposit on spark plugs. To overcome this ethylene dibromide is added. Lead bromide will be formed which will go out with the exhaust gases. This lead bromide will cause atmospheric pollution.

Presence of sulphur compounds in petrol all reduce the effectiveness of TEL.

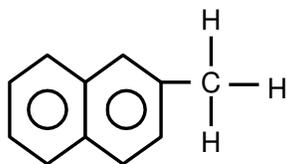
5.5.2 CI Engine (Diesel Engine)

In a diesel engine the fuel is exploded not by a spark but by the application of heat and pressure. In the CI engine, air alone is compressed. This will result in the cylinder temperature going upto as high as 300°C . Now when the diesel oil is injected or sprayed it must get ignited spontaneously. The combustion products will expand and the power stroke will begin.

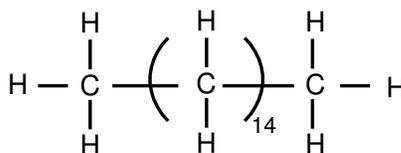
Knocking which will occur when burning will not occur even after the compression stroke is over and the diesel oil is sprayed. As a result more fuel will have to be injected automatically and sudden ignition might result and then the whole oil will burn. This delayed ignition will result in an uncontrolled excessive combustion and produce what is referred to as the 'diesel knock'. Hence while in SI engine knocking is the result of premature or too early ignition, in CI engines the knocking is the result of delayed ignition or ignition lag.

Cetane number

The diesel engine fuels consist of longer chain hydrocarbons than internal combustion engines. The suitability of a diesel fuel is indicated by its cetane value. This 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)



n - hexadecane
(Cetane number = 100)

Addition of 'pre-ignition dopes' like ethyl nitrite, acetone peroxide etc. enhances the cetane number of a diesel fuel.

Diesel oil or gas oil is the usual diesel engine fuel.

- It is obtained between 250-320°C during fractional distillation of crude petroleum.
- It contains 85% carbon and 12% hydrogen.
- It has a calorific value of 11000 kcal/kg.

The hydrocarbon constituents of diesel fuel have the ignition quality order as follows.

n – alkanes > naphthalenes > alkenes > branched alkanes > aromatics

Hence from the above, the hydrocarbons which are poor gasoline fuels are quite good diesel fuels.

Addition of ethyl nitrate, isoamyl nitrate etc. will increase the cetane number.

High Speed, Medium Speed and Low Speed Diesels

High Speed Diesel

- Time lag is about $1/500^{\text{th}}$ of a second in getting the diesel droplets heated to the ignition point - very brief.
- Diesel with cetane numbers 45 to 60 serve the purpose.

Medium Speed Diesel

- Cetane number of medium speed diesel is about 35.

Low Speed Diesel

- Cetane number of low speed diesel is about 25.

S.No.	Petrol	Diesel
1.	This is the low boiling fraction of petroleum.	Contains C_{10} to C_{16} hydrocarbons and constitutes the high boiling fraction of petroleum.

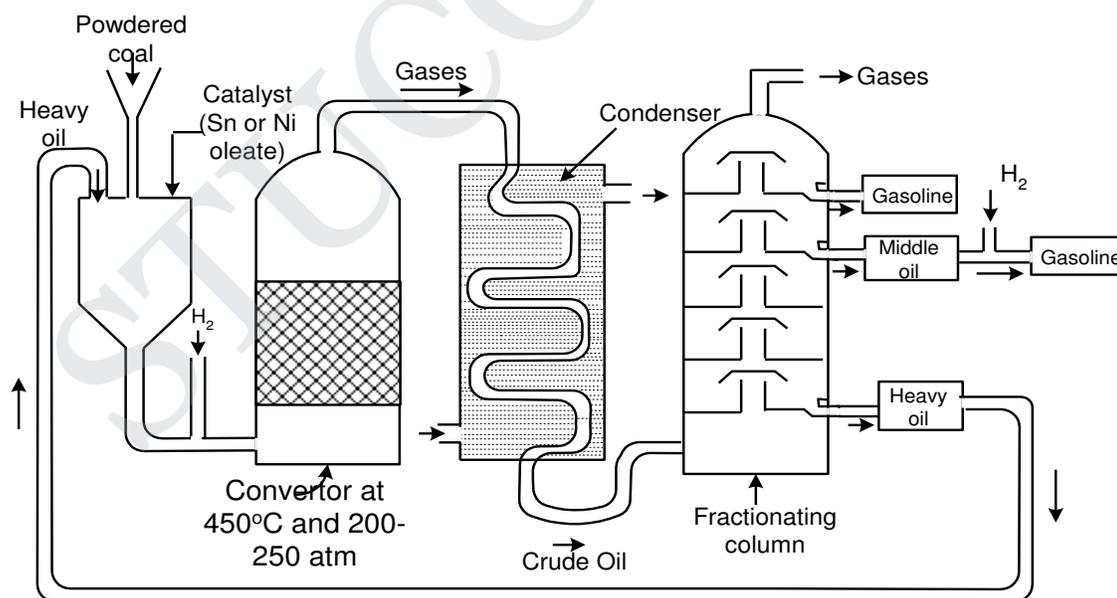
2.	It is the fuel for spark ignition engines	It is the fuel for compression ignition engines
3.	Knocking is the result of premature ignition	Knocking occurs due to delay in the ignition.
4.	Knocking is measured in terms of octane rating.	Knocking is measured in terms of cetane rating.
5.	Adding of TEL improves the anti-knock property.	Doping with isoamyl nitrate improves anti-knocking
6.	Thermal efficiency is low	High thermal efficiency
7.	Consumption is more	Consumption is less

5.6 SYNTHETIC PETROL (HYDROGENATION OF COAL)

Coal contains about 4.5% hydrogen compared to about 18% in petroleum based on 100 grams of carbon. Hence compared to petroleum, coal is a hydrogen deficient compound.

If coal is reacted with hydrogen under high temperature and pressure, solid coal will get converted to liquid fuels. The preparation of liquid fuels from solid coal is known as hydrogenation of coal.

5.6.1 Bergius Process



Powdered coal, heavy oil and catalysts such as nickel oleate or tin oleate are used. The low ash coal is powdered (coal dust) well and made into a paste with heavy oil. Thereafter the catalysts viz. tin or nickel oleate is added. The mixture is heated with hydrogen at 450°C and at 200-250 atm. pressure for about 1.5 hours. Under these conditions coal undergoes hydrogenation and forms

saturated hydrocarbons. These decompose under the existing high temperature and pressure conditions to give low-boiling liquid hydrocarbons. The gaseous mixture from the converter is led to a condenser where a liquid resembling crude oil is obtained.

The crude oil is then fractionated and gives

- (i) gasoline
- (ii) middle oil
- (iii) heavy oil

Yield of gasoline is about 60% of the powdered coal used.

Middle oil is again hydrogenated in presence of solid catalysts to give more gasoline.

Heavy oil is used again to make a paste with fresh coal powder.

5.7 GASEOUS FUELS

5.7.3 Liquefied Petroleum Gas (LPG) or bottled gas or refinery gas

The approximate composition of LPG is 70% n-butane, 17% isobutane, 11% n-propane and the rest being butylene and ethane. Its calorific value is about 27800 kcal/m³.

It is the byproduct obtained during the cracking of heavy oils or from natural gas. It consists of hydrocarbons of such volatility that they can exist as gas under atmospheric pressure. They can however be readily liquified under pressure.

LPG is supplied under pressure in containers under trade names such as Indane, Bharat gas etc. LPG is dehydrated, desulphurised and traces of organic sulphides (mecaptans) which have odour are added so that a gas leak can be easily detected.

Uses:

- As it can be easily liquified it can be economically stored and transported in cylinders.
- It is used as a domestic fuel.
- It is also used as an industrial fuel
- Also used as a motor fuel

Advantage of LPG over gasoline as a motor fuel

- Cheaper
- High knock resistance
- Burns cleanly
- Increased engine life

Disadvantages of LPG over gasoline as a motor fuel

- Only in engines working under high compression ratios use of LPG is advantageous.
- Always handling of LPG will be under pressure.
- As the odour is faint detection of leakage may not be easy.

5.7.4 Compressed Natural Gas

It is a potential alternative for gasoline fuels for spark ignition engines. Compressed Natural Gas is a fossil fuel substitute for petrol and diesel. Its combustion does produce greenhouse gases but it is still a more environmentally clean alternative.

It is made by compressing natural gas (mainly methane) to less than 1% of its volume at standard atmospheric pressure. It is stored & distributed in hard containers at a normal pressure of 200-220 bar in cylindrical or spherical shapes.

CNG is used in the traditional internal combustion engine cars that have been converted into bi-fuel vehicles (gasoline/CNG).

CNG's volumetric energy density is estimated to be 42% of LNG's and 25% of diesels. It has to be hence compressed to high pressures of the order of 200 bars.

CNG cylinders can be made of steel, aluminium or plastic. Lightweight composite cylinders are especially beneficial for vehicular use as they result in remarkable weight reduction when compared to the previously used steel and aluminium cylinders. This leads to lower fuel consumption.

Advantages

The advantage of CNG when used as a fuel in spark-ignition engines are

- 1) It is a light weight gas
- 2) It has high ignition temperature
- 3) Octane number is 130
- 4) No need for adding any anti-knock additive as the octane number is 130.
- 5) Environmental pollution is less as the emission of CO and unburnt hydrocarbons are minimum.
- 6) Does not carbonize the spark plugs.
- 7) Life of the engine is more when CNG is used
- 8) CNG is almost insoluble in the engine oil, unlike petrol. So the oil lasts longer

Limitations of CNG

- 1) Trunk space has to be more
- 2) They require heavy cylinders to store the natural gas at high pressure.
- 3) CNG driven vehicles have shorter operating range when compared to petrol driven vehicles.

5.8. Power alcohol

When ethyl alcohol is blended with petrol at concentration of 5-10%. It is called power alcohol. In other words absolute alcohol (100% ethyl alcohol) is also called power alcohol. Ethyl alcohol is used in an internal combustion (IC) engine. The addition of ethyl alcohol to petrol increases its octane number. When ethyl alcohol is blended with diesel it is called E Diesel.

Manufacture

Step:1

Manufacture of ethyl alcohol

Ethyl alcohol can be synthesized by fermentation of carbohydrates (sugar materials). Fermentation of molecules which is the residue left after the crystallization of sugar, with yeast generates alcohol. This fermentation yields only about 20 % alcohol.



Concentration of alcohol can be increased up to 97.6% by fractional distillation yields rectified spirit. The concentration of alcohol cannot be increased by distillation above 97.6 %. Because it forms a constant boiling mixture with water. The constant boiling point has a lower boiling point than alcohol.

Step:2

Conversion of ethyl alcohol into power alcohol.

But for IC engine, 100% alcohol (absolute alcohol) is prepared by removing last trace of water from rectified spirit. It can be done by the following two methods.

- i) alcohol containing trace of water, is distilled with benzene. When benzene passes over with a portion of alcohol and water, it leaves behind absolute (power)alcohol.
- ii) alcohol is distilled in the presence of dehydrating agent, which holds water.

Finally absolute alcohol is mixed with petrol at concentration of 5-10% to get power alcohol.

Properties

- Power alcohol has a lower calorific values(7000K.Cal/Kg)
- It has high octane number(90)
- Its anti-knocking properties are good.
- It generates 10% more power than the gasoline of same quality.
- Its compression ratio is also high.

Uses:It is used as a very good fuel in motors.

5.8.1 Advantages and disadvantages of power alcohol

Advantages

1. It is cheaper than petrol
2. If any moisture is present, power alcohol absorbs it.
3. As ethyl alcohol contains oxygen atoms complete combustion occurs, so emission of CO₂, hydrocarbon particulates are reduced.

Disadvantages

1. As the calorific value of power alcohol (7000 cal/gm) is lower than petrol (11,500cal/gm), specially designed engine is required.
2. Output power is reduced upto 35%
3. Due to its high surface tension, atomization of power alcohol is difficult, so it causes starting trouble.
4. It may undergo oxidation to give acetic acid, which corrodes engine part.
5. As it contains oxygen atoms, the amount of air required for combustion is less therefore the engine and carburetor need to be modified.

5.9. BIO-DIESEL

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

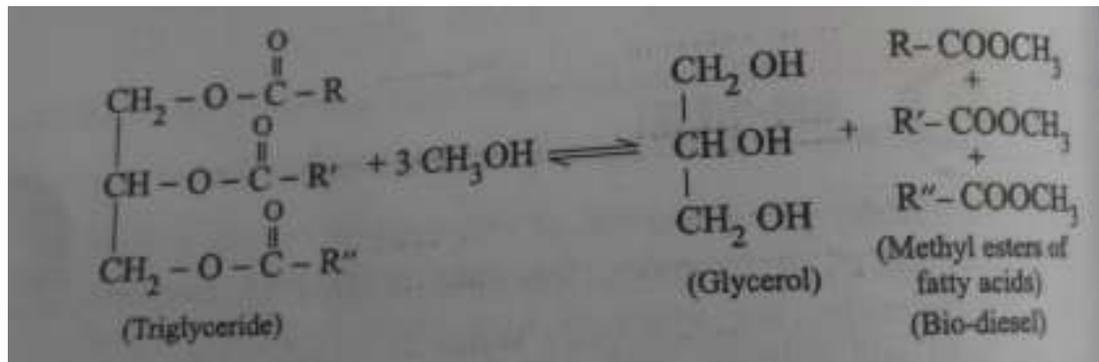
Problem in using vegetable oils directly.

1. As the viscosity of vegetable oils are high, atomization is very poor and hence inefficient mixing of oil with air leads to incomplete combustion.
2. Oxidation and thermal polymerization of vegetable oil cause deposit formation.
3. Their high viscosity causes misfire and ignition delay.
4. Their high volatility and consequent high flash point leads to more deposit formation.
5. The use of vegetable oils as direct fuel requires modification of the conventional diesel engine design.

Manufacture: trans-etherification (or) alcoholysis.

The above problems are overcome by reducing the viscosity of the vegetable oils by the process known as trans-etherification 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, soybean oil, mustard oil, etc) with excess of methanol in presence of catalyst to give mono ethyl ester of long chain fatty acid and glycerin. It is allowed to stand for some time and glycerin is separated.

Equation

Methyl ester of fatty acid, thus formed are called Bio-Diesel is defined as mono-alkyl ester of long chain fatty acid derived from vegetable oils or fats. It is a pure fuel before blending with conventional diesel fuel. Bio-diesel can be blended with petroleum diesel.

5.9.1. Advantages and Disadvantages of Bio diesel.**Advantages**

- Bio-diesel is biodegradable.
- It is from renewable resources.
- The gaseous pollutant are lesser as compared to the vegetable oils.
- Bio-diesel can be produced from different types of vegetable oils.
- Best engine performance and less smoke emission are achieved.

Disadvantages.

1. Bio-diesel gels in cold weather.
2. As Bio-diesel are hygroscopic, Bio-Diesel can absorb water from atmosphere.
3. Bio-diesel decreases the horse power of the engine.
4. Bio-diesel degrades and softens the rubber and plastics that are used in some old cars.
5. Bio-diesel has about 10% higher nitrogen-oxide (NO_x) emission than conventional petroleum.

5.10 ANALYSIS OF FLUE GAS – ORSAT'S APPARATUS

Flue gas refers to gases such as CO₂, O₂ and CO which came out from the combustion chamber. To have an idea if the combustion of the fuel is complete or not we analyse these flue gases in the Orsat's apparatus.

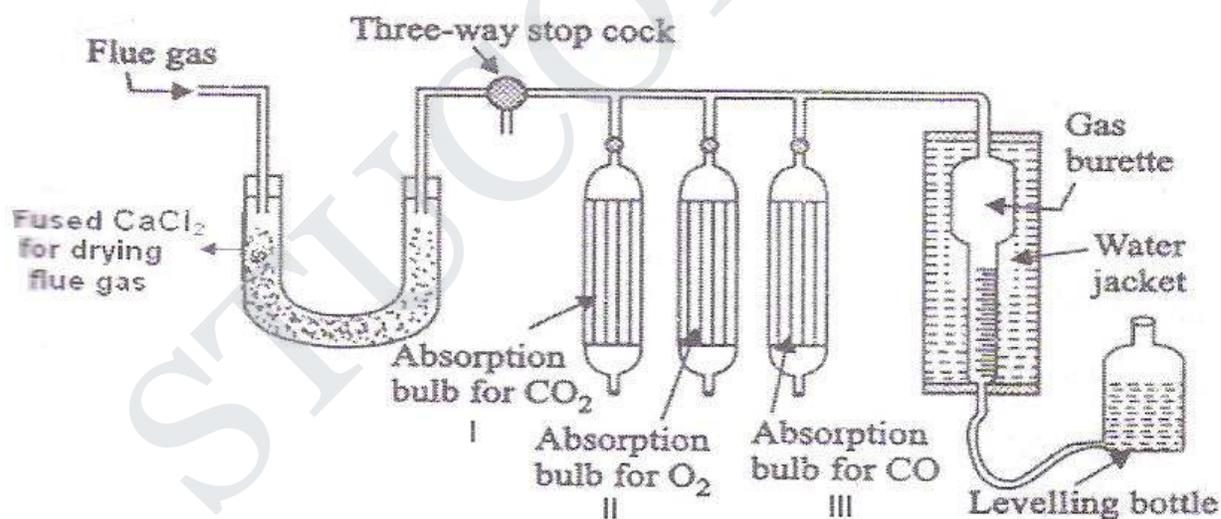
(a) Principle

If the flue gas has more of CO it means the combustion is incomplete. This means the fuel is being wasted. It also means that the oxygen available for combustion is insufficient. If the flue gas contains a lot of oxygen it would mean that the oxygen supply is in excess and that combustion is complete.

The CO_2 , O_2 and CO which come out from the combustion chamber are determined in the Orsat's apparatus by absorbing them in KOH, alkaline pyrogallic acid and ammoniacal cuprous chloride respectively.

Orsat's apparatus consists of a water-jacketed measuring burette connected in series to a set of three absorption bulbs through stop-cocks. At the other end is a three-way stop cock, the free end of which is connected to a U-tube packed with glass wool. This will prevent the entry of smoke particles etc.

The graduated burette is surrounded by a water jacket. This water jacket will keep the temperature of the gas, constant during the experiment. The lower end of the burette is connected to a water reservoir by means of a long rubber tube. The level of water in the 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.



The first bulb contains KOH solution and it absorbs CO_2 . The second bulb has alkaline pyrogallic acid and it can absorb CO_2 and O_2 . The third bulb contains ammoniacal cuprous chloride and it can absorb CO_2 , O_2 and CO. Hence it is a must that the flue gases be first passed through the KOH bulb where CO_2 will be absorbed, then through alkaline pyrogallic acid bulb when only oxygen will be absorbed (as CO_2 has already been removed) and finally through ammoniacal cuprous chloride bulb, where only CO will be absorbed.

(b) Working**Step 1**

The flue gas is passed through the three way stop cock and the reservoir is lowered to draw the gas into the burette. But the sample gas being drawn in will be mixed with some air too. Hence the 3-way stop-cock is opened to the atmosphere and the gas is pushed out by raising the reservoir. The process of sucking and exhausting of the gas is repeated 3-4 times so as to expel the air from the apparatus. Finally gas is sucked into the burette. The volume of the flue gas is adjusted to 100 ml at atmospheric pressure.

Step 2 (Absorption of CO₂)

The 2-way stop-cock of the first absorption bulb- containing caustic potash solution is opened and all the gas is forced into this bulb by raising the reservoir. This process is repeated several times to ensure complete absorption of the CO₂. Now the stop-cock of bulb A is closed. The volume of the residual gases in the burette is noted after equalizing the water level both in the burette and water reservoir. The difference between the original volume (100 CC) and the volume of the gases after CO₂ absorption gives the volume of CO₂ absorbed.

Step 3 (Absorption of oxygen)

The stopcock of bulb A is closed and bulb B is opened. Oxygen present in the flue gas is absorbed by alkaline pyrogallic acid. The procedure thereafter is the same as followed for bulb A.

Step 4 (Absorption of CO)

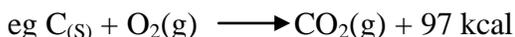
The stopcock of bulb-B is now closed and that of bulb C opened. The ammoniacal cuprous chloride will absorb the CO present in the flue gas. The procedure thereafter is the same as followed for bulb-A.

The total volume of the flue gas analysed is 100 ml. Hence the volumes of the constituents obtained will be their percentages.

The residual gas left after the absorption of CO₂, O₂ and CO is taken as that of nitrogen.

5.11. THEORETICAL AIR FOR COMBUSTION**5.11.1 Combustion of fuels**

Combustion is an exothermic chemical reaction which is accompanied by the development of heat and light at a rapid rate, so that the temperature rises considerably



The rate of combustion depends on

- 1) the nature of the fuel
- 2) the temperature
- 3) concentration of the fuel and air or oxygen

The rate of combustion can be increased by

- 1) preheating the fuel and air
- 2) increasing the surface area of the fuel
- 3) increasing the pressure of air or oxygen used for combustion.

The aim of combustion is to get the maximum amount of heat from a combustible material in the shortest time and to use this heat for various purposes.

Calculation of minimum quantity of air required for the complete combustion of 1 kg of solid and liquid fuel.

To achieve efficient combustion of the fuel it is necessary that there should be

- a) Intimate mixing of sufficient quantity of air with the combustible matter.
- b) Sufficient time should be given for the combustible process to be completed. If not combustion will be incomplete.

Combustion involves the elements such as C, H, S and oxygen in the fuel. Nitrogen, ash and CO₂ (if any) present in the fuel being incombustible will not take up any oxygen during combustion.

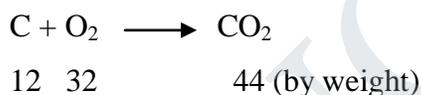
Air contains 21% of oxygen by volume and 23% of oxygen by mass.

1 kg of oxygen is supplied by $1 \times 100/23 = 4.35$ kg of air

Similarly 1m³ of oxygen is supplied by $1 \times 100 / 21 = 4.76$ m³ of air

Hence from the amount of oxygen required by the fuel, the weight or volume of air required can be calculated.

Combustion of Carbon



12 parts by weight of C requires 32 parts by weight of oxygen for complete combustion.

\therefore C parts by weight of carbon requires = $32 \times C / 12 = 2.76 C$

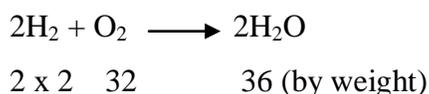
Combustion of Hydrogen

If the fuel has oxygen it will be in combination with hydrogen. Hence this hydrogen will not be available for combustion. This hydrogen in combination with oxygen will have to be deducted from the total hydrogen in the fuel.

Quantity of hydrogen available for combustion reaction will be $[H - O/8]$

Where H = total quantity of hydrogen and O is the total quantity of oxygen in the fuel.

In water the quantity of hydrogen in combination with oxygen is one eighth of the weight of oxygen.

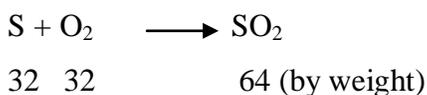


4 parts by weight of hydrogen requires 32 parts by weight of oxygen for complete combustion

\therefore $H - O/8$ part by weight of hydrogen requires.

$$\frac{[(H - O/8) \times 32] / 4}{4} = 8 (H - O/8)$$

Combustion of Sulphur



32 parts by wt of sulphur requires 32 parts by weight of oxygen for complete combustion.

$$\therefore S \text{ part by weight of sulphur requires} = \frac{32 \times S}{32} = S$$

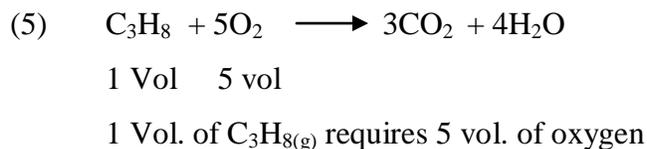
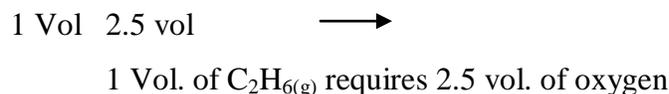
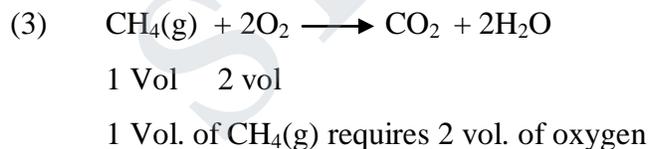
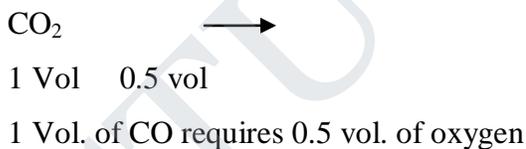
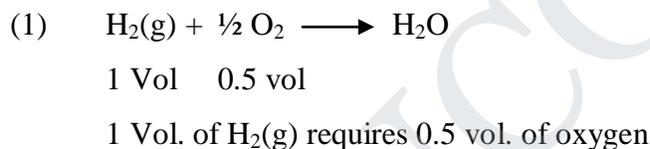
Theoretical amount of oxygen required for the complete combustion of 1 kg of solid or liquid fuel

$$= 2.67C + 8 [H - O/8] + S$$

Since the percentage of oxygen in air by weight is 23, the amount of air required for combustion of 1 kg of fuel

$$= \frac{100}{23} \left[2.67C + 8 \left(H - \frac{O}{8} \right) + S \right] \text{ kg}$$

Volume of air required for complete combustion of Gaseous combustible matters



Hence combustion reaction equations we can calculate the quantity of oxygen required by weight or volume.

The following should be borne in mind while calculating the amount of air required for complete combustion of a fuel.

- 1) The combustion reaction equation should be written.
- 2) From the above equation the amount or volume of the oxygen required by the elements or compounds present in the fuel can be calculated.
- 3) If oxygen is mentioned in the problem, the weight or volume of the oxygen present in the fuel should be subtracted from the total oxygen required by the other elements or compounds.
- 4) N_2 , CO_2 and H_2O will not burn and they do not require any oxygen. Hence their value if mentioned in the problem can be ignored.
- 5) Finally the volume of air required by the fuel can be obtained by multiplying the total volume of oxygen required by 100/21 (air contains 21% oxygen by volume)

The weight of the air required by the fuel can be found by multiplying the total amount of oxygen required by 100/23 (air contains 23% oxygen by weight)

- 6) In actual practice more than the theoretical amount of air is necessary to achieve complete combustion.

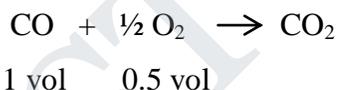
$$\begin{array}{l} \text{Excess air as a percentage} \\ \text{of the theoretical air} \end{array} = \text{Theoretical air} \times \frac{100 + \text{excess air}}{100}$$

5.11.2 Problems based on volume of air

- 1) Calculate the volume of air (volume percentage of oxygen in air = 21) required for the complete combustion of 1 litre of CO.

Solution:

Combustion equation for CO is



For complete combustion,

One volume of CO requires 0.5 volume of oxygen

We know that,

21 litres of oxygen is present in 100 litres of air

$$\therefore 0.5 \text{ litre of oxygen is present in } \frac{100 \times 0.5}{21} = 2.38 \text{ litres of air}$$

\therefore Volume of air required for the complete

combustion of one litre of CO = 2.38 litres

2) A gas used in an internal combustion engine had the following composition by volume $H_2 = 45\%$, $CH_4 = 36\%$, $CO = 15\%$, $N_2=4\%$. Find the volume of air required for the combustion of $1m^3$ of the gas.

Solution:

The combustion equation for the various constituents of the gas is given by,



For complete combustion,

Two volumes of hydrogen requires one volume of oxygen

$$\therefore 0.45 m^3 \text{ of hydrogen requires } \frac{1 \times 0.45}{2} = 0.225 m^3 \text{ of oxygen}$$



1 vol. 2 vol.

For complete combustion,

One volume of methane requires two volumes of oxygen

$$\therefore 0.36 m^3 \text{ of methane requires } \frac{2 \times 0.36}{1} = 0.72 m^3 \text{ of oxygen}$$



2 vol. 1 vol.

For complete combustion,

two volumes of methane requires two volumes of oxygen

$$\therefore 0.15 m^3 \text{ of CO requires } 1 \times 0.15 / 2 = 0.075 m^3 \text{ of oxygen}$$

iii) Nitrogen is non-combustible

$$\text{Total volume of oxygen required} = 0.225 + 0.72 + 0.075$$

the complete combustion of

all the given constituents

$$\text{of the gas} = 1.02 m^3$$

We know that,

21 litres of oxygen is present in 100 litres of air

$\therefore 1.02 \text{ m}^3$ of oxygen is present in $1.02 \times 100 / 21 = 4.857 \text{ m}^3$ of air

\therefore Volume of air required for complete

combustion of 1 m^3 of the gas $= 4.857 \text{ m}^3$

3) A gaseous fuel has the following composition by volume. Methane = 5%, Hydrogen = 20%, Carbonmonoxide = 25%, $\text{CO}_2=6\%$ and rest nitrogen. If 20% excess air is used for combustion, then calculate the volume of air supplied per m^3 of fuel and composition of dry flue gases.

Solution:

1 m^3 of fuel contains

CH_4 - $5/100 = 0.05 \text{ m}^3$

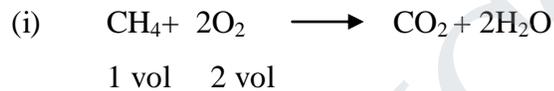
H_2 - $20/100 = 0.20 \text{ m}^3$

CO - $25/100 = 0.25 \text{ m}^3$

CO_2 - $6/100 = 0.06 \text{ m}^3$

N_2 - $1 - (0.05 + 0.20 + 0.25 + 0.06) = 0.44 \text{ m}^3$

The combustion equation for the various constituents of the gas is given by,



For complete combustion,

one volume of methane requires two volumes of oxygen

$\therefore 0.05 \text{ m}^3$ of methane requires $\frac{2 \times 0.05}{1}$

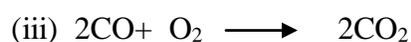
$= 0.1 \text{ m}^3$ of oxygen



For complete combustion,

Two volumes of hydrogen requires one volume of oxygen

$\therefore 0.20 \text{ m}^3$ of hydrogen requires $\frac{0.20 \times 1}{2} = 0.100 \text{ m}^3$ of oxygen



2 vol 1 vol

For complete combustion,

Two volumes of CO requires one volume of oxygen

$$\therefore 0.25 \text{ m}^3 \text{ of CO requires } \frac{0.25 \times 1}{2} = 0.125 \text{ m}^3 \text{ of oxygen}$$

(i) N_2 of CO_2 are non-combustible constituents. Therefore no oxygen is required for burning.

$$\begin{aligned} \text{So total volume of oxygen required} &= 0.1 + 0.1 + 0.125 \\ \text{for complete combustion} &= 0.325 \text{ m}^3 \end{aligned}$$

$$\begin{aligned} \therefore \text{Volume of air required per m}^3 \\ \text{of the gaseous fuel} &= 0.325 \times \frac{100}{21} \end{aligned}$$

$$\begin{aligned} \text{Volume of air required using} \\ \text{20\% excess air for combustion} \\ \text{per m}^3 \text{ of the fuel} &= 0.325 \times \frac{100}{21} \times \frac{120}{100} \\ &= 1.857 \text{ m}^3 \end{aligned}$$

Calculation for composition of dry flue gases



1 Volume of methane on combustion gives one volume of CO_2

$$\begin{aligned} 0.05 \text{ m}^3 \text{ of methane on combustion will give } &1 \times 0.05 \text{ m}^3 \\ &= 0.05 \text{ m}^3 \text{ of } \text{CO}_2 \end{aligned}$$



2 volumes of CO gives on combustion 2 volumes of CO_2

$$\begin{aligned} \therefore 0.25 \text{ m}^3 \text{ of CO on combustion will give } &\frac{2}{2} \times 0.25 \\ &= 0.25 \text{ m}^3 \text{ of } \text{CO}_2 \end{aligned}$$

$$\begin{aligned} \text{CO}_2 \text{ present in } 1 \text{ m}^3 \text{ of fuel} &= 0.06 \text{ m}^3 \\ \text{So total CO}_2 \text{ present in the dry flue gas} &= 0.05 + 0.25 + 0.06 \\ &= 0.36 \text{ m}^3 \end{aligned}$$

$$\begin{aligned} \text{Oxygen content in the flue gas} &= 20 \\ \text{as 20\% excess air is taken} &= 0.325 \times \frac{20}{100} \\ &= 0.065 \text{ m}^3 \end{aligned}$$

$$\text{Nitrogen per m}^3 \text{ of gaseous fuel} = 0.44 \text{ m}^3$$

$$\begin{aligned} \text{Nitrogen in the volume of air} &= 77 \\ \text{required (using 20\% excess)} &= 1.857 \times \frac{77}{100} \\ &= 1.4299 \end{aligned}$$

$$\begin{aligned} \therefore \text{Nitrogen in the flue gas} &= 0.44 + 1.4299 \\ &= 1.8699 \text{ m}^3 \end{aligned}$$

$$\therefore \text{CO}_2 = 0.36 \text{ m}^3$$

$$\text{O}_2 = 0.065 \text{ m}^3$$

$$\text{N}_2 = 1.8699 \text{ m}^3$$

$$\text{Total} = 2.2949 \text{ m}^3$$

$$\begin{aligned} \text{Percentage of CO}_2 &= \frac{0.36}{2.2949} \times 100 \\ &= 15.69\% \end{aligned}$$

$$\begin{aligned} \text{Percentage of N}_2 &= \frac{1.869}{2.2949} \times 100 \\ &= 81.44\% \end{aligned}$$

$$\begin{aligned} \text{Percentage of O}_2 &= \frac{0.065}{2.2949} \times 100 \\ &= 2.83\% \end{aligned}$$

5.11.3 Problems based on weight of air

4) A sample of coal was found to contain C = 80%, H₂ = 5%, O₂ = 1%, N₂ = 2%, remaining being ash. Calculate the amount of minimum air required for the complete combustion of 1 kg of coal sample.

Solution:

1 kg of coal sample contains

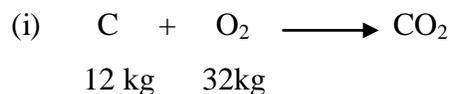
$$\text{C} \quad - \quad 80/100 = 0.80 \text{ kg}$$

$$\text{H}_2 \quad - \quad 5/100 = 0.05 \text{ kg}$$

$$\text{O}_2 \quad - \quad 1/100 = 0.01 \text{ kg}$$

$$\text{N}_2 \quad - \quad 2/100 = 0.02 \text{ kg}$$

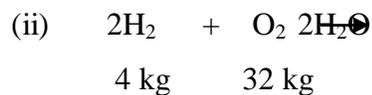
The combustion equation for the various constituents of the gas is given by,



For complete combustion

12 kg of carbon requires 32 kg of oxygen,

$$\therefore 0.8 \text{ kg of carbon requires } \frac{32 \times 0.8}{12} = 2.133 \text{ kg of O}_2$$



For complete combustion

4 kg of H₂ requires 32 kg of oxygen,

$$\therefore 0.05 \text{ kg of H}_2 \text{ requires } \frac{32 \times 0.05}{4} = 0.4 \text{ kg of O}_2$$

(iii) Nitrogen is non-combustible. Therefore no oxygen is required for burning.

$$\begin{aligned} \therefore \text{Total amount of oxygen required} &= 2.133 + 0.4 \\ &= 2.533 \text{ kg} \end{aligned}$$

$$\text{But the amount of oxygen already} = 0.01 \text{ kg}$$

$$\begin{aligned} \therefore \text{Net amount of oxygen required} &= \text{Total amount for complete combustion of} \\ &\text{oxygen present in fuel} - \text{Amount of all the constituents already present in fuel} \\ &= 2.533 - 0.01 \\ &= 2.523 \text{ kg} \end{aligned}$$

We know that,

23 kgs of oxygen is present in 100 kgs of air

$$\therefore 2.523 \text{ kg of oxygen is present in } \frac{2.523 \times 100}{23} = 10.970 \text{ kg of air}$$

\therefore Minimum amount of air required = 10.970 kg

for complete combustion of

1 kg of coal

5) A coal sample on analysis gives C = 80%, S = 1%, H₂ = 4.5%, O₂ = 2% and rest ash.

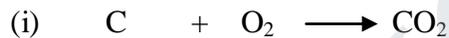
Find the theoretical amount of air required per 2 kg of coal burnt .

Solution:

1 kg of coal sample contains.

$$\begin{aligned} \text{C} &= 80/100 = 0.8 \text{ kg} \\ \text{S} &= 1/100 = 0.01 \text{ kg} \\ \text{H}_2 &= 4.5/100 = 0.045 \text{ kg} \\ \text{O}_2 &= 2/100 = 0.02 \text{ kg} \end{aligned}$$

The combustion equation for the various constituents of the gas is given by



$$12 \text{ kg} \quad 32 \text{ kg}$$

For complete combustion,

12 kg of carbon requires 32 kg of oxygen

$$\therefore 0.8 \text{ kg carbon requires } \frac{32 \times 0.8}{12} = 2.133 \text{ kg of O}_2$$



$$4 \text{ kg} \quad 32 \text{ kg}$$

For complete combustion,

4 kg of H₂ requires 32 kg of oxygen,

$$\therefore 0.045 \text{ kg H}_2 \text{ requires } \frac{32 \times 0.045}{4} = 0.36 \text{ kg of O}_2$$



32 kg 32 kg

For complete combustion,

32 kg of S requires 32 kg of oxygen

$$\therefore 0.01 \text{ kg of S requires } \frac{32 \times 0.01}{32} = 0.01 \text{ kg of O}_2$$

(iv) Ash is non-combustible. Therefore no oxygen is required for burning.

$$\begin{aligned} \therefore \text{Total amount of oxygen required} &= 2.133 + 0.36 + 0.01 \\ &= 2.503 \text{ kg} \end{aligned}$$

But the amount of oxygen already present in the fuel = 0.02 kg

$$\begin{aligned} \text{Net amount of oxygen required for complete combustion of oxygen all the constituents already present in fuel} &= \text{Total amount} - \text{Amount of Oxygen} \\ &= 2.503 - 0.02 \\ &= 2.483 \text{ kg} \end{aligned}$$

We know that,

23 kg of oxygen is present in 100 kgs of air

$$\begin{aligned} \therefore 2.483 \text{ of oxygen is present in } &\frac{2.483 \times 100}{23} \\ &= 10.796 \text{ kg of air} \end{aligned}$$

Minimum amount of air required for complete combustion of 1 kg of coal = 10.796 kg

Minimum amount of air required for complete combustion of 2 kg of coal = 10.796 x 2 = 21.592

7. Calculate the mass of air needed for the complete combustion of 5 kg of coal containing C = 80%, H = 15%, O = rest

Solution:

1 kg of coal sample contains

$$C = 80 / 100 = 0.8 \text{ kg}$$

$$H = 15 / 100 = 0.15 \text{ kg}$$

$$\begin{aligned} \text{oxygen} &= 1 - (0.8 + 0.15) \\ &= 0.05 \text{ kg} \end{aligned}$$

$$\begin{aligned} \text{Mass of air required} &= \frac{100}{23} \left[2.67C + \left(H - \frac{O}{8} \right) 8 + S \right] \\ \text{for complete combustion} & \end{aligned}$$

of 1 kg of coal

$$= \frac{100}{23} \left[(2.67 \times 0.8) + \left(0.15 - \frac{0.05}{8} \right) 8 + 0 \right]$$

$$= 14.3 \text{ kg}$$

Hence mass of air required for the complete combustion of 5 kg coal = $14.3 \times 5 = 71.5$ kg

8. A fuel is found to contain C = 90% H = 6%, S = 2.5% O=1% and ash = 0.5%. Calculate the amount of air required for the complete combustion of 1 kg of fuel. If 25% excess air is used for combustion calculate the amount of dry products in the flue gas.

Solution:

$$\begin{aligned} \text{(i) } C &= \frac{90}{100} = 0.9 \text{ kg} \end{aligned}$$

$$\begin{aligned} H &= \frac{6}{100} = 0.06 \text{ kg} \end{aligned}$$

$$\begin{aligned} S &= \frac{2.5}{100} = 0.025 \text{ kg} \\ &= \frac{1}{100} \end{aligned}$$

$$O = \frac{\quad}{100} = 0.01 \text{ kg}$$

$$\text{Ash} = \frac{0.5}{100} = 0.005 \text{ kg}$$

Amount of air required for the complete combustion of 1 kg of fuel = $\left[\frac{100}{23} \cdot 2.67C + \left(H - \frac{O}{8} \right) 8 + S \right]$

$$= \left[\frac{100}{23} (2.67 \times 0.9) \left(0.06 - \frac{0.01}{8} \right) 8 + 0.025 \right]$$

$$= 12.6 \text{ kg}$$

ii) Calculation of dry products when 25% excess air is used



Carbon

12 kg of carbon on combustion gives 44 kg of CO₂. So 0.9 kg of carbon present in the fuel will give

$$= \frac{44}{12} \times 0.9 \text{ kg of } CO_2$$

$$= 3.3 \text{ kg}$$

Sulphur



32 kg of sulphur on combustion gives 64 kg of SO₂. So 0.025 kg of sulphur present in fuel will give

$$= \frac{64}{32} \times 0.025 = 0.05 \text{ kg}$$

Nitrogen

Nitrogen present in 12.6 kg of air

$$= 12.6 \times \frac{77}{100} \text{ kg}$$

$$\begin{aligned} \text{Nitrogen present when 25\% excess air is used} &= 12.6 \times \frac{77}{100} \times \frac{125}{100} \\ &= 12.115 \text{ kg} \end{aligned}$$

Oxygen

Oxygen present in the fuel = 0.01 kg

$$\text{Oxygen present when 12.6 kg of air} = 12.6 \times \frac{23}{100} \text{ kg}$$

$$\begin{aligned} \text{Oxygen present when 25\% excess air is used} &= 12.6 \times \frac{23}{100} \times \frac{125}{100} = 3.626 \text{ kg} \end{aligned}$$

∴ Total amount of dry products

in the flue gas

$$\begin{aligned} &= \text{C} + \text{S} + \text{N} + \text{O} \\ &= 3.3 + 0.05 + 12.115 + 3.626 \\ &= 19.091 \text{ kg} \end{aligned}$$

$$\begin{aligned} \% \text{ CO}_2 &= (3.3 / 19.091) \times 100 \\ &= 17.28\% \end{aligned}$$

$$\begin{aligned} \% \text{ SO}_2 &= 0.05 / 19.091 \times 100 \\ &= 0.26\% \end{aligned}$$

$$\begin{aligned} \% \text{ N}_2 &= 12.115 / 19.091 \times 100 \\ &= 63.34\% \end{aligned}$$

$$\begin{aligned} \% \text{ O}_2 &= 3.626 / 19.091 \times 100 \\ &= 19.02\% \end{aligned}$$

9. Calculate the weight and volume of air required for the complete combustion of 1 kg coke or carbon.

Solution:



12 kg of carbon for combustion requires = 32 kg of oxygen

$$1 \text{ kg of carbon will require} = \frac{32}{12} \times 1 = 2.67 \text{ kg of oxygen}$$

∴ Wt of air required for
complete combustion of $= \frac{100}{23} \times 2.67 = 11.61$ kg of air
1 kg of coke or carbon

ii) Based on the fact that

(a) 22.4 l of any gas at NTP has a mass equal to its gram molecular weight.

(b) Molecular mass of air is taken as 28.94 g/mol

28.94 g mole⁻¹ of air will occupy 22.4 l

$$\begin{aligned} \therefore 11.61 \times 1000 \text{ gm of air will occupy} \\ &= \frac{22.4}{28.94} \times 11.61 \times 1000 \\ &= 8986.3 \text{ L} \end{aligned}$$

Ignition Temperature (IT)

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

Spontaneous ignition temperature (SIT)

It is defined as “the minimum temperature at which the fuel catches fire spontaneously without external heating”.

UNIT V – ENERGY SOURCES AND STORAGE DEVICES

5.1 INTRODUCTION

For our energy requirement, we mainly depend upon the conventional sources of energy like coal, petroleum, natural gas, etc., These sources are limited in quantity and can be exhausted in near future. This is because of their continuous and rapid use.

To overcome this energy crises, the scientists have accelerated the search and use of non-conventional (renewable) sources of energy like wind energy, solar energy, nuclear energy, etc.

5.2 Nuclear Fission

When U²³⁵ is bombarded by thermal neutron (low energy neutron), it splits into two approximately equal parts with the liberation of large amount of energy.

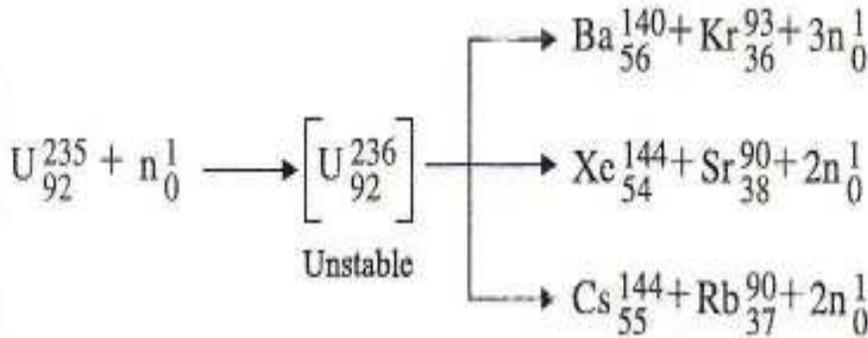
5.2.1 Definition

Nuclear fission is defined as “**the process of splitting of heavier nucleus into two (or) more smaller nuclei with simultaneous liberation of large number of energy**”.

5.2.2 Mechanism of nuclear fission

When U²³⁵ is bombarded by thermal neutron (slow moving), unstable U²³⁶ is formed. The unstable

U^{236} then divides into two approximately equal nuclei with the release of neutrons and large number of energy



Illustration

During the nuclear fission a large amount of energy is released.

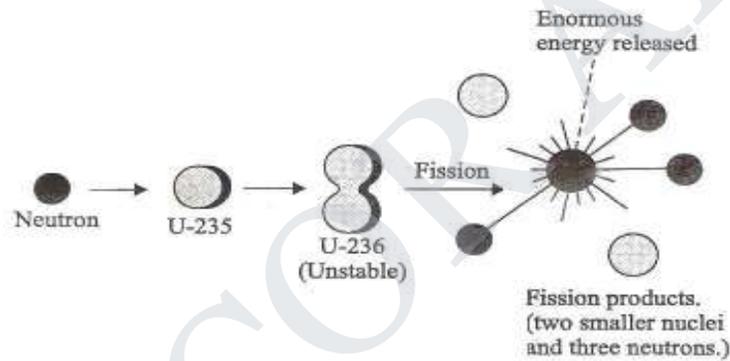


Fig. 5.1 The fission process illustrated

5.2.3 CHARACTERISTICS OF NUCLEAR FISSION

- ❖ A heavy nucleus such as (U^{235} (or) Pu^{239}) is bombarded by slow moving neutrons, split into two or more smaller nuclei.
- ❖ Two or more neutrons are produced by fission of each nucleus.
- ❖ Large quantities of energy are produced as a result of conversion of small mass of nucleus into energy.
- ❖ All the fission fragments are radioactive, giving off β and γ radiations.
- ❖ The atomic weights of fission fragments range from about 70 to 160.
- ❖ All the fission reactions are a self-propagating chain-reactions fission products contain neutrons (secondary neutrons) which further cause fission in other nuclei.
- ❖ The nuclear chain reactions can be controlled and maintained steadily by absorbing a desired number of neutrons. This process is used in nuclear reactor.
- ❖ Every secondary neutron, released in the fission process, does not strike a nucleus, some escape

into air and hence a chain reaction cannot be maintained.

- ❖ **Multiplication factor:** The number of neutrons, resulting from a single fission is known as the Multiplication factor. When the value of multiplication is less than 1, a chain reaction does not take place.

5.2.4 Advantages and disadvantages of nuclear fission energy

Advantages of nuclear fission energy over fossil fuels energy

1. A small amount of nuclear fuel (U235) gives a large amount of energy while large quantity of fossil fuel is required to produce large amount of heat.
2. In a nuclear power plant, the nuclear fuel is inserted once to get energy over a long period of time. But, in a thermal power plant, fossil fuel is to be supplied continuously to get the energy.

Disadvantages of nuclear fission energy over fossil fuels energy

1. Nuclear fission causes more serious pollution problems than burning fossil fuels.
2. The biggest problem of using nuclear fission energy is the safe disposal of nuclear waste. But no such problem is faced in the disposal of fossil fuels.

5.3 NUCLEAR FUSION

Nuclear fusion is defined as “**the process of combination of lighter nuclei into heavier nuclei, with simultaneous liberation of large amount of energy**”. Nuclear fusion occurs in sun.

Example:

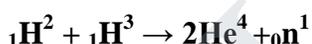


Fig. 5.2 The fusion process illustrated

5.3.1 CHARACTERISTICS OF NUCLEAR FUSION

1. Unlike nuclear fission, there is no limit on the amount of nuclear fusion that can occur.
2. It is possible only when the distance between the nuclei is of the order of one Fermi.
3. The amount of energy in fusion is 4 times more compared to that of fission.

5.3.2 Difference between nuclear fission and fusion

S.No	Nuclear fission	Nuclear fusion
1.	It is the process of breaking of heavier	It is the process of combination of

	nucleus.	lighter nuclei.
2.	It emits radioactive rays	It does not emit any kind of radioactive rays.
3.	It occurs ordinary temperature.	It occurs high temperature($>10^6$)
4.	The mass number and atomic number of new elements are lower than that of parent nuclei.	The mass number and atomic number of product is higher than that of starting elements.
5.	It gives rise to chain reaction	It does not rise to chain reaction
	It emits neutrons	It emits positrons
6.	It can be controlled	It cannot be controlled

5.4 NUCLEAR CHAIN REACTION

In the nuclear fission reaction the neutrons emitted from the fission of U^{235} atom may hit another U^{235} nuclei and cause fission producing more neutrons and so on. Thus, a chain of self-sustaining nuclear reactions will set up with the release of enormous amount of energy. But the amount of energy released will be less than expected. Thus the fission of U^{235} by slow moving neutrons is a chain reaction.

5.4.1 Definition

A fission reaction, where the neutrons from the previous step continue to propagate and repeat the reaction is called nuclear chain reaction.

Reason for less energy

Some of the neutrons, released in the fission of U^{235} , may escape from the surface to the surroundings or may be absorbed by U^{235} present as impurity. This will result in breaking of the chain and the amount of energy released will be less than expected.

5.4.2 Criteria for nuclear chain reaction

- ❖ For a nuclear chain reaction to continue sufficient amount of U^{235} must be present to capture the neutrons, otherwise neutrons will escape from the surface.

Critical mass

The minimum amount of fissionable material (U^{235}) required to continue the nuclear chain reaction is called critical mass.

The critical mass of U^{235} lies between 1 kg to 100kg.

(a) Super critical mass

If the mass of the fissionable material (U^{235}) is more than the critical mass, it is called

super critical mass.

(b) Sub critical mass

If the mass of the fissionable material is smaller than the critical mass; it is called sub critical mass.

- ❖ Thus the mass greater or lesser than the critical mass will hinder the propagation of the chain reaction.

Illustration

When U^{235} nucleus is hit by a thermal neutron, it undergoes the following reaction with the release of three neutrons.



Each of the three neutrons, produced in the above reaction, strikes another U^{235} nucleus causing 9 subsequent reactions. This 9 reaction further give rise to 27 reactions. This process of propagation of the reaction by multiplication in threes at each fission is called Chain reaction.

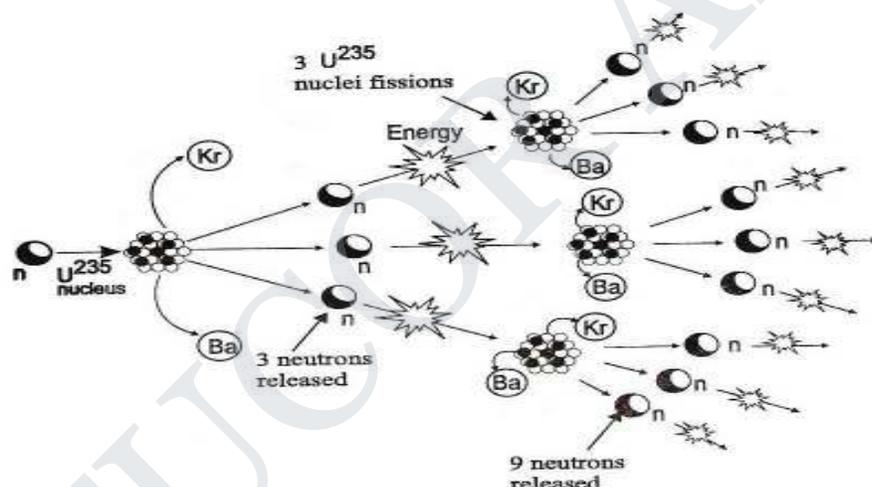


Fig. 5.3 U^{235} fission chain reaction illustrated

5.5 NUCLEAR ENERGY

The enormous amount of energy released during the nuclear chain reaction of heavy isotope like U^{235} or Pu^{239} is called nuclear energy.

5.5.1 DEFINITION

The energy released by the nuclear fission is called nuclear fission energy or nuclear energy.

Illustration

The fission of U^{235} or Pu^{239} occurs instantaneously, producing enormous amount of energy in the form of heat and radiation.

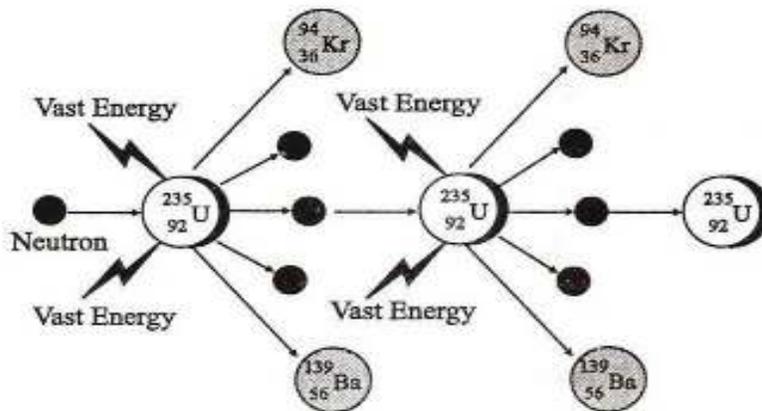


Fig. 5.4 Nuclear energy illustrated

5.5.2 CAUSE OF THE RELEASE OF ENERGY

The enormous amount of energy released during the nuclear fission is due to the loss in some mass, when the reaction takes place. It has been observed that 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 Einstein equation.

$$E = mc^2$$

Where,

c = velocity; m = loss in mass and E = energy

5.5.3 Hazards of using nuclear energy

The radiation is harmful to the living organisms. The long and constant exposure of living organisms to these radiations causes the following disease.

1. Damage the structure of cells in the human body.
2. Cancer and blindness.
3. Genetic disorder in a human body.
4. Sterility in young generation

5.5.4 Applications of nuclear energy

1. Electricity generation
2. Sources of pure water
3. Health care
4. Agriculture

5.6 TYPES OF NUCLEAR FISSION REACTION

5.6.1. Uncontrolled nuclear fission reaction

If a nuclear fission reaction is made to occur in an uncontrolled manner, then the energy released can be used for many destructive purposes.

Ex: Atom Bomb

5.6.2. Controlled nuclear fission reaction

If a nuclear fission reaction is made to occur in an controlled manner, then the energy released can be used for many constructive purposes.

Ex: Nuclear Reactor

5.7 NUCLEAR REACTOR (OR) PILE: If a nuclear fission reaction is made to occur in a controlled manner, then the energy released can be used for many constructive purposes.

5.7.1 DEFINITION

The arrangement or equipment used to carry out fission reaction under controlled conditions is called a nuclear reactor.

Example:

The energy released (due to the controlled fission of U^{235} in a nuclear reactor) can be used to produce steam which can run turbines and produce electricity.

5.7.2 Classification of nuclear reactors

I. Based on neutron energy and moderator

1. Thermal neutron reactors

In these reactors, nuclear fission reaction is brought out by slow moving neutrons. These are further classified into various types

(a) Light water moderated reactors (LWR)

In these reactors, ordinary water is used as moderators and coolant. These are cheaper and have excellent safety and stability when compared to other nuclear reactors.

These are further classified into

- (i) Boiling water reactors (BWR)
- (ii) Pressurized water reactors (BWR)
- (iii) Supercritical water reactors (BWR)

(b) Heavy water moderated reactors (HWR)

Heavy water is used as a moderator

(c) Graphite moderated reactors (GMR)

Graphite is used as a moderator

- (i) Gas cooled reactors
- (ii) Water cooled reactors

2. Fast neutron reactors

In these reactors nuclear fission is brought out by unmoderated fast moving (high energy) neutrons. These are generally cooled by liquid metal.

II. Based on fuel used

1. Burner

Here, nuclear fuel is burnt to produce heat or electrical energy.

2. Converter (or) Breeder type reactors

II. Based on purpose

- (a) Power reactor
- (b) Breeder reactor
- (c) Materials testing reactor

5.7.3 COMPONENTS OF A NUCLEAR REACTOR

The main components of the nuclear reactor are

1. Fuel rods

The fissionable materials used in the nuclear reactor are enriched U^{235} or Pu^{239} . The enriched fuel is used in the reactor in the form of rods or strips.

Example: U^{235} ; Pu^{239} (obtained from U^{238})

Function: It produces heat energy and neutrons which initiates the nuclear chain reaction. The heat should be removed efficiently during the fission process.

2. Control rods

To control the fission reaction (rate), movable rods, made of cadmium (or) boron, are suspended between fuel rods. These rods can be lowered or raised. They control the fission reaction by absorbing excess neutrons. If the rods are deeply inserted inside the reactor, they will absorb more neutrons and the reaction become very slowly. On the other hand, if the rods are pushed outwards, they will absorb less neutrons and the reaction will be very fast.

Example:



Function: It controls the nuclear chain reaction and avoids the damage of the reactors.

3. Moderators

The substance used to slow down the neutrons is called moderates.

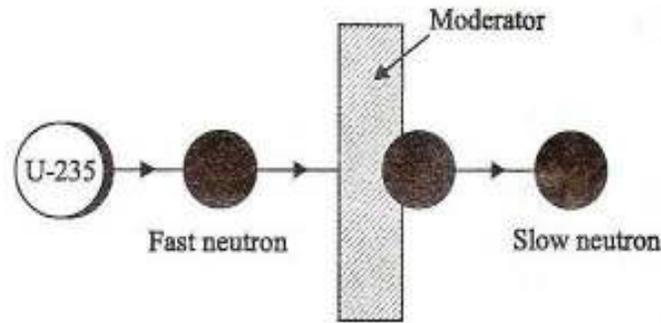


Fig. 5.5 Function of a moderator

When the fast moving neutrons collide with moderator they lose energy and gets slow down.

Example: Ordinary water, Heavy water, Graphite, Beryllium

Function: The kinetic energy of fast neutrons (1MeV) is reduced to slow neutrons (0.25eV)

4. Coolants

In order to absorb the heat products during fission, a liquid called coolant is circulated in the reactor core. It enters the base of the reactor and leaves at the top. The heat carried by out-going liquid is used to produce steam.

Example: Water and heavy water, Liquid metals like Na, K and Air

Function: It cools the fuel core.

5. Pressure vessel

It encloses the core and also provides the entrance and exit passage for coolant. Holes at the top of the vessel are provided to insert or pull out the control rods.

Function: It withstands the pressure as high as 200 kg/cm².

6. Protective shield

The nuclear reactor is enclosed in a thick massive concrete shield (more than 10 meters thick).

Function: The environment and operating personnel's are protected from destruction in case of leakage of radiation.

7. Turbine

The steam generated in the heat exchanger is used to operate a steam turbine, which drives a generator to produce electricity.

5.7.4 LIGHT WATER NUCLEAR REACTOR

Light-water nuclear -power plant is the one, in which U²³⁵ fuel rods are submerged in water.

Here the water acts as coolant and moderator.

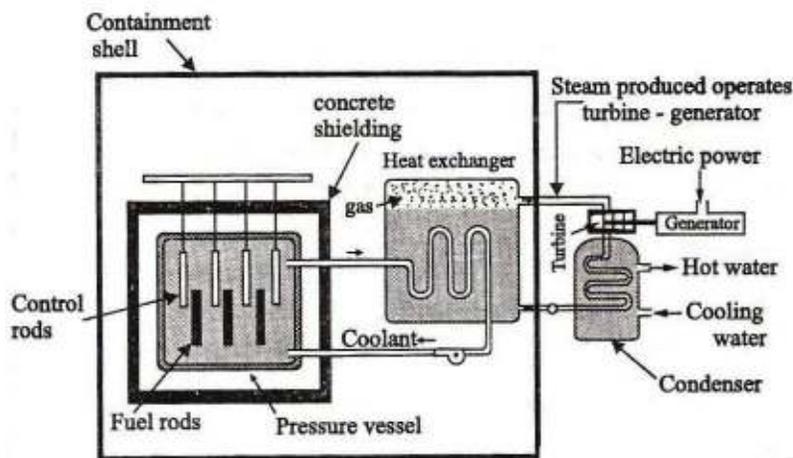


Fig. 5.6 Light water nuclear power plant

Working

The fission reaction is controlled by inserting or removing the control rod of B¹⁰ automatically from the spaces in between the fuel rods. The heat emitted by fission of U²³⁵ in the fuel core is absorbed by the coolant (light water). The heated coolant (water at 300°C) then goes to the heat exchanger containing sea water. The coolant here, transfers heat to sea water, which is converted into steam. The steam then drives the turbines, generating electricity.

Pollution

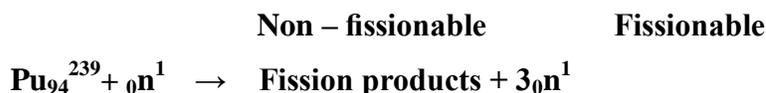
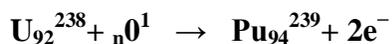
Though nuclear power plants are very important for production of electricity, they will cause a serious danger to environments.

Problem on disposal of reactor waste

Disposal of reactor waste is another important problem because the fission products viz., Ba¹³⁹ and Kr⁹² are themselves radioactive. They emit dangerous radiation for several hundred years. So waste is packed in concrete barrels, which are buried deep in the sea.

5.8 BREEDER REACTOR

Breeder reactor is the one which convert non-fissionable material (U²³⁸, Th²³²) into fissionable materials (U²³⁵, Th²³³). Thus the reactor produces more fissionable materials than it consumes.



In breeder reactor, of the three neutrons emitted in the fission of U²³⁵, only one is used in propagating the fission chain with U²³⁵. The other two are allowed to react with U²³⁸. Thus, two fissionable atoms of U²³⁵ are produced for each atom of U²³⁵ consumed. Therefore, the breeder reactor produces more fissionable material than it uses. Hence Pu²³⁹ is a **man-made nuclear fuel**

- ❑ It is generally used in cold places, which houses are kept in hot condition using solar heat collectors.

Solar water heater

It consists of an insulated box inside of which is painted with black paint. It is also provided with a glass lid to receive and store solar heat. Inside the box it has black painted copper coil, through which cold water is allowed to flow in, which gets heated up and flows out into a storage tank. From the storage tank water is then supplied through pipes.

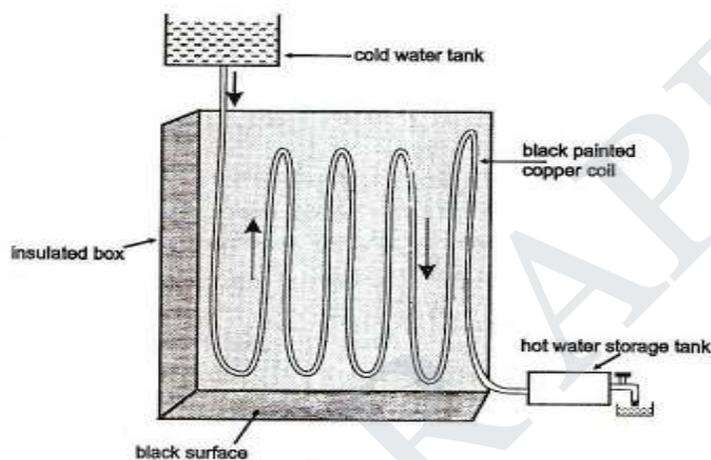


Fig. 5.8 Solar water heater

5.9.2 Photo conversion

Photo conversion involves conversion of light energy directly into electrical energy.

Methods of photo conversion

- Photo conversion can be made by the following method.
- Photo galvanic cell or Solar cell.

5.10 PHOTO GALVANIC CELL OR SOLAR CELL

Definition

Photo galvanic cell is the one, which converts the solar energy (energy obtained from sun) directly into electrical energy.

Principle

The basic principle involved into the solar cell is based on the photovoltaic (PV) effect. When the solar rays fall on a two layer of semi-conductor devices, a potential difference between the two layers is produced. This potential difference causes flow of electrons and produces electricity.

Construction

A solar cell consists of a p-type semiconductor (such as Si doped with B) and n-type semiconductor (such as Si doped with P). They are in close contact with each other.

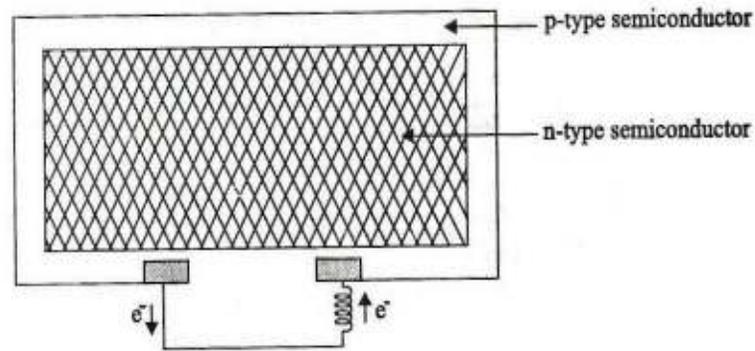


Fig5.9 Solar cell

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. There by potential difference between two layers is created, which causes flow of electrons (ie., an 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.

5.10.1 Applications of solar cells

1. Lighting purpose

Solar cells can be used for lighting purpose. Nowadays electrical street lights are replaced by solar street lights.

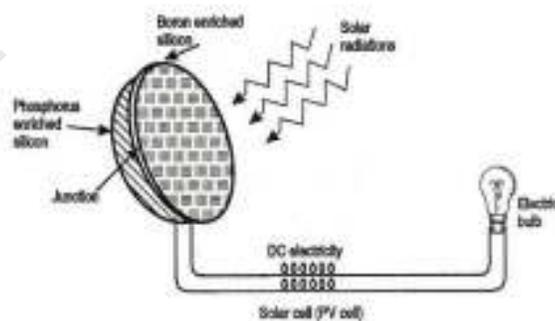


Fig. 5.10 Solar light

2. Solar pumps run by solar battery

When a large number of solar cells are connected series it form a solar battery. Solar battery produces more electricity which is enough to run, water pump, street-light etc. They are also used in remote areas where conventional electricity supply is a problem.

Solar cells are used in calculators, electronic watches, radios and TVs.

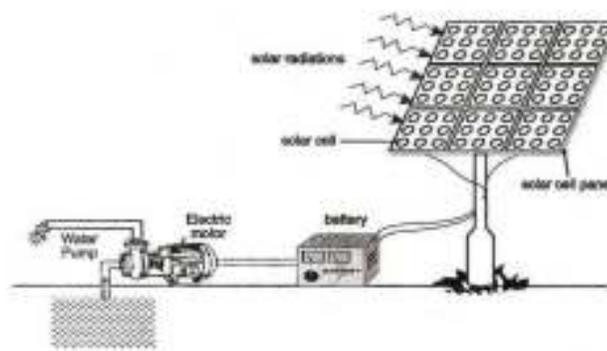


Fig. 5.11 Solar pump run by solar cells (Battery)

3. Solar cells are superior to other type of cells, because these are non-polluting and eco-friendly.
4. Solar energy can be stored in Ni-Cd batteries and lead acid batteries.
5. Solar cells can be used to drive vehicles.
6. Solar cells, made of silicon, are used as a source of electricity in space craft and satellites.

5.10.2 Advantages of solar cells

1. Solar cells can be used in remote and isolated area, forests and hilly regions.
2. Maintenance cost is low.
3. Solar cells are noise and pollution free.
4. Their lifetime is long.

Disadvantages

- ✓ Capital cost is higher.
- ✓ Storage of energy is not possible.

5.11 WIND ENERGY

Moving air is called wind. Energy recovered from the force of the wind is called wind energy. The energy possessed by wind is because of its high speed. The wind energy is harnessed by making use of wind mills.

5.11.1 Methods of harnessing wind energy

1. Wind mills

The strike of blowing wind on the blades of the wind mill makes it rotating continuously. The rotational motion of the blades drives a number of machines like water pump, flour mills and electric generators.

Now a day's wind mill uses large sized propeller blades and is connected to a generator through a shaft. Wind mills are capable of generating about 100 kW electricity.

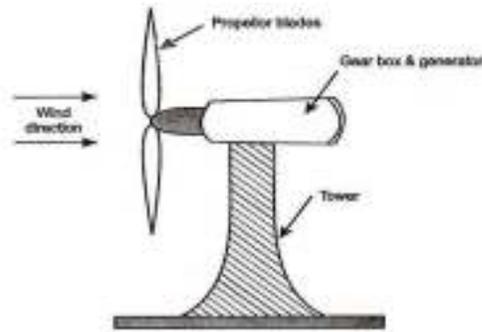


Fig. 5.12 Wind mill

2. Wind farms

When a large number wind mills are installed and joined together in a definite pattern it forms a wind farm. The wind farms produce a large amount of electricity.

Condition

The minimum speed required for satisfactory working of a wind generator is 15 km/hr.

3. Others methods

Other methods adopted for harnessing wind energy are

- (a) Sky sail.
- (b) Ladder mill.
- (c) Kite ship (Large free flying sails.)
- (d) Sky wind power (Flying electric generator.)
- (e) Briza technologies (Hovering wind turbine)
- (f) Sequoia automation (The kite wind generator).

5.11.2 Advantages of wind energy

- (i) It does not cause any air pollution.
- (ii) It is very cheap and economic.
- (iii) It is renewable.
- (iv) It does not cause any pollution.

Disadvantages

- ✓ Public resists for locating the wind forms in polluted areas due to noise generated by the machines and loss of aesthetic appearance.
- ✓ Wind forms located on the migratory routes of birds will cause hazards.
- ✓ Wind forms produce unwanted sound.
- ✓ Wind turbines interfere with electromagnetic signals(TV, Radio signals).

5.11.3 Use of wind energy

1. Used to move the sail boats in lakes, rivers and seas.

2. Used to operate water pumps.

BATTERIES AND FUEL CELLS

6.1 INTRODUCTION

In electrochemical cells, the chemical energy is converted into electrical energy. The cell potential is related to free energy change. In an electrochemical cell, the system does work by transferring electrical energy through an electric circuit. Thus free energy change for a reaction is a measure of the maximum useful work that can be obtained from a chemical reaction.

i.e., $\Delta G =$ maximum useful work

But we know that

Maximum useful work = nFE

When a cell operates, work is done on the surroundings (flow of electricity).

$$\Delta G = -nFE$$

OR

$$\Delta G < 0$$

Decrease in free energy is indicated by negative sign.

One of the main uses of the galvanic cells is the generation of portable electrical energy. These cells are known as batteries.

6.1.1 Battery

A battery is an arrangement of several electrochemical cells connected in series that can be used as a source of direct electric current.

A cell: It contains only one anode and cathode.

A Battery: It contains several anode and cathode.

6.1.2 Requirements of a battery

A useful battery should fulfil the following requirements.

- It should be light and compact for easy transport.
- It should have long life both, when it is being used and when it is not used.
- The voltage of the battery should vary appreciably during its use.

6.2 TYPES OF BATTERY

1. Primary Battery (or) Primary cells (or) Non-reversible Battery

In these cells, the electrode and the electrode reactions cannot be reversed by passing an external electrical energy. The reactions occur only once after use they become dead. Therefore, they are **not chargeable**. **Examples: Dry cell, mercury cell.**

2. Secondary Battery or Secondary cells or Reversible Battery

In these cells, the electrode reactions can be reversed by passing an external electrical energy. Therefore, they can be chargeable by passing electric current and used again and again. These are

also called **Storage cell** or **Accumulators**.

Examples: Lead acid storage cell, Nickel-cadmium cell.

3. Flow Battery or Fuel cell

In these cells, the reactants, products and electrolytes are continuously passing through the cell. In this chemical energy gets converted into electrical energy.

Example: Hydrogen-Oxygen fuel cell.

6.3 Dry Cell or Leclache's Cell

Description

A dry cell consists of a zinc cylinder, which acts as anode. This zinc cylinder is filled with an electrolyte consisting of NH_4Cl , ZnCl_2 and MnO_2 in the form of paste using starch and water.

A carbon rod acts as cathode, is immersed in the electrolyte in the cell. The zinc cylinder has an outer of cardboard case. During use, the zinc cylinder gets consumed and the end, it will develop holes which are responsible for leakages.

Working

When the cell is working, zinc losses electrons and Zn^{2+} ions gets dissolved in the electrolyte. The electrons pass through the circuit and are consumed at cathode. This causes discharge of NH_4^+ ions from the electrolyte.

Cell reactions

Anode:



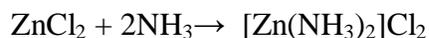
Cathode:



Overall reaction:



In cathode reaction, Mn is reduced from +4 oxidation state to +3 oxidation state. The liberation of NH_3 gas, which disturbs the current flow, is prevented by a reaction of NH_3 with Zn^{2+} .



6.3.1 Advantages of alkaline battery over dry battery

- ❖ This dry cell do not have an indefinite life, because NH_4Cl being acidic corrodes the zinc container, even if it is not used.
- ❖ When current is drawn rapidly from it, produces build up on the electrodes, so voltage drop occurs.

Uses: It is used in calculators, watches etc.

6.4 LEAD ACID STORAGE CELL OR LEAD ACCUMULATOR OR ACID STORAGE CELL

Storage cell

A lead acid storage cell is secondary battery, which can operate both 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 electrolytic cell.

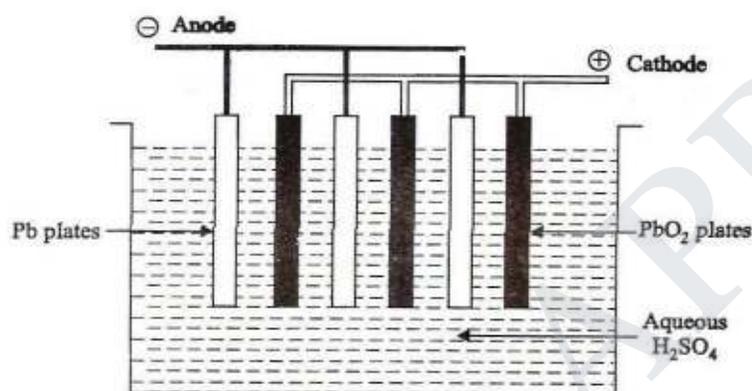


Fig. 6.2 Lead storage cell

Description

A lead acid storage battery consists of a number of (3 to 6) voltaic cells connected in series to get 6 to 12 V battery. In each cell, the anode is made of lead. The cathode is made of lead dioxide or a grid made of lead, packed with lead dioxide. A number of lead plates (anodes) are connected in parallel and a number of lead dioxide plates (cathodes) are also connected in parallel. Various plates are separated from the adjacent ones by insulators like rubber or glass fibre. The entire combinations is then immersed in dil. sulphuric acid (38 percentage by mass) having a density of 1.30 gm/ml. The cell may be represented as;

Cell representation:

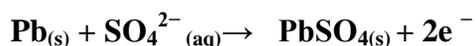


Working (Discharging)

When the lead acid storage battery operates, the following reaction occurs.

Anode

Lead is oxidized to Pb^{2+} ions, which further combines with SO_4^{2-} forms insoluble PbSO_4 .

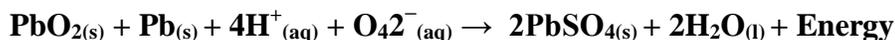


Cathode

PbO_2 is reduced to Pb^{2+} ions, which further combines with SO_4^{2-} forms insoluble PbSO_4



Overall reaction:



From the above cell reactions it is clear that, lead sulphate is precipitated at both the electrode and sulphuric acid is used up. As a result, the concentration of sulphuric acid decreases and hence the density of sulphuric acid falls below 1.2 gm/ml. So the battery needs recharging.

Recharging the Battery

The cell can be charged by passing electric current in the opposite direction. The electrode reaction is reversed. As a result, Pb is deposited on anode and lead dioxide on the cathode. The density of sulphuric acid also increases.

The net reaction during charging is,



Advantages of lead acid battery

- It is made easily.
- It produces very high current.
- The self-discharging rate is low when compared to other rechargeable batteries.
- it also acts effectively at low temperature.

Disadvantages of lead acid batteries

- Recycling of this battery causes environmental hazards.
- Mechanical strain and normal bumping reduces battery capacity.

Uses

- ❖ Lead storage cell is used to supply current mainly in automobiles such as cars, buses, trucks, etc.,
- ❖ It also used in gas engine ignition, telephone exchanges, hospitals, power stations, etc.,

6.6 LITHIUM BATTERY

Lithium- ion battery is a secondary battery. As in lithium cell, it does not contain metallic lithium as anode. As the name suggests, the movement of lithium ions are responsible for charging and discharging. Lithium -ion cell has the following three components.

- Cathode-Lithium metal oxide
- Anode-Porous carbon
- Electrolyte- Polymer gel

Construction

The positive electrode is typically made from a layers of chemical compound called lithium-cobalt oxide (LiCoO_2)

The negative electrode is made from layers of porous carbon.

Both the electrodes are dipped in a polymer gel electrolyte and separated by a separator, which is a perforated plastic and allows the lithium ions to pass through.

Working (Charging)

During charging Li^+ ions flow from the positive electrode to the negative electrode through the electrolyte. Electrons also flow from the positive electrode to the negative electrode through the wire. The electrons and Li^+ ions combine at the negative electrode and deposit there as Li.

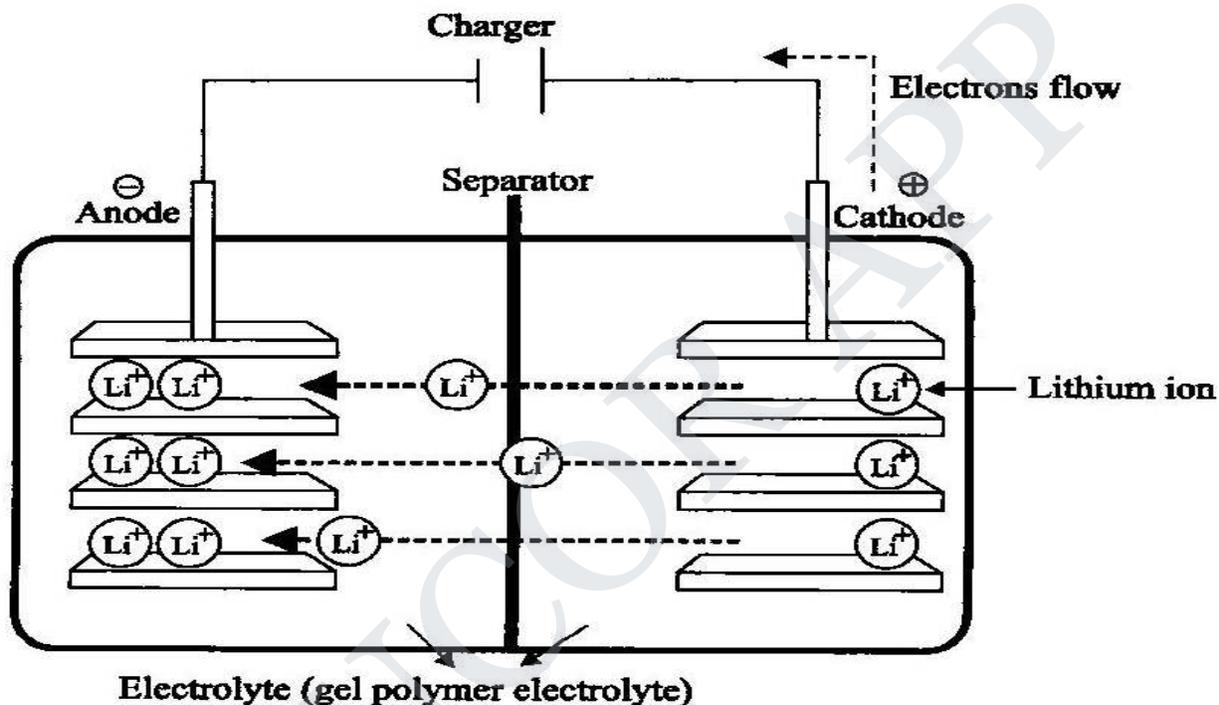


Fig. 9.3 Lithium-ion cell during charging

Fig. 6.4 Solid state lithium battery

Discharging

During discharging, the Li^+ ions flow back through the electrolyte from negative electrode to the positive electrode. Electrons flow from the negative electrode to the positive electrode through the wire. The Li^+ ions and electrons combine at the positive electrode and deposit there as Li.



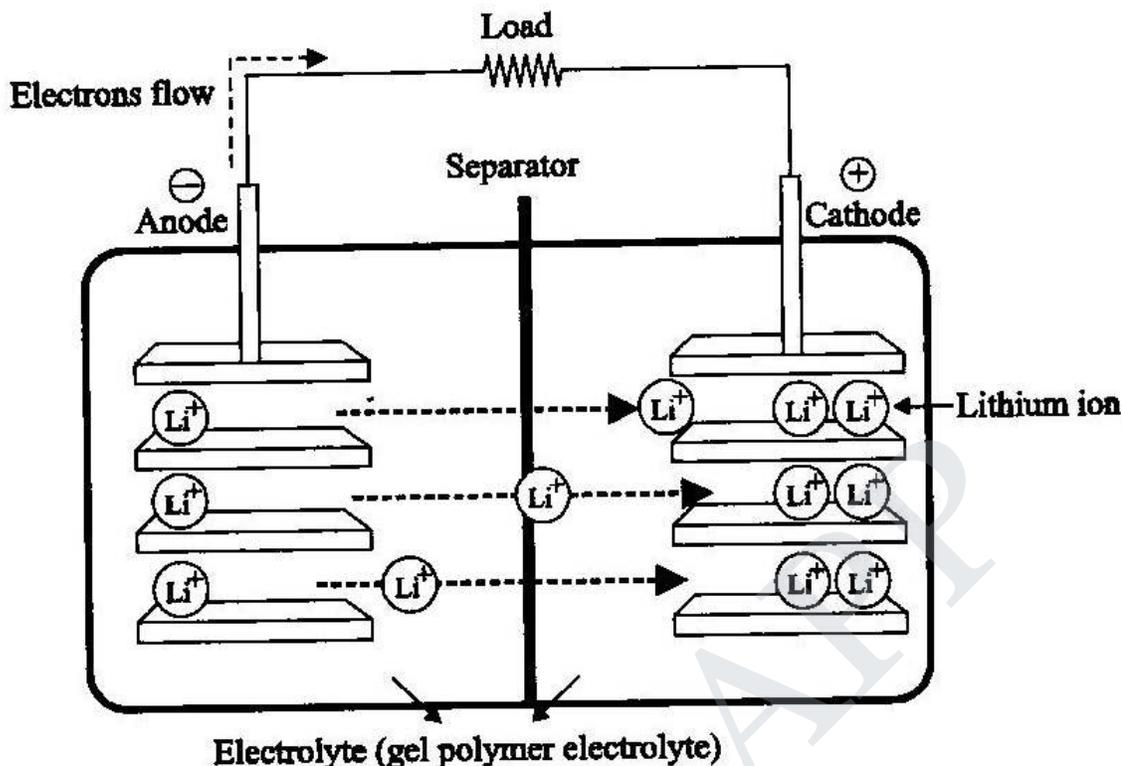


Fig. 9.4 Lithium-ion cell during discharging

6.6.1 Advantages

- Lithium-ion batteries are high voltage and light weight batteries.
- It is smaller in size.
- It produces three time the voltage of Ni-Cd batteries.

Uses

It is used in cell phone, note PC, portable LCD TV and semiconductor driven audio, etc.,

6.7 FUELL CELLS

Definition

Fuel cell is a voltaic cell, which converts the chemical energy of the fuels directly into electrical energy without combustion. It converts the energy of the fuel directly into electricity. In these cells, the reactants, products and electrolytes pass through the cell.

Fuel + Oxygen → oxidation products + Electricity.

Examples: Hydrogen-oxygen fuel cell: Methyl alcohol-oxygen fuel cell.

6.7.1 Hydrogen-Oxygen fuel cell

Hydrogen-Oxygen fuel cell is the simplest and most successful fuel cell, in which the fuel-hydrogen and the oxidizer-oxygen and the liquid electrolyte are continuously passed through the

cell.

Description

It consists of two porous electrodes anode and cathode. These porous electrodes are made of compressed carbon containing a small amount of catalyst (Pt, Pd, Ag). In between the two electrodes an electrolyte solution such as 25 percentage KOH or NaOH is filled. The two electrodes are connected through the voltmeter.

Working

Hydrogen (the fuel) is bubbled through the anode compartment, the cathode compartment, where it is oxidized. The oxygen (oxidizer) is bubbled through the cathode compartment, where it is reduced.

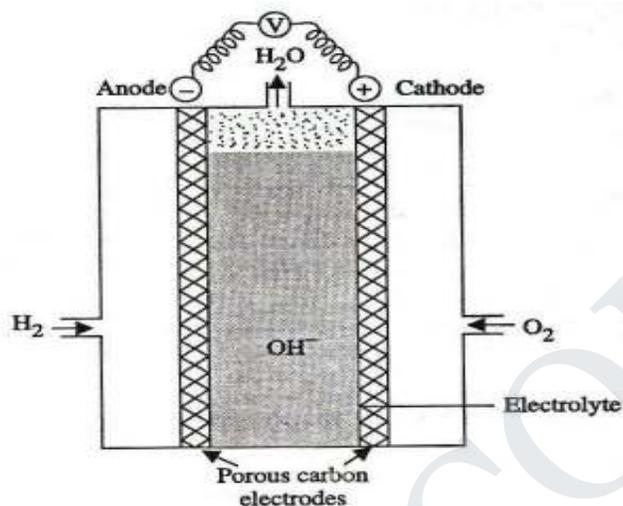


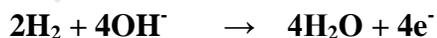
Fig. 6.6 Hydrogen-oxygen fuel cell

At anode

Hydrogen molecules are oxidized at the anode with the liberation of electrons which then combine with hydroxide ions to form water.



At cathode



The electrons produced at the anode pass through the external wire to the cathode, where it is absorbed by oxygen and water to produce hydroxide ions.

The emf of the cell = 0.8 to 1.0 V

Fuel Battery

When a large number of fuel cells are connected in series, it forms fuel battery.

6.7.2 Advantages of fuel cells

- Fuel cells are efficient and take less time for operation.
- It is pollution free technique.
- It produces electric current directly from the reaction of a fuel and an oxidiser.
- It produces drinking water.

Disadvantages

- Fuel cell cannot store electric energy as other cells do.
- Electrode is expensive and short lived.
- Storage and handling of hydrogen gas is dangerous.

Applications

- ❖ Hydrogen-Oxygen fuel cells are used as auxiliary energy source in space vehicles, submarines or other military-vehicles.
- ❖ In case of Hydrogen-Oxygen fuel cells, the product of water is proved to be a valuable source of fresh water by the astronauts.

6.8 SUPER CAPACITOR

Super capacitor is a high capacitor with capacitance value much higher than other capacitor. They store 10 to 100 times more energy per unit volume and deliver charge much faster than batteries.

Unlike ordinary capacitors, super capacitors, do not use the conventional solid electric, but rather they use electrostatic double- layer capacitance.

DESIGN OF SUPER CAPACITOR

Super capacitor consists of two electrodes separated by an ion-permeable membrane and dipped in an electrolyte, containing positive and negative ions, connecting both the electrodes.

WORKING

When the electrodes are connected to the power source, ions in the electrolyte from electric double layers of opposite polarity to the electrodes polarity, creating an electric field between them.

For example, positively polarized electrodes will have a layer of negative ions at the electrode/electrode interface. Similarly negatively polarized electrodes will have a layer of positive ions at the electrode/electrode interface.

This electric field polarizes the dielectric so its molecules lineup in the opposite direction to the field and reduce its strength. Its mean that its stores more electrical energy at an electrode/electrode interface.

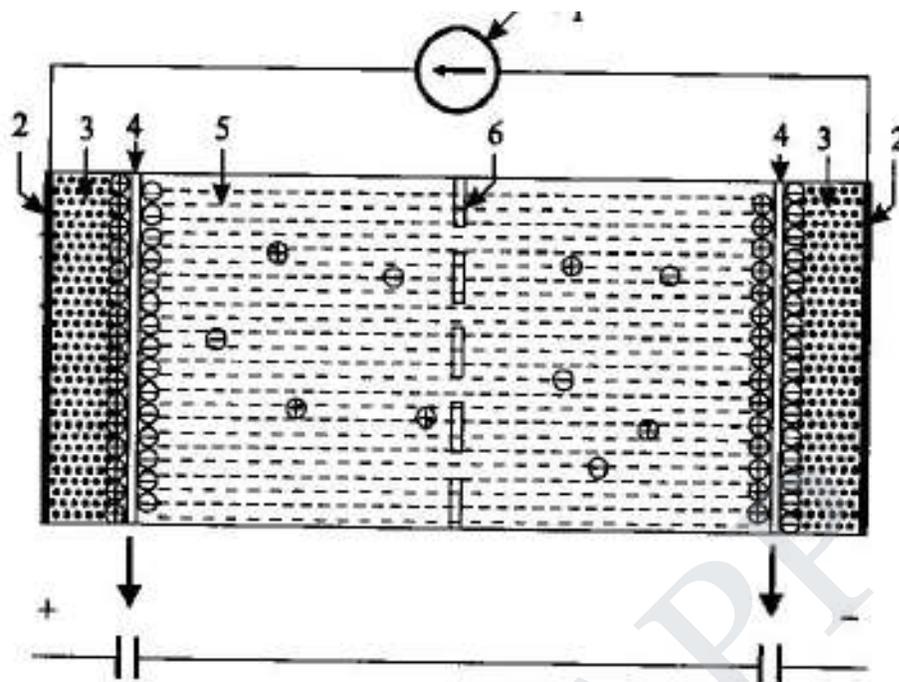


Fig. 9.6 Typical construction of a super capacitor

- | | |
|--|---------------------------|
| 1. Power source | 2. Collector |
| 3. Polarized electrode | 4. Helmholtz double layer |
| 5. Electrolyte having positive and negative ions | |
| 6. Separator | |

Advantages

- ✓ It is highly safe
- ✓ Its life time is very high
- ✓ It can be cycled millions of time
- ✓ It can be charged in seconds

Disadvantages

- ✓ Cost per Watt is high
- ✓ It cannot be used as source for continuous power supply
- ✓ If higher voltage is require the cells must be connected in series
- ✓ High self- discharge.