

**OBJECTIVES:**

- To understand about the water technology.
- To get the information on electrochemical cells, batteries, fuels and combustion.
- To study about the corrosion and protective coatings.
- To gain knowledge on adsorption phenomena.

**INTENDED OUTCOME:**

- This course will create an impact on the students and make them to realize the modern utility on electrochemical cells, batteries, fuels and combustion process, corrosion and adsorption methods.

**UNIT I WATER TECHNOLOGY****(9)**

Sources-Characteristics – Specification for drinking water, BIS &WHO-Alkalinity – Types of alkalinity and determination – Hardness – Types and estimation by EDTA method (problems) - Domestic water treatment – Disinfection methods (Chlorination, Ozonation, UV treatment) – Boiler feed water – Requirements – Disadvantages of using hard water in boilers – Internal conditioning (Phosphate, Calgon and Carbonate conditioning methods) – External conditioning – Demineralization process – Desalination - Reverse osmosis.

**UNIT II ELECTROCHEMISTRY AND STORAGE DEVICES****(9)**

Electrochemical cells – EMF – Measurement of emf – Single electrode potential – Nernst equation – Reference electrodes –Standard Hydrogen electrode -Calomel electrode – Ion selective electrode – Glass electrode and measurement of pH – Electrochemical series – Significance – Potentiometric titrations (Redox -  $\text{Fe}^{2+}$  vs dichromate) –Electrolytic conductance-application (conductometric titration)-Batteries-Primary batteries-Leclanche cell- Secondary batteries- Lead acid battery. An introduction to Fuel Cell-  $\text{H}_2$ - $\text{O}_2$  Fuel Cell.

**UNIT III FUELS AND COMBUSTION****(9)**

Coal - Proximate and Ultimate analysis - Metallurgical coke - Manufacture by Otto-Hoffman method - Petroleum processing and fractions - Synthetic petrol - Bergius and Fischer-Tropsch method - Knocking - Octane number and Cetane number - Gaseous fuels - Water gas, Producer gas, Combustion of fuel- Introduction-GCV-NCV-Flue gas analysis.

**UNIT IV CORROSION SCIENCE****(9)**

Chemical and Electrochemical corrosion - Galvanic corrosion - Differential aeration corrosion - Corrosion control - Sacrificial anode and Impressed current cathodic methods - Corrosion inhibitors - Protective coatings – Organic coatings-Paints - Constituents and functions –Inorganic coatings- Metallic coatings - Electroplating (Au) and Electro less plating (Ni) - Surface conversion coating - Hot dipping.

**UNIT V SURFACE CHEMISTRY AND PHASE RULE****(9)**

Introduction-Adsorption-Types, adsorption of gases on solids, adsorption of solutes from solutions, Adsorption isotherms-Freundlich adsorption isotherm-Langmuir adsorption isotherm- Role of adsorbents in industries (catalysis and water softening).

Phase Rule: Definition -Phase diagrams – one component water system, two component Ag-Pb system.

**TEXT BOOKS:**

| S. No. | AUTHOR(S) NAME    | TITLE OF THE BOOK            | PUBLISHER                                                 | YEAR OF PUBLICATION |
|--------|-------------------|------------------------------|-----------------------------------------------------------|---------------------|
| 1.     | Dr. Vairam.S      | Engineering Chemistry        | Gems Publishers, Coimbatore.                              | 2014                |
| 2.     | Dr.Ravikrishnan.A | Engineering Chemistry I & II | Sri Krishna Hi tech Publishing Company (P) Ltd., Chennai. | 2012                |

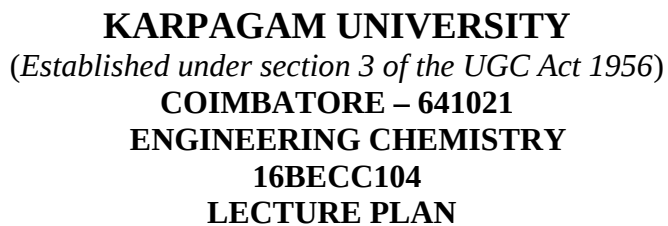
**REFERENCES:**

| S. No. | AUTHOR(S) NAME              | TITLE OF THE BOOK                                                                | PUBLISHER                                                         | YEAR OF PUBLICATION |
|--------|-----------------------------|----------------------------------------------------------------------------------|-------------------------------------------------------------------|---------------------|
| 1.     | Raman Sivakumar             | Engineering Chemistry I &II                                                      | McGraw-Hill Publishing Co.Ltd., 3 <sup>rd</sup> Reprint NewDelhi. | 2013                |
| 2.     | Kuriakose. J.C. and Rajaram | Chemistry in Engineering and Technology. Vol. I & II<br>5 <sup>th</sup> edition. | Tata McGraw Hill Publishing Company, New Delhi.                   | 2010                |
| 3.     | Jain, P.C. and Monika Jain  | Engineering Chemistry.                                                           | Dhanpat Rai Publishing Company (P) Ltd., New Delhi.               | 2009                |
| 4.     | Dara.S.S                    | Text book of Engineering Chemistry.                                              | S.Chand & Co.Ltd., New Delhi                                      | 2008                |
| 5.     | Sharma.B. K                 | Engineering Chemistry                                                            | Krishna Prakasam Media (P) Ltd., Meerut                           | 2001                |

**WEBSITES:**

1. <http://www.studynotes.ie/leaving-cert/chemistry/>
2. <http://www.rejinpaul.com/2011/04/engineering-chemistry-ii-second.html>
3. <http://www.learnerstv.com/Free-chemistry-Video-lectures-ltv044-Page1.htm>
4. <http://ocw.mit.edu/courses/#chemistry>
5. <http://www.chem.qmul.ac.uk/surfaces/sec>





## UNIT I

**HOURS REQUIRED: 12**

## UNIT II

**HOURS REQUIRED: 12**

| S.No | Topics                                                                | Hours |
|------|-----------------------------------------------------------------------|-------|
| 1.   | Electrochemical cells – reversible and irreversible cells             | 1     |
| 2.   | EMF – measurement of emf                                              | 1     |
| 3.   | Single electrode potential                                            | 1     |
| 4.   | Nernst equation                                                       | 1     |
| 5.   | Reference electrodes –Standard Hydrogen electrode , Calomel electrode | 1     |
| 6.   | Tutorial (Topics 1 to 5)                                              | 1     |
| 7.   | Ion selective electrode – glass electrode and measurement of pH       | 1     |
| 8.   | Electrochemical series – significance                                 | 1     |
| 9.   | Potentiometer titrations (redox - $\text{Fe}^{2+}$ vs dichromate)     | 1     |
| 10.  | Batteries -Primary batteries - Secondary batteries                    | 1     |
| 11.  | Tutorial (Topics 7 to 10)                                             | 1     |
| 12.  | Unit test                                                             | 1     |

**UNIT III****FUELS AND ROCKET PROPELLANTS****HOURS REQUIRED: 12**

| S.No | Topics                                                           | Hours |
|------|------------------------------------------------------------------|-------|
| 1.   | Introduction –Fuels, solid fuels, Coal - Proximate analysis      | 1     |
| 2.   | Ultimate analysis of coal                                        | 1     |
| 3.   | Metallurgical coke – Manufacture by Otto-Hoffman oven's method   | 1     |
| 4.   | Petroleum processing and fractions                               | 1     |
| 5.   | Synthetic petrol - Bergius and Fischer-Tropsch method            | 1     |
| 6.   | Tutorial (Topics 1 to 5)                                         | 1     |
| 7.   | Knocking -- Octane number and Cetane number                      | 1     |
| 8.   | Gaseous fuels – Water gas, Producer gas, CNG and LPG             | 1     |
| 9.   | Fuel Cell -H <sub>2</sub> -O <sub>2</sub> Fuel Cell-Applications | 1     |
| 10.  | Rocket Engines-Types-Basic Principles, Mass fraction.            | 1     |
| 11.  | Tutorial (Topics 7 to 10)                                        | 1     |
| 12.  | Unit test                                                        | 1     |

**UNIT IV****CORROSION SCIENCE****HOURS REQUIRED: 12**

| S.No | Topics                                                    | Hours |
|------|-----------------------------------------------------------|-------|
| 1.   | Introduction to corrosion Chemical corrosion and types    | 1     |
| 2.   | Electrochemical corrosion and types                       | 1     |
| 3.   | Galvanic corrosion - Differential aeration corrosion      | 1     |
| 4.   | Corrosion control                                         | 1     |
| 5.   | Corrosion inhibitors                                      | 1     |
| 6.   | Tutorial (Topics 1 to 5)                                  | 1     |
| 7.   | Protective coatings - Paints - Constituents and functions | 1     |
| 8.   | Metallic coatings - Electroplating (Au)                   | 1     |
| 9.   | Electroless plating (Ni)                                  | 1     |
| 10.  | Surface conversion coating and Hot dipping.               | 1     |
| 11.  | Tutorial (Topics 7 to 10)                                 | 1     |
| 12.  | Unit test                                                 | 1     |

**UNIT V****SURFACE CHEMISTRY****HOURS REQUIRED: 12**

| S.No | Topics                                                                                              | Hours |
|------|-----------------------------------------------------------------------------------------------------|-------|
| 1.   | Introduction-Adsorption-Types, adsorption of gases on solids, adsorption of solutes from solutions, | 1     |
| 2.   | Adsorption isotherms-Freundlich adsorption isotherm                                                 | 1     |
| 3.   | Langmuir adsorption isotherm                                                                        | 1     |
| 4.   | Industrial adsorbent materials                                                                      | 1     |
| 5.   | Tutorial (Topics 1 to 4)                                                                            | 1     |
| 6.   | Role of adsorbents in catalysis water softening                                                     | 1     |
| 7.   | Role of adsorbents in water softening                                                               |       |

|     |                            |   |
|-----|----------------------------|---|
| 8.  | Emulsion-Types-water/oil   | 1 |
| 9.  | oil/water                  | 1 |
| 10. | Applications of adsorption | 1 |
| 11. | Tutorial (Topics 6 to 10)  | 1 |
| 12. | Unit test                  | 1 |

#### TEXT BOOKS:

| S. No. | Author(s) Name  | Title of the book            | Publisher                                                     | Year of Publication  |
|--------|-----------------|------------------------------|---------------------------------------------------------------|----------------------|
| 1.     | Dr.S.Vairam     | Engineering Chemistry        | Gems publishers                                               | Revised edition 2014 |
| 2.     | Ravikrishnan, A | Engineering Chemistry I & II | Sri Krishna Hi tech Publishing Company Private Ltd., Chennai. | 2008                 |

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| S. No. | Author(s) Name             | Title of the book                     | Publisher                                           | Year of Publication  |
|--------|----------------------------|---------------------------------------|-----------------------------------------------------|----------------------|
| 1.     | Dr.V.Veeraiyan             | Engineering Chemistry I & II          | VRB Publishers Pvt. Ltd., Chennai                   | Revised edition 2012 |
| 2.     | Jain, P.C. and Monika Jain | Engineering Chemistry                 | Dhanpat Rai Publishing Company (P) Ltd., New Delhi. | 2007                 |
| 3.     | Dara, S.S                  | A text book of Engineering Chemistry. | S.Chand & Co.Ltd., New Delhi                        | 2006                 |
| 4.     | Sharma, B. K               | Engineering Chemistry                 | Krishna Prakasam Media (P) Ltd., Meerut             | 2001                 |

#### WEBSITES:

1. [www.chemistry.org/portal/Chemistry](http://www.chemistry.org/portal/Chemistry)
2. [chemfinder.cambridgesoft.com](http://chemfinder.cambridgesoft.com)
3. [www.sciencedirect.com](http://www.sciencedirect.com)
4. [www.electrochem.org](http://www.electrochem.org)

## UNIT-I WATER TECHNOLOGY

### Introduction

97% of the water on the Earth is salt water, and only 3% is fresh water of which slightly over two thirds is frozen in [glaciers](#) and [polar](#) ice caps. The remaining unfrozen freshwater is mainly found as groundwater, with only a small fraction present above ground or in the air.

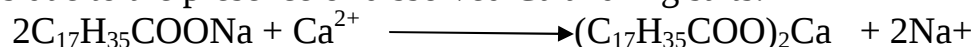
The process of removing all types of impurities from water and making it fit for domestic or industrial purposes is called water technology.

### Hard water and soft water

#### Hard water

Water, which does not produce lather with soap solution, but produces white precipitate is called Hard water.

This is due to the presence of dissolved Ca and Mg salts.



#### 2. Soft water

Water, which produces lather readily with soap solution is called soft water.

This is due to the absence of Ca and Mg salts.

## HARDNESS OF WATER

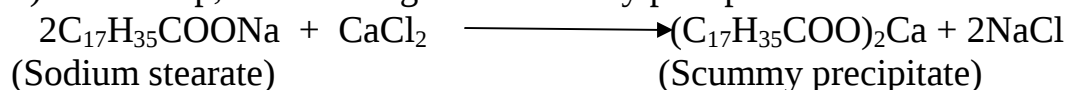
### 1. Hardness of water

If the water produces lather with soap, it is soft water.

If the water does not produce lather with soap, it is called as Hard water. The property is known as hardness. But it will produce a scummy white precipitate. The hardness is due to  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  ions and their salts.

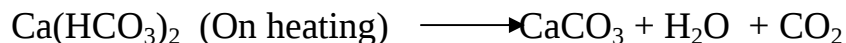
### 2. Test for hardness:

- Eriochrome Black – T indicator gives red colour in hard water.
- With soap, hard water gives a scummy precipitate.

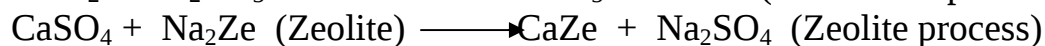


**3. Types of Hardness:**

**a) Temporary Carbonate hardness :** The hardness due to carbonates and bicarbonates can be removed by simple boiling. So, they are known as temporary or carbonate or alkaline hardness.



**b) Permanent hardness ( Non-carbonate):** The hardness due to chlorides and sulphates cannot be removed by simple boiling. They need special methods like lime soda process and zeolite process. This hardness is called as “Permanent hardness or Non-carbonate or non alkaline hardness.

**4. Units of hardness:**

i) ppm ii) mg/L iii) degree Clarkes iv) Degree French

1 ppm – 1 part by weight of  $\text{CaCO}_3$  equivalent hardness /  $10^6$  parts of water

1 mg/L – 1mg of  $\text{CaCO}_3$  / 1 Lr of water

Clarkes Degree –  $^{\circ}\text{Cl}$  – 1 part of  $\text{CaCO}_3$  equivalent hardness / 70,000 parts of water

1 Degree French –  $^{\circ}\text{F}$  – 1 part of  $\text{CaCO}_3$  equivalent hardness /  $10^5$  parts of water

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

**5.  $\text{CaCO}_3$  equivalence:**

Hardness is expressed in  $\text{CaCO}_3$  equivalence. Because,

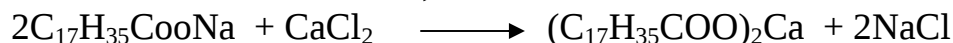
i) It is the most insoluble and easily precipitable salt.

ii) Its molecular weight is 100 and equivalent weight is 50. As these are whole numbers, it is very easy to use them in calculations

**5. Detection of hardness:**

It can be detected in two ways.

i) When the water is treated with soap solution, If it prevents lathering and forms white scum, the contains hardness.



ii) Water containing hardness, gives wine red colour with EBT indicator at Ph 9-10.

### How Hard Is The Water?

The degree of hardness of the water is classified in terms of its calcium carbonate concentration as follows:

| Hardness rating | Concentration of Calcium Carbonate (mg/L) | Concentration of Calcium Carbonate (grains/US gallon) |
|-----------------|-------------------------------------------|-------------------------------------------------------|
| Soft            | 0 to <75                                  | 0 to <5.2                                             |
| Medium hard     | 75 to <150                                | 5.2 to <10.5                                          |
| Hard            | 150 to <300                               | 10.5 to <21                                           |
| Very hard       | 300 and greater                           | 21 and greater                                        |

### ALKALINITY

Alkalinity is a measure of a water's ability to neutralize acid. Depending on pH, water can contain three types of alkalinity: carbonate ( $\text{CO}_3$ ), bicarbonate ( $\text{HCO}_3$ ) and hydroxide ( $\text{OH}$ ). Since bicarbonate alkalinity is the specie that exists at a pH range of 4.3 to 8.3, it predominates in natural waters. The carbonate ion begins to appear at  $\text{pH} > 8.3$  and hydroxide at  $\text{pH} > 10$ .

#### Definition:

The acid neutralizing capacity is known as alkalinity. It is due to  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ .

#### 1.Aim:

To determine the type and amount of alkalinity of the water sample

#### 2.Chemicals required:

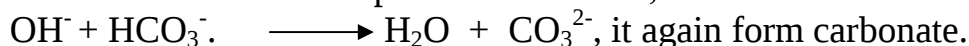
$\text{NaOH}$ ,  $\text{HCl}$ , Sample water, Phenolphthalein, Methyl orange

#### 3.Principle:

There are five types of alkalinity.

i)  $\text{OH}^-$  only   ii)  $\text{CO}_3^{2-}$  only   iii)  $\text{HCO}_3^-$ .only   iv)  $\text{OH}^-$  and  $\text{CO}_3^{2-}$    v)  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ .

The other combinations are not possible. Because,



The possible reactions are

- $\text{OH}^- + \text{H}^+ \longrightarrow \text{H}_2\text{O}$
- $\text{CO}_3^{2-} + \text{H}^+ \longrightarrow \text{HCO}_3^-$  ( Half neutralization of carbonate)



Phenolphthalein can be used as indicator for 1 & 2. But not for 3.

Methyl orange is used for all 1, 2 & 3 reactions.

4. Formula table:

| S.No | Case                | $\text{OH}^-$ | $\text{CO}_3^{2-}$ | $\text{HCO}_3^-$ |
|------|---------------------|---------------|--------------------|------------------|
| 1    | P=0                 | Nil           | Nil                | M                |
| 2    | P=M                 | P=M           | Nil                | Nil              |
| 3    | $P = \frac{1}{2} M$ | Nil           | 2P                 | Nil              |
| 4    | $P > \frac{1}{2} M$ | $2P - M$      | $2(M - P)$         | Nil              |
| 5    | $P < \frac{1}{2} M$ | Nil           | 2P                 | $(M - 2P)$       |

5. Short Procedure

| S.No | Content        | Titration-I<br>Standardisation of HCl | Titration-II<br>Alkalinity estimation                           |
|------|----------------|---------------------------------------|-----------------------------------------------------------------|
| 1    | Burette        | HCl acid                              | Standard HCl                                                    |
| 2    | Pipette(20 ml) | Standard NaOH                         | Water sample                                                    |
| 3    | Indicator      | Phenolphthalein                       | i)Phenolphthalein<br>ii) Methyl orange                          |
| 4    | Endpoint       | Disappearance of pink colour          | i)Disappearance of pink colour<br>ii) Appearance of pink colour |

**6. Calculation:**

**Step-1 : Standardisation of HCl**

Volume of NaOH ( $V_1$ ) = 20ml

Strength of NaOH ( $N_1$ ) = 0.1N

Volume of HCl ( $V_2$ ) = x ml

Strength of HCl ( $N_2$ ) = ?

As per volumetric principle,  $V_1N_1 = V_2N_2$

$$N_2 = V_1N_1 / V_2$$

**Step -2 : Estimation of alkalinity:**

(let us consider  $P=8$  and  $M = 10$ , as  $P>1/2 M$ , this comes under case (iv). We are having  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  alkalinity)

**a) Amount of OH<sup>-</sup>**

Volume of HCl (V<sub>1</sub>) = (2P – M ) ml

Strength of HCl (N<sub>1</sub>) = From step 1

Volume of water (V<sub>2</sub>) = 20 ml

Strength of OH<sup>-</sup> in water (N<sub>2</sub>) = ?

As per volumetric principle, V<sub>1</sub>N<sub>1</sub> = V<sub>2</sub>N<sub>2</sub>

$$N_2 = V_1 N_1 / V_2$$

Amount of OH<sup>-</sup> in water = N<sub>2</sub> X 50 X 1000 ppm

( we are multiplying by 50 as it is eq.wt of CaCO<sub>3</sub>.

We are multiplying by 1000 to convert it for gram to milligram)

**b) Amount of CO<sub>3</sub><sup>2-</sup>**

Volume of HCl (V<sub>1</sub>) = 2(M-P ) ml

Strength of HCl (N<sub>1</sub>) = From step 1

Volume of water (V<sub>2</sub>) = 20 ml

Strength of CO<sub>3</sub><sup>2-</sup> in water (N<sub>2</sub>) = ?

As per volumetric principle, V<sub>1</sub>N<sub>1</sub> = V<sub>2</sub>N<sub>2</sub>

$$N_2 = V_1 N_1 / V_2$$

Amount of CO<sub>3</sub><sup>2-</sup> in water = N<sub>2</sub> X 50 X 1000 ppm

( we are multiplying by 50 as it is eq.wt of CaCO<sub>3</sub>.

We are multiplying by 1000 to convert it for gram to milligram)

**Determination of Hardness of water**

The determination of water hardness is a useful test that provides a measure of quality of water for households and industrial uses. Originally, water hardness was defined as the measure of the capacity of the water to precipitate soap.

**ESTIMATION OF HARDNESS BY EDTA METHOD:**

**1. Aim:** To estimate the amount of hardness present in the given water sample.

**2. Chemicals required:**

a) Standard hard water – 1g CaCO<sub>3</sub> + dil. HCl – made up to 1 Lr.

b) EDTA solution – 4 gms of EDTA sodium salt / 1 Lr of water

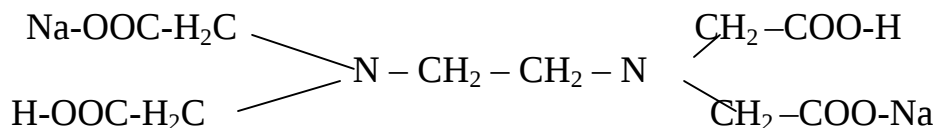
c) EBT Indicator – 0.5g EBT / 100 ml alcohol

d) Ammonia buffer – 67.5g Ammonium chloride +570ml Ammonia– made up to 1Lr

**3. Principle:**

EDTA stands for Ethylene Di amine Tetra Acetic acid. As it is insoluble in water, we use its disodium salt.

Structure of EDTA:

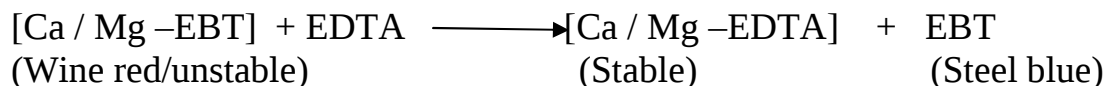


- By nature, Eriochrome Black T indicator is blue in colour. When EBT indicator is added to water sample, it forms a wine red coloured unstable Ca-Mg-EBT complex.

-This reaction is carried out under a basic  $\text{P}^{\text{H}}$  of 8- 10 using ammonia buffer.

- $\text{Ca}^{2+} / \text{Mg}^{2+}$  in water + EBT  $\longrightarrow$  [Ca / Mg –EBT] unstable wine red complex

-When EDTA is titrated against the complex, EDTA replaces all the EBT and forms a stable Ca / Mg –EDTA complex. The liberated EBT indicates the end point as steel blue.



-So, the end point is the colour change from wine red to steel blue.

**4. Short Procedure:**

| S.No | Content                | Titration-I<br>Standardisation<br>of EDTA | Titration-II<br>Total Hardness  | Titration-III<br>permanent<br>Hardness |
|------|------------------------|-------------------------------------------|---------------------------------|----------------------------------------|
| 1    | Burette                | EDTA                                      | Standard EDTA                   | Standard EDTA                          |
| 2    | Pipette(20 ml)         | Std. Hardwater                            | Sample water                    | Boiled water                           |
| 3    | Additional<br>solution | 10ml of $\text{NH}_3$<br>buffer           | 10ml of $\text{NH}_3$<br>buffer | 10ml of $\text{NH}_3$<br>buffer        |
| 4    | Indicator              | EBT                                       | EBT                             | EBT                                    |
| 5    | Endpoint               | Wine red to steel<br>blue                 | Wine red to steel<br>blue       | Wine red to steel<br>blue              |
| 6    | Volume                 | $V_1$                                     | $V_2$                           | $V_3$                                  |

**5. Calculation:****Step1 – Standardisation of EDTA**

$$\begin{aligned}
 1 \text{ ml of Std. Hard water} &= 1 \text{ mg of CaCO}_3 \text{ (Given)} \\
 \text{So, } 20 \text{ ml of Std. Hard water} &= 20 \text{ mg of CaCO}_3 \\
 V_1 \text{ ml of EDTA is required for} &= 20 \text{ mg of CaCO}_3 \\
 \text{Therefore, } 1 \text{ ml of EDTA} &= 20 / V_1 \text{ mg of CaCO}_3
 \end{aligned}$$

**Step 2: Finding Total hardness:**

$$\begin{aligned}
 20 \text{ ml of sample water required} &= V_2 \text{ ml of EDTA} \\
 &= V_2 \times \frac{20}{V_1} \text{ mg of CaCO}_3 \\
 \text{Therefore, } 1000 \text{ ml of sample requires} &= V_2 \times \frac{20}{V_1} \times 1000 \text{ mg of CaCO}_3 \\
 \text{Hence, total hardness} &= \frac{V_2}{V_1} \times 1000 \text{ ppm}
 \end{aligned}$$

**Step 3: Finding Permanent hardness:**

$$\begin{aligned}
 20 \text{ ml of boiled water required} &= V_3 \text{ ml of EDTA} \\
 &= V_3 \times \frac{20}{V_1} \text{ mg of CaCO}_3 \\
 \text{Therefore, } 1000 \text{ ml of boiled sample requires} &= V_3 \times \frac{20}{V_1} \times 1000 \text{ mg of CaCO}_3 \\
 \text{Hence, permanent hardness} &= \frac{V_3}{V_1} \times 1000 \text{ ppm}
 \end{aligned}$$

$$\text{Step 4 : Temporary hardness} = \text{Total hardness} - \text{permanent hardness}$$

**Treatment of water for domestic supply****Stages in the purification process.****Screening**

It is the process of removing floating materials.

**Aeration**

The process of mixing water with air is known as aeration. The main purpose of aeration is

- (a) to remove dissolved gases
- (b) to remove ferrous and manganous salts

**Sedimentation**

It is the process of removing suspended impurities.

**Coagulation**

It is the method to remove finely divided clay, silica. In this method coagulant like alum is added to water.

**Filtration**

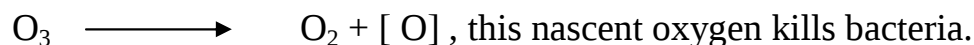
It is the process of removing bacteria, colour, taste, odour, suspended particle from water using filter beds.

**Sterilization or disinfection**

The process of destroying harmful bacteria is known as Sterilization or disinfection. The following methods are employed for sterilization

By boiling for 10 – 15 minutes, water can be sterilized. But it affects the taste and can not be used for higher volume water.

By using Ozone, (with the usual dosage of 2-3ppm for 10 – 15 minutes in disinfection tank) we produce nascent oxygen which is powerful disinfectant. Its excess is not harmful, since it is unstable and decomposes into oxygen. But, it is costly. It cannot be used and stored for long time as it is unstable.



By passing UV radiations from mercury vapour lamp, the swimming pool water can be sterilized. But it is costly and turbid water cannot be treated.

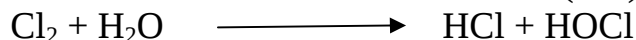
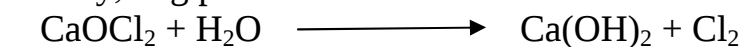
By chlorination:

a) Chlorine gas or solution bubbling will kill bacteria.

b) Adding chlorine and ammonia (2:1) will form chloramine. It decomposes slowly to release chlorine which kills bacteria. Its excess does not produce any irritating odour. It imparts a good taste to treated water.



c) Bleaching powder ( $\text{CaOCl}_2$ ) reacts with water and forms hypochlorous acid which kills bacteria. Generally, 1kg powder is used for 1000 kilolitres of water.



(Hypochlorous acid which kills bacteria)

It should be noted that chlorine should be always added a little higher than the *break point chlorination* for perfect disinfection.

**Breakpoint chlorination:**

The point at which the added chlorine completely removes bacteria,  $\text{NH}_3$ , Organic and inorganic impurities is known as “Breakpoint chlorination”.

The water contains: a) Bacteria b) Ammonia c) Organic impurity (sewage)

d) Inorganic salt impurities (Effluents,  $\text{H}_2\text{S}$ , Fe salts)

1. When we add chlorine, first it kills bacteria and oxidizes some inorganic impurities.

2. The added chlorine is completely consumed. (a).

3. Further addition of chlorine is used to combine with ammonia to form chloramines compounds. So, the residual chlorine content is increased upto (b).

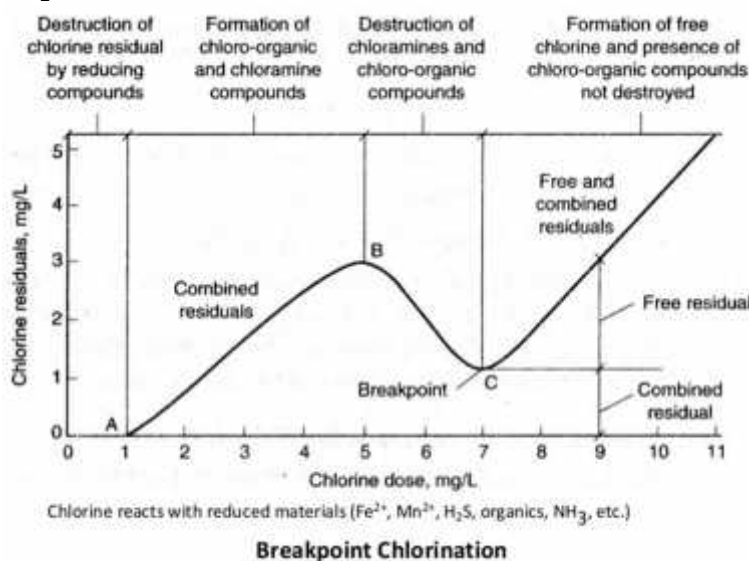
4. As saturation level is attained, the chloramines begin to decompose to release chlorine which is utilized to remove all the types organic and inorganic impurities. So, residual

chlorine level decreases. (c).

5. At point (c), the added chlorine removes all the types of impurities. So, the point is known as “ Break point chlorination”.

6. After this point, further addition of chlorine is not at all utilized and simply increases the residual chlorine content.(along CD)

Diagram for break point chlorination:



*Advantages of break point chlorination: (Significance)*

i) It is used to remove Bacteria , Ammonia ,Organic impurity (sewage) ,Inorganic salt impurities ( Effluents,  $\text{H}_2\text{S}$  , Fe salts) from water.

ii) It prevents the growth of any weeds in water.

### **BOILER FEED WATER**

The setup used to produce steam in industries is known as ‘Boiler’. Water is fed to the boiler and heated to produce steam. The water fed into the boiler is known as “Boiler feed water”.

| S.No | Requirements for boiler water                   | If not, it will cause |
|------|-------------------------------------------------|-----------------------|
| 1    | Free from hardness causing salts                | Sludge and scale      |
| 2    | Free from oil and greases                       | Foaming               |
| 3    | Free from dissolved salts, suspended impurities | Caustic embrittlement |
| 4    | Free from dissolved gases, suspended salts      | Boiler corrosion      |

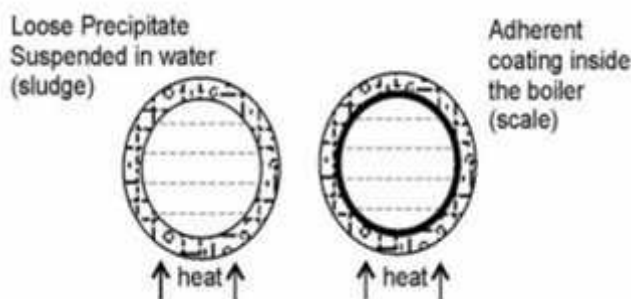
**1.Sludge and scale:**

If the water contains hardness causing salts like  $\text{MgSO}_4$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{Ca}(\text{HCO}_3)_2$

On evaporation, the salts are precipitated to produce *scale and sludge*.

| No | Sludge                                                                                                                                | Scale                                                                                                                                                                   |
|----|---------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 1  | Loose, slim, non-adherent precipitate                                                                                                 | Hard, thick, adherent precipitate                                                                                                                                       |
| 2  | Due to salts like $\text{MgSO}_4$ , $\text{MgCl}_2$                                                                                   | Due to salts like $\text{CaSO}_4$ , $\text{Ca}(\text{HCO}_3)_2$                                                                                                         |
| 3  | Due to poor conductance, they decrease the boiler efficiency to lesser extent and causing chocking in the pipelines.                  | Due to poor conductance, they decrease the boiler efficiency to maximum extent, cause reduced fuel economy, improper boiling, boiler explosion etc.,                    |
| 4  | It can be prevented by periodical replacement of concentrated hard water by fresh water. This process is known as “blow down” method. | It can be prevented by special methods like external treatment of ion exchange, Internal carbonate, phosphate, Calgon conditioning & Mechanical hard scrubbing methods. |

Diagram:

**2. Priming and Foaming:**

Due to rapid boiling, the steam may carry some water droplets along with it. This is called *wet steam*. The process of wet steam production is called *Priming*. It can reduce the heat of the steam and cause corrosion in the pipelines.

**Priming is due to:**

- Improper design of boiler
- High water level
- High velocity of steam
- Uneven boiling

**Priming can be controlled by**

- i) Proper boiler design
- ii) Maintaining proper water level
- iii) Proper boiling

If oils and greases are present, they produce bubbles on the water surface. This will increase the wet steam production. This is known as “*Foaming*”.

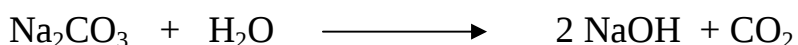
Foaming is prevented by adding

- i) Anti foaming agents (e.g.) synthetic poly amides , castor oil
- ii) Coagulants (e.g.) Aluminum hydroxide

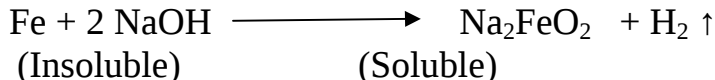
Foaming and priming are collectively known as ‘*Carry over*’.

**3. Caustic Embrittlement:**

It is the intercrystalline cracking of boiler due to NaOH. NaOH content is increased due to the dissolved salts like  $\text{Na}_2\text{CO}_3$  which is added during internal treatment.



This NaOH occupies the hair line cracks of boiler metal and converts the insoluble Fe into soluble Sodium Ferroate. Thus it makes the cracks bigger in bents, joints and crevices.



Prevention of caustic embrittlement:

1. As softening agent, we can use sodium phosphate instead of sodium carbonate.
2. The hair line cracks can be sealed by waxy materials like Tannin and Lignin

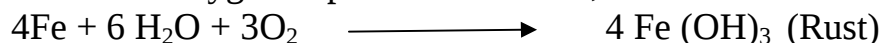
**4.Boiler Corrosion**

It may be due to three major reasons:

- i) Dissolved Oxygen    ii) Dissolved  $\text{CO}_2$     iii) Dissolved salts like  $\text{MgCl}_2$

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

Dissolved oxygen in presence of water, causes corrosion.

**Prevention from oxygen:****a) Chemical method -**

Adding Sodium Sulphite:  $2 \text{Na}_2\text{SO}_3 + \text{O}_2 \longrightarrow 2 \text{Na}_2\text{SO}_4$

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

Adding Hydrazine:  $\text{N}_2\text{H}_4 + \text{O}_2 \longrightarrow \text{N}_2 + 2 \text{H}_2\text{O}$

This method results in inert gas and pure water, it is preferred.

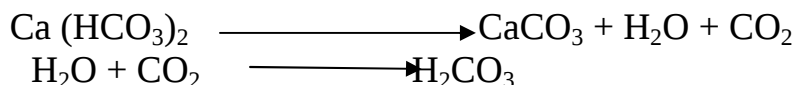
**b) Mechanical deaeration method:**

This is based on the principle that at high temperature and low pressure and high exposed area, the solubility of gases in water is decreased. So, the water is fed into the

mechanical deaerator which is provided with vacuum pump, heaters and perforated plates. The out coming water will be free from dissolved gases.

**ii) Corrosion due to Carbon – di – oxide:**

Salts like Calcium bicarbonate on heating produces  $\text{CO}_2$ .  $\text{CO}_2$  dissolves in water to form carbonic acid which corrodes the boiler metal.

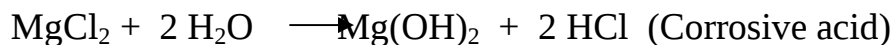


**Prevention from  $\text{CO}_2$**

1. Chemical method: By adding calculated amount of ammonium hydroxide  
 $2\text{NH}_4\text{OH} + \text{CO}_2 \longrightarrow (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}$
2. Mechanical deaeration method ( similar to oxygen method)

**iii) Corrosion due to Dissolved salts like  $\text{MgCl}_2$**

Dissolved salts like  $\text{MgCl}_2$  cause acid formation. This will be prevented by alkali neutralisation.



**SOFTENING OR CONDITIONING METHOD**

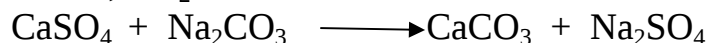
Water used for industrial purposes should be free from hardness producing substances, suspended impurities and dissolved gases etc. The process of removing hardness producing substances from water is known as softening or conditioning of water.

**INTERNAL TREATMENT BY BOILER COMPOUNDS:**

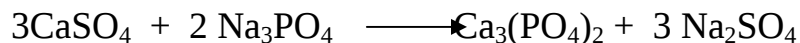
The residual salts that are not removed by external methods can be removed by adding some chemicals directly into the boiler water. These chemicals are known as 'Boiler compounds'. This method is known as 'Internal treatment'.

E.g: Carbonate conditioning, Phosphate conditioning and Calgon conditioning

**a) Carbonate conditioning:** Used for low pressure boilers. Here the salts like  $\text{CaSO}_4$  are converted to easily removable  $\text{CaCO}_3$ . But sometimes it produces  $\text{NaOH}$ ,  $\text{CO}_2$  and hence Carbonic acid. So it is less preferred.



**b) Phosphate conditioning:** Used for high pressure boiler. No risk of  $\text{CO}_2$  liberation.



Three types of Phosphate salts are used:

$\text{Na}_3\text{PO}_4$  – Tri sodium Phosphate – Used for highly acidic water

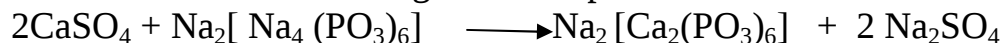
$\text{Na}_2\text{HPO}_4$  – Disodium hydrogen Phosphate – Used for slightly acidic water

$\text{NaH}_2\text{PO}_4$  – Sodium di hydrogen phosphate – Used for alkaline water

**c) Calgon conditioning:**

Calgon is the trade name of sodium hexa meta phosphate-  $\text{Na}_2[\text{Na}_4(\text{PO}_3)_6]$ .

With calcium ions it forms a soluble complex and prevents scale and sludge formation. It is used for high and low pressure boilers.



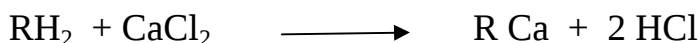
**EXTERNAL TREATMENT METHOD:****Ion exchange method (Demineralisation)**

Working:

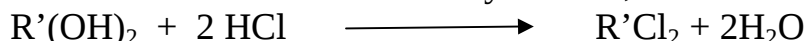
1. Here all the cations and anions are completely removed . It uses two cylinders of cation exchange cylinder and anion exchange cylinder filled with resins.
2. Resins are linear, insoluble, cross linked , organic polymers. There are 2 types.
  - a) **Cation exchange resins** –  $\text{RH}_2$  (e.g) Sulphonated coals ,  $\text{RSO}_3\text{H}$
  - b) **Anion exchange resins** .  $\text{R}'(\text{OH})_2$  (e.g) Urea-formaldehyde resin, Amines

$\text{R}-\text{NH}_2$

3. The water is fed into cylinder –I where all the cations are replaced by  $\text{RH}_2$  Resins.



4. The cation free water is fed to cylinder II, where all the anions are replaced.

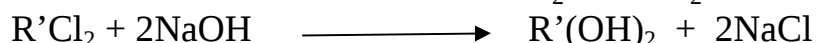
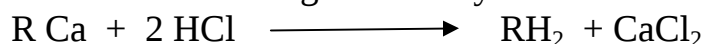


5. So, the resultant water is free from all types of ions.

**Regeneration:**

On prolonged use, as all the resins are exhausted, there will be no  $\text{H}^+$  or  $\text{OH}^-$  ions to exchange the unwanted ions. So, they have to be regenerated.

Cation resins are regenerated by  $\text{HCl}$  and anion resins by  $\text{NaOH}$ .

**Advantages of Ion exchange method:**

- i) Very good for use in high pressure boilers also.
- ii) It can treat highly acidic or alkaline water.
- iii) We can get pure water as hardness as low of 2 ppm.

**Drawbacks of Ionexchange method:**

- i) Expensive
- ii)  $\text{Fe}$ ,  $\text{Mn}$  cannot be removed as they form complexes with resins
- iii) Cannot be used for turbid water as they clog the resins.

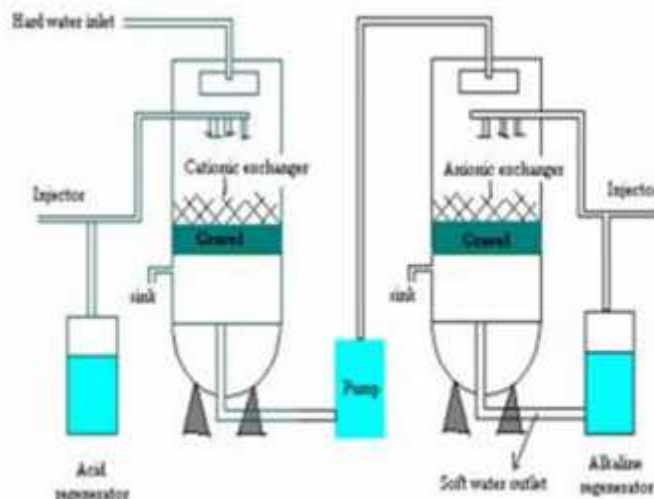


Fig4.10. Demineralization process

## DESALINATION

### Reverse Osmosis Method: (Desalination)

1. Removal of common salt (NaCl) from water is called 'Desalination'. Fresh water contains dissolved solids less than 1000ppm. Brackish water 1000 to 35000ppm.

Sea water contains greater than 35000ppm. Reverse osmosis is used to convert sea and brackish water to fresh water.

2. Osmosis: When two different concentrated solutions are separated by a semi permeable membrane, due to osmotic pressure, low concentrated solvent flows to higher one. This is known as osmosis.

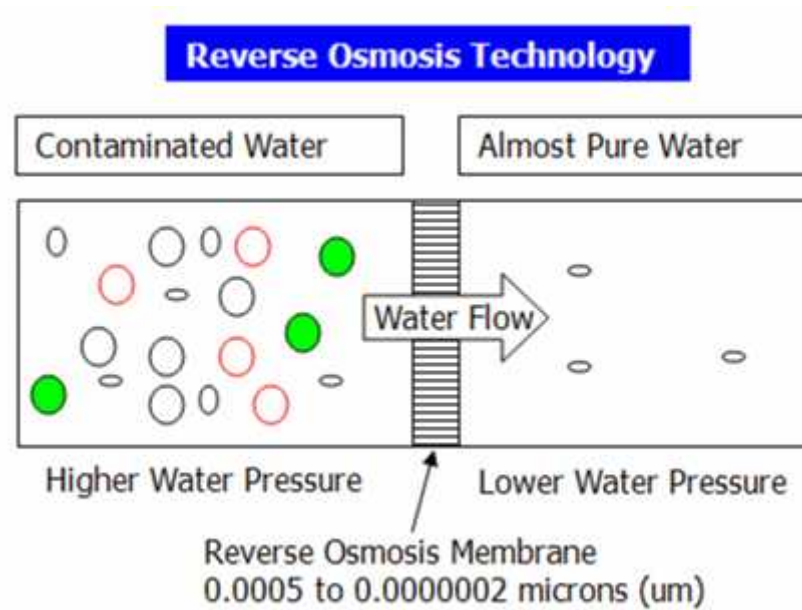
3. But when we apply an excess and opposite Hydrostatic pressure to overcome the osmotic pressure, then higher concentrated solvent will flow to the lower one. This is known as reverse osmosis.

4. During this RO process, only the water flows across the membrane and it prevents the salt migration. So, this method is also called as 'Super filtration'. The membrane is made up of cellulose acetate or cellulose butyrate.

### Advantages of Reverse Osmosis:

1. High life time
2. Removes ionic, non-ionic and colloidal impurities.
3. Low capital cost.

## 4. Simple operational procedure.



**KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21.****FACULTY OF ENGINEERING****DEPARTMENT OF SCIENCE AND HUMANITIES****ENGINEERING CHEMISTRY****UNIT-I****WATER TECHNOLOGY****PART –B**

1. What is hardness?
2. What are the hardness causing salts?
3. How temporary hardness can be removed?
4. Give the difference between soft and hard water?
5. Give the requirements of drinking water?
6. Calcium carbonate is chosen as standard in water analysis Why?
7. Define alkalinity
8. How is alkalinity classified?
9. How is alkalinity determined?
10. What is Coagulation?
11. What are disfectants? Give examples?
12. What is Break Point Chlorination?
13. Give the requirements of boiler feed water?
14. What are the problems encountered in boiler feed water?
15. Give the difference between scales and sludge?
16. Define priming and forming?
17. What is meant by carry over? How is it caused?
18. What is caustic embrittlement? How is it prevented?
19. What is meant by boiler corrosion? How is it prevented?
20. What is blow down operation?
21. What is carbonate conditioning?
22. What is Calgon conditioning?
23. What is Phosphate conditioning?
24. What is desalination?
25. What is meant by reverse osmosis?

**PART – C**

1. Explain with a neat sketch the various steps in the treatment of water for domestic supply
2. Define the term desalination? Describe the desalination by Reverse Osmosis method
3. What is the principle of EDTA method? Describe the estimation of hardness of water by EDTA method
4. What is the principle and method involved in the determination of different types of alkalinity of water?
5. Describe the demineralization process of water softening. Explain the reactions involved
6. Write notes on boiler compounds
7. Discuss in detail the problems caused due to the usage of hard water in boiler?
8. Discuss the various methods of sterilization process
9. Explain phosphate and calgon methods of internal treatment of hard water.

## UNIT II

### ELECTROCHEMISTRY

Electrochemistry is a branch of chemistry, deals with the chemical applications of electricity. It mainly deals with the chemical reactions produced by passing electric current through an electrolyte or the production of electric current through chemical reactions.

#### **Conductors**

A substance or material that allows electric current to pass through it is called a *conductor*. The ability of a material to conduct electric current is called *conductance*.

**Examples:** All metals, graphite, fused salts, aqueous solutions of acids, bases, etc.,

#### **Non-Conductors (or) Insulators**

Materials which do not conduct electric current are called non-conductors or insulators.

**Examples:** Plastics, wood, most of the non metals, etc.

#### **Types of Conductors**

The conductors are broadly classified into two types as follows.

##### **1. Metallic conductors (or) Electronic conductors**

Metallic conductors are solid substances, which conduct electric current due to the movement of electrons from one end to another end. The conduction decreases with increase of temperature.

**Examples:** All metals, graphite.

##### **2. Electrolytic Conductors**

Electrolytic conductors conduct electric current due to the movement of ions in solution or in fused state. The conduction increases with increase of temperature.

**Examples:** Acids, bases, electrovalent substances.

#### **Types of Electrolytic Conductors**

The electrolytic conductors are further sub-classified into three types as follows.

##### **(a) Strong electrolytes**

Strong electrolytes are substances, which ionize completely almost at all dilutions.

**Examples:**  $HCl$ ,  $NaOH$ ,  $NaCl$ ,  $KCl$ , etc.,

##### **(b) Weak electrolytes**

Weak electrolytes are substances, which ionise to a small extent even at high dilutions.

**Examples:**  $\text{CH}_3\text{COOH}$  ,  $\text{NH}_4\text{OH}$  ,  $\text{CaCO}_3$  , *etc.*

**(c) Non electrolytes**

Non electrolytes are substances, which do not ionise at any dilutions.

**Examples:** Glucose, sugar, alcohol, petrol, *etc.*,

## **CELL TERMINOLOGY**

### **1. Current**

Current is the flow of electrons through a wire or any conductor.

### **2. Electrode**

Electrode is a material (or) a metallic rod/bar/strip which conducts electrons.

### **3. Anode**

Anode is the electrode at which oxidation occurs.

### **4. Cathode**

Cathode is the electrode at which reduction occurs.

### **5. Electrolyte**

Electrolyte is a water soluble substance forming ions in solution, and conduct an electric current.

### **6. Anode Compartment**

Anode compartment is the compartment of the cell in which oxidation half-reaction occurs. It contains the anode.

### **7. Cathode Compartment**

Cathode compartment is the compartment of the cell in which reduction half reaction occurs. It contains the cathode.

### **8. Half-cell**

Half cell is a part of a cell, containing electrode dipped in an electrolytic solution. If oxidation occurs at the electrode that is called oxidation half cell. If reduction occurs at the electrode that is called reduction half cell.

### **9. Cell**

Cell is a device consisting two half cell. The two half cells are connected through one wire.

**CELLS**

A cell is a device which converts electrical energy into chemical energy (or) chemical energy into electrical energy. Generally a cell consists of two half cells. Each half cell consists of an electrode dipped in an electrolytic solution. These two half cells are connected through one wire.

**Types of cells**

Based on the type of reaction, occurring in a cell, cells are classified into two types

1. Electrolytic cells
2. Electrochemical cells (or) voltaic cell (or) galvanic cells

**1. Electrolytic cells**

Electrolytic cells are the cells in which electrical energy is used to bring about the chemical reaction.

**Example:** Electrolysis, electroplating, etc.

**2. Electrochemical cells (or) Galvanic cells**

Electro chemical cells are the cells in which chemical energy is converted into electrical energy.

**Example:** Daniel cell

**REDOX REACTIONS**

Reactions in which oxidation and reduction takes place simultaneously are known as redox reactions.

**Oxidation**

It is a process, which involves loss of electrons by a substance.

**Reduction**

It is a process, which involves gain of electrons by a substance.

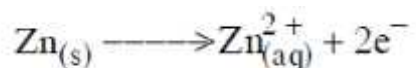
It is known that if a substance loses electrons, another substance must accept these electrons. Similarly, if a substance accepts electrons, another substance must supply these electrons. Thus, redox (oxidation and reduction) reactions always go side-by-side.

**Illustration****Zinc metal in copper sulphate solution**

If zinc metal is placed in a copper sulphate solution, the following oxidation and reduction reactions takes place.

**Oxidation**

Zinc atom (Zn) loses two electrons and gets oxidized to zinc ion  $\text{Zn}^{2+}$

**Reduction**

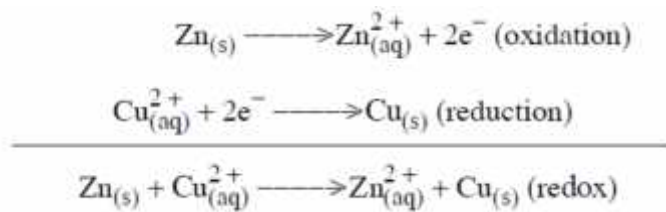
Copper ion  $\text{Cu}^{2+}$  gains two electrons, liberated by Zn and gets reduced to copper (Cu).



Each of the above reactions is known as half reaction. The reaction, in which loss of electrons takes place, is called oxidation half-reaction, while the reaction, in which gain of electrons takes place is called reduction half-reaction.

**Overall redox reaction**

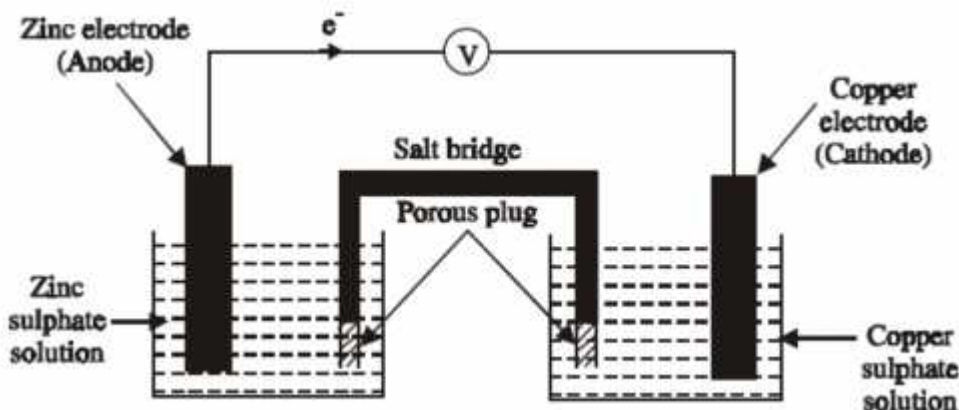
It is obtained by adding the two half-reactions. Thus,

**ELECTROCHEMICAL CELLS**

Galvanic cells are electrochemical cells in which the electrons, transferred due to redox reaction, are converted into electrical energy.

**Cell device (Construction)**

Galvanic cell consists of a zinc electrode dipped in 1M  $\text{ZnSO}_4$  solution and a copper electrode dipped in 1M  $\text{CuSO}_4$  solution. Each electrode is known as a half cell. The two solutions are inter connected by a salt bridge and the two electrodes are connected by a wire through a voltmeter.



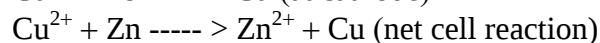
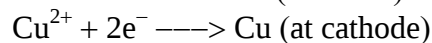
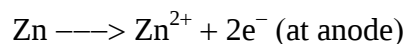
### Reactions occurring in the cell

#### At anode

Oxidation takes place in the zinc electrode by the liberation of electrons, so this electrode is called negative electrode or anode.

#### At cathode

Reduction takes place in the copper electrode by the acceptance of electrons, so this electrode is called the positive electrode or cathode.



The electrons liberated by the oxidation reaction flow through the external wire and are consumed by the copper ions at the cathode.

### Salt bridge

It consists of a U-tube containing saturated solution of KCl or  $\text{NH}_4\text{NO}_3$  in agar-agar gel. It connects the two half cells of the galvanic cells.

#### Functions of salt bridge

- (i) It eliminates liquid junction potential.
- (ii) It provides the electrical continuity between the two half cells.

### Conditions for a cell to act as standard cell

The conditions for an electrochemical cell to act as a standard cell are

- (i) The e.m.f of the cell is reproducible.
- (ii) The temperature-coefficient of e.m.f (change in e.m.f with temperature) should be very low.

**Representation of a galvanic cell (or) Cell diagram**

- (i) A galvanic cell consists of two electrodes anode and cathode.
- (ii) The anode is written on the left hand side while the cathode is written on the right hand side.
- (iii) The anode must be written by writing electrode metal first and then electrolyte. These two are separated by a vertical line or a semicolon. The electrolyte may be written by the formula of the compound (or) by ionic species.

**Examples**

- (a)  $\text{Zn}/\text{Zn}^{2+}$  (or)  $\text{Zn}/\text{ZnSO}_4$  (or)  $\text{Zn}; \text{Zn}^{2+}$
- (b) Standard hydrogen electrode  
 $\text{Pt}, \text{H}_2 (1 \text{ atm}); \text{H}^+ (1 \text{ M})$
- (iv) The cathode must be written by writing electrolyte first and then the electrode metal. These two are separated by a vertical line or a semicolon.

**Example:**

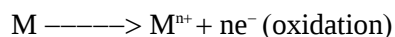
- $\text{Cu}^{2+}/\text{Cu}$  (or)  $\text{CuSO}_4/\text{Cu}$  (or)  $\text{Cu}^{2+}; \text{Cu}$
  - (v) The two half cells are separated by a salt bridge, which is indicated by two vertical lines.
- Using the above representation, the galvanic cell is represented as follows.

$\text{Zn} / \text{ZnSO}_4 (1 \text{ M}) // \text{CuSO}_4 (1 \text{ M}) / \text{Cu}$   
 (or)  $\text{Zn} / \text{Zn}^{2+} (1 \text{ M}) // \text{Cu}^{2+} (1 \text{ M}) / \text{Cu}$   
 (or)  $\text{Zn}; \text{Zn}^{2+} (1 \text{ M}) // \text{Cu}^{2+} (1 \text{ M}); \text{Cu}$

**ELECTRODE POTENTIAL****Origin of Electrode Potential**

A metal (M) consists of metal ions  $\text{M}^{n+}$  with valence electrons. When the metal (M) is placed in a solution of its own salt, any one of the following reactions will occur.

- (i) Positive metal ions may pass into the solution.



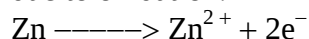
- (ii) Positive metal ions from the solution may deposit

**Illustration**

In order to understand the origin of electrode potential, the following two examples are considered.

**Example-1      Zn electrode dipped in ZnSO<sub>4</sub> solution**

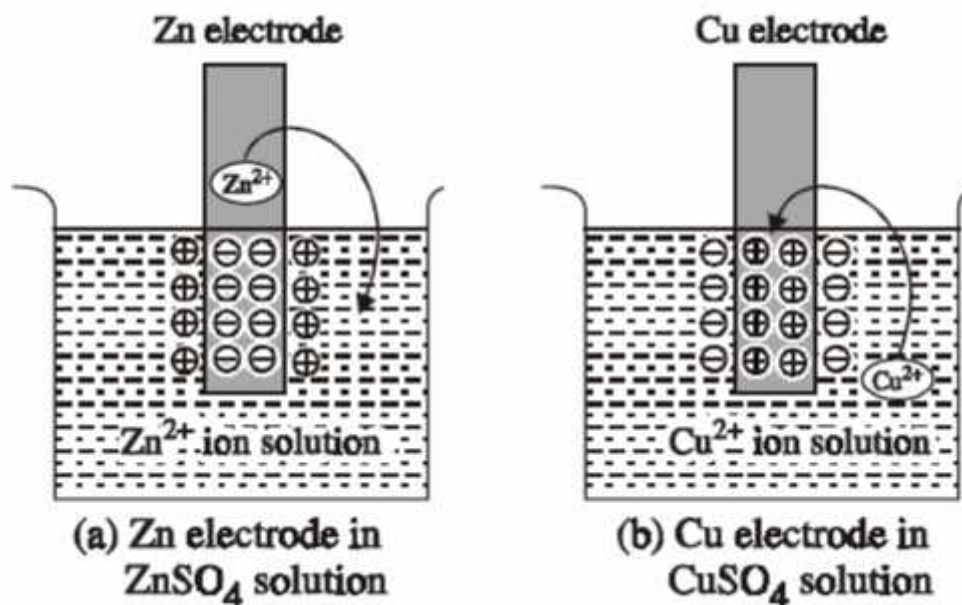
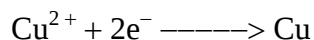
When Zn electrode is dipped in ZnSO<sub>4</sub> solution, Zn goes into the solution as  $\text{Zn}^{2+}$  ions due to oxidation.



Now, the Zn electrode attains a negative charge, due to the accumulation of valence electrons on the metal. The negative charges developed on the electrode attract the positive ions from solution. Due to this attraction the positive ions remain close to the metal.

**Example -2 Cu electrode dipped in CuSO<sub>4</sub> solution**

When Cu electrode is dipped in CuSO<sub>4</sub> solution, Cu<sup>2+</sup> ions from the solution deposit over the metal due to reduction.



Now, the Cu electrode attains a positive charge, due to the accumulation of Cu<sup>2+</sup> ions on the metal. The positive charges developed on the electrode attract the negative ions from solution. Due to this attraction, the negative ions remain close to the metal. Thus, a sort of layer (positive (or) negative ions) is formed all around the metal. This layer is called Helmholtz electrical double layer. This layer prevents further passing of the positive ions from or to the metal. A difference of potential is consequently set up between the metal and the solution. At equilibrium, the potential difference becomes a constant value, which is known as the electrode potential of a metal.

**Factors affecting electrode potential**

The rate of the above reactions depend on

- (i) The nature of the metal.
- (ii) The temperature.

(iii) The concentration of metal ions in solution.

### Single electrode potential

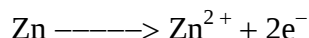
It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

### Standard electrode potential

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of 1 molar concentration at 25°C.

### Oxidation potential

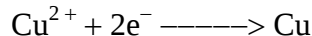
If oxidation occurs at the electrode, at equilibrium, the potential of the electrode is oxidation potential.



Thus, the tendency of an electrode to lose electrons is called the oxidation potential.

### Reduction potential

If reduction occurs at the electrode, at equilibrium, the potential of the electrode is reduction potential.



Thus, the tendency of an electrode to gain electrons is called the reduction potential.

## NERNST EQUATION FOR ELECTRODE POTENTIAL

Consider the following redox reaction



For such a redox reversible reaction, the free energy change ( $\Delta G$ ) and its equilibrium constant ( $K$ ) are inter related as

$$\begin{aligned}\Delta G &= -RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \\ &= \Delta G^{\circ} + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \dots\dots (1)\end{aligned}$$



where,

$\Delta G^\circ$  = Standard free energy change

The above equation (1) is known as *Van't Hoff isotherm*.

The decrease in free energy ( $-\Delta G$ ) in the above reaction will produce electrical energy. In the cell, if the reaction involves transfer of 'n' number of electrons, then 'n' faraday of electricity will flow. If E is the emf of the cell, then the total electrical energy (nEF) produced in the cell is

$$\begin{aligned} -\Delta G &= nEF \\ \text{(or)} \\ -\Delta G^\circ &= nE^\circ F \end{aligned} \quad \text{..... (2)}$$

where,

$-\Delta G$  = decrease in free energy change.

(or)  $-\Delta G^\circ$  = decrease in standard free energy change.

Comparing equation 1 and 2, it becomes

$$-nEF = -nE^\circ F + RT \ln \frac{[M]}{[M^{n+}]} \quad \text{.....(3)}$$

Dividing the above equation (3) by  $-nF$

[  $\therefore$  the activity of solid metal  $[M] = 1$  ]

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

$$\text{In general, } E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

(or)

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

(or)

$$E = E^{\circ} + \frac{2.303 RT}{nF} \log [M^{n+}] \quad \text{.....(4)}$$

When,  $R = 8.314 \text{ J/K/mole}$ ;  $F = 96500 \text{ coulombs}$  ;  
 $T = 298 \text{ K (25}^{\circ}\text{C)}$ , the above equation becomes

$$E = E^{\circ}_{\text{red}} + \frac{0.0591}{n} \log [M^{n+}] \quad \text{.....(5)}$$

$$\text{In general, } E = E^{\circ}_{\text{red}} + \frac{0.0591}{n} \log C$$

Similarly for oxidation potential

$$E = E^{\circ}_{\text{oxi}} - \frac{0.0591}{n} \log [M^{n+}] \quad \text{..... (6)}$$

The above equation 5&6 are known as “Nernst equation for single electrode potential”.

### Applications of Nernst equations

#### (Electrode Potential)

1. Nernst equation is used to calculate electrode potential of unknown metal.
2. Corrosion tendency of metals can be predicted.
3. It is used to calculate the EMF of a cell.
4. Concentration of the reactant can be calculated using the electrode potential.
5. Concentration of the solution in galvanic cell can be determined.
6. pH of a solution can be calculated by measuring the emf.
7. Applications of emf series

**Problems**

*What is the potential of a lead electrode that is in contact with a solution of 0.015 M  $\text{Pb}^{2+}$  ions. Standard electrode potential ( $E^\circ$ ) for  $\text{Pb} \longrightarrow \text{Pb}^{2+} + 2e^-$  is 0.13 volt.*

**Solution**

Std. oxidation potential is given as

**Given**

Concentration of  $(\text{Pb}^{2+}) = 0.015 \text{ M}$

$E^\circ = +0.13 \text{ V}$  (std. oxidation potential of Pb)

$\therefore$  The Nernst equation for oxidation potential of Pb is

$$E = E^\circ - \frac{2.303 RT}{nF} \log [\text{Pb}^{2+}]$$

$$E = E^\circ - \frac{0.0591}{n} \log [\text{Pb}^{2+}]$$

$$= 0.13 - \frac{0.0591}{2} \log [0.015]$$

$$= 0.13 - 0.02955(-1.824)$$

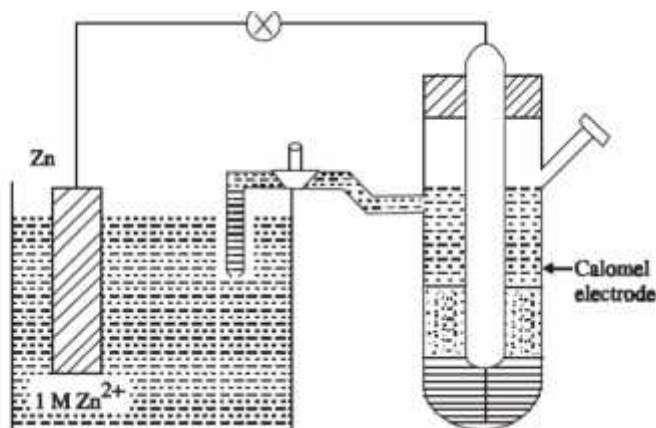
$$= 0.13 + 0.0539$$

Oxidation potential of Pb = 0.184 volt.

**MEASUREMENT OF SINGLE ELECTRODE POTENTIAL**

It is impossible to determine the absolute value of a single electrode potential. But, we can measure the potential difference between two electrodes potentiometrically, by combining them to form a complete cell. For this purpose, 'reference electrode' is used. Standard hydrogen electrode(SHE) is the commonly used reference electrode, whose potential has been arbitrarily fixed as zero. The emf of the cell is measured and it is equal to the potential of electrode.

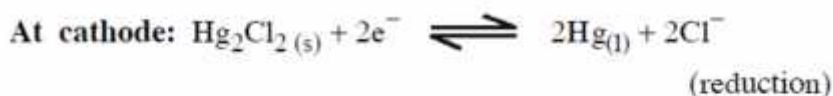
It is very difficult to set up a hydrogen electrode. So other electrodes called secondary reference electrodes like calomel electrodes are used.



### Example

To measure the electrode potential of Zn, a cell is made by combining the saturated calomel electrode with Zn electrode, the potential of which is to be determined. Since the reduction potential of the coupled Zn electrode is less than of calomel electrode  $\approx 0.2422 \text{ V}$ , the calomel electrode will act as cathode and zinc electrode will act as anode.

The following cell reaction will occur in the above cell



The emf of the above cell is measured and the electrode potential is calculated from the emf as follows

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

$$E_{\text{cell}} = E_{\text{cal}} - E_{\text{Zn}}$$

$$\begin{aligned} E_{\text{Zn}} &= E_{\text{cal}} - E_{\text{cell}} \\ &= +0.2422 - 1.0025 \end{aligned}$$

$$E_{\text{Zn}} = -0.7603 \text{ volt}$$

ie., the reduction potential of Zn electrode =  $-0.7603 \text{ volt}$ .

**ELECTROCHEMICAL SERIES**

The standard electrode potential (reduction) of a number of electrodes values are determined potentiometrically by combining the electrode with the another standard electrodes, whose electrode potential is zero.

**Definition**

When various electrodes (metals) are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, then the arrangement is called electrochemical series.

| Electrode                          | Electrode reaction                                        | $E^\circ$ , volts | Nature                        |
|------------------------------------|-----------------------------------------------------------|-------------------|-------------------------------|
| $\text{Li}^+/\text{Li}$            | $\text{Li}^+ + e \rightleftharpoons \text{Li}$            | - 3.01            | Anodic<br>↑                   |
| $\text{Mg}^{2+}/\text{Mg}$         | $\text{Mg}^{2+} + 2e \rightleftharpoons \text{Mg}$        | - 2.37            |                               |
| $\text{Pb}^{2+}/\text{Pb}$         | $\text{Pb}^{2+} + 2e \rightleftharpoons \text{Pb}$        | -1.12             |                               |
| $\text{Zn}^{2+}/\text{Zn}$         | $\text{Zn}^{2+} + 2e \rightleftharpoons \text{Zn}$        | - 0.76            |                               |
| $\text{Fe}^{2+}/\text{Fe}$         | $\text{Fe}^{2+} + 2e \rightleftharpoons \text{Fe}$        | -0.44             |                               |
| $\text{Sn}^{2+}/\text{Sn}$         | $\text{Sn}^{2+} + 2e \rightleftharpoons \text{Sn}$        | - 0.136           | Pt-reference<br>↓<br>Cathodic |
| $\text{H}^+/\text{H}_2$            | $2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$          | 0.00              |                               |
| $\text{Cu}^{2+}/\text{Cu}$         | $\text{Cu}^{2+} + 2e \rightleftharpoons \text{Cu}$        | + 0.34            |                               |
| $\text{Ag}^+/\text{Ag}$            | $\text{Ag}^+ + e \rightleftharpoons \text{Ag}$            | + 0.80            |                               |
| $\text{Au}^+/\text{Au}$            | $\text{Au}^+ + e \rightleftharpoons \text{Au}$            | + 1.50            |                               |
| $\frac{1}{2}\text{F}_2/\text{F}^-$ | $\frac{1}{2}\text{F}_2 + e \rightleftharpoons \text{F}^-$ | + 2.87            |                               |

**Significance of emf series (or) Applications of electrochemical series (or)**

**Applications of Nernst equation (or) Importance of electrode potential**

The emf series (electrode potential) provide valuable information as given below.

### 1. Calculation of standard emf of the cell

The standard emf of a cell can be calculated if the standard electrode potential values are known using the following relation.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{R.H.E}} - E^{\circ}_{\text{L.H.E}}$$

### 2. Relative ease of oxidation (or) reduction

Higher the value of standard reduction potential (+ve value) greater is the tendency to get reduced. (i.e. Metals on the top (–ve value) are more easily ionised) (oxidised).

(a) The fluorine has higher positive value of standard reduction potential  $+2.87 \text{ V}$ , and shows higher tendency towards reduction.

(b) The lithium has highest negative value ( $-3.01 \text{ V}$ ) and shows higher tendency towards oxidation.

### 3. Displacement of one element by the other

Metals which lie higher in the emf series can displace those elements which lie below them in the series.

For example, we may know whether Cu will displace

Zn from the solution or vice-versa. We know that standard reduction potential of Cu & Zn.

i.e.,  $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$  and  $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ .

So,  $\text{Cu}^{2+}$  has a great tendency to acquire Cu form, than  $\text{Zn}^{2+}$  has for acquiring Zn form.

### 4. Determination of standard free energy change $\Delta G$ and equilibrium constant for the reaction

Standard electrode potential can also be used to determine the standard free energy change  $\Delta G$  and equilibrium constant  $K$  for the reaction. We know that

$$-\Delta G^{\circ} = RT \ln K = 2.303 RT \log K$$

$$\log K = \frac{-\Delta G^{\circ}}{2.303 RT}$$

$$= \frac{nFE^{\circ}}{2.303 RT} \quad [\because -\Delta G^{\circ} = nFE^{\circ}]$$

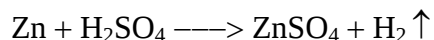
The equilibrium constant for the cell reaction can be calculated.

### 5. Hydrogen displacement behaviour

Metals with negative reduction potential (i.e., the metals placed above  $\text{H}_2$  in the emf series) will displace the hydrogen from an acid solution.

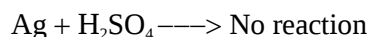
**Example:**

Zinc reacts with dil  $\text{H}_2\text{SO}_4$  to give  $\text{H}_2$  but Ag does not, why?



$$E^\circ_{\text{Zn}} = -0.76 \text{ volt}$$

The metal with positive reduction potential (ie., the metals placed below  $\text{H}_2$  in the emf series) will not displace the hydrogen from an acid solution.



$$E^\circ_{\text{Ag}} = +0.80 \text{ volt}$$

### Predicting Spontaneity (or) feasibility of Redox Reactions

Spontaneity of redox reaction can be predicted from the emf  $\square$  value of the complete cell reaction ( $\Delta G = -nFE^\circ$ ).

(i) If  $E^\circ$  of the cell is positive, the reaction is spontaneous (or) feasible

(ii) If  $E^\circ$  of the cell is negative, the reaction is not spontaneous (or) not feasible

In general, an element having lower reduction potential can displace another metal having higher reduction potential from its salt solution spontaneously.

### 1.3 REFERENCE ELECTRODES (STANDARD ELECTRODES)

The electrode, whose electrode potential is known or arbitrarily fixed as zero is called reference electrode.

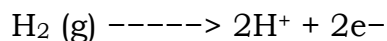
#### 1.3.1 Primary Reference Electrode (Standard Hydrogen electrode)

##### Construction

- Platinum electrode consists of Pt foil connected in a Pt wire and sealed in glass tube.
- when its dipped in a 1N HCl,  $\text{H}_2$  gas at 1 atmospheric pressure is passed and it forms a standard hydrogen electrode.
- The electrode potential of SHE is zero at all temperatures

It is represented as,  
 $\text{Pt}, \text{H}_2 (1 \text{ atm}) / \text{H}^+ (1 \text{ M}); E^\circ = 0 \text{ V}$

Anode reaction



Cathode reaction

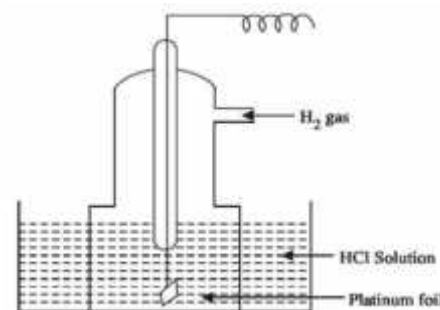
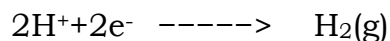


Fig. 1.2 Hydrogen electrode

##### Limitations

- It requires hydrogen gas and is difficult to set up and transport.
- It requires considerable volume of test solution.
- The solution may poison the surface of the platinum electrode.

iv. The potential of the electrode is altered by changes in barometric pressure.

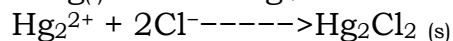
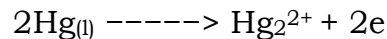
### 1.3.2 Secondary Reference Electrode - Saturated Calomel Electrode

#### Construction

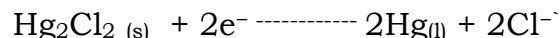
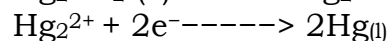
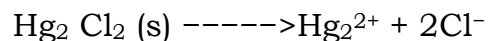
- It consists of a glass tube contain Hg at bottom over mercurous chloride is placed.
- Remaining portion is filled with saturated KCL.
- The bottom of the tube is sealed with platinum wire
- The side tube is used for making electrical contact with salt bridge

Calomel electrode is represented as  
 $\text{Hg}, \text{Hg}_2\text{Cl}_2, \text{KCl}(\text{Saturated Solution}); E^0 = 0.2422$

If the electrode acts as anode the reaction is



If the electrode acts as cathode the reaction is



The electrode potential depends on the activity of the chloride ions.

|               |               |
|---------------|---------------|
| 0.1 N KCl     | = + 0.3338 V  |
| 1.0 N KCl     | = + 0.2800 V  |
| Saturated KCl | = + 0.2422 V. |

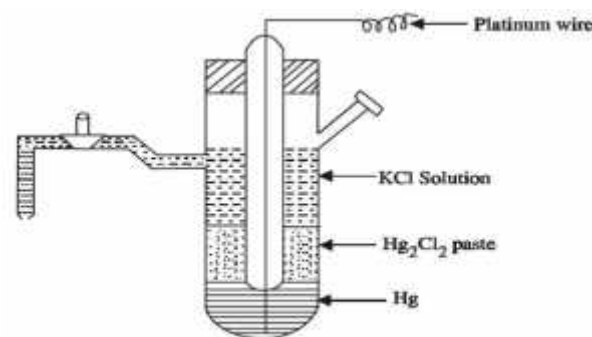


Fig. 1.3 Calomel electrode

#### Measurement of single electrode potential of Zn using calomel electrode

To measure the electrode potential of Zn, it made by connected with saturated calomel electrode. Calomel electrode act as cathode zinc act as anode

$$E_{\text{cell}} = E^{\circ}_{\text{right}} - E^{\circ}_{\text{left}}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cal}} - E^{\circ}_{\text{Zn}}$$

$$E^{\circ}_{\text{Zn}} = E^{\circ}_{\text{cal}} - E_{\text{cell}}$$

$$= + 0.2422 - 1.0025$$

$$E^{\circ}_{\text{Zn}} = - 0.7603 \text{ volt .}$$

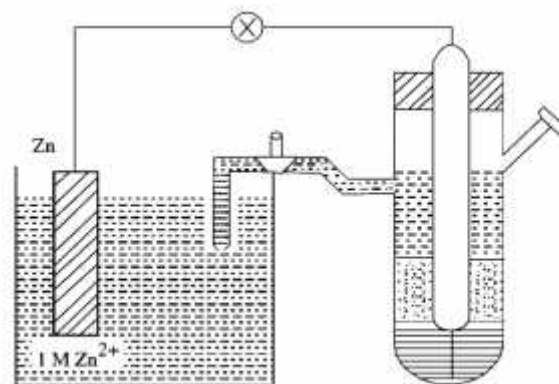


Fig. 1.4 Measurement of electrode potential (Zn)

### 1.3.3 Ion-Selective Electrodes (ISE)

Ion-selective electrodes are the electrodes having the ability to respond only to a particular ions, and develop potential, ignoring the other ions in a mixture totally.

#### Glass Electrode (Internal Reference Electrode)

- It consists of thin walled glass bulb(special type of glass) containing Pt wire in 0.1 M HCL Pt,0.1 M HCL / Glass
- Its used as internal reference electrode
- The Ph of the solution specially colored solutions can be measured
- The glass membrane act as ion exchange resin & equilibrium set in between  $\text{Na}^+$  ions of glass and  $\text{H}^+$  ions in solution
- The potential difference vary with  $\text{H}^+$  ion concentration and EMF

$$E_G = E_G^0 + 0.0592 \text{ pH}$$

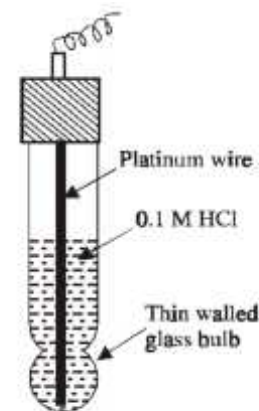


Fig. 1.5 Glass electrode

#### Determination of pH of a Solution using Glass Electrode

The glass electrode is placed in the under test solution & coupled with calomel electrode

$$\begin{aligned} E_{\text{cell}} &= E_{\text{right}} - E_{\text{left}} \\ E_{\text{cell}} &= E_{\text{cal}} - E_G \\ &= E_{\text{cal}} - (E_G^0 + 0.0592 \text{ pH}) \\ &= E_{\text{cal}} - E_G^0 - 0.0592 \text{ pH} \\ \text{pH} &= \frac{E_{\text{cal}} - E_G^0 - E_{\text{cell}}}{0.0592} \\ \therefore E_{\text{cal}} &= 0.2422 \text{ V} \\ \therefore \text{pH} &= \frac{0.2422 - E_G^0 - E_{\text{cell}}}{0.0592} \end{aligned}$$

#### Advantages of Glass Electrode

- It can be easily constructed
- The results are accurate.
- It is not easily poisoned.
- Equilibrium is rapidly achieved.

#### Disadvantages (Limitations)

- Since the resistance is quite high, special electronic potentiometers are employed for measurement.
- The glass electrode can be used in solutions only with pH range of 0 to 10.

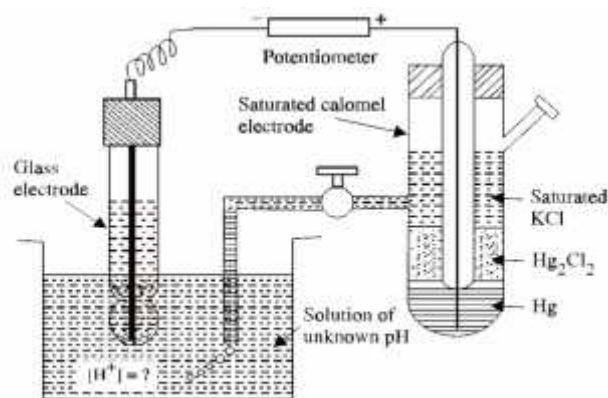


Fig. 1.6 Determination of pH by using glass electrode

**Applications of ISE**

Used for determining the concentration of cations like  $H^+$ ,  $Na^+$ ,  $K^+$  etc

Used for the determination of hardness of  $Ca^{2+}$  and  $Mg^{2+}$

Used for determining the concentration of anions like  $CN^-$ ,  $NO_3^-$ ,  $S^{2-}$  etc

Used for determining the PH of the solution using glass sensing electrode

**1.8 EMF OF A CELL**

Electromotive force is defined as, "the difference of potential which causes flow of current from one electrode of higher potential to the other electrode of lower potential.

$$EMF = \left\{ \begin{array}{l} \text{Standard reduction} \\ \text{potential of right hand} \\ \text{side electrode} \end{array} \right\} - \left\{ \begin{array}{l} \text{Standard reduction} \\ \text{potential of left} \\ \text{hand side electrode} \end{array} \right\}$$

**1.8.1 Measurement of EMF of a cell**

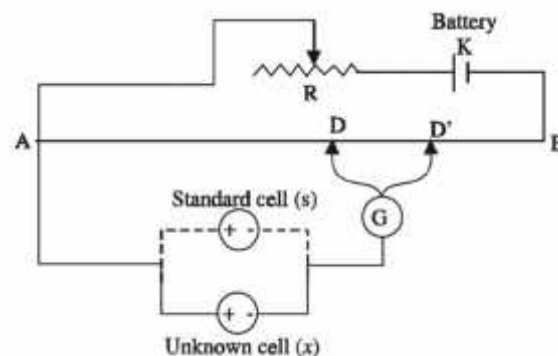
The potential difference or emf of a cell can be measured on the basis of Poggendorff's compensation principle.

Here the emf of the cell is just opposed or balanced by an emf of standard cell (external emf), so that no current flows in the circuit.

- It consists of uniform wire AB and storage battery K is connected to the ends A and B of the wire through rheostat R
- The cell of unknown emf is connected to the series by positive pole to A and negative pole to sliding contact D through galvanometer G.
- The sliding contact is moved along the wire AB till no current flows the galvanometer
- The distance AD is measured the emf is directionally proportional to distance AD
- Then the unknown cell is replaced by a standard cell. the distance is AD'.

$$\frac{\text{Emf of the unknown cell } x}{\text{Emf of the standard cell } s} = \frac{\text{Length AD}}{\text{Length AD'}} \quad \frac{E_x}{E_s} = \frac{AD}{AD'}$$

$$\therefore \text{Emf of the unknown cell} = E_x = \frac{AD}{AD'} \times E_s$$



### 1.8.2 Factors affecting EMF of a cell

Nature of the electrolytes and electrodes.  
Concentration and composition of the electrolytes.  
pH and temperature of the solution.

### 1.8.3 Applications of EMF measurements

1. Determination of standard free energy change and equilibrium constant.

The standard free energy change of a reaction can be calculated by

$$-\Delta G^\circ = nFE^\circ$$

2. Determination of pH by using a standard hydrogen electrode.  $E = \frac{-2.303RT}{nF} \text{pH}$
3. Solubility of a sparingly soluble salt can be determined.
4. Valency of an ion can be determined.
5. Potentiometric titrations can be carried out.
6. Hydrolysis constant can also be determined.

## 1.9 REVERSIBLE AND IRREVERSIBLE CELLS

### 1. Reversible Cells

A cell which obeys the following three conditions of thermodynamic reversibility is called a reversible cell.

- (i) If the Daniel cell is connected to an external source of emf equal to 1.1 volt, no current flows and also no chemical reaction takes place in the cell.
- (ii) If the external emf is made slightly less than 1.1 volt, a small amount of current flows from the cell and a small chemical reaction occurs.
- (iii) If the external emf is made slightly greater than 1.1 volt, the current will flow in the opposite direction.

### 2. Irreversible Cells

Cells which do not obey the conditions of thermodynamic reversibility are called irreversible cells. Zinc-Silver cell is an example for an irreversible cell. It is represented as

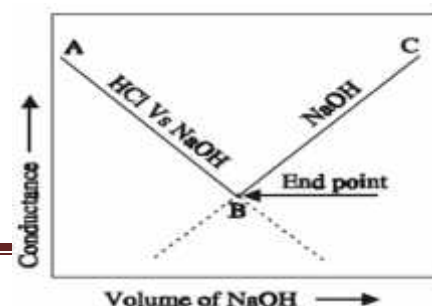
## 1.10 CONDUCTOMETRIC TITRATION

### Principle

Conductometric titration is a volumetric method based on the measurement of conductance of the solution during the titration.

The conductance of a solution depends on

- (i) the number and charge on the free ions, and



- (ii) the mobility of the ions.

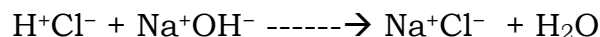
### 1.10.1 Types of conductometric titrations

- Acid-Base titrations.
- Precipitation titrations.
- Redox (oxidation-reduction) titrations.
- Replacement titrations etc

### 1.10.2 Acid-Base titration

#### Strong acid Vs Strong base (HCl Vs NaOH)

- Known amount of acid (HCl) is taken in the conductivity cell and the alkali (NaOH) in the burette.
- Initially conductivity of HCL is High due to fast moving  $H^+$  ions
- As the NaOH is added gradually, conductance will be going on decreasing until the acid has been completely neutralized (indicated by the line AB).
- This is due to the replacement of fast moving  $H^+$  ions by slow moving  $Na^+$  ions.
- The point 'B' indicates complete neutralization of all  $H^+$  ions (end point).
- After the end point further addition of NaoH will increase the fast moving  $OH^-$  ions



On plotting the conductance against the volume of NaoH added, the two lines intersect at a point 'B' gives the end point. This corresponds to the volume of NaOH required for neutralization.

### 1.10.3 Advantages of conductometric titration

- It gives more accurate end point.
- It is also used for the analysis of dilute solutions and weak acids.
- Since the end point is detected graphically

### 1.10.4 Disadvantages of Conductometric Titration

- Only limited number of redox titration can be carried out.
- It becomes less accurate and less satisfactory

## 1.11 POTENTIOMETRIC TITRATIONS

### Principle

Emf of a cell depends upon the concentration of electrolytes with the electrodes are in contact. The potentiometric titrations involve the measurement of emf between reference electrode and an indicator electrode, with the addition of the titrant.

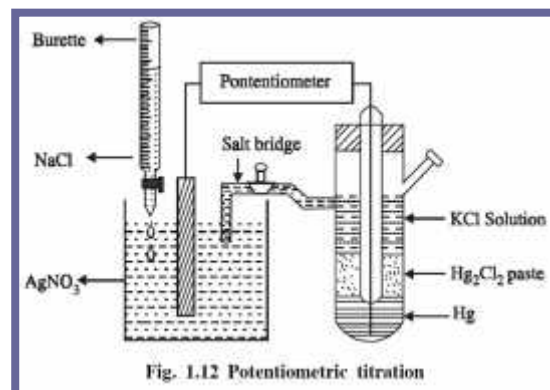
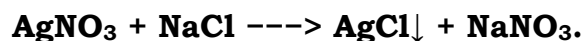


Fig. 1.12 Potentiometric titration

### 1.11.1 Types of potentiometric Titration

#### 1. Precipitation titration ( $\text{AgNO}_3$ Vs $\text{NaCl}$ )

- $\text{AgNO}_3$  solution is taken in a beaker and indicator electrode is placed in it.
- Then its connected to the calomel electrode to form galvanic cell its connected to potentiometer and its  $E_{\text{cell}}$  is determined.
- When  $\text{AgNO}_3$  is titrated against to the  $\text{NaCl}$  the emf will be decreasing to the  $\text{Ag}^+$  concentration decreases



- At the end point, emf is suddenly decreases. After the end point there is no noticeable change in the potential.

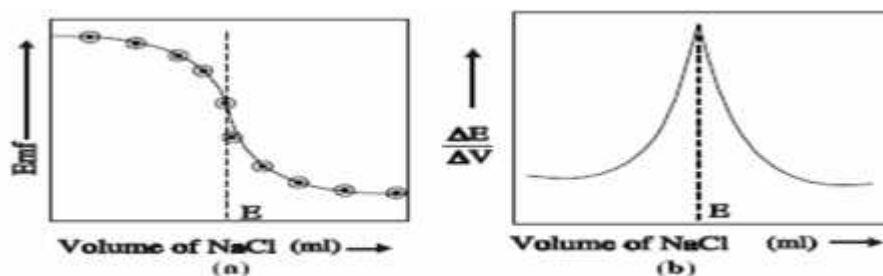


Fig. 1.13  $E_{\text{cell}}$  Vs Vol. of  $\text{NaCl}$

- When the emf is plotted against the volume of  $\text{NaCl}$  added a curve of the type shown in figure 1.13 is obtained.
- The end point is the point, where the slope of the curve is maximum.
- The graph vs volume of  $\text{NaCl}$  is plotted as above to get the accurate end point.

#### 2. Redox titration ( $\text{FeSO}_4$ Vs $\text{K}_2\text{Cr}_2\text{O}_7$ )

- $\text{FeSO}_4$  solution is taken in a beaker and indicator electrode is placed in it.
- Then its connected to the calomel electrode to form galvanic cell its connected to potentiometer and its  $E_{\text{cell}}$  is determined.
- When  $\text{FeSO}_4$  is titrated against to the  $\text{K}_2\text{Cr}_2\text{O}_7$  the emf will be increasing to the  $\text{Fe}^{3+}$  concentration increases
- At the end point, emf is suddenly increases. After the end point there is no noticeable change in the potential.

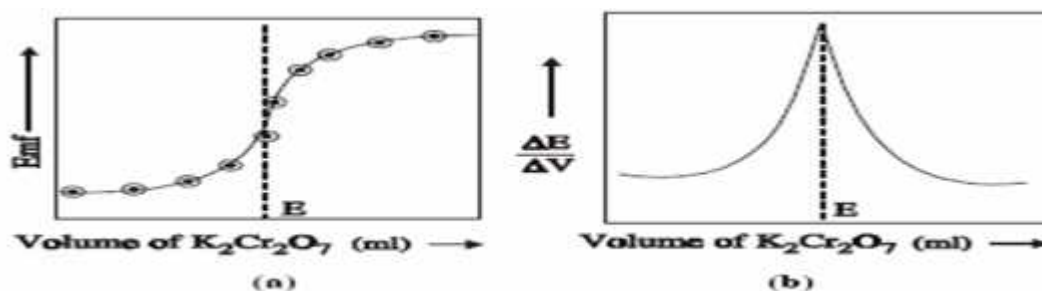


Fig. 1.14  $E_{\text{cell}}$  Vs Vol. of  $\text{K}_2\text{Cr}_2\text{O}_7$

- 
- When the emf is plotted against the volume of  $K_2Cr_2O_7$  added a curve of the type shown in figure is obtained.
- The end point is the point, where the slope of the curve is maximum.
- The graph vs volume of  $K_2Cr_2O_7$  is plotted as above to get the accurate end point.

#### 1.11.2 Advantages of potentiometric titrations

1. The necessary apparatus required is cheap and easily available.
2. This method can be used for coloured solution.
3. Very dilute solutions can be titrated with accuracy.
4. Several components may be titrated in the same solution.



**KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21.**

**FACULTY OF ENGINEERING**

**DEPARTMENT OF SCIENCE AND HUMANITIES**

**ENGINEERING CHEMISTRY**

**UNIT-II**

**ELECTROCHEMISTRY**

**PART – B**

1. What is cell? Mention its types.
2. State single electrode potential
3. State standard electrode potential
4. Define the terms (i) single electrode potential (ii) Electrochemical cells.
5. What are reversible and irreversible cells?
6. Define emf
7. List the factors affecting emf of a cell
8. What are the limitations of standard hydrogen electrode?
9. Write the limitations of hydrogen electrode
10. Write the conditions for an electrochemical cell to act as a standard cell
11. What is reference electrode? Give an example
12. Define electrode potential
13. What is an ion selective electrode?
14. How is  $p^H$  of a solution determined using glass electrode
15. Mention the advantages of potentiometric titration
16. Distinguish between metallic and electrolytic conductors.
17. What is electrochemical series?
18. Mention the significance of emf series.
19. Zinc reacts with dilute  $H_2SO_4$  to give hydrogen but Ag does not-Explain.
20. How will you predict the spontaneity of a redox system using emf
21. What is redox titration? Give an example.
22. Mention the advantages of conductometric titration.
23. What are the requirements of a good battery?
24. What are batteries? How do they differ from a cell?
25. What is alkaline battery?
26. What are the advantages of alkaline battery over dry cell?
27. Write the charging and discharging of lead storage battery and give its uses
28. What is a storage cell? Write the cell representation of lead accumulator?
29. Write a few disadvantages of fuel cells?
30. What are the components of  $H_2$ - $O_2$  fuel cell?
31. What are the applications of  $H_2$ - $O_2$  fuel cell?
32. Write the electrode reactions of  $H_2$ - $O_2$  fuel cell?

**PART – C**

1. Derive Nernst equation for EMF of a cell. Give its significance
2. Define emf. How can it be measured potentiometrically?
3. What are Reference Electrodes? Explain the types with neat diagrams and mention their uses.
4. What are reference electrodes? Describe calomel electrode with a neat diagram.
5. Describe the construction and working of calomel electrode & hydrogen Electrode
6. Describe glass electrode. How can it be used for determining the  $P^H$  of a solution.
7. What is irreversible cell explain the irreversibility taking a suitable example
8. What is electrochemical series? Give its applications with suitable examples.
9. What is the principle underlying conductometric titration? Explain acid-base titrations with neat graph.
10. Explain the conduct metric titration of strong acid by strong base.
11. Explain the principle involved in potentiometric titration. Write an experimental procedure for carrying out the titration of redox reaction.
12. What are fuel cells? Explain the construction and working of a fuel cell
13. What is reversible battery? Describe the construction and working of lead acid storage battery with reactions occurring during charging and discharging?

### UNIT-III

### FUELS AND COMBUSTION

#### DEFINITION- FUEL

A fuel is defined as any combustible substance, which when burnt produces heat and is used for domestic and industrial purposes.

#### CLASSIFICATION OF FUELS

Fuels are classified into two types based on their (i) occurrence and (ii) the state of aggregation.

Based on occurrence

(i) Natural (or) Primary fuels:

These fuels occur in nature as such

Examples: Wood, peat, coal, petroleum etc

(ii) Artificial (or) secondary fuels:

These are derived from primary fuels.

Examples: Charcoal, coke, kerosene, petrol etc

Based on the state of aggregation:

(i) Solid fuels : Wood, peat, coal and coke etc

(ii) Liquid fuels: Most of the liquid fuels are obtained from petroleum. The combustible elements in all liquid fuels are carbon and hydrogen.

Examples: Paraffins, olefins, naphthalenes and aromatics.

(iii) Gaseous fuels: The gaseous fuels of engineering importance are natural gas, coal gas, producer gas, oil gas etc

#### COAL

It is a solid fuel, produced from accumulation of vegetable debris due to partial decay and alteration by the action of heat and pressure over millions of years

#### ANALYSIS OF COAL:

##### (i) Proximate analysis of coal

To assess the quality of coal proximate analysis was carried out

Proximate analysis of coal

It involves the determination of percentage of

- (i) Moisture content
- (ii) Volatile matter
- (iii) Ash content
- (iv) Fixed carbon in coal

##### Moisture content

About 1 gm of powdered air dried coal sample is taken in a crucible, and it is heated at 100-105°C in an electric hot air oven for 1 hour. The loss in

weight of the sample is found out and the percentage of moisture is calculated as

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

**Volatile matter**

After the analysis of moisture content the crucible with residual coal sample is covered with a lid, and it is heated at  $950 \pm 20^\circ\text{C}$  for 7 minutes in a muffle furnace. The loss in weight of the sample is found out and the percentage of volatile matter is calculated as

$$\% \text{ of volatile matter in coal} = \frac{\text{loss of weight of the coal}}{\text{Weight of moisture free coal}} \times 100$$

**Ash content**

After the analysis of volatile matter, the crucible with residual coal sample is heated without lid at  $700^\circ \pm 50^\circ\text{C}$  for half an hour in a muffle furnace. The loss in weight of the sample is found out and the percentage of ash content is calculated as

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

**Fixed carbon**

It is determined by subtracting the sum total of moisture, Volatile and ash contents from 100

% of ash content in coal =  $100 - (\% \text{ of (moisture content + volatile matter + ash content)})$

Importance of Proximate analysis

**Moisture content**

High percentage of moisture is undesirable because

- (i) It reduces the calorific value of the coal
- (ii) Moisture in coal consumes more heat in the form of latent heat of evaporation and hence more heat is to be applied to the coal.
- (iii) It increases the transport cost

**Volatile matter**

High percentage of volatile matter is undesirable because

- (i) It reduces the calorific value of the coal
- (ii) Large proportion of fuel on heating will distill over as vapour, which escapes out unburnt.
- (iii) Coal with high percentage of volatile matter burns with a long flame with high smoke.
- (iv) The coal containing high percentage of volatile matter does not coke well.

### Ash content

High percentage of ash content is undesirable because

- (v) It reduces the calorific value of the coal
- (vi) Ash causes hindrance to heat flow as well as produces clinkers, which blocks the air supply through the fuel.
- (vii) It increases the transporting, handling and storage costs.
- (viii) It involves additional cost in ash disposal

### Fixed carbon

- (ix) High percentage of fixed carbon is desirable because higher the percentage of fixed carbon in a coal, Greater is its calorific value.
- (x) The percentage of fixed carbon helps in designing the furnace and the shape of the fire box.

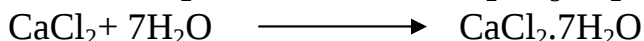
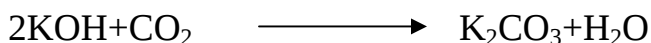
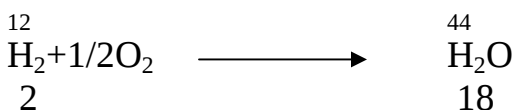
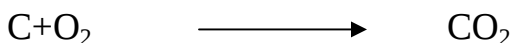
### Ultimate Analysis Of Coal

The ultimate analysis of coal consists of determination of carbon, hydrogen, sulphur, nitrogen and oxygen.

Procedure for ultimate analysis

Carbon and hydrogen:

About 1-2 g of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. Carbon and hydrogen of coal are converted into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The gaseous products of combustion are absorbed in  $\text{KOH}$  and  $\text{CaCl}_2$  of known weights respectively. The increase in weights of these tubes are then determined.



Percentage of carbon:  $\frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Weight of coal taken} \times 44}$

-----  
Weight of coal taken x 44

$$\text{Percentage of hydrogen: } \frac{\text{Increase in weight of weight of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal taken} \times 18}$$

Nitrogen:

About 1 g of accurately weighed powdered coal is heated with concentrated sulphuric acid along with potassium sulphate catalyst in a long necked flask. After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard solution. The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the percentage of nitrogen in coal can be calculated as follows

Percentage of Nitrogen:  $\frac{\text{Volume of acid used} \times \text{normality}}{\text{Weight of coal taken}}$

Sulphur:

It is determined from the washings obtained by a known mass of coal, used in bomb calorimeter for determination of a calorific value. During this determination, sulphur is converted into sulphate. The washings are treated with barium chloride solution, when barium sulphate is precipitated. This precipitate is filtered, washed and dried to get a constant weight.

Percentage of sulphur =  $\frac{\text{Weight of barium sulphate} \times 32 \times 100}{\text{Weight of coal taken in bomb} \times 233}$

Ash

Its determination is carried out as in proximate analysis

Oxygen

The sum of percentage of carbon, hydrogen, nitrogen, sulphur and ash is subtracted from 100 to get the percentage of oxygen.

Percentage of oxygen =  $100 - \% \text{ of (C+H+N+S+Ash)}$

Significance of ultimate analysis

1. Greater the percentage of carbon and hydrogen, better the quality and calorific value of coal
2. A good coal should have less nitrogen content
3. Sulphur contributes to calorific value of coal, but high sulphur content leads to atmospheric pollution
4. High oxygen content of coal contributes to high moisture, low calorific value and low coking power.

## Manufacture of Metallurgical coke

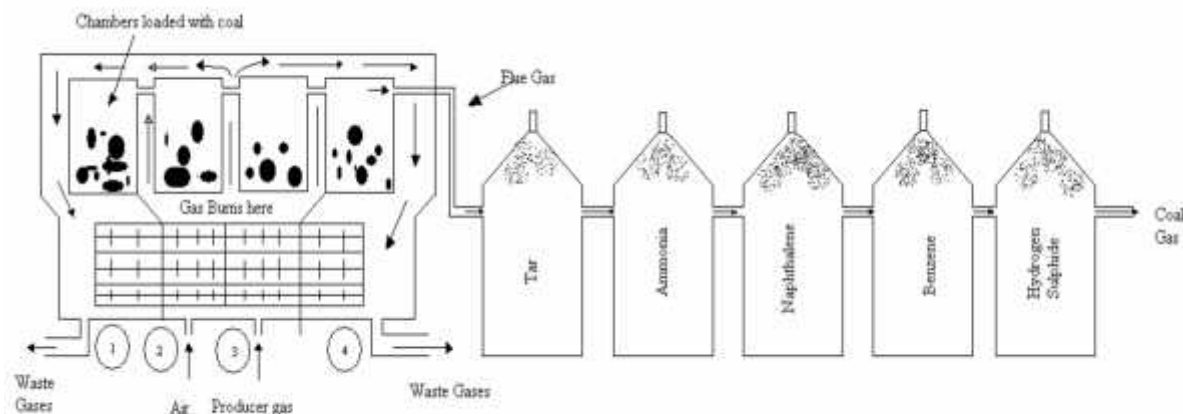
There are so many types of ovens are used for the manufacture of metallurgical coke. But the important one is Otto-Hoffman's by-product oven method.

### Otto-Hoffman's by-product oven method

In order to

- (i) Increase the thermal efficiency of the carbonization process.
- (ii) Recover valuable by product (like coal gas, ammonia, benzol oil, tar, etc.).

Otto Hoffman developed modern by-product coke oven



### Otto Hoffmann's by product oven

The by product coke oven consists of number of silica chambers, Each chamber is about 10 -12 m long, 3-4m height and 0.4 -0.45m wide. Each chamber is provided with a charging hole at the top, a gas off take valve and iron door at each ends for discharging coke.

Coal is introduced into the silica chamber and the chamber is closed. The chambers are heated to 1200 degree Celsius by burning the preheated air and the producer gas mixture in the interspaces between the chambers

The air and gas are preheated by sending them through 2<sup>nd</sup> and 3<sup>rd</sup> for regenerators. Hot flue gases produced during the carbonization are allowed to pass through 1<sup>st</sup> and 4<sup>th</sup> regenerators until the temperature has been raised to 1000 degree Celsius. While 1<sup>st</sup> and 4<sup>th</sup> regenerators are heated by hot flue gases. The 2<sup>nd</sup> and 3<sup>rd</sup> regenerators are used for heating the incoming air and gas mixture. For economical heating, the direction of inlet gases and flue gases are changed frequently. The above system of recycling the flue gases to produce heat energy known as the regenerative system of heat economy. When the process is complete, the coke is removed and quenched with water.

Time taken for complete carbonization is about 12-20 hours. The yield coke is about 70%.

The valuable by products like coal gas, tar, ammonia, H<sub>2</sub>S and benzol etc... can be recovered from flue gas

**Recovery of by products:****(i) Tar:**

The flue gas is first passed through a tower in which liquor ammonia is sprayed. Tar and dust get dissolved and collected in a tank below, which is heated by steam coils to recover back ammonia sprayed.

(ii) **Ammonia:** The gases are then passed through another tower in which water is sprayed. Here ammonia gets converted to NH<sub>4</sub>OH.

(iii) **Naphthalene:** The gases are then passed through another tower in which cool water is sprayed. Here naphthalene gets condensed.

(iv) **Benzene:** The gases are passed through another tower, where petroleum is sprayed. Here benzene gets condensed to liquid.

(v) **H<sub>2</sub>S:** The remaining gases are then passed through a purifier, packed with moist Fe<sub>2</sub>O<sub>3</sub>. Here H<sub>2</sub>S is retained.

The final gas left out is called coal gas which is used as gaseous fuel.

**Advantages of Otto Hoffman's process:**

- 1, Valuable by products like ammonia, coal gas, naphthalene etc., are recovered.
- 2, The carbonization time is less.
3. Heating is done externally by producer gas.

**SYNTHETIC PETROL**

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

Based on its availability, petrol is classified into two types.

(a) Natural petrol

**Natural Petrol:**

The petrol obtained from natural resources is known as Natural petrol.

**Synthetic Petrol:**

In countries like Germany and South Africa, which do not contain petroleum deposits, petrol is derived from non- petroleum sources, such as oil shales, lignites and bituminous coals. The other name for synthetic petrol is gasoline.

Petrol synthesized either by polymerization of low molecular mass olefins and alkanes (or) from finely powdered coal and heavy oil is called synthetic petrol.

## SYNTHESIS OF SYNTHETIC PETROL

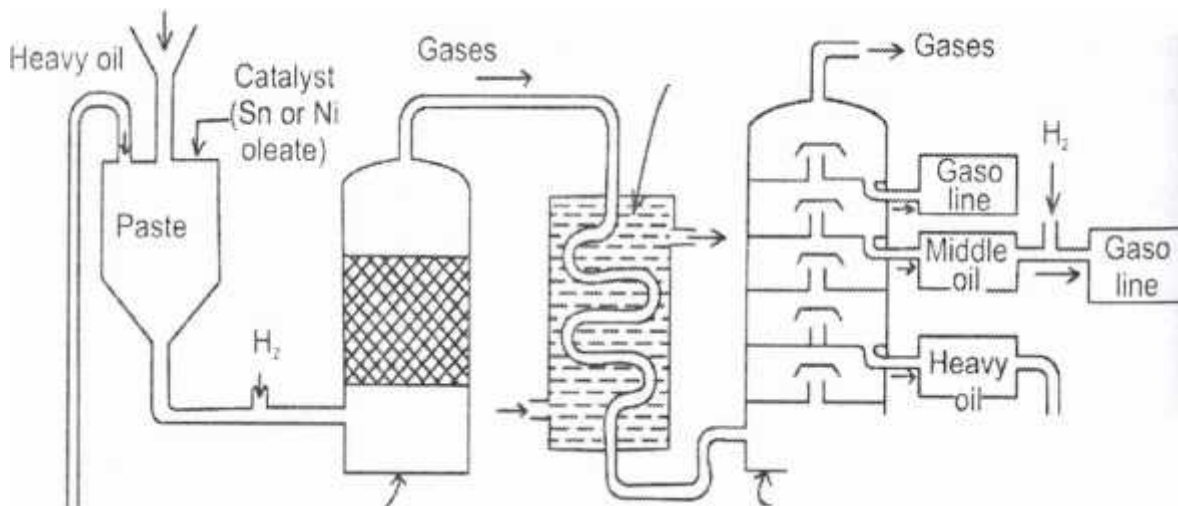
### Bergius process: Bergius process of hydrogenation of coal to gasoline

1. In this process, low ash coal pulverized to a fine powder, is converted into a paste, with heavy oil and a catalyst, composed of tin (or) nickel oleates.
2. This mixture is then sent to a converter maintained at  $450^{\circ}\text{C}$  and a pressure of 200 to 250 atmospheres, where it meets with Hydrogen gas

3. The combination of the hydrogen with the carbon framework of the coal yields various

Hydrocarbons from wax to gases.

4. The high molecular weight hydrocarbons are decomposed further at the high temperature prevailing in the converter giving lower hydrocarbons
5. The out coming gases are led to condenser, where a liquid resembling crude oil is obtained, which is then fractionated to get (1) gasoline (ii) middle oil and (iii) Heavy oil



6. The heavy oil is used again for making paste with fresh coal dust.
7. The middle oil is hydrogenated in vapour - phase in presence of a solid catalyst to yield more gasoline.
8. The yield of gasoline is about 60% of the coal dust used.

### Fischer - Tropsch Method

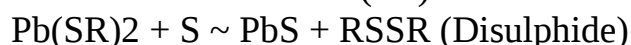
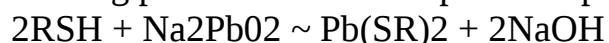
Water gas ( $\text{CO} + \text{H}_2$ ), produced by passing steam over heated coke, is mixed with hydrogen.

1. The gas is purified by passing through  $\text{Fe}_2\text{O}_3$  to remove  $\text{H}_2\text{S}$  and then into a mixture of  $\text{Fe}_2\text{O}_3 \cdot \text{Na}_2\text{CO}_3$  to remove organic sulphur compounds.

- The purified gas is compressed to 5 - 25 atm and then led through a converter maintained at about 200- 300°C.
- A mixture of saturated and unsaturated hydrocarbons results
- The reaction is exothermic, so out coming gaseous mixture is led to a cooler, where a liquid resembling crude oil is obtained
- The crude oil thus obtained is then fractionated to yield (i) gasoline and (ii) high-boiling heavy oil.
- The heavy oil is reused for cracking to get more gasoline.

#### Refining of Synthetic Petrol:

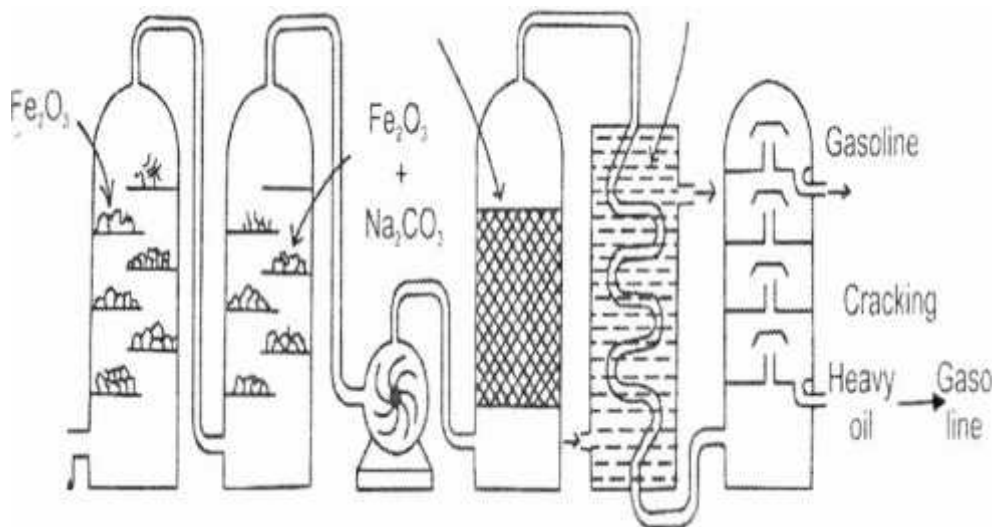
(1) The sulphur compounds are, generally, removed by treating gasoline with an alkaline solution of sodium plumbite with controlled addition of sulphur. This refining process converts sulphur compounds into disulphides.



The PbS is removed by filtration. Disulphide in gasoline is also objectionable, so they are also extracted with a suitable solvent.

(2) Usually, olefins and coloring matter of gasoline are removed by percolating gasoline through "fullers earth", which adsorbs preferentially only the colours and olefins.

(3) After the refining of gasoline, some inhibitors are added to it. These retard the oxidation reactions, thereby improving storing qualities of gasoline.



#### KNOCKING

In an internal combustion engine, a mixture of gasoline vapour and air is used as a fuel. After the initiation of the combustion reaction by spark in the cylinder, flame should spread rapidly and smoothly through the gas mixture, thereby the expanding gas drives the piston down the cylinder. The ratio of the gaseous

volume in the cylinder at the end of the suction stroke to the volume at the end of compression stroke of the piston is known as compression ratio. The efficiency of the internal combustion engine increases with the compression ratio.

But high compression ratio depends upon the nature of the constituents present in the gasoline used. In certain circumstances, due to the presence of some constituents in the gasoline used, the rate of oxidation becomes so great that the last portion of the fuel air mixture gets ignited instantaneously producing an explosive violence known as knocking. The knocking results in loss of efficiency, Since this ultimately decreases the compression ratio.

The phenomena of knocking are not known. However it is noted that the tendency of the fuel constituents knocks in the following order

Straight chain paraffin's (n-paraffins) > branched chain paraffin's (isoparaffines > olefines > cycloparaffines (naphthalene's) > aromatics

Thus, olefines of the same carbon chain length possess better antiknock properties than the corresponding paraffines and so on

### OCTANE NUMBER

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

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

Thus if a sample of petrol gives as much of knocking as a mixture of 75 parts of iso octane and 25 parts of n – heptanes, then its octane number is taken as 75. fuels with octane rating greater than 100 are quite common nowadays and they are rated by comparison with a blend of iso – octane with tetra ethyl lead (TEL) which greatly diminishes the knocking tendency of any hydrocarbon with which it is mixed. The value of octane number in such cases is determined by extrapolation.

### IMPROVEMENT OF ANTIKNOCKING CHARACTERISTICS

The octane number of many poor fuels can be raised by the addition of externally poisonous materials like tetra ethyl lead (TEL) ,  $(\text{C}_2\text{H}_5)_4\text{Pb}$  or diethyl telluride,  $(\text{C}_2\text{H}_5)_2\text{Te}$  . In motor fuel about 1.5ml of TEL is added per litre of petrol.

TEL is able to convert a gasoline into branched chain hydrocarbons by alkylation and polymerization.

Triptane (2,2,3-trimethyl butane) has octane number 124 and is a better antiknocking agent than TEL.

Tetramethyl lead,  $(\text{TEL}, (\text{CH}_3)_4\text{Pb})$  has been found better than TEL.

A new compound cyclopentadienyl manganese carbonyl is now used as antiknock agent because it also avoids lead pollution.

Isomerisation, alkylation, aromatization, reformation etc, also increase the octane number of fuels.

### **MECHANISM**

Petrol to which TEL is added is called leaded petrol. The mode of action of TEL is still a matter of controversy. According to the most accepted theory, TEL is converted into cloud of finely divided lead oxide particle in the cylinder and these particles react with any hydrocarbon peroxide molecules formed, thereby slowing down the chain oxidation reaction and thus decreasing the chance of any early detonation.

TEL is more effective on saturated hydrocarbons than on unsaturated ones. The presence of sulphur compounds in petrol reduces the effectiveness of the TEL.

### **DISADVANTAGES**

TEL forms lead oxide, which deposits on spark plug which is harmful to the engine. In order to remove it, ethylene dibromide is added. During burning, lead bromide is formed

which evaporates away in the heat engines and goes out together with exhaust gases out together with exhaust gases. This creates atmospheric pollution for human beings.

### **CETANE NUMBER**

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

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

The cetane number of a diesel fuel can be raised by the addition of small quantity of certain pre-ignition dopes like ethyl nitrite, isoamyl nitrite, acetone peroxide.

## GASEOUS FUELS

### a. Water Gas:

It is a mixture of CO and H with small amount of N<sub>2</sub>. The Average Composition of water gas is as follows

| Constituents                     | Percentage (%) |
|----------------------------------|----------------|
| CO                               | 41             |
| H <sub>2</sub>                   | 51             |
| N <sub>2</sub>                   | 4              |
| Co <sub>2</sub> +Ch <sub>4</sub> | rest           |

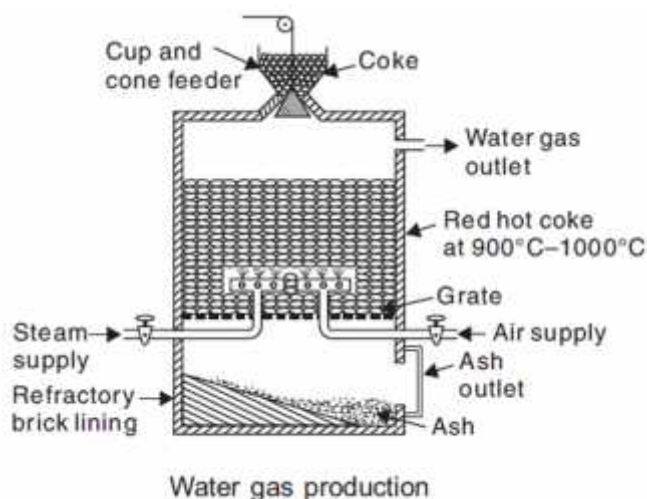
**Its calorific value is about 2800 kcal/m<sup>3</sup>**

### Manufacture:

The water gas producer consists of a tall steel vessel, lined inside with refractory bricks. It is provided with the cup of cone feeder at the top and a side opening for water gas exit.

At the bottom it is provided with two inlet pipes for passing air and steam

When steam and little air is passed alternatively over a red hot coke maintained at about 900-1000 degree Celsius in a reactor, water gas is produced



### Various Reactions

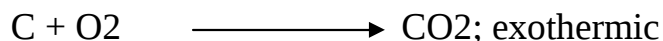
The reactions of water gas production involves the following two steps

**I-step:**

In the first stage, steam is passed through the red hot coke where CO & H<sub>2</sub> gases are produced. The reaction is endothermic. Hence, the temperature of the coke bed falls.

**II-step**

In the second stage, in order to raise the temperature of the coke bed to 1000 degree Celsius, the steam supply is temporarily cut off and air is blown in, the reaction is exothermic



Thus the steam-run and air-blow are repeated alternatively to maintain proper temperature.

**Uses**

1. It is used for the production of h<sub>2</sub> and the Synthesis of ammonia
2. It is used to synthesis gasoline in Fischer-Tropsch process
3. It is used as an illuminating gas and fuel.
4. It is also used in the manufacture of power alcohol and carbureted water gas (water gas + oil gas)

**b.Liquid Petroleum Gas (or) Liquefied Petroleum Gas (LPG)**

Liquefied Petroleum Gas is shortly known as LPG. It is also known as Refinery gas or bottled gas.

LPG is obtained as a by-product from natural gas or during the cracking of heavy oils. It mainly consists of butane and propane. It can be readily liquefied under pressure, so it can be economically stored and transported in cylinders. In order to find out the leakage of LPG, small amounts of odourous mercaptans are added to give warning.

The average composition of LPG by Hindustan Petroleum is given below:

| Constituent gas | Percentage in household LPG |
|-----------------|-----------------------------|
| n - Butane      | 27.2                        |
| Isobutane       | 24.7                        |
| Butylene        | 42.8                        |
| Propylene       | 2.5                         |
| Propane         | 2.8                         |

**(c) Compressed Natural Gas (CNG):**

CNG is natural gas compressed to a high pressure of about 1000 atmosphere. A cylinder containing 15 Kg of Compressed Natural Gas contains 20 m<sup>3</sup> or 20000 litres of natural gas at one atmospheric pressure. CNG is now used as substitute for petrol and diesel since it is less pollution causing fuel. During its combustion, no sulphur and nitrogen gases are evolved. Also, no carbon particles are ejected. Hence, it is a better fuel for automobiles. On the other hand, the initial cost of engine designed to use CNG as fuel is so high. In Delhi, for all buses, taxis and auto to use CNG as a fuel is mandatory.

Advantages of CNG over LPG:

- (i) CNG is a much safe fuel than gasoline and diesel.
- (ii) The conversion of gasoline operated automobiles into CNG operated vehicle is very easy
- (iii) The operating cost of CNG fuel is much lower.
- (iv) Producer gas

**Definition**

Producer gas is a mixture of CO and N<sub>2</sub>.

Composition:

The composition of producer gas is

CO = 22 - 30%

N<sub>2</sub> = 52 - 55%

H<sub>2</sub> = 8-12%

CO<sub>2</sub> = 3%

**Manufacture**

Producer gas is prepared by passing air mixed with small amounts of steam over a red hot coke maintained at 4000°C in a special type reactor called "gas producer". It consists of a steel vessel lined inside with refractory bricks. It is provided with a cup and cone arrangement at the top for feeding coke and a side tube for producer gas. The gas producer has one inlet for passing air and steam and one outlet for removing ash at the bottom.

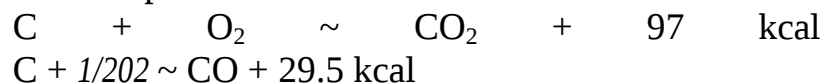
This involves following zones:

**Ash zone**

It is the lowest zone consisting of mainly ash. The temperature of supplied air and steam is increased as they pass through this zone.

**Combustion zone:**

This is also known as oxidation zone .. In this zone, carbon burns to form CO and CO<sub>2</sub>. The temperature of this zone is about 11 00°C.



**Reduction zone:**

It is the upper zone in which  $\text{CO}_2$  and steam combines with red hot coke to liberate  $\text{H}_2$  and  $\text{CO}$ .

**Calorific value:**

The calorific value of producer gas is 1300 Kcal/m<sup>3</sup>.

**Uses:**

Producer gas is

- (i) Used for heating furnaces like open-hearth, muffle furnaces.
- (ii) Used as a reducing agent in metallurgical operations.

**THEORETICAL CALCULATION OF CALORIFIC VALUE OF A FUEL**

The calorific value of a fuel can be approximately calculated by using the amounts of the constituents of the fuel. The higher calorific values of some of the chief combustible constituents are:

| Constituent      | hydrogen | carbon | sulphur |
|------------------|----------|--------|---------|
| HCV<br>(Kcal/Kg) | 34.500   | 8080   | 2240    |

The oxygen, if present in the fuel, is assumed to be present in combined form with hydrogen i.e., in the form of fixed hydrogen ( $\text{H}_2\text{O}$ ). So, the amount of hydrogen available for combustion

= Total mass of hydrogen in fuel - Fixed hydrogen

= Total mass of hydrogen in fuel – (1/8) mass of oxygen in the fuel

**DULONG'S FORMULA**

For the calculation of High calorific value of the fuel the following Dulong's formula is used.

**HCV (or) GCV**

$$= \frac{1}{100} [8,080C + 34,500(H - \frac{O}{8}) + 2,240S] \text{ Kcal/Kg}$$

Where C, H, O and S are the percentage of Carbon, Hydrogen, Oxygen and Sulphur in the fuel respectively. In this formula, oxygen is assumed to be present in combination with hydrogen as water.

Lower Calorific Value (LCV) is calculated using the formula,

**HCV (or) NCV**

$$= [\text{HCV} - \frac{9}{100}H \times 587] \text{ Kcal/Kg}$$

$$= [\text{HCV} - (0.09H \times 587)] \text{ Kcal/Kg}$$

This is based on the fact that 1 part of H by mass gives 9 parts of  $\text{H}_2\text{O}$  and latent

heat of steam is 587 Kcal/Kg.

**PROBLEMS:**

- (1) Calculate the gross and net calorific value of coal having the following compositions: carbon = 85%, hydrogen = 8%, Sulphur = 1 %, nitrogen = 2%, ash = 4%, latent heat of steam = 587 Kcal/Kg.

**SOLUTION:**

Gross calorific value (GCV)

$$= 1/100 [8,080C + 34,500(B - O/8) + 2,240S] \text{ Kcal/Kg}$$

$$= 1/100 [(8,080 \times 85) + 34,500(8 - \underline{0/8}) + (2,240 \times 1)] \text{ kcal/kg}$$

$$= 1/100[965,040] \text{ Kcal/Kg} = 9,650.4 \text{ Kcal/Kg}$$

Net calorific value (NCV)

$$= (\text{GCV} - 0.09H \times 587) \text{ Kcal/Kg}$$

$$= [9,650.4 - (0.09 \times 8 \times 587)] \text{ Kcal/Kg}$$

$$= 9,227.8 \text{ Kcal/Kg}$$

- (2) A coal has the following composition by weight: C = 90%, O = 3%, S = 0.5%, N = 0.5% and ash = 2.5%. Net calorific value of the coal was found to be 8,490.5 Kcal/Kg. Calculate the percentage of hydrogen and higher calorific value of coal.

**SOLUTION:**

$$\text{Lower calorific value (LCV)} = (\text{HCV} - 0.09H \times 587) \text{ Kcal/Kg}$$

$$(\text{i.e.}) 8,490.5 \text{ Kcal/Kg} = (\text{HCV} - 0.09H \times 587) \text{ Kcal/Kg}$$

$$(\text{i.e.}) \text{HCV} = (8,490.5 + 52.8H) \text{ Kcal/Kg} \quad \dots\dots\dots 1$$

Higher calorific value (HCV)

$$= 1/100[8,080C + 34,500(H - \underline{O/8}) + 2,240S] \text{ Kcal/Kg}$$

$$= 1/100[8,080(90) + 34,500(H - 3/8) + 2,240(0.5)] \text{ Kcal/Kg}$$

$$= [7,272 + 345H - 129.4 + 11.2] \text{ Kcal/Kg}$$

$$\text{HCV} = [7,153.8 + 345H] \text{ Kcal/Kg} \quad \dots\dots\dots 2$$

Comparing equations (1) and (2), we get

$$8,490.5 + 52.8H = 7,153.8 + 345H$$

$$(\text{or}) 292.2H = 8,490.5 - 7,153.8$$

$$292.2H = 1,336.7$$

$$1336.7$$

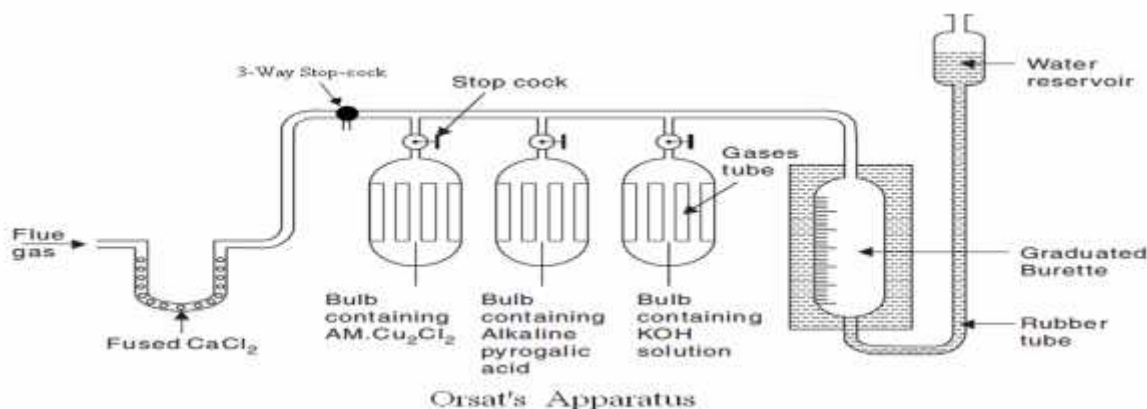
$$\% \text{ of H} = \frac{\quad}{292.2} = 4.575\%$$

### Flue Gas Analysis (ORSAT METHOD)

The mixture of gases like ( $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ , etc) coming out from a combustion chamber is called as flue gases. The Analysis of a flue gas would give an idea about the complete or incomplete combustion process. The analysis of flue gas is carried out by using orsat's apparatus

#### Description of orsat's apparatus

It consists of a horizontal tube. At one end of this tube, U-tube containing fused  $\text{CaCl}_2$  is connected through the 3-way stop cock. The other end of this tube is connected with a graduated burette. The burette is surrounded by a water jacket to keep the temperature of the gas constant. The lower end of the burette is connected to the water reservoir by means of a rubber tube. The level of the water in the burette can be raised or lowered by raising or lowering the reservoir.



The horizontal tube is also connected with three different absorption bulbs I, II, and III for absorbing  $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ .

**I-Bulb** contains 'potassium hydroxide' solution, and it absorbs only  $\text{CO}_2$

**II-Bulb** contains 'alkaline pyrogallol' solution, and it absorbs  $\text{CO}_2$  and  $\text{O}_2$ .

**III-Bulb** contains 'ammoniacal cuprous chloride solution' and it absorbs  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{CO}$

#### Working

The 3-way stop-cock is opened to the atmosphere and the reservoir is raised, till the burette is completely filled with water and air is excluded from the burette. The 3-way stop-cock is now connected to the flue gas supply and the flue gas is sucked into the burette and the volume of flue gas is adjusted to 100cc by rising and lowering the reservoir. Then the 3-way stop cock is closed

##### (a) Absorption of $\text{CO}_2$

The stopper of the absorption bulb-I, containing  $\text{KOH}$  solution, is opened and all the gas is passed into the bulb-I by raising the level of water in the

burette. The gas enters into the bulb-I, where  $\text{CO}_2$  present in the flue gas is absorbed by  $\text{KOH}$

The gas is again sent to the burette. This process is repeated several times to ensure the complete absorption of  $\text{CO}_2$ . The decrease volume of flue gas in the burette indicated the volume of  $\text{CO}_2$  in 100 cc flue gas

**(b)Absorption of  $\text{O}_2$**

Stop-cock of bulb-I is closed and stop cock of bulb-II is opened. The gas is again sent into the absorption bulb-II where  $\text{O}_2$  present in the flue gas is absorbed by alkaline pyrogallol. The decrease in volume of the flue gas in the burette indicated the volume of  $\text{O}_2$ .

**(c)Absorption of  $\text{CO}$**

Now stop-cock of bulb-II is closed and the stop-cock of bulb-III is opened. The remaining gases sent into the absorption bulb-III, where  $\text{CO}$  present in the flue gas is absorbed by ammoniacal cuprous chloride, the decrease in the volume of flue gas in the burette indicated with volume of  $\text{CO}$ , The remaining gas in the burette after the absorption of  $\text{CO}_2$ ,  $\text{O}_2$ , &  $\text{CO}$  is taken as nitrogen

**Significance (or) uses of flue gas Analysis**

- 1, Flue gas analysis gives an idea about the complete or incomplete combustion process.
- 2, If the flue gas contains considerable amount of  $\text{CO}$ , it indicates that incomplete combustion is occurring and it also indicates that the short supply of  $\text{O}_2$
- 3, If the flue gases contains considerable amount of  $\text{O}_2$ , it indicates that complete combustion is occurring and also it indicates that the excess of  $\text{O}_2$  is supplied.

**KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21.****FACULTY OF ENGINEERING****DEPARTMENT OF SCIENCE AND HUMANITIES****ENGINEERING CHEMISTRY****UNIT –III****FUELS AND COMBUSTION****PART – B**

1. What is the significance of analyzing sulphur in coal
2. What is metallurgical coke? How it differs from coal?
3. Discuss the principle steps in the refining of crude petroleum.
4. What is synthetic petrol?
5. Define knocking
6. Explain the mechanism of knocking.
7. Define cetane number.
8. Define octane number
9. What is the disadvantage of using tetraethyl lead in petrol?
10. Write down the influence of chemical structure on knocking.
11. Give the composition and uses of water gas
12. Give the composition and uses of producer gas
13. How water gas is superior to producer gas?
14. What is flue gas?

**PART – C**

1. Write in detail about the proximate analysis of a coal?
2. Discuss ultimate analysis of coal.
3. What is the significance of proximate and ultimate analysis of coal?
4. Explain the manufacture of metallurgical coke by otto Hofmann method
5. What is meant by crude petroleum? Discuss the principle steps of its refining.
6. How is synthetic petrol synthesized by Bergius and Fischer tropesch process
7. Explain the causes, mechanism and prevention of knocking of petrol in IC engines.
8. Explain the composition, manufacture and uses of producer gas and water gas.
9. Explain the flue gas analysed using Orsat's apparatus?

## UNIT – IV

### Corrosion Science

#### Corrosion

##### a) Corrosion

The slow and continuous destruction of metals and alloys by the action of environment is known as corrosion.

##### b) Classification of Corrosion

Based on the environment to which it is exposed, corrosion is divided into two types:

- Dry (or) Chemical Corrosion
- Wet (or) Electrochemical Corrosion

#### Chemical (Or) Dry Corrosion

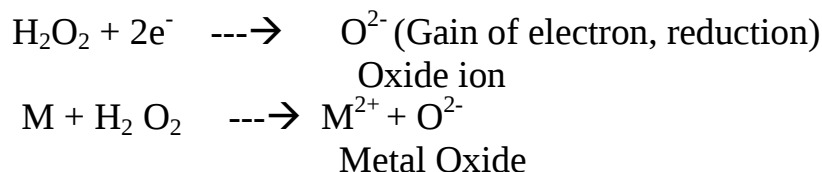
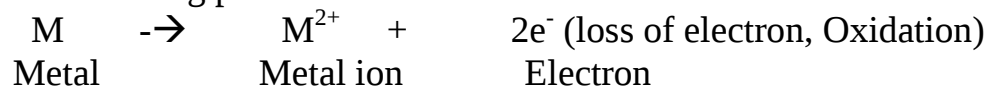
Dry or Chemical corrosion refers to the direct attack on the metallic surfaces by atmospheric gases like  $O_2$ ,  $H_2$ ,  $H_2S$ ,  $SO_2$ ,  $N_2$  and Halogens. Attack of metals by liquid metals is also referred to as dry corrosion. There are three main types of chemical corrosion.

- i. Oxidation Corrosion (or) Corrosion by oxygen gas
- ii. Corrosion by other gases like hydrogen, chlorine, etc.,
- iii. Liquid-metal corrosion

#### 1. Oxidation Corrosion

Usually, this type of corrosion is brought about by the direct attack of oxygen at low or high temperatures on metals in the absence of moisture. In general, at ordinary temperatures metals are slightly attacked. However, alkali and alkaline earth metals are rapidly oxidised even at low temperatures. At high temperatures, almost all the metals are oxidised.

The reactions taking place in oxidation corrosion are:



**Mechanism**

Usually, oxidation first occurs at the surface of the metal and resulting metal oxide scale forms a barrier that tends to restrict further oxidation. In order to continue the oxidation process, either the metal must diffuse outwards through the scale to the underlying metal. Generally, both the transfers occur, but the outward diffusion of metal is much more rapid than the inward diffusion of oxygen. This is because the metal ion is appreciably smaller than the oxide ion and hence higher mobility.

**Role of Oxide Film**

The nature of oxide layer plays an important role in oxidation corrosion

$$\text{Metal} + \text{Oxygen} \longrightarrow \text{Metal oxide}$$

(Corrosion product)

When oxidation starts with a thin layer of oxide is formed on metal surface and the nature of this film decides the further action. If,

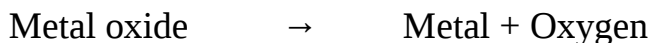
**(a)THE OXIDE LAYER IS STABLE**

If the oxide layer formed is stable and impervious in nature, it behaves as protective coating thereby further corrosion is prevented.

Example: The oxide films formed on Al, Sn, Pb, Cu, Pt, etc. are stable, tightly adhering and impervious in nature.

**(b)THE OXIDE LAYER IS UNSTABLE**

If the oxide layer formed is unstable, it decomposes into the metal and oxygen.



Consequently, oxidation corrosion is not possible in such a case.

Example: The oxides of Ag, Au, and Pt are unstable and hence do not undergo oxidation corrosion.

**(c)THE OXIDE LAYER IS VOLATILE**

The oxide layer formed is volatile in nature, it evaporates as soon as it is formed, thereby leaving fresh metallic surface for further attack. This causes rapid and continuous corrosion leading to excessive corrosion.

Example: Molybdenum oxide ( $\text{Mo O}_3$ ) is volatile.

**(d)THE OXIDE LAYER IS POROUS**

If the oxide layer formed is porous or having cracks that leads to excessive corrosion. i.e., the atmospheric oxygen may attack the metallic surface through

the pores or cracks of the layer, thereby the corrosion continues till the entire metal is completely converted into its oxide.

Example: Iron oxide is porous in nature.

### e) THE OXIDE LAYER IS PROTECTIVE OR NON-PROTECTIVE

#### i) Pilling-Bedworth rule (or) Pilling-Bedworth ratio

If the volume of the metal oxide is greater than the volume of the metal from which it is formed, then the oxide layer formed is protective and non-porous in nature. On the other hand, if the volume of the metal oxide is less than the volume of the metal, then the oxide layer formed is porous and non-protective in nature. This is known as Pilling-Bedworth rule.

Example: The volume of oxides of Cu, Al, Pb, and Sn is greater than the volume of the metal and forms a coherent, protective layer. On the other hand, the volume of oxides of Li, K, Na and Mg is less than the volume of the metal and forms porous and non-protective oxide layer.

#### (ii) Corrosion by Other gases:

Other gases present in the atmosphere like SO<sub>2</sub>, CO<sub>2</sub>, Cl<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>S can also attack metals. The extent of corrosion depends on the chemical affinity of environment to metals and nature of corrosion products.

Example:

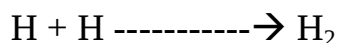
(a) Formation of chloride layer on silver prevents further attack of Ag, since the silver chloride is non-porous and protective.

(b) On the other hand, stannic chloride (SnCl<sub>4</sub>) formed on tin metal is volatile and hence corrosion is not prevented.

Metals are also corroded by hydrogen under specific conditions. Metals combine with H<sub>2</sub>S to liberate atomic hydrogen.

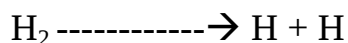


The atomic hydrogen is highly reactive and penetrate the metal and occupies the voids. The atomic hydrogen recombine inside the metals.



This types of reaction are taking place inside the metals and develop pressures which may cause fissures and blisters. This phenomenon is referred to as hydrogen embrittlement.

Atomic hydrogens are formed by dissociation of  $H_2$  gas at high temperatures.



This atomic hydrogen is highly reactive and combines with C, S, O or N present in metals. For example, atomic hydrogen combines with carbon in steel to give  $CH_4$  gas. The collection of these gases inside the metal develops pressures that lead to cracking of metal surface. This method of decreasing the carbon content in steel by heating with hydrogen is known as decarburization.

### **(iii)Liquid metal corrosion**

This type of corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. Such corrosion occurs in devices used for nuclear power.

The corrosion reaction involves either

- (a) Dissolution of a solid metal by a liquid metal.
- (b) Internal penetration of the liquid metal into the solid metal.
- (c) Both the modes of corrosion cause weakening of the solid metal.

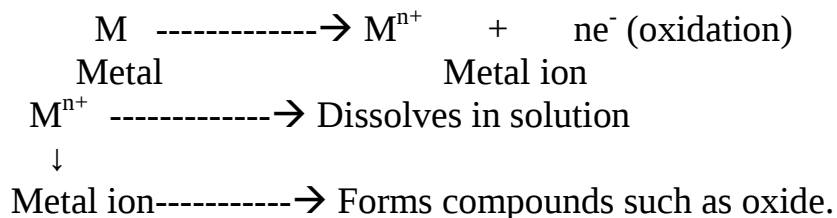
## **WET (OR) ELECTROCHEMICAL CORROSION**

This type of corrosion refers to the destruction of metals by acids, alkalis and other aqueous neutral reagents. Electrochemical corrosion takes place under two conditions.

- (i) When a metal comes in contact with conducting liquids (Electrolytes).
- (ii) When two dissimilar metals are in contact in the presence of a conducting liquid.

Under these conditions, one part of the metal becomes anodic and other part cathodic. At anodic area, oxidation reaction takes place, so anodic metal is destroyed either by dissolving in solution or by forming compounds such as oxide etc., Hence, corrosion always occurs at anodic areas.

**At anode:**



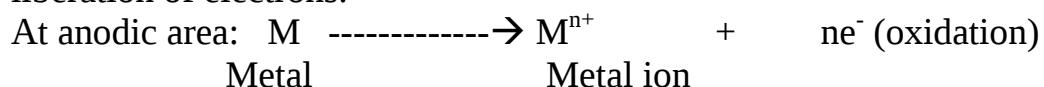
On the other hand, at cathode reduction reaction takes place. Usually, the metallic ions ( $M^{2+}$ ) formed at anode and the non-metallic ions ( $OH^-$ ,  $O^{2-}$  etc.) formed at cathode diffuses towards each other through conducting medium and form a corrosion product somewhere between anode and cathode.

The rate of electrochemical reaction depends on

- (a) If corrosion product goes into solution, the corrosion rate continues the same.
- (b) The corrosion product is an insoluble compound, acts as barrier, the corrosion rate will be reduced.

### Mechanism

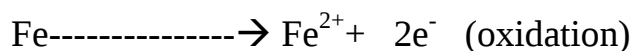
Electrochemical corrosion involves the flow of electrons from anodic area to cathodic area. At anodic area, the dissolution of metals take place with the liberation of electrons.



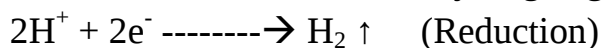
The electrons released at anode moves towards cathodic area through metal and are consumed there. So, at cathode the reduction reaction takes place either by evolution of hydrogen or by absorption of oxygen depending upon the nature of corrosive environment.

#### (a) Evolution of hydrogen type corrosion

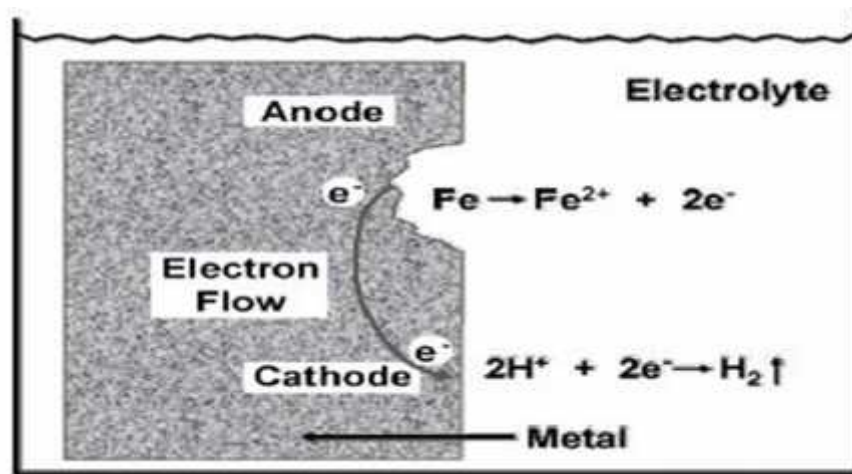
- Usually, this type of corrosion takes place in acidic environment. i.e., solutions containing industrial wastes or mineral acids like HCl.
- At the anodic area, metal dissolves in solution liberating free electrons.
- Consider the metal like iron; the anodic reaction is dissolution of iron as ferrous ions with the liberation of electrons.



- From anode to cathode, these electrons flow through the metal where  $H^+$  ions of acidic solution are eliminated as hydrogen gas.



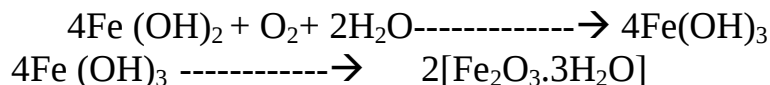
- The overall reaction is  $Fe + 2H^+ \xrightarrow{\hspace{1cm}} Fe^{2+} + H_2 \uparrow$
- According to the above reaction, displacement of hydrogen ions from acidic solution by metal ions takes place.
- Consequently, it is obvious that all metals which lie above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen gas.



**Fig 3. Mechanism of evolution of hydrogen type corrosion**

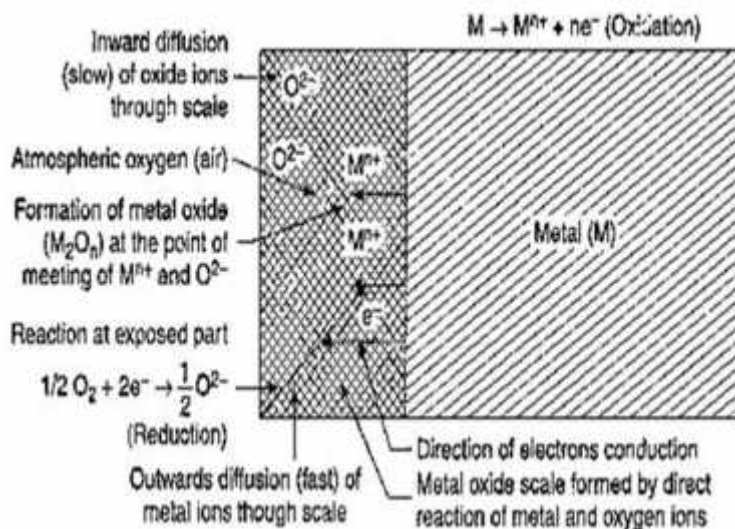
**(b Absorption of oxygen type corrosion)**

- This type of corrosion takes place in neutral aqueous solutions like NaCl in the presence of oxygen or slightly alkaline medium.
- The best example for this type of corrosion is rusting of iron.
- Usually, the iron surface is coated with a thin film of iron oxide.
- If, this iron oxide film develops some cracks, anodic areas are created on the surface while remaining part of the metal acts as cathodes.
- At anodic area, the iron metal dissolves as ferrous ions with liberation of electrons.
 
$$\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^- \text{ (oxidation)}$$
- At cathodic area, the liberated electrons flow from anode to cathode through iron metal, where electrons are intercepted by the dissolved oxygen to form hydroxide ions
 
$$\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow 2\text{OH}^- \text{ (Reduction)}$$
- The  $\text{Fe}^{2+}$  ions at anode and  $\text{OH}^-$  ions at cathode diffuse and when they meet, ferrous hydroxide is precipitated.
 
$$\text{Fe}^{2+} + \text{OH}^- \longrightarrow \text{Fe}(\text{OH})_2$$
- If enough oxygen is present, ferrous hydroxide is easily oxidised to ferric hydroxide and this product is called yellow rust which actually corresponds to  $2[\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}]$ .



Yellow Rust

- If limited supply of oxygen is present, the corrosion product is black anhydrous magnetite,  $\text{Fe}_3\text{O}_4$ .



**Fig . 4. Mechanism of absorption of oxygen type corrosion**

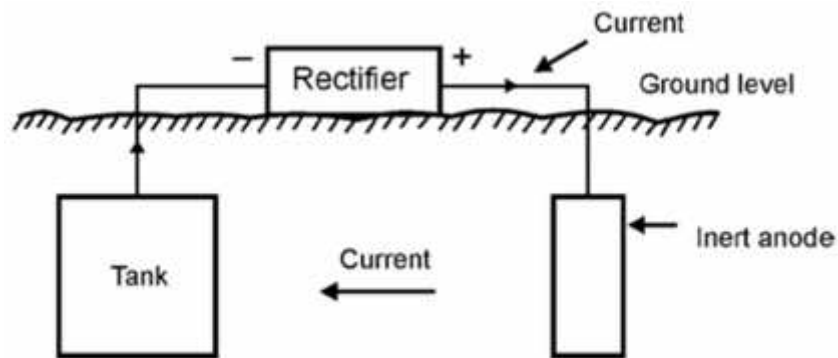
## CATHODIC PROTECTION

The principle of this method is to force the metal to behave like a cathode by connecting it to a powerful anode metal plate. These are of two kinds

### a) Sacrificial anodic protection

In this method, the metallic structure to be protected is connected through a metallic wire to a more anodic metal so that all the corrosion will take place only on the anodic metal. The artificially made anode thus gets gradually corroded protecting the original metallic structure. This process is otherwise known as sacrificial anodic protection. Metals commonly used as sacrificial anodes are zinc, magnesium, aluminium and their alloys. This method is used

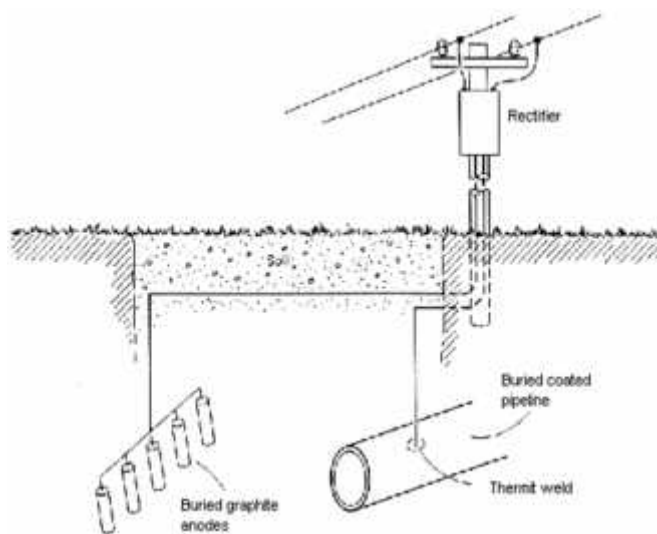
- To protect underground pipelines, cables etc., from soil corrosion
- To prevent the corrosion of ship hulls and other marine devices
- Insertion of Mg sheets into domestic water boilers to prevent the formation of rust.



### Cathodic protection by means of sacrificial anodes

#### b) Impressed current cathodic protection:

In this method an impressed direct current (DC) is sent in the opposite direction of the corrosion current to nullify it and the corroding metal is converted from an anode to cathode. This can be done by connecting the negative terminal of the battery to the metallic structure to be protected, and the positive terminal to an inert anode. Inert anodes used for this purpose are graphite or platinised titanium. The anode is buried in a “back fill” contacting coke, breeze, gypsum, bentonite and sodium sulphate. The “black fill” provides a surrounding for good electrical conductivity of anode. The other terminal of the battery is connected to the metallic structure to be protected. Hence the current from the external system is impressed on the metallic structure to be protected which acts as the cathode. This kind of corrosion control is usually applied to underground water pipelines, oil pipelines, transmission lines, marine pipes, ships, etc.,



**Impressed-current cathodic protection of a buried pipeline using graphite anodes****Corrosion Inhibitors**

A corrosion inhibitor is a substance when added in a small concentration to an environment reduces the corrosion rate of a metal exposed to that environment. Inhibitors often play an important role in the oil extraction and processing industries where they have always been considered to be the first line of defence against corrosion.

**Types of corrosion inhibitors****1. Anodic inhibitors**

Anodic inhibitors usually act by forming a protective oxide film on the surface of the metal causing a large anodic shift of the corrosion potential. This shift forces the metallic surface into the passivation region. They are also sometimes referred to as passivators. Chromates, nitrates, tungstate, molybdates are some examples of anodic inhibitors.

**2. Cathodic inhibitors**

Cathodic inhibitors act by either slowing the cathodic reaction itself or selectively precipitating on cathodic areas to limit the diffusion of reducing species to the surface.

The rates of the cathodic reactions can be reduced by the use of cathodic poisons. However, cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking since hydrogen can also be absorbed by the metal during aqueous corrosion or cathodic charging. The corrosion rates can also be reduced by the use of oxygen scavengers that react with dissolved oxygen. Sulfite and bisulfite ions are examples of oxygen scavengers that can combine with oxygen to form sulfate.

**3. Mixed Inhibitors**

Mixed inhibitors work by reducing both the cathodic and anodic reactions. They are typically film forming compounds that cause the formation of precipitates on the surface blocking both anodic and cathodic sites indirectly. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal forming a protective film. The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the occurrence of rust water.

In aerated hot water systems, sodium silicate protects steel, copper and brass. However, protection is not always reliable and depends heavily on pH. Phosphates also require oxygen for effective inhibition. Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites, however, they are very useful in situations where non-toxic additives are required.

#### **4. Volatile Corrosion Inhibitors**

Volatile Corrosion Inhibitors (VCI), also called Vapor Phase Inhibitors (VPI), are compounds transported in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine, are transported with steam to prevent corrosion in the condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH towards less acidic and corrosive values.

In closed vapor spaces, such as shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene-amine are used. When these inhibitors come in contact with the metal surface, the vapor of these salts condenses and is hydrolyzed by any moisture to liberate protective ions. It is desirable, for an efficient VCI, to provide inhibition rapidly while lasting for long periods. Both qualities depend on the volatility of these compounds; fast action wanting high volatility while enduring protection requires low volatility.

#### **PAINTS**

Paint is the mechanical dispersion of one or more fine pigments in a medium (thinner + vehicle). When paint is applied to a metal surface, the thinner evaporates, while the vehicle undergoes slow oxidation leading to formation of a pigmented film.

##### **Requisites of a good paint:**

A good paint should

- Spread easily on the metal surface.
- Adhere well on the surface.
- Possess a stable colour.
- Possess a high hiding (covering) power.
- Be corrosion and water resistant.
- Give a glossy film.

**Constituents of paint and their functions**

**1. Pigments:** Pigments are solid and non-producing substances in the paint.

**Functions**

- Gives colour and opacity to the film.
- Provides strength to the film.
- Protects the film by reflecting the destructive UV rays.

*Examples:*

- Black pigment: Lamp black, Carbon black
- White pigment: White lead ( $2\text{PbCO}_3\text{Pb(OH)}_2$ )  
Lithophone (75%  $\text{BaSO}_4$  + 25% Zn S)
- Red pigment: Venetian red ( $\text{Fe}_2\text{O}_3$  and  $\text{CaSO}_4$ )  
Indian red ( $\text{Fe}_2\text{O}_3$ )
- Green pigment: Chromium oxide
- Blue pigment: Prussian blue  $\text{Fe}_4(\text{Fe(CN)}_6)_3$

**2. Vehicles or drying oils**

Vehicles are the film-forming constituents in paints. These are high molecular weight fatty acids present in vegetable and animal oils. They form the non-volatile portion of paints.

**Functions**

- They form a protective film by process of oxidation and polymerisation of the oil.
- They impart water repellancy, toughness and durability to the film.
- They hold the pigment particles together on the metal surface. *Examples:* Linseed oil, dehydrated castor oil.

**3. Extenders or Filters:** These are white or colourless pigments which forms the bulk of the paint.

**Functions**

- Reduces the cost of the paint.
- Retards the settling of the pigment in paints.
- Prevents shrinkage and cracking.

- Modifies the shades of the pigments. *Examples:* Talc, gypsum, china-clay, etc.,

#### 4. Thinners or Solvents

Thinners generally contains solvents and form the volatile portion of a medium. It easily evaporates after application of the paint.

##### Functions

- Reduce the viscosity of the paint, so that it can be easily applied to the surface.
- Dissolve the oil, pigments, etc. and produces a homogenous mixture.
- Increase the elasticity of the film.
- Increase the penetrating power of the vehicle.

**5. Driers:** These are substances used to accelerate the process of drying.

##### Functions

- They act as oxygen-carriers or catalysts.
- They provide oxygen, which is essential for oxidation and polymerism of the drying oil. *Examples:* Metallic soaps, Linoleates and resonates of Co, Mn and Pb.

#### 6. Plasticisers

Chemicals added to paints to provide elasticity to the film and to prevent cracking of the film are called plasticisers. *Examples:* Triphenyl phosphate, tricresyl phosphate, etc.

#### 7. Anti-skinning agents

These are chemicals added to paints to prevent gelling and skinning of the paints. *Examples:* Polyhydroxy phenol.

### Electroplating

#### i) Principle

The basic principle of electroplating is coating the coating metal on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal. The base metal to be plated is made cathode of an electrolytic cell, whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity.

**ii). Definition**

Electroplating is the process in which the coating metal is deposited on the vase metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal

**Objectives of Electroplating****1. On metals**

1. To increase the resistance to corrosion of the coated metal.
2. To improve the hardness and physical appearance of the article.
3. To increase the decorative and commercial values of the article.
4. To increase resistance to chemical attack.
5. To improve the properties of the surface of the article.
- 6.

**2. On non-metals**

1. To increase strength.
2. To preserve and decorate the surfaces of non-metals like plastics, wood, glass, etc.
3. For making the surface conductivity by utilization of light weight, non-metallic materials.

**Theory**

During electroplating, the concentration of electrolyte solution should remain unaltered. This is possible only in any one of the following ways.

1. If the anode is made of coating metal itself in the electrolytic cell, during electrolysis, the concentration of electrolytic bath remains unaltered, since the metal ions deposited from the bath on cathode are replenished continuously by the reaction of free anions with the anode.
2. If the anode is made of an inert material like graphite, electrolyte (salt of coating metal) should be added continuously to maintain the concentration of the coating metal ions in the bath.

## ELECTROPLATING OF GOLD OVER COPPER OBJECT

### Process

The copper object, to be plated, is first treated with dil.HCl or dil H<sub>2</sub>SO<sub>4</sub>. The cleaned object is then made cathode and gold foil as the anode. AuCl<sub>3</sub> solution is taken as the electrolyte. When the current is passed through the solution, gold dissolves in the electrolyte and deposits uniformly on the copper object.

### i). Various Chemical Reactions



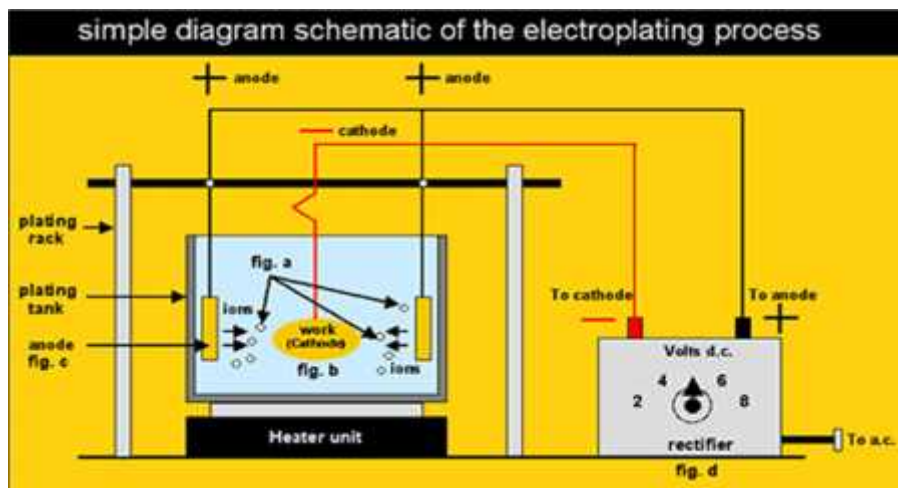
at cathode : On passing current , Au<sup>3+</sup> ions move to the cathode and get deposited there as Au metal



at anode: The free chloride ions migrate to the gold anode and dissolves an equivalent amount of Au to form AuCl<sub>3</sub>



To get strong, adherent and smooth deposit certain additives (glue, gelatin, etc.,) and for brightness of deposit, brightening agents are added to the bath. Optimum temperature (60°C), optimum current density (1-10 Ma/cm<sup>2</sup>) and low metal ion concentrations are favourable conditions for good deposit



### Electroplating of gold

#### ii). Characteristics of gold plating:

1. The deposits of gold are used for electrical and electronic applications.
2. It is used for high quality decorations and high oxidation resistant coatings.
3. For jewellery very thin coating is given (0.05-1.0 microns)

**iii). Applications of gold plating:**

1. It is used for electrical and electronics applications
2. It is used as jewellery.
3. It is used for high quality decorations

**Surface Conversion Coatings**

Common conversion coatings processes are briefly discussed in this section, including oxide coatings, phosphate coatings, and chromate coatings.

**1. Oxide Coatings:** The oxide coatings are in fact a corrosion product which is a thin, usually less than 2.5  $\mu\text{m}$  (.00001 in) oxide with good adhesion. The oxide treatments are done by heat, chemicals, or electrochemical reactions.

- **Gun-bluing-type oxidations** are done by heating the metals, generally steel, at 370°C (700°F) in a steam atmosphere. An oiled gun bluing provides *some atmospheric corrosion resistance*, but little protection on wear and other corrosion.
- **Chemical baths** produce coatings similar to a gun bluing coating by immersion techniques.
- **Black oxide** treatments are done by proprietary chemicals. Some *pastes* can be rubbed on surfaces to produce similar results. Black oxide can be applied on steel, copper, and most stainless steel.
- **Anodizing** is produced by *electrochemical conversion*. The anodizing process, usually performed on aluminum for protection and cosmetic purposes, builds up both on the surface as well as into the metal. Thin coatings, 2  $\mu\text{m}$  to 25  $\mu\text{m}$  (100  $\mu\text{in}$  to 1000  $\mu\text{in}$ ) can be coated on most aluminums. Thick coatings from 25 to 75  $\mu\text{m}$  (1000 to 3000  $\mu\text{in}$ ) are *more durable and abrasion resistant* than above chemical conversion oxide coatings. This oxide layer can be made in *different colors* depending on the post chemistries that are employed. The anodized parts are quite durable and do not tarnish and maintain their cosmetic appearance for a long period of time. Anodized coatings are usually dielectric in nature.

**2. Phosphate Coatings:**

Phosphate coatings are processes of *chemical conversion* on a metal surface to produce thin adherent phosphate compound coatings. The phosphate crystals formed on the surfaces of materials can be iron, zinc, or manganese phosphates.

Among these phosphates, manganese phosphate is more suitable for wear applications. Phosphate coatings are usually applied to carbon steel, low-alloy steel, and cast iron. They can also be applied to zinc, cadmium, aluminum, and tin. Phosphate processes are hard to apply on high alloys for these alloys are likely immune to the phosphoric acid. In short, phosphating is one of the most useful non-metallic coatings.

### 3. Chromate Coatings:

Chromate coatings, similar to phosphate coatings, are processes of *chemical conversion*. But the chromate coatings are formed by the reaction of water solutions of chromic acid or chromium salts. The coatings can be applied to aluminum, zinc, cadmium, and magnesium. The coatings usually have good *atmospheric corrosion resistance*. Chromate coatings are widely used in protecting *common household products*, such as screws, hinges, and many hardware items with the yellow-brown appearance.

### Hot Dip Galvanizing

Hot-dip deposition is used to increase corrosion and wear resistance. Coatings of all low melting-point metals and alloys (which can be melted without undesirably changing the substrate) are deposited. The process is carried out by immersing a pre-treated (cleaned, etched, etc.) substrate in a bath of molten metal or alloy for a specific time (from 0.5 to 5 minutes). Limitations are the melting temperature of the coating metal (less than 1300 C), the difference of melting-points between the coating material and the substrate, the brittleness of the coating layers, and the shape of the substrate (no small openings.).

The first use of hot dip galvanizing on steel was some work reported by the Frenchman P J Malouin in 1742. A French patent was issued to Sorel in 1837 and an English patent to H V Craufurd in the same year. Very little has changed in the process since that time. Zinc is very successful as a protective coating for steel because in most environments to which steel will be subjected, zinc will act as the anode; ie it will dissolve in preference to the steel. In simplistic terms, while there is zinc on the surface the steel will be protected from corrosion.

Hot dip galvanizing is one of a number of methods available to the surface finisher for applying a zinc coating to an item. Other techniques include electroplating, mechanical plating, and sherardising, painting with zinc-rich coatings and zinc spraying or metallising. In the hot dip galvanizing process, a

uniform coating of metallurgically bonded zinc-iron alloy layers and pure zinc is produced. The life expectancy of zinc coatings is independent on the coating process – an equivalent coating of zinc will provide the same life expectancy regardless of the coating process.

Hot dip galvanizing will provide over 80 microns of zinc coating, while zinc electroplates are normally less than 25 micron. The hot dip galvanizing process is widely used in a number of applications, particularly constructional. The pictorial representation of the galvanizing is shown in the figure below.



**Galvanizing steel tubes in order to prevent them from rusting**

**KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21.****FACULTY OF ENGINEERING****DEPARTMENT OF SCIENCE AND HUMANITIES****ENGINEERING CHEMISTRY****UNIT-IV****CORROSION SCIENCE****PART – B**

1. Define corrosion.
2. What is dry corrosion?
3. State Pilling Bedworth rule.
4. What is wet corrosion?
5. Give two differences between dry and wet corrosion.
6. What is differential aeration corrosion?
7. What is waterline corrosion?
8. What is pitting corrosion?
9. What is cathodic protection?
10. What is galvanising?
11. How is galvanic corrosion prevented?
12. What is electroplating?
13. What is meant by hydrogen embrittlement?
14. What are the factors influencing rate of corrosion depending on nature of metal?
15. What is the principle involved in impressed cathodic current method of protection of corrosion?
16. Steel screw in a brass marine hardware corrodes-explain.
17. What is deactivation? Give examples.
18. What are inhibitors? Give an example each for anodic and cathodic inhibitors.
19. Give the function of driers in paint. Give 2 examples of driers.
20. What are the essential constituents of paint?
21. What are metallic coatings?
22. What are the advantages of electroless plating over electroplating?
23. What are the requisites of a good paint?
24. Define throwing power.
25. What is the function of extenders in the paint?
26. What is electroless plating?
27. Mention two differences between electroplating and electroless plating.
28. What are the reasons for failure of paint?
29. What are the various steps of electroless plating?
30. What are the characteristics of gold plating?

**PART – C**

1. Define corrosion of metals. What are different types of corrosion?
2. What is chemical corrosion? Explain the mechanism of chemical corrosion.
3. What is electrochemical corrosion? Explain the mechanism of electrochemical corrosion by rusting of iron as an example.
4. Differentiate between chemical corrosion and electrochemical corrosion.
5. What are corrosion inhibitors? Classify different type of inhibitors with examples.
6. Explain inhibition of corrosion by sacrificial anodic protection and impressed cathodic current protection method.
7. What is paint? What are the constituents and functions of paints?
8. What are the protective coatings? How do protective coatings help in controlling corrosion.
9. What are the main objectives of electroplating .Give an account of the method used in electroplating of gold.
10. What is Electroplating? How are the metals protected by electroplating and give an account of its application.
11. What is electroless plating? Write short note on electroless nickel plating and discuss its application.

## UNIT V

### SURFACE CHEMISTRY AND PHASE RULE

**Adsorption:** Concentration or assimilation of a gas (or liquid) at the surface of a solid (or liquid)

**Occlusion.:** The adsorption of gases on the surface of solids

**Adsorbent:** The material providing the surface upon which adsorption occurs

**Adsorbate:** The substance adsorbed or attached to the surface of adsorbent

Ex: Charcoal, Silica gel, Alumina gel, Clay, etc.

**Desorption.:** The removal of adsorbed substance from the surface

#### Exothermic nature of adsorption

- Occurs *spontaneously* as the unbalanced or residual forces acting along the surface
- The adsorbent has a *tendency to attract and retain* molecules of other species
- Results in *decrease in the residual forces*, thereby resulting decrease of surface energy, which in turn appears in the form of heat.
- The amount of heat evolved when 1 mole of any gas (or vapour) is adsorbed on a solid adsorbent surface, is called "*enthalpy (or heat) of adsorption*".

#### Adsorption and Absorption:

**Absorption:** Substance assimilated is uniformly distributed throughout the body of the solid or liquid

| Adsorption                                                                                                                                        | Absorption                                                                                     |
|---------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------|
| 1. Concentration or assimilation of a gas (or a liquid) at the surface of a solid (or liquid)                                                     | The substance assimilated is uniformly distributed throughout the body of the solid or liquid. |
| 2. A surface phenomenon                                                                                                                           | A bulk phenomenon                                                                              |
| 3. A fast process                                                                                                                                 | A slow process                                                                                 |
| 4. Equilibrium is attained easily                                                                                                                 | Attainment of equilibrium takes some time                                                      |
| 5. It depends upon the surface area of the adsorbent. Consequently, adsorption is more rapid on finely divided or more rough surface of adsorbent | No such effect is there                                                                        |

#### CLASSIFICATION OF ADSORPTION

##### Based on the force of attraction

##### Physical adsorption (or physisorption) or van der Waals adsorption:

- The adsorbed molecules are held to the surface of the adsorbent by weak physical or van der Waal's forces.
- e.g: Adsorption of various gases by charcoal belongs to this type.

##### Chemical adsorption or chemisorption or activated adsorption:

- The adsorbed molecules are held by chemical bonds.
- e.g: Adsorption of oxygen on tungsten, and on charcoal

**Differences between Physical adsorption and Chemical adsorption**

| Physical adsorption (Physisorption)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | Chemical adsorption (Chemisorption)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>1. Adsorption is completely <i>reversible</i>, since the molecules are not tightly retained by the adsorbent</p> <p>2. <i>Forces</i> responsible for such adsorption are <i>very weak</i></p> <p>3. <i>Multilayer adsorption occurs</i>, i.e., adsorbed layer may be several molecules thick, since the van der Waal's forces can extend from one layer to another</p> <p>4. Heat of adsorption is about <i>20-40 kcal/mol</i> as</p> <p>5. Involves <i>very small or little activation energy</i></p> <p>6. The <i>equilibrium is established rapidly</i></p> <p>7. Adsorption is appreciable only at <i>temperature below the boiling point</i> of the adsorbate, and it decreases with rise in temperature</p> <p>8. The rate of adsorption <i>increases with the increase of pressure or concentration of the adsorbate</i>. Near saturation pressure, multilayers are formed</p> <p>9. The amount of adsorption on a surface is <i>more function of the adsorbate</i> than the adsorbent.</p> <p>10. <i>No surface compound</i> formation takes place</p> <p>11. It is <i>not very specific</i> in nature</p> | <p>Adsorption is <i>irreversible</i>, since molecules are tightly retained by adsorbent</p> <p><i>Forces</i> responsible for such adsorption are <i>quite strong</i></p> <p><i>Adsorption leads to , utmost, a monolayer</i></p> <p>Heat of adsorption is about <i>40-400 kcal/mol</i></p> <p>Involves <i>appreciable activation energy</i></p> <p>Establishment of <i>equilibrium requires time</i></p> <p><i>Adsorption can occur at high temperatures</i></p> <p>The rate of adsorption <i>decreases with the increase of pressure or concentration of the adsorbate</i>. Near saturation pressure, adsorption rate decreases, since the adsorption is confined only to upper surface layer of adsorbent</p> <p>The amount of adsorption is <i>characteristic of both adsorbate and adsorbent</i>.</p> <p>Adsorbent</p> <p>Actual <i>surface compound formation</i> between the adsorbent and adsorbate takes place</p> <p>It is <i>highly specific</i> in nature</p> |

**ADSORPTION OF GASES ON SOLIDS****Factors affecting the adsorption of gases on solid surfaces****(1) Nature of the gas:**

- Easily liquefiable gases (like HCl, NH<sub>3</sub>, Cl<sub>2</sub>, etc.) are adsorbed more easily than the permanent gases (like H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, etc.).
- The ease of liquefaction of a gas depends upon its critical temperature
- The higher the critical temperature (T<sub>c</sub>), the more easily the gas is liquefied and consequently, more readily it is adsorbed.

**(2) Nature of adsorbent:**

- Greater the surface area of the adsorbent, greater is its adsorption capacity.
- Charcoal and silica gel are excellent adsorbents, since their structure is highly porous and hence, possess large internal surface areas.
- Activated charcoal and finely divide solid substances are better adsorbents.

### (3) Activation of adsorbent:

Activation leads to increase in the surface area i.e., adsorbing power of the adsorbent

#### i) Creation of roughness

- Mechanical rubbing of metallic adsorbents,
- Subjecting to some chemical reactions of metallic adsorbents

#### ii) Increasing effective area

- Sub-dividing the solid adsorbents into finer particles and hence, increasing surface area
- Strong heating in superheated steam of some adsorbents, e.g., when charcoal is subjected to the action of superheated steam, its pores are opened, thereby Adsorption activity increases.

### (4) Effect of pressure:

- The extent of adsorption ( $x/m$ ) or ( $S$ ) (where  $x$  is the mass of adsorbate, gas, and  $m$  is the mass of the adsorbent) depends upon the pressure.

#### Adsorption isotherm

- A graph plotted between magnitude of adsorption and pressure, at constant temperature.
- The extent of adsorption ( $x/m$ ) increases with increasing pressure ( $P$ ) and becomes maximum at  $P_s$ , called the saturation pressure.

### (5) Effect of temperature:

- **Adsorption isobar** is a graph plotted between magnitude of adsorption and temperature, at constant pressure.
- Since adsorption is an exothermic reaction, with an increase in temperature, the amount adsorbed ( $x/m$ ) should decrease.
- However, in case of chemisorption, the amount adsorbed ( $x/m$ ) initially increases and then decreases, because chemisorption (like an ordinary chemical reaction) requires some activation energy.
- Adsorption isobars can be used to distinguish between physical and chemical adsorptions.
- Thus, in physical adsorption, there is a regular decrease in extent of adsorption as temperature increases; whereas in chemisorption, there is initial increase and then decrease in extent of adsorption as temperature increases.

## ADSORPTION OF SOLUTES FROM SOLUTIONS

*Solid surfaces adsorb solutes from solutions in two ways*

### 1) Solid substances adsorb dissolved substances (solute) from solutions

*Activated animal charcoal adsorbs*

- Colouring matter present in sugar solution, thereby making the latter colourless.
- Certain acids like acetic and oxalic present in water, thereby acid concentration in water decreases.
- Ammonia from solutions of  $\text{NH}_4\text{OH}$  and phenolphthalein from solution of acids or bases

### 2) An adsorbent adsorbs certain solute from solution in preference to other solutes.

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

### Factors influencing adsorption of solutes from solution

#### 1) Effect of temperature and concentration

##### Positive adsorption:

- Concentration of the adsorbate is more on the surface of the adsorbent than in the bulk
- Adsorption from solution increases with rise of temperature and increase in concentration of solution.
- Freundlich adsorption equation is found applicable
- e.g., In the concentrated solution of KCl, charcoal adsorbs KCl rather than water and this leads decrease in concentration of KCl in solution.

##### Negative adsorption:

- Concentration of the adsorbate is less on the surface of the adsorbent than in the bulk
- Adsorption from solution decreases with rise of temperature and decrease in concentration of solution.
- e.g. In the dilute solutions of KCl, charcoal adsorbs water, thereby the salt concentration is increased

#### 2) Effect of surface area

- Adsorption increases with increase in surface area of the adsorbent

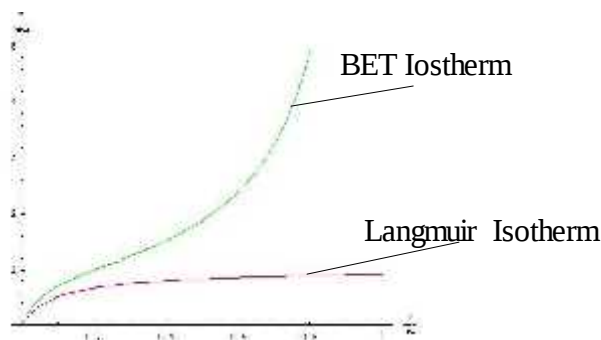
### ADSORPTION ISOTHERMS

A graph plotted between the magnitude of adsorption and pressure at constant temperature

#### Types of adsorption Isotherms

##### Type I: Monomolecular layer adsorption

- Postulated by Langmuir
- The rate of adsorption increases with the increase of pressure or concentration of the adsorbate until it reaches the saturation pressure
- Further increase in pressure will not increase the amt of adsorption
- E.g., Adsorption of  $N_2$  or  $H_2$  on charcoal



**Type II: Multimolecular layer adsorption: BET adsorption theory**

- The amt of adsorption increases with increase in pressure
- Additional layer formation due to the extension of vander waals force
- e.g., Adsorption of N<sub>2</sub> on Pt at -195 C
- e.g., Adsorption of Br<sub>2</sub> on silica at 80C

**Type III: Capillary condensation with multimolecular layer formation**

- Condensation of gases in the minute capillary pores of adsorbent
- Multimolecular layer formation
- e.g.: Adsorption of benzene on silica gel at 50C

e.g.: Adsorption of H<sub>2</sub>O vapour on activated Carbon at 100C

**FREEUNDLICH'S ADSORPTION ISOTHERM**

For Adsorption of gases on solids

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

For Adsorption of solutes on solid in solutions

$$x/m = KC^{1/n}$$

Where

$x/m$  = extent of adsorption  $x$  =

mass of the adsorbate  $M$  = mass

of the adsorbent  $P$  = Pressure

$C$  = concentration of the solute

$K$  = constant and  $n$  = constant, whole number

From the adsorption isotherm, the following observations can easily be made: (i) At low pressure, the graph is almost straight line, thereby indicating

$x/m \propto P$  or  $x/m = KP$

(ii) At high pressure, the graph becomes almost parallel to X-axis, thereby indicating  $x/m =$  constant or  $x/m \propto P^0$  or  $x/m = K$

(iii) At intermediate pressure,  $x/m$  depends on 0 to 1 power of pressure (i.e., fractional power of pressure). This may be expressed as

$x/m \propto P^{1/n}$  or  $x/m = KP^{1/n}$  : Where  $n$  is a whole number

- On taking the logarithm of both sides, the above expression assumes the form:  $\log x/m = \log K + 1/n \log P$  or  $\log x/m = \log K + 1/n \log C$
- Thus, if  $\log x/m$  is plotted against  $\log P$  or  $\log C$ , a straight line would be obtained. The slope of the curve will give  $1/n$ ; while the intercepts on  $\log x/m$  axis at  $P = 0$  or  $C = 0$  would give  $K$

**Limitations:**

- Purely empirical basis
- Valid upto certain pressure and invalid at high pressure
- Fails when concentration of adsorbate is very high
- $K$  and  $n$  are not temperature independents, vary with temperature

**LANGMUIR'S THEORY OF ADSORPTION****Assumptions or Postulates**

1. Valencies at the surface of adsorbent atoms are not fully satisfied
2. The residual valency force on the surface of adsorbent is effective only up to a small distance (about  $2 \times 10^{-8}$  cm) and hence, the adsorbed gas layer is only one molecule thick.

3. The phenomenon of adsorption consists of two opposing processes, namely, condensation of the molecules of the adsorbate on the surface of the adsorbent and evaporation or desorption of the adsorbed molecules from the surface of the adsorbent.
4. A dynamic equilibrium is set up, when the rate of condensation becomes equal to the rate of evaporation.
5. There is no interaction between the adjacent adsorbed molecules
6. The adsorbed gas molecule do not move around on the surface.

#### Langmuir's adsorption equation.

$$w = \frac{bP}{1 + aP} \dots\dots\dots (1)$$

$w$  = *amt of the adsorbate per gm of adsorbent*

$P$  = *Pressure*

$a, b$  are constants

The equation(1) may be re-written as:

$$P/w = 1/b + aP/b$$

Thus, if we plot  $P/w$  against  $P$ , we should get a straight line.

**Merits:** This equation has found valid in all cases.

**Case I:** At very low pressures,  $aP$  becomes negligible in comparison with 1, hence, equation (1) reduces to:

$$w = bP = bP_1 \dots\dots\dots (2)$$

i.e., amount of adsorption per unit weight of adsorbent at a given temperature is directly proportional to the pressure of the gas at low pressures.

**Case II:** At high pressures,  $aP$  is very high as compared with 1 and, therefore, (1) takes the form

$$w = \frac{bP}{aP} = \frac{b}{a} = \text{constant} \dots\dots\dots (3)$$

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

**Case III:** At intermediate pressure, equation 3 becomes

$$w = \frac{b}{aP^{1/n}} \\ = \text{constant } P^{1/n} \dots\dots\dots (4)$$

where  $n$  is whole number. Equation (4) is Freundlich's adsorption isotherm

#### Limitations

This equation does not explain the multilayer formation. Multi layer formation is explained by BET adsorption isotherm

### APPLICATIONS OF ADSORPTION

#### (1) Activated charcoal

- Gas masks in which all undesirable (toxic) gases are adsorbed selectively by charcoal; while purified air passes through its pores.
- Removing colouring matter of sugar solution and the decoloration of vinegar.
- Charcoal adsorption filters are used for removing organic matter from drinking water
- Production of vacuum in Dewar's flask.

#### (2) Silica and alumina gels

- Removing moisture and for controlling humidity of room.
- Silica gel has been employed for drying air, used in blast furnaces.

#### (3) Adsorption chromatography.

- Selective adsorption by alumina, magnesia, etc., has been used for separating different pigments

(4) Arsenic poisoning

- Colloidal ferric hydroxide is administered which adsorbs the arsenic poison and retains it and can thus be removed from the body by vomiting.

(5) Fuller's earth

- Refining petroleum and vegetable oils, due to its good adsorption capacity for unwanted materials.

(6) Heterogeneous catalysis

- Contact process
- Haber's process
- Hydrogenation of oils.

(7) Lake test for  $Al^{3+}$

- Adsorption of litmus colour by  $Al(OH)_3$  precipitate.

(8) Mordants ( alum)

- Dying cloth, adsorb the dye particles, which otherwise do not stick to the cloth.

(9) Measurement of surface area

- Surface area of powder and rough surface can be measured (BET method)

(10) Water Conservation

- The adsorbed stearic acid on the surface of water minimizes evaporation of water

(11) Ore Dressing

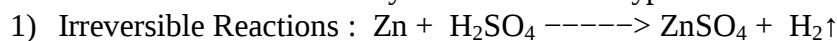
- Froth floatation process: Low grade sulphide ores are freed earthy impurities

## UNIT V

### PHASE RULE

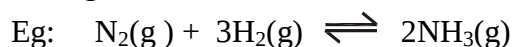
#### INTRODUCTION

All chemical reactions are broadly classified into 2 types:



2) Reversible reactions:

(a) Homogeneous reversible reactions



(b) Heterogeneous reversible reactions



The reversible reactions are represented by 2 arrows in the opposite directions. The homogeneous reversible reactions can be studied by the law of mass action and the heterogeneous reversible reactions using the phase rule, given by Willard Gibbs (1874) which is defined as,

#### PHASE RULE:

If the equilibrium between any numbers of phases is not influenced by gravitational/electrical/magnetic forces but is influenced by pressure, temperature and concentration, then the number of degrees of freedom (F) is related to the number of components (C) and the number of phases (P) as:  $F = C - P + 2$

#### EXPLANATION OF TERMS WITH EXAMPLES

##### (1) PHASE (P):

PHASE is defined as, “any homogeneous physically distinct and mechanically separable portions of a system which is separated from other parts of the system by definite boundaries”.

##### a) Gaseous phase (g):

All gases are completely miscible and have no boundaries between them. Hence all gases constitute a single phase.

Eg: Air, a mixture of  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$  and water vapor, etc., constitutes a single phase.

##### (b) Liquid Phase (l):

The number of liquid phases depends on the number of liquids present and their miscibility's.

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

(e.g.) Benzene – Water system.

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

(e.g.) Alcohol - Water system.

##### (c) Solid Phase (s):

Every solid constitutes a separate single phase.

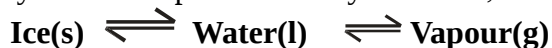
(e.g.) *Decomposition of  $\text{CaCO}_3$*



It involves 3 phases namely solid  $\text{CaCO}_3$ , solid  $\text{CaO}$  and gaseous  $\text{CO}_2$

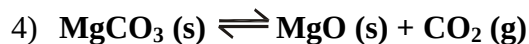
**OTHER EXAMPLES:**

- 1) A water system has 3 phases namely one solid, one liquid and one gaseous phase.



- 2) A solution of a substance in a solvent constitutes only one phase. (e.g.) Sugar solution in water.

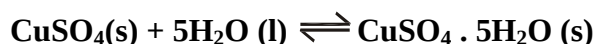
- 3) An emulsion of oil in water forms two phases



It involves 3 phases, solid  $\text{MgCO}_3$ , solid  $\text{MgO}$  and gaseous  $\text{CO}_2$ .

- 5) Rhombic sulphur (s)  $\rightleftharpoons$  Monoclinic sulphur (s). It forms 2 phases.

- 6) Consider the following heterogeneous system.



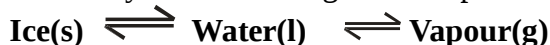
It involves 3 phases namely, 2 solids and 1 liquid phase.

**2. COMPONENT (C):**

Component is defined as, “the minimum number of independent variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation”.

**Examples:**

- (a) Consider a water system consisting of three phases.



The chemical composition of all the three phases is  $\text{H}_2\text{O}$ . Hence the number of component is one.

- (b) Sulphur exists in 4 phases namely rhombic, monoclinic, liquid and vapour, but the chemical composition is only sulphur. Hence it is a one component system.

- (c) Thermal decomposition of  $\text{CaCO}_3$



The system has 3 phases namely, solid  $\text{CaCO}_3$ , solid  $\text{CaO}$  and gaseous  $\text{CO}_2$  and 2 components, as the composition of each of the above phases can be expressed as equations considering any two of the three components present. When  $\text{CaCO}_3$  and  $\text{CaO}$  are considered as components, the chemical equations are:

| Phase           | Components                    |
|-----------------|-------------------------------|
| $\text{CaCO}_3$ | $\text{CaCO}_3 + 0\text{CaO}$ |
| $\text{CaO}$    | $0\text{CaCO}_3 + \text{CaO}$ |
| $\text{CO}_2$   | $\text{CaCO}_3 - \text{CaO}$  |



This system has 3 phases and 2 components namely,  $\text{PCl}_3$  and  $\text{Cl}_2$ .

(e) An aqueous solution of  $\text{NaCl}$  is a two component system. The constituents are  $\text{NaCl}$  and  $\text{H}_2\text{O}$ .



It is also a two component system as components are  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{H}_2\text{O}$ .

(g) In the dissociation of  $\text{NH}_4\text{Cl}$ , the following equilibrium occurs.



The system consists of 2 phases namely solid  $\text{NH}_4\text{Cl}$  and the gaseous mixture containing  $\text{NH}_3 + \text{HCl}$ . When  $\text{NH}_3$  and  $\text{HCl}$  are present in equivalent quantities the composition of both the phases can be represented by  $\text{NH}_4\text{Cl}$  and hence the system will be a one component system.

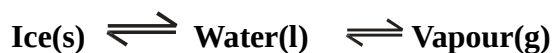
### **3. DEGREE OF FREEDOM (F)**

Degree of freedom is defined as, “the minimum number of independent variable factors like temperature, pressure and concentration, which must be fixed in order to define the system completely”.

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

#### **Examples:**

(a) Consider the following equilibrium



These 3 phases will be in equilibrium only at a particular temperature and pressure. Hence, this system does not have any degree of freedom, so it is non-variant (or) zero-variant (or) in-variant system.

(b) Consider the following equilibrium



Here liquid water is in equilibrium with water vapour. Hence any one of the degrees of freedom such as temperature (or) pressure has to be fixed to define the system. Therefore the degree of freedom is one.

(c) For a gaseous mixture of  $\text{N}_2$  and  $\text{H}_2$ , both the pressure and temperature must be fixed to define the system. Hence, the system is bivariant

### **PHASE DIAGRAM**

Phase diagram is a graph obtained by plotting one degree of freedom against the other.

#### **Types of Phase Diagrams**

##### **(i) P-T Diagram**

If the phase diagram is plotted between temperature and pressure, the diagram is called P -T diagram. P -T diagram is used for one component system.

**(ii) T-C Diagram**

If the phase diagram is plotted between temperature and composition, the diagram is called T-C diagram. T-C diagram is used for two component system

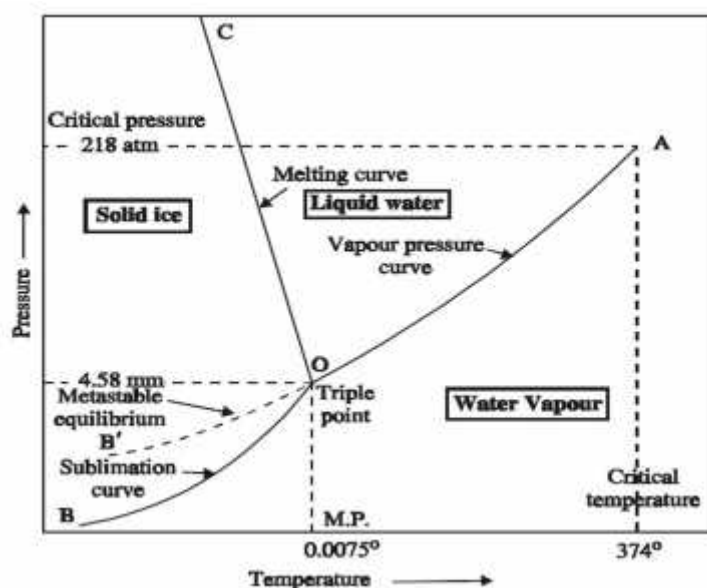
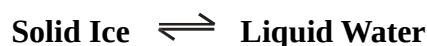
**Uses of Phase Diagram:**

It helps in

- (i) Predicting whether an eutectic alloy (or) a solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.
- (ii) Understanding the properties of materials in the heterogeneous equilibrium system.
- (iii) Studying of low melting eutectic alloys, used in soldering.

**APPLICATIONS OF PHASE RULE - TO ONE COMPONENT SYSTEM****The Water System**

Water exists in 3 possible phases, namely solid ice, liquid water and water-vapour. Hence, there can be three forms of equilibria, each involving two phases such as.



The phase diagram for the water system is as follows and it contains curves, areas, and triple point

**Curve OA**

The curve OA is called vapourisation curve, it represents the equilibrium between water and vapour.

At any point on the curve the following equilibrium will exist.



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

### **Curve OB**

The curve OB is called sublimation curve of ice, it represents the equilibrium between solid ice and water-vapour.

At any point on the curve the following equilibrium will exist.

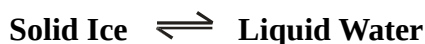


This equilibrium (i.e.line OB) will extend up to the absolute zero ( $- 273^{\circ}\text{C}$ )  
Beyond absolute zero only solid ice will exist and no water-vapour.

### **Curve OC**

The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water.

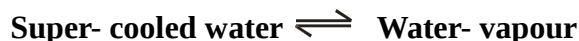
At any point on the curve the following equilibrium will exist.



The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure

### **CurveOB'(Metastable Equilibrium)**

The curve OB' is called vapour pressure curve of the super-cooled water (or) metastable equilibrium where the following equilibrium will exist.



Sometimes water can be cooled below its freezing point ( $0^{\circ}\text{C}$ ) without the formation of ice, this water is called super-cooled water.

Super cooled water is unstable and it can be converted into solid ice by "seeding" (or) by slight disturbance.

### **Along the curves OA,OB,OC and OB'**

The no. of phases(P) is 2 ,component(C) is 1 and the degree of freedom of the system is one i.e., univariant. This is predicted by the phase rule:

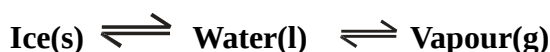
$$F = C - P + 2; F = 1 - 2 + 2; F = 1$$

Therefore, either temperature (or) pressure must be fixed to define the system.

### **Point'O'(Triplepoint)**

The three curves OA, OB and OC meet at a point „O“, where three phases namely solid ice, liquid water and water-vapour are simultaneously at equilibrium.

This point is called triple point, at this point the following equilibrium will exist



At this point the no. of phases(P) is 3, component(C) is 1 and the degree of freedom of the system is zero i.e., nonvariant. This is predicted by the phase rule:

$$F = C - P + 2; F = 1 - 3 + 2; F = 0$$

This takes place only at a constant temperature (0.0075°C) and pressure (4.58 mm of Hg).

### **Areas**

Areas AOC, BOC, AOB represents liquid water, solid ice and water-vapour respectively where the no. of phases(P) and component(C) are one. Hence the degree of freedom of the system is two i.e., bivariant. This is predicted by the phase rule:

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

Therefore, both temperature and pressure must be fixed to define the system at any point in the areas.

## **TWO COMPONENT ALLOY SYSTEM (or) MULTI COMPONENT EQUILIBRIA**

### **Reduced Phase Rule (or) Condensed System**

The maximum number of degree of freedom for a two component system will be three, when the system exists as a single phase.

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

In order to represent the conditions of equilibrium graphically, it requires three co-ordinates, namely P, T and C. This requires three dimensional graph, which cannot be conveniently represented on paper. Therefore, any two of the three variables must be chosen for graphical representation.

A Solid-liquid equilibrium of an alloy 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 phase rule becomes

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

This equation is called reduced phase rule (or) condensed phase rule.

### **Classification of Two Component System**

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

- (i) Simple eutectic formation.
- (ii) (a) Formation of compound with congruent melting point.  
(b) Formation of compound with incongruent melting point.
- (iii) Formation of solid solution.

#### **(i) Simple Eutectic Formation**

A binary system having two substances, which are completely miscible in the liquid state, but completely immiscible in the solid state, is known as eutectic (easy melt) system. They do not react chemically. Of the different mixtures of two substances, a mixture having the lowest melting point is known as the eutectic mixture.

**(ii)(a) Formation of compound with congruent melting point**

The binary alloy system with two substances form one or more compounds with definite proportions. Of the compounds, a compound is said to have congruent melting point, if it melts exactly at a constant temperature into liquid, having the same composition as that of the solid.

**(ii) (b) Formation of compound with incongruent melting point**

Of the above compounds, a compound is said to have incongruent melting point, if it decomposes completely at a temperature below its melting point forming a new solid phase with a different composition from that of the original.

**(iii) Formation of solid solution**

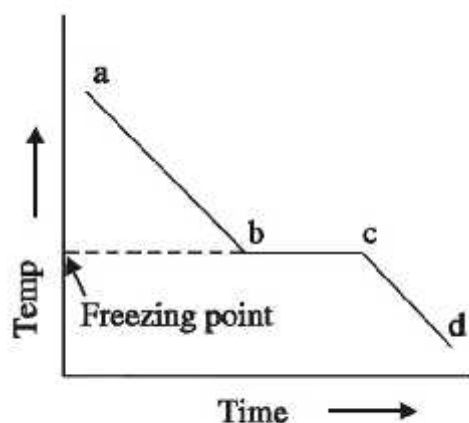
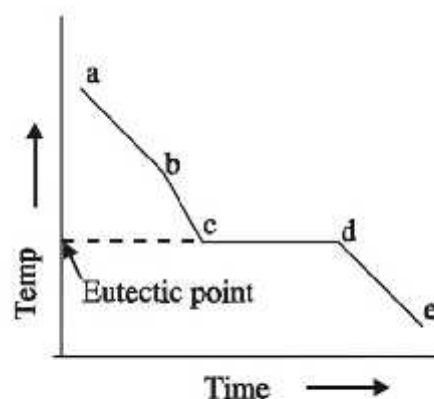
A binary system in which two substances, especially metals, are completely miscible in both solid and liquid states form solid solutions and their mixing takes place in the atomic levels. This happens only when the atomic radius of the two metals not differ by more than 15%.

**EXPERIMENTAL METHOD OF CONSTRUCTION OF A SIMPLE EUTECTIC PHASE DIAGRAM****Thermal Analysis (or) Cooling Curves**

Thermal analysis is a method of studying the cooling curves of various compositions of a system during solidification. The shapes of the freezing point curves for any system (involving metals) can be determined by thermal analysis. The form of cooling curves indicates the composition of the solid.

**Example 1:**

A pure solid substance in the fused state is allowed to cool slowly and the temperature is noted at different time intervals. Then a graph is plotted between temperature and time and it is the cooling curve for the pure solid substance.

**Cooling curve of pure solid****Cooling curve of a mixture A+B**

Initially the rate of cooling of liquid melt is continuous from „a“ till the point „b“, where solid begins to appear. Then the temperature remains constant until the liquid melt is completely solidified and solidification completes at the point „c“.

The horizontal line „bc“ represents the equilibrium between the solid and liquid melt. After the point „c“, along the curve „cd“ cooling of solid mass begins and the temperature begins to decrease.

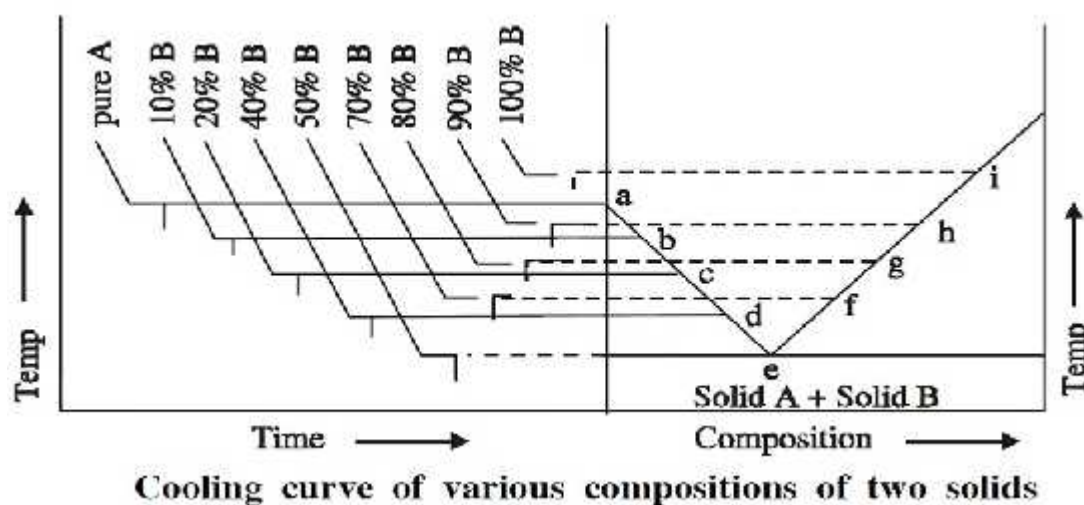
**Example 2:**

If a mixture of two substances (say A and B) in the fused state are allowed to cool slowly, the cooling curve is obtained as above:

Initially the rate of cooling of liquid melt is continuous from 'a' till the point 'b'. When it reaches the point 'b' one substance (either A or B) begins to solidify out of the melt. This is indicated by a break where the rate of cooling is different. On further cooling at the break point 'c' the second substance also begins to solidify. Now the temperature remains constant until the liquid melt is completely solidified, which forms the eutectic mixture along the line 'cd'. After the break point 'd' cooling of solid mass begins. The temperature of horizontal line „cd“ gives the eutectic temperature.

The experiment are repeated for different compositions of A and B and the various cooling curves are recorded.

From the cooling curves of various compositions, the main phase diagram can be drawn by taking composition in X-axis and the temperature in Y-axis.

**Uses of Cooling Curves:**

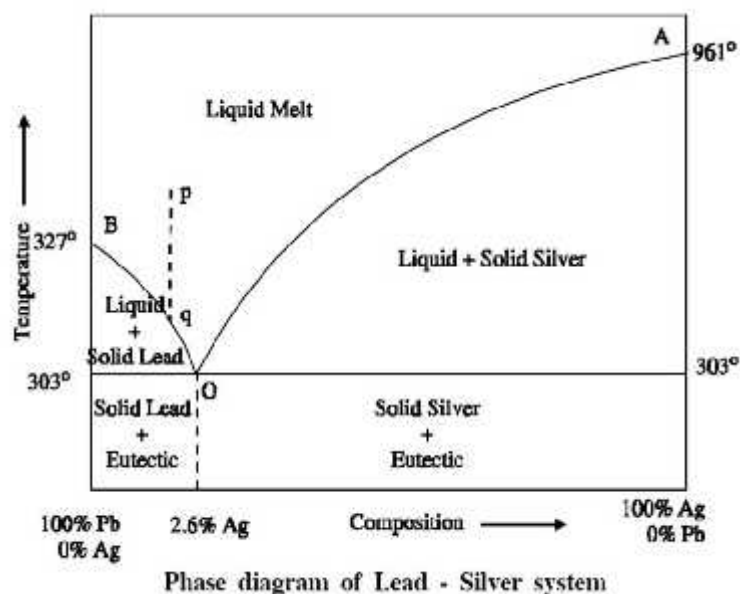
1. Melting point and eutectic temperature can be noted.
2. Percentage purity of the compounds can be noted.
3. The behavior of the compounds can be clearly understood.
4. The composition corresponding to its freezing point yields the composition of the alloy.
5. The phase diagram for any two component system can be obtained.

**BINARY ALLOY SYSTEM (OR) THE SIMPLE EUTECTIC SYSTEM****The Lead-Silver System**

The Lead-Silver system is studied at constant pressure and the vapour phase is ignored. Hence the condensed phase rule is used:

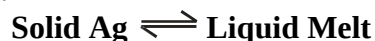
$$F' = C - P + 1$$

The phase diagram of lead-silver system is shown as follows. It contains curves, areas and eutectic point.



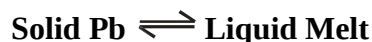
### (i) Curve AO

The curve AO is known as freezing point curve of silver. Point A is the melting point of pure Ag (961°C). The curve AO shows the melting point depression of Ag by the successive addition of Pb. Along this curve AO, solid Ag and the melt are in equilibrium.



### (ii) Curve BO

The curve BO is known as freezing point curve of lead. Point B is the melting point of pure lead (327°C). The curve BO shows the melting point depression of Pb by the successive addition of Ag. Along this curve BO, solid Pb and the melt are in equilibrium.



### Along the curves AO and BO

The degree of freedom according to reduced phase rule is as follows:

$$F' = C - P + 1; F' = 2 - 2 + 1; F' = 1$$

The system is univariant which means either temperature (or) composition must be fixed to define the system.

### (iii) Point 'O' (Eutectic point)

The curves AO and BO meet at point „O“ at a temperature of 303°C, where three phases (solid Ag, solid Pb and their liquid melt) are in equilibrium.



According to reduced phase rule equation.

$$F' = C - P + 1; F' = 2 - 3 + 1; F' = 0$$

The system is non-variant.

The point „O“ is called eutectic point or eutectic temperature and its corresponding composition, 97.4%Pb + 2.6%Ag, is called eutectic composition.

Below this point the eutectic compound and the metal solidify.

**(iv) Area**

The area above the line AOB has a single phase (molten Pb+Ag) or liquid melt. According to reduced phase rule the degree of freedom.

$$F' = C - P + 1; F' = 2 - 1 + 1; F' = 2$$

The system is bivariant which means both the temperature and composition have to be fixed to define the system completely.

The area below the line AO (solid Ag + liquid melt), below the line BO (solid Pb + liquid melt) and below the point „O“ (Eutectic compound + solid Ag or solid Pb) have two phases and hence the system is univariant

$$F' = C - P + 1; F' = 2 - 2 + 1; F' = 1.$$

**Application of Pattinson's process for the desilverisation of argentiferous lead**

The argentiferous lead, having a very small amount of silver (say 0.1%), is heated to a temperature above its melting point, so that the system has only the liquid phase represented by the point „p“ in the phase diagram .

It is then allowed to cool where the temperature decreases along the line „pq“. As soon as the point „q“ is reached, Pb is crystallised out and the solution will contain relatively increasing amounts of „Ag“. On further cooling, more and more of „Pb“ is separated along the line „BO“. The melt continues to be richer and richer in Ag until the point „O“ is reached, where the percentage of Ag rises to 2.6%.

Thus, the process of raising the relative proportions of Ag in the alloy is known as Pattinson's process.

**Uses of Eutectic system**

1. Suitable alloy composition can be predicted.
2. Making solders, used for joining two metal pieces together.

**Differences between Melting point, Eutectic point and Triple point**

**1.Melting Point:** It is the temperature at which the solid and liquid phases, having the same composition, are in equilibrium.



**2. Eutectic Point:** It is the temperature at which two solids and a liquid phase are in equilibrium

**3. Triple Point**

It is the temperature at which three phases are in equilibrium.



All the eutectic points are melting points

All the melting points need not be eutectic points.

Similarly all the eutectic points are triple points, but all the triple points need not be eutectic points.

**Uses (or) merits of phase rule**

1. Applicable to both physical and chemical equilibria.
2. A convenient method to classify the equilibrium systems in terms of phases, components and degree of freedom.
3. Indicates that different systems having the same degrees of freedom behave similarly.
4. Decides whether the given number of substances remains in equilibrium or not.
5. Applicable to macroscopic systems without considering their molecular structures.
6. Does not consider the nature (or) amount of substances in the system.

**Limitations of phase rule**

1. Phase rule can be applied only for the heterogeneous systems in equilibrium.
2. Only three variables like P, T & C are considered, but not electrical, magnetic and gravitational forces.
3. All the phases of the system must be present under the same conditions of pressure and temperature.
4. Solid and liquid phases must not be in finely divided state, otherwise deviations occur

**KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21.****FACULTY OF ENGINEERING****DEPARTMENT OF SCIENCE AND HUMANITIES****ENGINEERING CHEMISTRY****UNIT -V****SURFACE CHEMISTRY AND PHASE RULE****PART – B**

1. Define adsorption.
2. Differentiate adsorption and absorption.
3. What are adsorbent and adsorbate?
4. Differentiate physisorption and chemisorption.
5. Give any four characteristics of adsorption.
6. What is the effect of pressure, temperature on physisorption and chemisorption.
7. What is positive adsorption? And negative adsorption. Give examples.
8. Define adsorption isotherms.
9. What is Freundlich isotherm? What are the limitations?
10. What are the assumptions of Langmuir adsorption isotherm?
11. List out any four important applications of adsorption.
12. What is homogeneous catalyst? What is heterogeneous catalyst?
13. Why the solid catalyst should be used as a fine powder?
14. What are promoters and catalytic poison?
15. Give two examples for cation and anion exchange resins?
16. What is zeolite process?
17. What are the applications of activated charcoal?
18. What are GAC and PAC?
19. What are the factors affecting adsorption of gases on solid?
20. What are the factors affecting adsorption from solutions?
21. How is arsenic poisoning removed from the body?
22. Define phase rule and indicate the terms involved in it.
23. What is condensed Phase rule? Or what is reduced phase rule?
24. What is eutectic point?
25. Write the significance of eutectic mixture.

**PART – C**

1. Differentiate physisorption and chemisorption?
2. Explain the factors affecting adsorption of gases on solids.
3. Explain the factors affecting adsorption of solutes from solutions.
4. What are the five types of isotherms possible? Draw and explain the cases with examples.
5. Derive Langmuir adsorption isotherm.
6. Bring out the role of adsorption in heterogeneous catalyst?
7. Explain the principle of adsorption in ion-exchange process of water treatment?
8. What are the common applications of adsorption?
9. How can the pollution be reduced by activated charcoal.
10. Draw a neat phase diagram and explain the lead-silver system? Briefly write about Pattinson's process.
11. Explain the application phase rule to a one component system.

## UNIT I

## WATER TECHNOLOGY

| Question                                                                                        | opt1                                                   | opt2                                   | opt3                           | opt4                            | Answer                                                 |
|-------------------------------------------------------------------------------------------------|--------------------------------------------------------|----------------------------------------|--------------------------------|---------------------------------|--------------------------------------------------------|
| Purest form of water is present in                                                              | River water                                            | Rain water                             | Stream water                   | Sea water                       | Rain water                                             |
| For the determination of alkalinity the indicator used is                                       | Methyl orange                                          | potassium chromate                     | EBT                            | Starch                          | Methyl orange                                          |
| In alkalinity determination the phenolphthalein end point colour change is                      | colourless to pink                                     | colourless to blue                     | pink to colourless             | yellow to pink                  | pink to colourless                                     |
| If phenolphthalein end point is greater than half the total titration then alkalinity is due to | Bicarbonate ions                                       | Hydroxide and Carbonate ions           | Hydroxide and Bicarbonate ions | Carbonate ions                  | Hydroxide and Carbonate ions                           |
| If P is less than half M (or T) then alkalinity is due to -                                     | Bicarbonate ions                                       | Hydroxide and Carbonate ions           | Carbonate and Bicarbonate ions | Carbonate ions                  | Carbonate and Bicarbonate ions                         |
| If P = M (or T) then alkalinity is due to -                                                     | Bicarbonate ions                                       | Hydroxide ions                         | Hydroxide and Bicarbonate ions | Carbonate ions                  | Hydroxide ions                                         |
| Magnesium bicarbonate & Calcium bicarbonate present in water cause                              | Temporary hardness                                     | Permanent hardness                     | Both                           | No Hardness                     | Temporary hardness                                     |
| 1 mg per litre =                                                                                | 1ppm                                                   | 0.1 ppm                                | 100 ppm                        | 10 ppm                          | 1ppm                                                   |
| 10 mg per litre =                                                                               | 1ppm                                                   | 0.1 ppm                                | 100 ppm                        | 10 ppm                          | 10 ppm                                                 |
| Temporary hardness is also called as                                                            | Carbonate hardness                                     | Non-carbonate hardness                 | Both A & B                     | None of these                   | Carbonate hardness                                     |
| Temporary hardness is removed by                                                                | Reverse osmosis                                        | Hehner's method (boiling)              | Electrodialysis                | Never removed                   | Hehner's method (boiling)                              |
| On boiling $\text{Ca}(\text{HCO}_3)_2$ present in water forms                                   | $\text{CaCO}_3$ , $\text{CO}_2$ & $\text{H}_2\text{O}$ | $\text{CaCO}_3$ & $\text{H}_2\text{O}$ | $\text{CaO}$ & $\text{CO}_2$   | $\text{CaCO}_3$ & $\text{CO}_2$ | $\text{CaCO}_3$ , $\text{CO}_2$ & $\text{H}_2\text{O}$ |
| Which of the calcium salts contributes to non-carbonate / permanent hardness?                   | Bicarbonate                                            | Sulphate                               | Carbonate                      | Hydroxide                       | Sulphate                                               |
| Unit of hardness is equivalent of -                                                             | $\text{CaCl}_2$                                        | $\text{CaSO}_4$                        | $\text{CaCO}_3$                | $\text{CaO}$                    | $\text{CaCO}_3$                                        |

|                                                                                             |                           |                                           |                                       |                                       |                                           |
|---------------------------------------------------------------------------------------------|---------------------------|-------------------------------------------|---------------------------------------|---------------------------------------|-------------------------------------------|
| Equivalent weight of Calcium Carbonate is                                                   | Equal to molecular weight | Half of molecular weight                  | Double the molecular weight           | triple the molecular weight           | Half of molecular weight                  |
| An example of complexometric titration is                                                   | EDTA Vs Hard water        | Strong acid Vs Hard water                 | AgNO <sub>3</sub> Vs hard water       | None                                  | EDTA Vs Hard water                        |
| Indicator used for the total hardness determination of water                                | Phenolphthalein           | Methyl orange                             | Methyl red                            | Eriochrome black-T                    | Eriochrome black-T                        |
| What is EDTA?                                                                               | A Complexing agent        | coagulant                                 | disinfectant                          | indicator                             | A Complexing agent                        |
| The colour of metal-EBT complex is                                                          | Blue                      | Wine red                                  | Black                                 | Pink                                  | Wine red                                  |
| The colour of metal-EDTA complex is                                                         | Blue                      | Wine red                                  | Colourless                            | Pink                                  | Colourless                                |
| Di-Sodium EDTA is used instead of EDTA because it is                                        | Readily soluble in water  | colourless                                | easily available                      | more reactive                         | Readily soluble in water                  |
| Hard water + pH 10 buffer + EBT indicator, the mixture is                                   | Wine red coloured         | Pink coloured                             | Blue coloured                         | Colourless                            | Wine red coloured                         |
| If boiled water sample is titrated with standard EDTA solution, then reading corresponds to | Total hardness            | Non-Carbonate hardness                    | Carbonate hardness                    | Temporary hardness                    | Non-Carbonate hardness                    |
| Ca-EDTA complex is _____ stable than Ca-EbT complex at pH 10.                               | less                      | equally                                   | more                                  | not equally                           | more                                      |
| The treatment used for the removal of biological impurities is                              | Softening                 | Coagulation                               | Sterilization                         | Sedimentation                         | Sterilization                             |
| The salt used for the removal of colloidal impurities is                                    | CuSO <sub>4</sub>         | Alum                                      | NaCl                                  | Chlorine                              | Alum                                      |
| Soft deposit at the bottom of the boiler is known as                                        | Foaming                   | Scale                                     | Corrosion                             | Sludge                                | Scale                                     |
| Scale is                                                                                    | Hard & Sticky substance   | Soft & Non-sticky substance               | easily removable                      | loose precipitate                     | Hard & Sticky substance                   |
| Hard Scales are formed due to                                                               | CaSO <sub>4</sub>         | CaCO <sub>3</sub>                         | Mg(HCO <sub>3</sub> ) <sub>2</sub>    | Ca(HCO <sub>3</sub> ) <sub>2</sub>    | CaSO <sub>4</sub>                         |
| Sludge formation is due to                                                                  | MgCO <sub>3</sub>         | Mg(OH) <sub>2</sub> and CaCO <sub>3</sub> | MgCl <sub>2</sub> and CO <sub>2</sub> | MgCO <sub>3</sub> and CO <sub>2</sub> | Mg(OH) <sub>2</sub> and CaCO <sub>3</sub> |
| Sludge is removed by                                                                        | Wire brush                | hammer                                    | electric shocks                       | Blow off                              | Blow off                                  |

|                                                                                                     |                                 |                                               |                                                                   |                                                                   |                                                                   |
|-----------------------------------------------------------------------------------------------------|---------------------------------|-----------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|
| To remove scale from boiler wall, it is treated with-                                               | EDTA solution                   | NaCl solution                                 | KOH solution                                                      | HCl                                                               | HCl                                                               |
| Priming is the formation of                                                                         | Wet steam                       | Dry steam                                     | Carbonated steam                                                  | Foamed steam                                                      | Wet steam                                                         |
| Violent or vigorous boiling of water leads to                                                       | Scale                           | Caustic embrittlement                         | Priming & foaming                                                 | Corrosion                                                         | Priming & foaming                                                 |
| Foaming is caused due to the presence of ____ in boiler.                                            | More dissolved salts            | Oil droplets                                  | Dissolved gases                                                   | NaOH                                                              | Oil droplets                                                      |
| Best oil used as antifoaming agent ( to prevent foaming) is                                         | Castor oil                      | Coconut oil                                   | Sunflower oil                                                     | Groundnut oil                                                     | Castor oil                                                        |
| Sodium carbonate in boiler water causes                                                             | Scale & Sludges                 | Priming & Foaming                             | Low pH corrosion                                                  | Caustic embrittlement                                             | Caustic embrittlement                                             |
| Caustic embrittlement occurs in _____ boilers                                                       | Low pressure                    | Medium pressure                               | High pressure                                                     | Low & Medium pressure                                             | High pressure                                                     |
| Corrosion of boiler is due to                                                                       | Dissolved N <sub>2</sub>        | Dissolved H <sub>2</sub>                      | Dissolved SO <sub>2</sub>                                         | Dissolved O <sub>2</sub>                                          | Dissolved O <sub>2</sub>                                          |
| Corrosion due to CO <sub>2</sub> is removed by adding                                               | NH <sub>4</sub> OH              | Na <sub>2</sub> SO <sub>4</sub>               | N <sub>2</sub> H <sub>4</sub>                                     | NH <sub>3</sub>                                                   | NH <sub>4</sub> OH                                                |
| Corrosion due to O <sub>2</sub> is removed by adding                                                | Na <sub>3</sub> PO <sub>4</sub> | Na <sub>2</sub> SO <sub>4</sub>               | N <sub>2</sub> H <sub>4</sub>                                     | NH <sub>3</sub>                                                   | N <sub>2</sub> H <sub>4</sub>                                     |
| To minimize boiler troubles, the optimum pH of the boiler feed water should be                      | 7                               | 5                                             | Above 10                                                          | 8 – 9                                                             | 8 – 9                                                             |
| Which of the following is not an internal treatment method for boiler feed water?                   | Phosphate conditioning          | Zeolite conditioning                          | Calgon conditioning                                               | carbonate conditioning                                            | Zeolite conditioning                                              |
| Calgon conditioning can be done by                                                                  | Trisodium Phosphate             | Sodium hexametaphosphate                      | Lignin                                                            | Sodium hydrogen phosphate                                         | Sodium hexametaphosphate                                          |
| The formula of Calgon                                                                               | Na <sub>3</sub> PO <sub>4</sub> | Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> | Na <sub>2</sub> [Na <sub>4</sub> P <sub>6</sub> O <sub>18</sub> ] | Na <sub>4</sub> [Na <sub>2</sub> P <sub>6</sub> O <sub>18</sub> ] | Na <sub>2</sub> [Na <sub>4</sub> P <sub>6</sub> O <sub>18</sub> ] |
| In phosphate conditioning the residual hardness is converted into – ( <i>Ca/Mg phosphate</i> )      | Loose precipitate               | Hard precipitate                              | soluble complex                                                   | insoluble complex                                                 | Loose precipitate                                                 |
| If boiler feed water is highly alkaline, then which ortho phosphate is used for internal treatment? | Na <sub>3</sub> PO <sub>4</sub> | Na <sub>2</sub> HPO <sub>4</sub>              | NaH <sub>2</sub> PO <sub>4</sub>                                  | NaPO <sub>3</sub>                                                 | NaH <sub>2</sub> PO <sub>4</sub>                                  |

|                                                                                                                     |                                                          |                                                         |                           |                                |                                                          |
|---------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------|---------------------------------------------------------|---------------------------|--------------------------------|----------------------------------------------------------|
| If boiler feed water is acidic, then which ortho phosphate is used for internal treatment                           | $\text{Na}_3\text{PO}_4$                                 | $\text{Na}_2\text{HPO}_4$                               | $\text{NaH}_2\text{PO}_4$ | $\text{NaPO}_3$                | $\text{Na}_3\text{PO}_4$                                 |
| Water free of all ions is obtained by                                                                               | deionization process                                     | reverse osmosis                                         | softening                 | electrodialysis                | deionization process                                     |
| Desalination of sea water by using ion-selective membranes is called                                                | Reverse Osmosis                                          | Ion-Exchange method                                     | Electrodialysis           | Softening                      | Electrodialysis                                          |
| The functional group of cation exchange resin is                                                                    | $\text{RH}^+$                                            | $\text{ROH}^-$                                          | $\text{R CH}_3$           | $\text{C}_6\text{H}_5\text{R}$ | $\text{RH}^+$                                            |
| The functional group of anion exchange resin is                                                                     | $\text{RH}^+$                                            | $\text{ROH}^-$                                          | $\text{R CH}_3$           | $\text{C}_6\text{H}_5\text{R}$ | $\text{ROH}^-$                                           |
| Regeneration of Anion exchange resin is done by                                                                     | dil $\text{Na}_2\text{SO}_4$                             | dil $\text{HCl}$                                        | dil $\text{NaOH}$         | 10 % $\text{NaCl}$             | dil $\text{NaOH}$                                        |
| Complete removal of all the salts from brackish water (sea water) is called                                         | Electrodialysis                                          | Demineralisation                                        | Deionisation              | Reverse osmosis                | Reverse osmosis                                          |
| Purification of saline water using semi permeable membranes is called                                               | Reverse Osmosis                                          | Ion-Exchange method                                     | Electrodialysis           | Ultrafiltration                | Reverse Osmosis                                          |
| The semipermeable membrane allows                                                                                   | Both solvent molecules and ions                          | Ions only                                               | Solvent molecules only    | Solute                         | Solvent molecules only                                   |
| The solvent from less concentrated solution moves into high concentrated solution through semipermeable membrane in | Electrodialysis                                          | Reverse Osmosis                                         | Osmosis                   | demineralisation               | Osmosis                                                  |
| Reverse Osmosis means movement of solvent from                                                                      | High concentrated solution to low concentrated solution. | Low concentrated solution to high concentrated solution | Both A & B                | None of the above              | High concentrated solution to low concentrated solution. |
| The opposition pressure applied to osmosis is                                                                       | Osmotic pressure                                         | Hydrostatic pressure                                    | electrostatic pressure    | pressure gauge                 | Hydrostatic pressure                                     |
| The life of semipermeable membrane used in RO is                                                                    | 1 year                                                   | 2 years                                                 | 3 years                   | 8 years                        | 1 year                                                   |

## UNIT II

## ELECTROCHEMISTRY AND STORAGE DEVICES

| Questions                                                           | opt1                                                         | opt2                                                                                              | opt3                                                         | opt4                                                                                              | Answer                                                                                            |
|---------------------------------------------------------------------|--------------------------------------------------------------|---------------------------------------------------------------------------------------------------|--------------------------------------------------------------|---------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|
| The type of reaction taking place in anode                          | Redox                                                        | Oxidation                                                                                         | Reduction                                                    | Precipitation                                                                                     | Oxidation                                                                                         |
| .An example for strong electrolyte is                               | Hydrochloric acid                                            | Acetic acid                                                                                       | Sugar                                                        | Glucose                                                                                           | Hydrochloric acid                                                                                 |
| An example for weak electrolyte is                                  | Hydrochloric acid                                            | Acetic acid                                                                                       | Sugar                                                        | Glucose                                                                                           | Acetic acid                                                                                       |
| Sodium chloride is called an electrolyte, because                   | Its molecule is made up of electrically charged particles.   | It is decomposed, when an electric current is passed through it.                                  | It breaks up into ions, when a current is passed through it. | It ionizes, when fused or dissolved in a proper solvent                                           | It ionizes, when fused or dissolved in a proper solvent                                           |
| Electrolyte can conduct electricity, because                        | Their molecules contain unpaired electrons, which are mobile | Their molecules contain loosely held electrons, which become free under the influence of voltage. | The molecules break up into ions, when a voltage is applied  | The molecules are broken up into ions, when the electrolyte is fused or dissolved in the solvent. | The molecules are broken up into ions, when the electrolyte is fused or dissolved in the solvent. |
| Which one of the following is an electrolyte?                       | $C_6H_6$                                                     | $CHCl_3$                                                                                          | $C_6H_5Cl$                                                   | NaCN                                                                                              | NaCN                                                                                              |
| Reduction takes place in -----                                      | Anode                                                        | Cathode                                                                                           | Electrolyte                                                  | Cell                                                                                              | Cathode                                                                                           |
| Electrolytic cell in which electrical energy is converted into      | Chemical energy                                              | Light energy                                                                                      | Heat energy                                                  | Sound energy                                                                                      | Chemical energy                                                                                   |
| Electrochemical cell is a device which is used to get _____ energy. | Thermal                                                      | Electrical                                                                                        | Chemical                                                     | Mechanical                                                                                        | Electrical                                                                                        |
| The emf of the daniel cell                                          | 1.1 V                                                        | 2 V                                                                                               | 0 V                                                          | 10 V                                                                                              | 1.1 V                                                                                             |
| The emf of the daniel cell can be calculated by the formula         | $E_{CELL} = E^0_{Zn} - E^0_{Cu}$                             | $E_{CELL} = E^0_{Cu} - E^0_{Zn}$                                                                  | $E_{CELL} = E^0_{Pb} - E^0_{Cu}$                             | $E_{CELL} = E^0_{Cu} - E^0_{Pb}$                                                                  | $E_{CELL} = E^0_{Zn} - E^0_{Cu}$                                                                  |
| The solution used in salt bridge is                                 | KCl                                                          | NaCl                                                                                              | KI                                                           | Sodium sulphate                                                                                   | KCl                                                                                               |

|                                                                                                     |                                        |                                        |                                     |                                  |                                        |
|-----------------------------------------------------------------------------------------------------|----------------------------------------|----------------------------------------|-------------------------------------|----------------------------------|----------------------------------------|
| .An electrochemical cell converts chemical energy into                                              | Electrical energy                      | Heat energy                            | light energy                        | Solar energy                     | Electrical energy                      |
| In galvanic series, a metal high in series is more _____.                                           | Anodic                                 | Cathodic                               | Corroded                            | Neutral                          | Anodic                                 |
| Electrical energy is converted into chemical energy in                                              | Electrolytic cell                      | Daniel cell                            | Fuel cell                           | Electroplating                   | Electrolytic cell                      |
| A galvanic cell converts                                                                            | electrical energy into chemical energy | chemical energy into electrical energy | electrical energy into heat energy  | chemical energy into heat energy | chemical energy into electrical energy |
| In the galvanic cell electrical energy is generated at the expense of                               | Free energy                            | Chemical energy                        | Heat energy                         | Heat energy                      | Chemical energy                        |
| Chemical energy is converted directly into electrical energy in                                     | a battery.                             | an electrical power plant              | an electrolytic cell.               | an automobile's engine.          | a battery.                             |
| Cells which obey the conditions of thermodynamic irreversibility are called                         | Reversible cell                        | Irreversible cell                      | Dry cell                            | Conductivity cell                | Reversible cell                        |
| Cells which do not obey the conditions of thermodynamic irreversibility are called                  | Reversible cell                        | Irreversible cell                      | Dry cell                            | Conductivity cell                | Irreversible cell                      |
| Tendency of an electrode to gain electron is                                                        | Oxidation potential                    | Reduction potential                    | Redox potential                     | Single electrode potential       | Reduction potential                    |
| Tendency of an electrode to lose electron is                                                        | Oxidation potential                    | Reduction potential                    | Redox potential                     | Single electrode potential       | Oxidation potential                    |
| The passage of electricity in the daniel cell, when zinc and copper electrode are connected to form | Cu to Zn in the cell                   | Cu to Zn outside the cell              | Zn to Cu in the cell                | Zn to Cu outside the cell        | Zn to Cu outside the cell              |
| The electrode potential is the tendency of metal                                                    | to gain the electron                   | loss the electron                      | either to loss or gain the electron | reactive                         | either to loss or gain the electron    |
| The vertical line // indicates                                                                      | Cathode                                | Anode                                  | Salt bridge                         | Electrolte                       | Salt bridge                            |

|                                                                                                                                                          |                                                  |                                                  |                                         |                                       |                                                  |
|----------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------|--------------------------------------------------|-----------------------------------------|---------------------------------------|--------------------------------------------------|
| In the electrochemical series elements are arranged in the                                                                                               | decreasing order of standard electrode potential | increasing order of standard electrode potential | increasing order of oxidation potential | increasing order of equivalent weight | increasing order of standard electrode potential |
| Zinc is above the copper in electrochemical series. So if standard zinc electrode and standard copper electrode are coupled to form a cell, in such cell | zinc is oxidized                                 | copper is oxidized                               | zinc gain electron                      | copper losses electron                | zinc is oxidized                                 |
| Which one of the following is a reversible cell                                                                                                          | Daniel cell                                      | Dry cell                                         | Zinc -silver cell                       | Lead -cadmium cell                    | Daniel cell                                      |
| The standard free energy $-\Delta G =$                                                                                                                   | $nfE$                                            | $RT/nF$                                          | $\ln k$                                 | $K$                                   | $nfE$                                            |
| The gas constant $R =$                                                                                                                                   | 8.314 J/K/mol                                    | 2.888 J/K/mol                                    | 96500 C                                 | 298 K                                 | 8.314 J/K/mol                                    |
| For measuring single electrode potential commonly used electrode is                                                                                      | Glass electrode                                  | SHE                                              | SCE                                     | Zinc electrode                        | SHE                                              |
| An example for reference electrode is                                                                                                                    | Calomel electrode                                | Glass electrode                                  | Silver electrode                        | Zinc electrode                        | Calomel electrode                                |
| The pH of the given solution can be measured by using                                                                                                    | Zinc electrode                                   | Calomel electrode                                | Standard hydrogen electrode             | Glass electrode                       | Glass electrode                                  |
| The electrode potential of standard hydrogen electrode is                                                                                                | 0 V                                              | 100 V                                            | 0.2422 V                                | 0.3526 V                              | 0 V                                              |
| Which among the following is the primary reference electrode                                                                                             | SHE                                              | SCE                                              | Glass electrode                         | Zinc electrode                        | SHE                                              |
| Ion selective electrode is                                                                                                                               | Glass electrode                                  | SHE                                              | SCE                                     | Zinc electrode                        | Glass electrode                                  |
| The concentration of hydrogen ion can be determined by using                                                                                             | Glass electrode                                  | Calomel electrode                                | Zinc electrode                          | Silver electrode                      | Glass electrode                                  |
| Which one of the following is not a reference electrode                                                                                                  | SHE                                              | SCE                                              | Glass electrode                         | Platinum electrode                    | Platinum electrode                               |
| Which one of the following is a internal reference electrode                                                                                             | SHE                                              | SCE                                              | Glass electrode                         | Platinum electrode                    | Glass electrode                                  |
| Emf is measured in                                                                                                                                       | Ampere                                           | Volts                                            | ev                                      | mho                                   | Volts                                            |

|                                                                                                   |                                                                 |                       |                           |                           |                                                                 |
|---------------------------------------------------------------------------------------------------|-----------------------------------------------------------------|-----------------------|---------------------------|---------------------------|-----------------------------------------------------------------|
| Which one of the following metal displaces H <sub>2</sub> with dil H <sub>2</sub> SO <sub>4</sub> | Zn                                                              | Ag                    | Cu                        | Au                        | Zn                                                              |
| If the emf of the cell is positive, The reaction is                                               | Spontaneous                                                     | Feasible              | Exothermic                | Endothermic               | Spontaneous                                                     |
| In the combination of metals Zn and Ag which will be acting as anode                              | Zn                                                              | Ag                    | Au                        | Fluoiride                 | Zn                                                              |
| Which one of the following is used in measuring emf of a solution                                 | Potentiometer                                                   | Ph meter              | Thermometer               | Voltmeter                 | Potentiometer                                                   |
|                                                                                                   |                                                                 |                       |                           |                           |                                                                 |
| The principle in which potentiometer works is                                                     | Poggendorff compensation principle                              | Heisen burg principke | Pauli exclusion principle | Aufbau principle          | Poggendorff compensation principle                              |
| The metal present in bottom of calomel electrode                                                  | Ag                                                              | Hg                    | Au                        | Zn to Cu outside the cell | Hg                                                              |
| The emf value ----- when Fe <sup>2+</sup> /K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>          | Increases                                                       | Decreases             | Remains constant          | unaltered                 | Increases                                                       |
| The coloured solution can be estinated by                                                         | Potentiometry                                                   | Volumetry             | Gravimetry                | Cyclic voltametry         | Potentiometry                                                   |
| Anode used in lead acid battery is                                                                | Lead                                                            | .Lead oxide           | Iron                      | Lithium                   | Lead                                                            |
| Storage cells are otherwise called                                                                | Accumulators                                                    | Fuel cells            | Flow cells                | Primary cells             | Accumulators                                                    |
| An example for redox titration is                                                                 | Fe <sup>2+</sup> /K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> | AgCl/NaOH             | HCl/NaOH                  | NaCl/NaOH                 | Fe <sup>2+</sup> /K <sub>2</sub> CR <sub>2</sub> O <sub>7</sub> |
| Battery is a type of _____ cell.                                                                  | Electrolytic                                                    | Electrochemical       | Chemo electric            | Thermal                   | Electrochemical                                                 |
| Dry cell is an example of _____ cell.                                                             | Primary                                                         | Secondary             | Electrochemical           | . Electrolytic            | Primary                                                         |
| _____ is acts as anode in dry / laclanche cell.                                                   | Carbon rod                                                      | Mn                    | Zn                        | .Fe                       | Fe                                                              |
| The ----- battery is used in automobiles                                                          | Lead acid                                                       | Lithium               | Alkaline                  | Lithium sulphur           | Zn                                                              |
| An example for non rechargeable battery                                                           | Dry cell                                                        | Lithium battery       | lead acid battery         | Lithium sulphur battery   | Dry cell                                                        |

|                                           |                    |                  |          |      |                    |
|-------------------------------------------|--------------------|------------------|----------|------|--------------------|
| The electrolyte used in lead acid battery | Dil sulphuric acid | NaCl             | HCl/NaOH | NaOH | Dil sulphuric acid |
| The anode used in alkaline battery        | Zn                 | Pb               | Cd       | Na   | Zn                 |
| The Cathode used in lead acid battery     | Pb                 | PbO <sub>2</sub> | Zn       | Cd   | PbO <sub>2</sub>   |

## UNIT III

## FUELS AND ROCKET PROPELLENTS

| Questions                                                                                                                       | opt1                                                 | opt2                                                               | opt3                                                 | opt4                                                                 | Answer                                               |
|---------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------|--------------------------------------------------------------------|------------------------------------------------------|----------------------------------------------------------------------|------------------------------------------------------|
| Gross and net calorific value of a fuel will be the same                                                                        | if its ash content is zero                           | if its carbon content is very low.                                 | if its hydrogen/hydrogen compound content is zero.   | under no circumstances.                                              | if its hydrogen/hydrogen compound content is zero.   |
| Presence of _____ in a dry gaseous fuel does not contribute to its calorific value.                                             | sulphur                                              | hydrogen                                                           | carbon                                               | oxygen                                                               | oxygen                                               |
| Which of the following constituents of coal is the most important in the production of coke?                                    | Moisture                                             | Volatiles                                                          | ash                                                  | Carbon                                                               | Carbon                                               |
| Low temperature carbonisation                                                                                                   | is mainly for producing the smokeless domestic coke. | produces less quantity of tar than high temperature carbonisation. | is meant for the production of 'metallurgical coke'. | produces higher quantity of gas than high temperature carbonisation. | is mainly for producing the smokeless domestic coke. |
| Calorific value of coal oven gas is around _____ Kcal/Nm <sup>3</sup> .                                                         | 900                                                  | 7500                                                               | 4200                                                 | 2000                                                                 | 7500                                                 |
| Bomb calorimeter can be used to determine the _____ of the coal.                                                                | sulphur content                                      | calorific value                                                    | Nitrogen content                                     | Oxygen content                                                       | sulphur content                                      |
| Coke having higher porosity has                                                                                                 | lower bulk density.                                  | higher strength.                                                   | lower reactivity.                                    | high density                                                         | lower strength.                                      |
| Net calorific value is the gross calorific value less the _____ heat of water in the product of combustion when cooled to 15°C. | sensible                                             | latent                                                             | sensible and latent                                  | evaporation                                                          | latent                                               |
| Fischer-Tropsch method aims at the                                                                                              | gasification of coal.                                | synthesis of gasoline (from water gas).                            | hydrogenation of coal to produce gasoline.           | Carbonization of coal                                                | synthesis of gasoline (from water gas).              |

|                                                                                |                                   |                                                   |                                                                    |                                                           |                                                                    |
|--------------------------------------------------------------------------------|-----------------------------------|---------------------------------------------------|--------------------------------------------------------------------|-----------------------------------------------------------|--------------------------------------------------------------------|
| Water gas constitutes mainly of                                                | CO & H <sub>2</sub>               | CO & N <sub>2</sub>                               | CO <sub>2</sub> & H <sub>2</sub>                                   | CH <sub>4</sub> & H <sub>2</sub>                          | CO & H <sub>2</sub>                                                |
| A good metallurgical coke should have very low                                 | porosity                          | sulphur & phosphorous content                     | fusion point of its ash                                            | hardness & strength                                       | sulphur & phosphorous content                                      |
| The typical rocket consumes fuel on the amount of                              | 8000 kg/s                         | 9000 kg/s                                         | 10000 kg/s                                                         | 11000 kg/s                                                | 10000 kg/s                                                         |
| A coal having higher volatile matter content, has lower                        | smoking tendency on burning.      | coke oven gas yield on carbonisation.             | chance of catching fire during storage in open space.              | ignition temperature.                                     | ignition temperature.                                              |
| Fixed carbon in coal is defined as                                             | that present in volatile matters. | the total quantity of carbon present in the coal. | hundred minus the percentage of volatile matter, ash and moisture. | the one which is present in the residue after combustion. | hundred minus the percentage of volatile matter, ash and moisture. |
| Quantity of coke produced from metallurgical coal may be around _____ percent. | 30                                | 75                                                | 50                                                                 | 95                                                        | 75                                                                 |
| Which of the following is called "blue gas" ?                                  | coke oven gas                     | water gas                                         | natural gas                                                        | producer gas                                              | water gas                                                          |
| The main product of high temperature carbonisation of coal is                  | coke                              | ammonia                                           | tar                                                                | coke oven gas                                             | coke                                                               |
| High temperature carbonisation of coal takes place at _____ °C.                | 2000                              | 1100                                              | 600                                                                | 1600                                                      | 1100                                                               |
| With increases in carbonisation temperature                                    | coke oven gas yield increases.    | tar yield increases.                              | hydrogen percentage in the coke oven gas decreases.                | methane percentage in the coke oven gas increases.        | hydrogen percentage in the coke oven gas decreases.                |
| Main constituent of natural gas is                                             | CH <sub>4</sub> (upto 90%)        | C <sub>2</sub> H <sub>6</sub>                     | C <sub>3</sub> H <sub>8</sub>                                      | H <sub>2</sub>                                            | CH <sub>4</sub> (upto 90%)                                         |

|                                                                                                          |                                                    |                          |                               |                    |                          |
|----------------------------------------------------------------------------------------------------------|----------------------------------------------------|--------------------------|-------------------------------|--------------------|--------------------------|
| Which of the following constituents of a fuel does not contribute to its calorific value on combustion ? | Hydrogen                                           | Sulphur                  | Carbon                        | Nitrogen           | Nitrogen                 |
| 'Fuel' can be defined as a substance which produces heat by                                              | combustion.                                        | condensation             | neturalization                | fusion.            | combustion.              |
| CaCl <sub>2</sub> is used to absorb _____ in the Ultimate analysis                                       | H <sub>2</sub> O                                   | CO <sub>2</sub>          | O <sub>2</sub>                | CO                 | H <sub>2</sub> O         |
| The gas coming out of OttoHoffma's by-product oven is                                                    | Coke oven gas                                      | water gas                | Producer gas                  | Blue gas           | Coke oven gas            |
| Fischer-Tropsch method is used to                                                                        | Crack the bigger hydrocarbon to simpler ydrocarbon | Produce synthetic petrol | To produce metallurgical coke | to reduce knocking | Produce synthetic petrol |
| Highest ranked coal is                                                                                   | Anthracite                                         | Lignite                  | Peat                          | Bitumeaneous coal  | Anthracite               |
| To remove moisture coal is heated to                                                                     | 105-110 C                                          | 925-950 C                | 750-800 C                     | 400-450 C          | 105-110 C                |
| Time taken to remove the moisture in Proximate analysis is                                               | 60min                                              | 7 min                    | 30 min                        | 45 min             | 60min                    |
| To remove volatile mater in coal is heated to                                                            | 105-110 C                                          | 925-950 C                | 750 C                         | 50 C               | 925-950 C                |
| Time taken to remove the volatile mater in Proximate analysis is                                         | 60min                                              | 7 min                    | 30 min                        | 45 min             | 7 min                    |
| _____ is used to remove CO <sub>2</sub>                                                                  | KOH                                                | CaCl <sub>2</sub>        | Cotton                        | KCl                | KOH                      |
| Kjeldkhl's method is used to estimate _____                                                              | Carbon                                             | Hydrogen                 | Nitrogen                      | Sulphur            | Nitrogen                 |
| Temperature maintained in the Otto Hoffman's oven is _____                                               | 500 C                                              | 700 C                    | 1000 C                        | 1500 C             | 1000 C                   |
| Time duration for the manufactuing of metellurgical coke in otto Hoffman's method                        | 11-18 hours                                        | 24-48 hours              | 20-24hours                    | 5-10hours          | 11-18 hours              |
| Crude petrolum contains _____ % of carbon                                                                | 79-87                                              | 10                       | 20-30                         | 50-70              | 79-87                    |

|                                                                                                  |                     |                                  |                                 |                                  |                     |
|--------------------------------------------------------------------------------------------------|---------------------|----------------------------------|---------------------------------|----------------------------------|---------------------|
| Fischer-Tropsch methods is used to produce                                                       | water gas           | Produce gas                      | Synthetic petrol                | Coke                             | Synthetic petrol    |
| Temperature maintained in the Fischer-Tropsch is                                                 | 200-300 °C          | 300-400 °C                       | 100-200 °C                      | 400-500 °C                       | 200-300 °C          |
| Pressure applied in Fischer-tropsch process is                                                   | 1-2 atm             | 5-25 atm                         | 25-100                          | 100-150                          | 5-25 atm            |
| Temperature maintained in the Bergius process is _____ °C                                        | 100                 | 200                              | 300                             | 400                              | 400                 |
| Pressure applied in Bergius process is                                                           | 1-2 atm             | 200-250 atm                      | 50-100                          | 100-150                          | 200-250 atm         |
| Octane Number of n-heptane is _____                                                              | 40                  | 50                               | 0                               | 75                               | 0                   |
| Octane Number of isooctane is _____                                                              | 10                  | 50                               | 70                              | 100                              | 100                 |
| Cetane Number of 2-methyl naphthalene is _____                                                   | 90                  | 35                               | 25                              | 0                                | 0                   |
| Cetane Number of n-hexadecane is _____                                                           | 100                 | 65                               | 75                              | 80                               | 100                 |
| Calorific value of producer gas is _____                                                         | 1000                | 1200                             | 1300                            | 1500                             | 1300                |
| Calorific value of Water gas is _____                                                            | 2800                | 2500                             | 1300                            | 2000                             | 2800                |
| Producer gas consists large % of                                                                 | N <sub>2</sub> & CO | N <sub>2</sub> & CO <sub>2</sub> | CO & CO <sub>2</sub>            | CO & H <sub>2</sub>              | N <sub>2</sub> & CO |
| Blue gas consists large % of                                                                     | CO & H <sub>2</sub> | N <sub>2</sub> & CO <sub>2</sub> | H <sub>2</sub> & N <sub>2</sub> | H <sub>2</sub> & CO <sub>2</sub> | CO & H <sub>2</sub> |
| Which form of energy source yields only water?                                                   | H <sub>2</sub>      | Biogas                           | Methane                         | O <sub>2</sub>                   | H <sub>2</sub>      |
| Which type of rocket fuel provides the best efficiency in terms of energy per mass of reactants? | solid fuel          | hypergolic fuel                  | petroleum fuel                  | cryogenic fuel                   | cryogenic fuel      |
| A fuel cell, in order to produce electricity, burns:                                             | Helium              | Nitrogen                         | Hydrogen                        | Oxygen                           | Hydrogen            |
| Fuel cells are                                                                                   | Carbon cell         | Hydrogen battery                 | Nuclear cell                    | Chromium cell                    | Hydrogen battery    |

|                                                                     |                                                                 |                                                    |                               |                                              |                                                                 |
|---------------------------------------------------------------------|-----------------------------------------------------------------|----------------------------------------------------|-------------------------------|----------------------------------------------|-----------------------------------------------------------------|
| Lignite, bituminous and anthracite are different ranks of           | Nuclear fuel                                                    | Coal                                               | Natural gas                   | Biogas                                       | Coal                                                            |
| Cruid oil is                                                        | Colourless                                                      | Odourless                                          | Smelly yellow to black liquid | Odourless yellow to black liquid             | Smelly yellow to black liquid                                   |
| The typical rocket ejects the burnt gases at speeds of over         | 2000 m/s                                                        | 3000 m/s                                           | 4000 m/s                      | 5000 m/s                                     | 4000 m/s                                                        |
| Thrust obtained by rocket engines is based on                       | Newtons third law                                               | omhs law                                           | boyle's law                   | charles's law                                | Newtons third law                                               |
| Propellents mass fraction will be around                            | 0.8-0.9                                                         | 1.0-1.1                                            | 0.5-0.6                       | 2.1-2.2                                      | 0.8-0.9                                                         |
| The knock in diesel engine occurs due to                            | instantaneous and rapid burning of the first part of the charge | instantaneous auto ignition of last part of charge | reduction of delay period     | slow burning of the first part of the charge | instantaneous and rapid burning of the first part of the charge |
| Ignition quality of diesel fuel oil is expressed by an index called | octane number                                                   | cetane number                                      | calorific value               | compression ratio                            | cetane number                                                   |
| Ignition quality of petrol fuel oil is expressed by an index called | octane number                                                   | cetane number                                      | calorific value               | compression ratio                            | octane number                                                   |

UNIT IV  
CORROSION SCIENCE

| Questions                                                                                          | opt1                                 | opt2                                    | opt3                           | opt4                             | Answer                                  |
|----------------------------------------------------------------------------------------------------|--------------------------------------|-----------------------------------------|--------------------------------|----------------------------------|-----------------------------------------|
| Corrosion is an example of                                                                         | Oxidation                            | Reduction                               | Electrolysis                   | Erosion                          | Oxidation                               |
| Corrosion is a process reverse of _____ of metal.                                                  | Destruction                          | Rusting                                 | Extraction                     | Galvanizing                      | Extraction                              |
| For corrosion of iron to takesplace                                                                | Presence of moisture only            | Presence of moisture & oxygen essential | Hydrogen is required           | A strong acid is necessary       | Presence of moisture & oxygen essential |
| Metal at the top of electromotive series is                                                        | Most stable                          | Least stable                            | Most noble                     | Most active                      | Most active                             |
| During electrochemical corrosion in acidic environment                                             | Oxygen evolution occurs              | Oxygen absorption occurs                | Hydrogen evolution takes place | Hydrogen absorption takes place. | Hydrogen evolution takes place          |
| In electrochemical corrosion                                                                       | Anode undergoes oxidation            | Cathode undergoes oxidation             | Both undergoes oxidation       | None.                            | Anode undergoes oxidation               |
| Non-volatile, film forming constituents of paint is called                                         | Drier                                | Pigment                                 | Thinner                        | Drying oil                       | Drying oil                              |
| The main objective of electroplating is                                                            | To increase the corrosion resistance | To decrease the corrosion resistance    | To increase the corrosion      | To decrease the corrosion        | To increase the corrosion resistance    |
| Aluminium forms                                                                                    | Stable oxide layer                   | Unstable oxide layer                    | Volatile oxide layer           | None.                            | Stable oxide layer                      |
| Dissolution of a solid metal by a liquid metal is a                                                | Oxidation corrosion                  | Corrosion by other gases.               | Liquid metal corrosion         | None.                            | Liquid metal corrosion                  |
| The metals used in sacrificial anodic protection are                                               | Mg, Al, Zn                           | Mg, Au, Pt                              | Mn, At, Zn                     | None.                            | Mg, Al, Zn                              |
| When a buried pipeline is protected from corrosion by connecting two magnesium block, it is called | Impressed voltage protection         | Sacrificial cathodic protection         | Sacrificial anodic protection  | Any of these                     | Sacrificial anodic protection           |

|                                                                                                                     |                                         |                                              |                                                                 |                                                                   |                                                                   |
|---------------------------------------------------------------------------------------------------------------------|-----------------------------------------|----------------------------------------------|-----------------------------------------------------------------|-------------------------------------------------------------------|-------------------------------------------------------------------|
| During wet corrosion                                                                                                | The anodic part undergoes oxidation     | Cathodic part undergoes oxidation            | Anodic part undergoes reduction                                 | Neither Cathodic nor Anodic parts undergo any changes.            | The anodic part undergoes oxidation                               |
|                                                                                                                     |                                         |                                              |                                                                 |                                                                   |                                                                   |
| In electroplating, cathode is                                                                                       | Coat metal                              | Base metal                                   | Noble metal                                                     | None.                                                             | Base metal                                                        |
| Corrosion by HCl can be avoided by the addition of                                                                  | Alkali                                  | Tannin                                       | Lignin                                                          | All of these                                                      | Alkali                                                            |
| Which of the following metals forms stable oxide layer                                                              | Aluminium                               | Gold                                         | Platinum                                                        | Calcium                                                           | Aluminium                                                         |
| Electrochemical corrosion can occur only if                                                                         | Oxygen is present in contact with metal | Air is present in contact with metal         | Liquid medium is in contact with metal                          | None                                                              | Liquid medium is in contact with metal                            |
| Electrode potential of std. hydrogen electrode is,                                                                  | 2                                       | -1                                           | 0                                                               | Highest                                                           | 0                                                                 |
| During galvanic corrosion more noble metal act as                                                                   | Anode                                   | Cathode                                      | Anode as well as cathode                                        | Corroding metal                                                   | Cathode                                                           |
| During corrosion of iron in aqueous solution                                                                        | Corrosion occurred at cathode           | Rust/Corrosion product is deposited at anode | Corrosion occurred at anode and rust is also deposited at anode | Corrosion occurred at anode and rust is also deposited at cathode | Corrosion occurred at anode and rust is also deposited at cathode |
| During oxygen concentration type corrosion, the corrosion                                                           | Occurred at more oxygenated             | Occurred at less oxygenated parts            | Is uniform through out                                          | Occurred at cathodic part                                         | Occurred at less oxygenated parts                                 |
| In acidic environment the electrochemical corrosion occurs with the replacement of H <sup>+</sup> ions by the metal | Iron                                    | Copper                                       | Iron and Copper                                                 | None                                                              | Iron                                                              |

|                                                                                   |                                                     |                                                     |                                        |                                             |                                                     |
|-----------------------------------------------------------------------------------|-----------------------------------------------------|-----------------------------------------------------|----------------------------------------|---------------------------------------------|-----------------------------------------------------|
| The deciding factor in atmospheric corrosion is                                   | Presence of oxygen in air                           | Humidity of air                                     | Presence of gases like SO <sub>2</sub> | Frequency of rain fall                      | Humidity of air                                     |
| The rate of corrosion of iron in atmosphere depends upon                          | The degree of pollution of the atmosphere           | The humidity of atmosphere                          | Frequency of rain fall                 | All of these factors                        | All of these factors                                |
| In waterline corrosion the maximum amount of corrosion takes place                | Along a line just below the level of water meniscus | Along a line just above the level of water meniscus | At the bottom of vessel                | Along a line at the level of water meniscus | Along a line just below the level of water meniscus |
| Galvanizing is the process of coating iron with,                                  | Zinc                                                | Nickel                                              | Copper                                 | Tin                                         | Zinc                                                |
| The following factors plays vital role in corrosion process                       | Temperature                                         | Solute concentration                                | Both                                   | None                                        | Both                                                |
| Anodic coating protects the underlined metal                                      | Due to its higher electrode potential               | Due to its noble character                          | Sacrificially                          | Due to both B And C                         | Sacrificially                                       |
| Food stuff containers should not be                                               | Electroplated                                       | Tinned                                              | Galvanized                             | All of these                                | Galvanized                                          |
| The process of Zinc coating over iron sheets by hot-dipping is called             | Anodizing                                           | Galvanizing                                         | Sheradizing                            | Tinning                                     | Galvanizing                                         |
| Which of the following used as a cathodic protection                              | Cd                                                  | Cu                                                  | Al                                     | Zn                                          | Al                                                  |
| The metals which do not form adherent oxide film on surface are                   | Iron and steel                                      | Nickel and Titanium                                 | Copper and Aluminium                   | Gold and Silver                             | Gold and Silver                                     |
| The corrosion by the mechanism of oxygen absorption can occur if                  | Electrolyte is neither neutral and nor acidic       | Electrolyte is neutral or acidic                    | Electrolyte is neutral or alkaline     | None                                        | Electrolyte is neutral or alkaline                  |
| Which of the following elements added to iron to improve its oxidation resistance | Chromium and aluminum                               | Magnesium                                           | Zinc                                   | Aluminium                                   | Chromium and aluminum                               |

|                                                                                                                        |                                            |                                              |                                                        |                  |                                            |
|------------------------------------------------------------------------------------------------------------------------|--------------------------------------------|----------------------------------------------|--------------------------------------------------------|------------------|--------------------------------------------|
| In the corrosion process by evolution of hydrogen                                                                      | the areas of anodes and cathodes are same  | the anodes have larger area than cathodes    | the cathodes have larger area than anodes              | None             | the anodes have larger area than cathodes  |
| An example of Inorganic inhibitors                                                                                     | Urea                                       | benzotriazole                                | Triazine                                               | Sodium nitrite   | Sodium nitrite                             |
| The drawback of inorganic inhibitors' is                                                                               | they are ineffective in acidic environment | they are ineffective in alkaline environment | before they become active, they have an induction time | None             | they are ineffective in acidic environment |
| Passivity is due to                                                                                                    | Lower EMF                                  | Higher EMF                                   | Oxide film                                             | All              | Oxide film                                 |
| This form of corrosion occurs due to concentration difference in a component                                           | Stress                                     | Inter-granular                               | Galvanic                                               | Uniform          | Inter-granular                             |
| Passivity is not reason for inertness of the following                                                                 | Al                                         | Au                                           | Ti                                                     | Ni               | Au                                         |
| Following equation is related to corrosion rate                                                                        | Faraday's equation                         | Nernst equation                              | Either                                                 | Neither          | Nernst equation                            |
| Difficult to monitor and very dangerous form of corrosion                                                              | Crevice                                    | Galvanic                                     | Stress                                                 | Pitting          | Pitting                                    |
| In order to form a protective oxide layer, the ratio of the volume of oxide formed to that of metal consumed should be | much greater than one                      | greater than one                             | less than one                                          | None             | greater than one                           |
| In the corrosion process by evolution of hydrogen                                                                      | the anodes have larger area than cathodes  | the cathodes have larger area than anodes    | the areas of anodes and cathodes are same              | none             | the anodes have larger area than cathodes  |
| The stainless steels owe their resistance to the presence of                                                           | Manganese                                  | Carbon                                       | Chromium                                               | Sulphur          | Chromium                                   |
| The highest percentage of chromium that can be added to steel is usually                                               | 15                                         | 18                                           | 10                                                     | 25               | 18                                         |
| Volatile oxidation corrosion product of a metal is,                                                                    | FeO                                        | Fe <sub>2</sub> O <sub>3</sub>               | Fe <sub>3</sub> O <sub>4</sub>                         | MoO <sub>3</sub> | MoO <sub>3</sub>                           |

|                                                                                              |                                |                                |                                  |                                                   |                                                   |
|----------------------------------------------------------------------------------------------|--------------------------------|--------------------------------|----------------------------------|---------------------------------------------------|---------------------------------------------------|
| Lower is PH, corrosion is                                                                    | Lower                          | Greater                        | Constant                         | None                                              | Greater                                           |
| Electrochemical corrosion takes place on                                                     | Cathodic area                  | Anodic area                    | Near cathode                     | Near anode                                        | Anodic area                                       |
| Chemical formula of Rust is,                                                                 | FeO                            | Fe <sub>2</sub> O <sub>3</sub> | Fe <sub>3</sub> O <sub>4</sub>   | Fe <sub>2</sub> O <sub>3</sub> .XH <sub>2</sub> O | Fe <sub>2</sub> O <sub>3</sub> .XH <sub>2</sub> O |
| Which of the following gases accelerates rusting of iron?                                    | SO <sub>2</sub>                | NO <sub>2</sub>                | CO <sub>2</sub>                  | All the above                                     | All the above                                     |
| Standard electrode potential of Fe <sup>2+</sup> /Fe is,                                     | + 1.44 V                       | - 1.44 V                       | + 0.44 V                         | - 0.44 V                                          | - 0.44 V                                          |
| Which of the following metal does not resist the corrosion process?                          | Fe                             | Ni                             | Pb                               | Cu                                                | Fe                                                |
| Pitting corrosion is a _____ accelerated attack.                                             | Localized                      | Non- localized                 | Diverse                          | granular                                          | Localized                                         |
| In waterline corrosion highly oxygenated parts act as                                        | Anodic                         | Cathodic                       | Corroded                         | None                                              | Cathodic                                          |
| Paints which are used to restrict corrosion are known as                                     | Antifouling paints             | Anticorrosion paints           | Marine paints                    | Special paints                                    | Anticorrosion paints                              |
| Caustic embrittlement, a type of stress corrosion contains deposition of corrosion products, | Fe <sub>3</sub> O <sub>4</sub> | NaFeO <sub>2</sub>             | Na <sub>2</sub> FeO <sub>2</sub> | K <sub>2</sub> FeO <sub>2</sub>                   | Na <sub>2</sub> FeO <sub>2</sub>                  |
| In galvanic series, a metal high in series is more _____.                                    | Cathodic                       | Anodic                         | Corroded                         | None                                              | Anodic                                            |
| Ratio of volumes of metal oxides to metal is known as                                        | Specific mass ratio            | Specific ratio                 | Volume ratio                     | Specific volume ratio                             | Specific volume ratio                             |
| More active metal used in sacrificial anodic protection method is known as,                  | Sacrificial anode              | Sacrificial cathode            | Active anode                     | Active cathode                                    | Sacrificial anode                                 |
| Identify the metal which is not employed as Sacrificial anode                                | Mg                             | Zn                             | Al                               | Na                                                | Na                                                |
| _____ is the process of coating Fe or steel with a zinc coating                              | Hot dipping                    | Tinning                        | Galvanizing                      | Painting                                          | Galvanizing                                       |
| Zn is more _____ than Fe.                                                                    | Corrosive                      | Electronegative                | Electropositive                  | None                                              | Electropositive                                   |

## UNIT V

## SURFACE CHEMISTRY

| Question                                                                                                          | opt1                                                                           | opt2                                     | opt3                                                               | opt4                                   | Answer                                                                         |
|-------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------|------------------------------------------|--------------------------------------------------------------------|----------------------------------------|--------------------------------------------------------------------------------|
| The Phenomenon of the assimilation of higher                                                                      | adsorption                                                                     | desorption                               | absorption                                                         | sorption                               | adsorption                                                                     |
| The solid on whose surface gas is adsorbed is                                                                     | adsorbent                                                                      | desorption                               | absorption                                                         | sorption                               | adsorbent                                                                      |
| When the concentration of the adsorbate is less on the surface of the adsorbent than in the bulk, it is termed as | positive adsorbtion                                                            | negative adsorbtion                      | positive desorbtion                                                | negative desorbtion                    | negative adsorbtion                                                            |
| Which of the following is true for the variation                                                                  | Adsorption is                                                                  | Adsorption                               | Adsorption                                                         | Adsorption first                       | Adsorption                                                                     |
| Physisorption                                                                                                     | is irreversible in                                                             | has highly                               | has high heat of                                                   | is generally                           | is generally                                                                   |
| Freundlich adsorption isotherm can be                                                                             | $x/m = (k_1 k_2 p) / ($                                                        | $x/m = (kp^{1/2})$                       | $x/m = (k_1 k_2 p)$                                                | $x/m = (1 + K_1 P)$                    | $x/m = (kp^{1/2})$                                                             |
| According to Freundlich's adsorption isotherm when the pressure of the gas is low                                 | the amount of gas adsorbed is directly proportional to the pressure of the gas | the adsorption attains a constant value. | the extent of adsorption does not increase as fast as the pressure | Adsorption is not affected by pressure | the amount of gas adsorbed is directly proportional to the pressure of the gas |
| The extent of adsorption of solutes from                                                                          | is usually                                                                     | is usually grater                        | increases with                                                     | decrease with                          | is usually grater                                                              |
| The process in which both absorption and                                                                          | desorption                                                                     | sorption                                 | adsorbent                                                          | adsorbate                              | sorption                                                                       |
| Chemisorption is called as                                                                                        | activated                                                                      | adsorption                               | negative                                                           | positive                               | activated                                                                      |
| Physisorption is also known as                                                                                    | adsorption                                                                     | vander waals                             | activated                                                          | multilayer                             | vander waals                                                                   |
| Adsorption of gases on the surface of a solid is                                                                  | occlusion                                                                      | collision                                | dissimilation                                                      | digestion                              | occlusion                                                                      |
| The variation of adsorption with pressure at a                                                                    | Chemisorption                                                                  | Physisorption                            | adsorption                                                         | absortiom                              | adsorption                                                                     |
| Langmuir adsorption isotherm is based on the assumption that adsorption is                                        | negative adsorption                                                            | positive adsorption                      | monolayer adsorption                                               | multilayer adsorption                  | monolayer adsorption                                                           |
| In case of chemisorption, the heat of adsorption is                                                               | low                                                                            | high                                     | medium                                                             | moderate                               | high                                                                           |
| In case of physisorption, the heat of adsorption is                                                               | low                                                                            | high                                     | medium                                                             | moderate                               | low                                                                            |
| In the case of physical adsorption, there is                                                                      | Temperature                                                                    | Temperature                              | Pressure                                                           | Concentration                          | Temperature                                                                    |

|                                                                                                                  |                                                                                                     |                                                                                   |                                                                    |                                                         |                                                         |
|------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|--------------------------------------------------------------------|---------------------------------------------------------|---------------------------------------------------------|
| For chemisorptions, which is wrong                                                                               | Surface compounds are formed                                                                        | It requires activation energy                                                     | It forms multimolecular layers on adsorbent                        | Irreversible                                            | It requires activation energy                           |
| The substance on whose surface adsorption takes place is called                                                  | Absorbate                                                                                           | Adsorbent                                                                         | Active substance                                                   | Emulsion                                                | Active substance                                        |
| A type of adsorption in which chemical bonds serve the function of holding gas molecule to the surface is called | Physical adsorption                                                                                 | Absorption                                                                        | Chemical adsorption                                                | Adsorbent                                               | Chemical adsorption                                     |
| Coconut charcoal is used for the adsorption of                                                                   | Gases                                                                                               | Liquids                                                                           | Solids                                                             | Colloids                                                | Liquids                                                 |
| The magnitude of gaseous adsorption does not depend upon                                                         | Temperature                                                                                         | Nature of the gas                                                                 | Pressure                                                           | Amount of the adsorbent                                 | Nature of the gas                                       |
| Palladium metal can take up a large volume of hydrogen. It is an example of                                      | Dissolution                                                                                         | Absorption                                                                        | Adsorption                                                         | Desorption                                              | Adsorption                                              |
| The multilayer adsorption of a gases on solids take place in                                                     | Sols                                                                                                | Chemisorption                                                                     | Physisorption                                                      | Catalyst                                                | Physisorption                                           |
| The solid that takes up gas, vapour or solute from a given solution is called                                    | adsorption                                                                                          | adsorbate                                                                         | adsorbent                                                          | Solvent                                                 | adsorbent                                               |
| Classification of adsorption of gases on solids is based on                                                      | The nature of adsorbent                                                                             | The nature of adsorbate                                                           | The nature of forces                                               | The effect of pressure                                  | The nature of adsorbent                                 |
| The type of forces between solid surface and the adsorbate molecules are                                         | Keesom forces                                                                                       | London forces                                                                     | Coulombic forces                                                   | Vander waals forces                                     | Vander waals forces                                     |
| According to the adsorption theory of catalysis , the speed of the reaction increases because                    | the conc of reactant molecules at the active centres of the catalyst becomes high due to adsorption | in the process of adsorption the activation energy of the molecules becomes large | adsorption produces heat which increases the speed of the reaction | adsorption lowers the activation energy of the reaction | adsorption lowers the activation energy of the reaction |

|                                                                                                                                |                                                            |                                                                      |                                                                   |                                                |                                                                      |
|--------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------|----------------------------------------------------------------------|-------------------------------------------------------------------|------------------------------------------------|----------------------------------------------------------------------|
| At the equilibrium position in the process of adsorption                                                                       | $\Delta H > 0$                                             | $\Delta H = T\Delta S$                                               | $\Delta H > T\Delta S$                                            | $\Delta H < T\Delta S$                         | $\Delta H = T\Delta S$                                               |
| Extent of physisorption of a gas increases with                                                                                | increase in temperature.                                   | decrease in temperature.                                             | decrease in surface area of adsorbent                             | decrease in strength of van der Waals forces   | decrease in temperature.                                             |
| Physical adsorption of a gaseous species may change to chemical adsorption with                                                | decrease in temperature                                    | increase in temperature                                              | increase in surface area of adsorbent                             | decrease in surface area of adsorbent          | increase in temperature                                              |
| In physisorption adsorbent does not show specificity for any particular gas because                                            | involved van der Waals forces are universal                | gases involved behave like ideal gases                               | enthalpy of adsorption is low                                     | it is a reversible process                     | involved van der Waals forces are universal                          |
| Which of the following is an example of absorption?                                                                            | Water on silica gel                                        | Water on calcium chloride                                            | Hydrogen on finely divided nickel                                 | Oxygen on metal surface                        | Water on calcium chloride                                            |
| Freundlich adsorption isotherm is given by the expression which of the following conclusions can be drawn from this expression | When $1/n = 0$ , the adsorption is independent of pressure | When $1/n = 0$ , the adsorption is directly proportional to pressure | When $n = 1$ , $x/m$ vs $p$ graph is a line parallel to $x$ -axis | When $n = 0$ , plot of $x/m$ vs $p$ is a curve | When $1/n = 0$ , the adsorption is directly proportional to pressure |
| Adsorption is always                                                                                                           | Endothermic                                                | Exothermic                                                           | Reversible                                                        | Irreversible                                   | Exothermic                                                           |
| In chemical adsorption, how many layers are adsorbed                                                                           | one                                                        | two                                                                  | multilayer adsorption                                             | zero                                           | one                                                                  |
| In physical adsorption, the gas molecules are held on solid surface by                                                         | Gravitational forces                                       | Chemical forces                                                      | Electrostatic forces                                              | Vander waals forces                            | Vander waals forces                                                  |

|                                                                                                      |                                                                           |                                                                                    |                                                                                                              |                                                                    |                                                         |
|------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------|------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|---------------------------------------------------------|
| Chemisorption                                                                                        | Involves the weak attractive interactions between adsorbent and adsorbate | Decreases with increase of temperature                                             | Involves multilayer formation of adsorbent on adsorbate                                                      | Is irreversible in nature                                          | Is irreversible in nature                               |
| A solid acts as an adsorbent because it has                                                          | A definite shape                                                          | Small pores in it                                                                  | A high lattice energy                                                                                        | Unsaturated Valencies                                              | Unsaturated Valencies                                   |
| What will be the effect of increase in temperature on physical adsorption                            | It will decrease                                                          | It will increase                                                                   | First increase then decrease                                                                                 | First decrease then increase                                       | It will decrease                                        |
| If the adsorbate is held on a surface by weak Vander Waal's forces, the adsorption process is called | Physical adsorption                                                       | Chemical adsorption                                                                | Enthalpy of adsorption                                                                                       | Heat of adsorption                                                 | Physical adsorption                                     |
| According to Langmuir adsorption isotherm, the amount of gas adsorbed at very high pressures         | Reaches a constant limiting value                                         | Goes on decreasing with pressure                                                   | Goes on increasing with pressure                                                                             | Increases first and decreases later with pressure                  | Reaches a constant limiting value                       |
| According to the adsorption theory of catalysis, the speed of the reaction increases because         | Adsorption lowers the activation energy of the reaction                   | In the process of adsorption, the activation energy of the molecules becomes large | The concentration of reactant molecules at the active centres of the catalyst becomes high due to adsorption | Adsorption produces heat which increases the speed of the reaction | Adsorption lowers the activation energy of the reaction |
| In Freundlich Adsorption isotherm, the value of $1/n$ is                                             | 1 in case of physical adsorption                                          | 1 in case of chemisorption                                                         | Between 0 and 1 in all cases                                                                                 | Between 2 and 4 in all cases                                       | Between 0 and 1 in all cases                            |
| Which of the following statements is incorrect                                                       | Enthalpy of                                                               | It occurs                                                                          | It occurs                                                                                                    | Under high                                                         | Enthalpy of                                             |

|                                                                                                                       |                                                                                                 |                                                                                                                  |                                                                                            |                                                                                                        |                                                                                              |
|-----------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------|
| Rate of physical adsorption increase with                                                                             | increase in temperature                                                                         | decrease in temperature                                                                                          | decrease in pressure                                                                       | decrease in surface area                                                                               | decrease in temperature                                                                      |
| The Langmuir adsorption isotherm is deduced                                                                           | The adsorbed                                                                                    | The adsorption                                                                                                   | The adsorption                                                                             | The heat of                                                                                            | The adsorption                                                                               |
| A plot of $\log x/m$ versus $\log p$ for the adsorption of a gas on a solid gives a straight line with slope equal to | n                                                                                               | 1/n                                                                                                              | $\log K$                                                                                   | - $\log K$                                                                                             | 1/n                                                                                          |
| In Langmuir's model of adsorption of a gas on a solid surface                                                         | the adsorption at a single site on the surface may involve multiple molecules at the same time. | the mass of gas striking a given area of surface is proportional to the pressure of the gas.                     | the mass of gas striking a given area of surface is independent of the pressure of the gas | the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered | the mass of gas striking a given area of surface is proportional to the pressure of the gas. |
| The extent of adsorption of a gas on a solid depends on                                                               | temperature of the gas                                                                          | adsorption of the gas                                                                                            | absorbption of the gas                                                                     | multilayer adsorption of gas                                                                           | temperature of the gas                                                                       |
| Identify the gas which is readily adsorbed by activated charcoal                                                      | Nitrogen                                                                                        | Oxygen                                                                                                           | Hydrogen                                                                                   | sulphurdioxide                                                                                         | sulphurdioxide                                                                               |
| According to adsorption theory of catalysis, the speed of the reaction increases because                              | adsorption produces heat which increases the speed of the reaction                              | the concentration of the reactant molecules at the active centres of the catalyst becomes high due to adsorption | in the process of adsorption, the activation energy of the molecules becomes large         | adsorption lowers the activation energy of the reaction                                                | adsorption lowers the activation energy of the reaction                                      |

|                                                                                                                                         |                                   |                              |                                                   |                                                      |                                                   |
|-----------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------|------------------------------|---------------------------------------------------|------------------------------------------------------|---------------------------------------------------|
| Which of the following characteristics is not correct for physical adsorption?                                                          | Adsorption on solid is reversible | Adsorption is spontaneous.   | Adsorption increases with increase in temperature | Both enthalpy and entropy of adsorption are negative | Adsorption increases with increase in temperature |
| The adsorption of gases on metal surfaces is called                                                                                     | occlusion                         | catalysis                    | collision                                         | dissimilation                                        | occlusion                                         |
| Physical adsorption is a                                                                                                                | reversible process                | irreversible process         | exothermic process                                | sometimes exothermic, sometimes endothermic process  | reversible process                                |
| Multi-molecular layers are formed in                                                                                                    | absorption                        | physical adsorption          | chemisorption                                     | reversible adsorption                                | chemisorption                                     |
| The relationship between equilibrium pressure of a gas and its amount adsorbed on the solid adsorbent at constant temperature is called | chemisorption                     | adsorption isobars           | adsorption isotherms                              | Physisorption                                        | adsorption isotherms                              |
| Freundlich isotherms is not applicable at                                                                                               | high pressure                     | low pressure                 | 273 K                                             | room temperature                                     | high pressure                                     |
| Adsorbate is that substance                                                                                                             | which concentrates on the surface | where adsorption takes place | which evaporates from the surface of metals       | where absorption takes place                         | which concentrates on the surface                 |
| Froth flotation process for the concentration of sulphide ore makes use of the process of                                               | adsorption                        | heterogeneous catalysis      | absorption                                        | equilibrium                                          | adsorption                                        |
| In physical adsorption the gas molecules are held to the solid surface by                                                               | hydrogen bond                     | sigma bond                   | pi bond                                           | van der Waal's forces                                | van der Waal's forces                             |
| The adsorption of hydrogen on charcoal is                                                                                               | physical adsorption               | chemical adsorption          | sorption                                          | desorption                                           | physical adsorption                               |

|                                                                                                                  |                                             |                                             |                                                      |                                                      |                                             |
|------------------------------------------------------------------------------------------------------------------|---------------------------------------------|---------------------------------------------|------------------------------------------------------|------------------------------------------------------|---------------------------------------------|
| Adsorption takes place with                                                                                      | decrease in enthalpy of the system          | increase in enthalpy of the system          | no change in enthalpy of the system                  | equilibrium at enthalpy of the system                | decrease in enthalpy of the system          |
| The ion-exchange resins are the compounds with                                                                   | high molecular masses                       | high surface tension                        | low viscosities                                      | high surface area                                    | high surface tension                        |
| Hard water is made soft by passing it through a column packed with high polymer resin. This process makes use of | cation-exchange                             | chromatographic analysis                    | adsorption of negatively charged ions                | heterogeneous catalysis                              | cation-exchange                             |
| Which of the following is not an application of adsorption?                                                      | gas masks                                   | heterogeneous catalysis                     | froth flotation process                              | softening of water by boiling                        | softening of water by boiling               |
| The process represented by the equation $R' H^+ + Na^+ \rightarrow R' Na^+ + H^+$ is                             | cation exchange                             | anion exchange                              | resin exchange                                       | chromatographic analysis                             | cation exchange                             |
| An anion exchange process is represented by                                                                      | $R'H^+ + Na^+ \leftrightarrow R'Na^+ + H^+$ | $R'OH + Cl^- \leftrightarrow R'Cl^- + OH^-$ | $2R Na^+ + Ca^{2+} \leftrightarrow R_2Ca^{2+} + 2Na$ | $2R Na^+ + Cl^{2-} \leftrightarrow R_2Cl^{2-} + 2Na$ | $R'OH + Cl^- \leftrightarrow R'Cl^- + OH^-$ |