SEMESTER I, II

17BECH103, 17BECH203 ENGINEERING CHEMISTRY 3 0 0 3

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 - Fe^{2+}vs dichromate) –Electrolytic conductance-application (conductometric titration)-Batteries-Primary batteries-Leclanche cell- Secondary batteries- Lead acid battery. An introduction to Fuel Cell-H_2-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.

Total: 45

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., 3rd Reprint NewDelhi.	2013
2.	Kuriakose. J.C. and Rajaram	Chemistry in Engineering and Technology. Vol. I & II 5th 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

KARPAGAM ACADEMY OF HIGHER EDUCATION
(*Established under section 3 of the UGC Act 1956*)
COIMBATORE – 641021
ENGINEERING CHEMISTRY
17BECH203 / 17BTCH203
LECTURE PLAN

TOTAL HOURS: 45

UNIT I - WATER TECHNOLOGY

HOURS REQUIRED: 9

S.No	Topics	Hours
1.	Introduction- Sources-Characteristics – Specification for drinking water, BIS &WHO	1
2.	Alkalinity – types of alkalinity and determination	1
3.	Hardness – Types and estimation by EDTA method Problems based on EDTA method	1
4.	Domestic water treatment- Disinfection methods (Chlorination, Ozonation. UV treatment)	1
5.	Boiler feed water – Requirements –boiler troubles	1
6.	Boiler corrosion	1
7.	Internal conditioning (Phosphate, Calgon and Carbonate conditioning methods)	1
8.	External conditioning – Demineralization process	1
9.	Desalination and Reverse osmosis	1

UNIT II - ELECTROCHEMISTRY AND STORAGE DEVICES

HOURS REQUIRED: 9

S.No	Topics	Hours
1.	Introduction , Electrolytic conductance-application (conductometric titration)	
2.	Electrochemical cells – reversible and irreversible cells,EMF – measurement of emf,	1
3.	Single electrode potential, Nernst equation	1
4.	Reference electrodes –Standard Hydrogen electrode , Calomel electrode	1
5.	Ion selective electrode – glass electrode and measurement of pH	1
6.	Electrochemical series – significance	1
7.	Potentiometric titrations (redox - Fe^{2+} vs dichromate)	1
8.	Batteries- Primary batteries-Leclanche cell- Secondary batteries- Lead acid battery	1
9.	Introduction to Fuel Cell- H_2-O_2 Fuel Cell	1

UNIT III - FUELS AND COMBUSTION

HOURS REQUIRED: 9

S.No	Topics	Hours
1.	Introduction –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.	Knocking –- Octane number and Cetane number	1
7.	Gaseous fuels – Water gas, Producer gas	1
8.	Combustion of fuel-Introduction-GCV-NCV, problems	1
9.	Flue gas analysis	1

UNIT IV - CORROSION SCIENCE

HOURS REQUIRED: 9

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.	Protective coatings - Paints - Constituents and functions	1
7.	Metallic coatings – Electroplating-Cu over Fe	1
8.	Electroless plating (Ni)	1
9.	Surface conversion coating- Hot dipping - Anodizing of Al	1

UNIT V - SURFACE CHEMISTRY AND PHASE RULE

HOURS REQUIRED: 9

S.No	Topics	Hours
1.	Introduction-Adsorption-Types, adsorption of gases on solids	1
2.	Aadsorption of solutes from solutions	1
3.	Adsorption isotherms-Freundlich adsorption isotherm	1
4.	Langmuir adsorption isotherm	1
5.	Role of adsorbents in industries-catalysis	1
6.	Role of adsorbents in industries- water softening	1
7.	Phase Rule: Definition -Phase diagrams	1
8.	One component water system	1
9.	Two component Ag-Pb system.	1

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

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2.	Kuriakose. J.C. and Rajaram	Chemistry in Engineering and Technology. Vol. I & II 5th 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

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1. http://www.studynotes.ie/leaving-cert/chemistry/
2. http://www.rejinpaul.com/2011/04/engineering-chemistry-ii-second.html
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5. http://www.chem.qmul.ac.uk/surfaces/sec

STAFF HoD

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.

$$2C_{17}H_{35}COONa + Ca^{2+} \longrightarrow (C_{17}H_{35}COO)_2Ca + 2Na+$$

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 Ca^{2+} , Mg^{2+} and SO_4^{2-} , Cl^- , CO_3^{2-}, HCO_3^- ions and their salts.

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2.Test for hardness:

a) Eriochrome Black – T indicator gives red colour in hard water.

b) With soap, hard water gives a scummy precipitate.

$$2C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca + 2NaCl$$

(Sodium stearate) (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.

$Ca(HCO_3)_2$ (On heating) $\xrightarrow{\quad}$ $CaCO_3 + H_2O + CO_2$

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.

$CaCl_2 + Na_2CO_3 \xrightarrow{\quad} CaCO_3 + 2NaCl$ (Lime soda process)

$CaSO_4 + Na_2Ze$ (Zeolite) $\xrightarrow{\quad}$ $CaZe + Na_2SO_4$ (Zeolite process)

4. Units of hardness:

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

1 ppm – 1 part by weight of $CaCO_3$ equivalent hardness / 10^6 parts of water

1 mg/L – 1mg of $CaCO_3$ / 1 Lr of water

Clarkes Degree – ^{0}Cl-1 part of $CaCO_3$ equivalent hardness / 70,000 parts of water

1 Degree French – ^{0}F – 1 part of $CaCO_3$ equivalent hardness / 10^5 parts of water

Therefore , 1ppm = 1mg/L = 0.07 ^{0}Cl = 0.1^{0}F

5.$CaCO_3$ equivalence:

Hardness is expressed in $CaCO_3$ equivalence. Because,

i) It is the most insoluble and easily precipitatable 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.

$2C_{17}H_{35}CooNa + CaCl_2 \xrightarrow{\quad} (C_{17}H_{35}COO)_2Ca + 2NaCl$

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 (CO3), bicarbonate (HCO3) and hydroxide (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 pH >8.3 and hydroxide at pH>10.

Definition:

The acid neutralizing capacity is known as alkalinity. It is due to OH^{-}, CO_3^{2-}, HCO_3^{-}.

1.Aim:

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

2.Chemicals required:

NaOH, HCl , Sample water, Phenolphthalein, Methyl orange

3.Principle:

There are five types of alkalinity.

i) OH^{-} only ii) CO_3^{2-} only iii) HCO_3^{-}.only iv) OH^{-} and CO_3^{2-} v) $CO_3^{2-}$and HCO_3^{-}.

The other combinations are not possible. Because,

$OH^{-} + HCO_3^{-}$. $\longrightarrow$ $H_2O + CO_3^{2-}$, it again form carbonate.

The possible reactions are

1. $OH^{-} + H^{+} \longrightarrow H_2O$
2. $CO_3^{2-} + H^{+} \longrightarrow HCO_3^{-}$ (Half neutralization of carbonate)

3. $HCO_3^- + H^+ \longrightarrow H_2O + CO_2$

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	OH^-	CO_3^{2--}.	HCO_3^-.
1	P=0	Nil	Nil	M
2	P=M	P=M	Nil	Nil
3	P = ½ M	Nil	2P	Nil
4	P > ½ M	2P – M	2(M – P)	Nil
5	P < ½ M	Nil	2P	(M – 2P)

5. Short Procedure

S.No	Content	Titration-I Standardisation of HCl	Titration-II Alkalinity estimation
1	Burette	HCl acid	Standard HCl
2	Pipette(20 ml)	Standard NaOH	Water sample
3	Indicator	Phenolphthalein	i)Phenolphthalein ii) Methyl orange
4	Endpoint	Disappearance of pink colour	i)Disappearance of pink colour 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 OH^- and CO_3^{2-} alkalinity)

a)Amount of OH^-

Volume of HCl (V_1) = (2P – M) ml
Strength of HCl (N_1) = From step 1
Volume of water (V_2) = 20 ml
Strength of OH^- in water (N_2)= ?
As per volumetric principle, $V_1N_1 = V_2N_2$
$N_2 = V_1N_1 / V_2$
Amount of OH^- in water = N_2 X 50 X 1000 ppm
(we are multiplying by 50 as it is eq.wt of $CaCO_3$.
We are multiplying by 1000 to convert it for gram to milligram)

b)Amount of CO_3^{2-}

Volume of HCl (V_1) = 2(M-P) ml
Strength of HCl (N_1) = From step 1
Volume of water (V_2) = 20 ml
Strength of CO_3^{2-} in water (N_2)= ?
As per volumetric principle, $V_1N_1 = V_2N_2$
$N_2 = V_1N_1 / V_2$
Amount of CO_3^{2-}in water = N_2 X 50 X 1000 ppm
(we are multiplying by 50 as it is eq.wt of $CaCO_3$.
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.

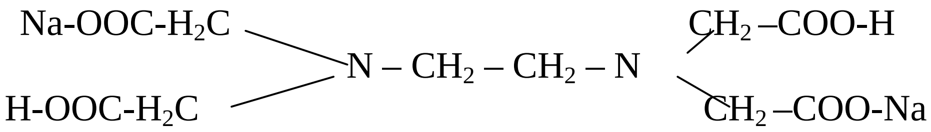
2. Chemicals required:

a) Standard hard water – 1g $CaCO_3$ + 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:



$$\begin{array}{lcl} Na\text{-}OOC\text{-}H_2C & & CH_2\text{–}COO\text{-}H \\ & N - CH_2 - CH_2 - N & \\ H\text{-}OOC\text{-}H_2C & & CH_2\text{–}COO\text{-}Na \end{array}$$

- 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 P^H of 8- 10 using ammonia buffer.

-Ca^{2+} / 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.

$$\underset{\text{(Wine red/unstable)}}{[Ca / Mg\text{–}EBT] + EDTA} \longrightarrow \underset{\text{(Stable)}}{[Ca / Mg\text{–}EDTA]} + \underset{\text{(Steel blue)}}{EBT}$$

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

4. Short Procedure:

S.No	Content	Titration-I Standardisation of EDTA	Titration-II Total Hardness	Titration-III permanent Hardness
1	Burette	EDTA	Standard EDTA	Standard EDTA
2	Pipette(20 ml)	Std. Hardwater	Sample water	Boiled water
3	Additional solution	10ml of NH_3 buffer	10ml of NH_3 buffer	10ml of NH_3 buffer
4	Indicator	EBT	EBT	EBT
5	Endpoint	Wine red to steel blue	Wine red to steel blue	Wine red to steel blue
6	Volume	V_1	V_2	V_3

5. Calculation:

Step1 – Standardisation of EDTA

1 ml of Std. Hard water = 1 mg of $CaCO_3$ (Given)

So, 20 ml of Std. Hard water = 20 mg of $CaCO_3$

V_1 ml of EDTA is required for = 20 mg of $CaCO_3$

Therefore, $\boxed{\text{1ml of EDTA} = 20 / V_1 \text{ mg of } CaCO_3}$

Step 2: Finding Total hardness:

20ml of sample water required = V_2 ml of EDTA

$$= \frac{V_2 \times 20}{V_1} \text{ mg of } CaCO_3$$

Therefore, 1000ml of sample requires = $\frac{V_2 \times 20}{V_1} \times \frac{1000}{20}$ mg of $CaCO_3$

Hence, total hardness = $\frac{V_2 \times 1000}{V_1}$ ppm

Step 3: Finding Permanent hardness:

20ml of boiled water required = V_3 ml of EDTA

$$= \frac{V_3 \times 20}{V_1} \text{ mg of } CaCO_3$$

Therefore, 1000ml of boiled sample requires = $\frac{V_3 \times 20}{V_1} \times \frac{1000}{20}$ mg of $CaCO_3$

Hence, permanent hardness = $\frac{V_3 \times 1000}{V_1}$ ppm

Step 4 : Temporary hardness = Total hardness – 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 bacterias is knows 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 miuntes 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.

$O_3 \longrightarrow O_2 + [O]$, this nascent oxygen kills bacteria.

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.

$Cl_2 + NH_3 \longrightarrow ClNH_2$ (Chloramine)+ HCl

c) Bleaching powder ($CaOCl_2$) reacts with water and forms hypochlorous acid which kills bacteria. Generally, 1kg powder is used for 1000 kilolitres of water.

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

(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, NH3, 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, H_2S , Fe salts)

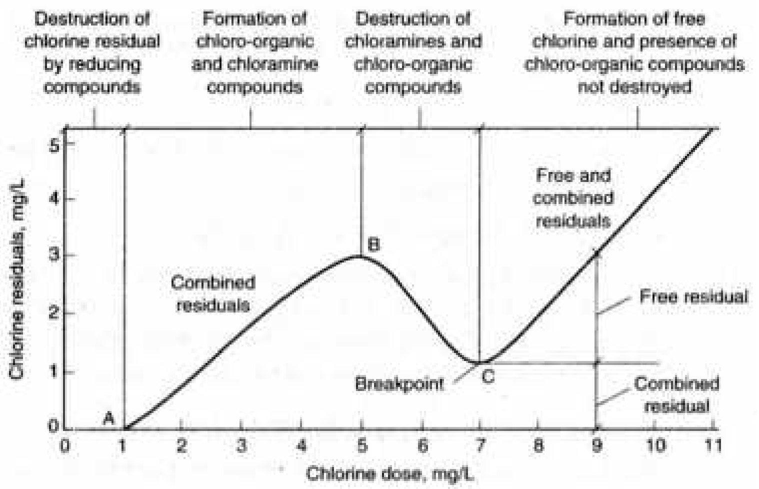
1. When we add chlorine, first it kills bacteria and oxidizes some inorganic impurities.
2. The added chlorine is completely consumed. (a).
3. Further addition of chlorine is used to combine with ammonia to form chloramines compounds. So, the residual chlorine content is increased upto (b).

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:



Chlorine reacts with reduced materials (Fe^{2+}, Mn^{2+}, H_2S, organics, NH_3, etc.)

Breakpoint Chlorination

Advantages of break point chlorination: (Significance)

i)It is used to remove Bacteria , Ammonia ,Organic impurity (sewage) ,Inorganic salt impurities (Effluents, H_2S , 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”.

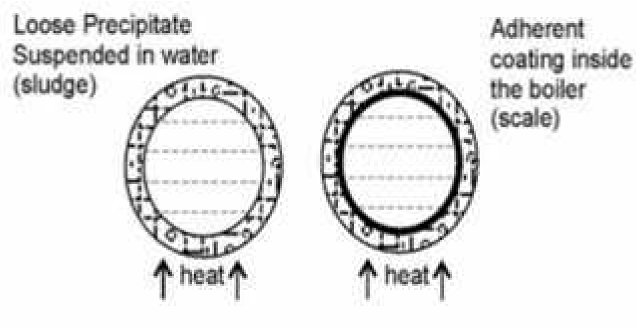
S.No	Requirements for boiler water	If not, it will cause
1	Free from hardness causing salts	Sludge and scale
2	Free from oil and greases	Foaming
3	Free from dissolved salts, suspended impurities	Caustic embrittlement
4	Free from dissolved gases, suspended salts	Boiler corrosion

1.Sludge and scale:

If the water contains hardness causing salts like $MgSO_4$, $MgCl_2$,$CaSO_4$, $Ca(HCO_3)_2$
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 $MgSO_4$, $MgCl_2$	Due to salts like $CaSO_4$, $Ca(HCO_3)_2$
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:

a) Improper design of boiler
b) High water level
c) High velocity of steam
d) 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 Na_2CO_3 which is added during internal treatment.

$$Na_2CO_3 + H_2O \longrightarrow 2\ NaOH + CO_2$$

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.

$$\underset{\text{(Insoluble)}}{Fe + 2\ NaOH} \longrightarrow \underset{\text{(Soluble)}}{Na_2FeO_2} + H_2 \uparrow$$

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 CO_2 iii) Dissolved salts like $MgCl_2$

<u>i)Corrosion Due to dissolved oxygen</u>:

Dissolved oxygen in presence of water, causes corrosion.

$$4Fe + 6\ H_2O + 3O_2 \longrightarrow 4\ Fe\ (OH)_3\ \text{(Rust)}$$

Prevention from oxygen*:*

a) Chemical method -

Adding Sodium Sulphite: $2\ Na_2SO_3 + O_2 \longrightarrow 2\ Na_2SO_4$

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

Adding Hydrazine: $N_2H_4 + O_2 \longrightarrow N_2 + 2\,H_2O$
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 vaccum 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 CO_2 . CO_2 dissolves in water to form carbonic acid which corrodes the boiler metal.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$
$$H_2O + CO_2 \longrightarrow H_2CO_3$$

Prevention from CO_2

1. Chemical method: By adding calculated amount of ammonium hydroxide
   $2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$
2. Mechanical deaeration method (similar to oxygen method)

iii)Corrosion due to Dissolved salts like $MgCl_2$

Dissolved salts like $MgCl_2$ cause acid formation. This will be prevented by alkali neutralisation.

$$MgCl_2 + 2\,H_2O \longrightarrow Mg(OH)_2 + 2\,HCl \text{ (Corrosive acid)}$$

Neutralisation: $HCl + NaOH \longrightarrow NaCl + H_2O$

SOFTENING OR CONDITIONING METHOD

Water used for industrial purposes should be free from hardness producing substances, suspended impurities and dissolves gases etc. The processing of remiving 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 $CaSO_4$ are converted to easlity removable $CaCO_3$. But sometimes it produces NaOH, CO_2 and hence Carbonic acid. So it is less preferred.

$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$

b)Phosphate conditioning: Used for high pressure boiler. No risk of CO_2 liberation.

$3CaSO_4 + 2\,Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 3\,Na_2SO_4$

Three types of Phosphate salts are used:

Na_3PO_4 – Tri sodium Phosphate – Used for highly acidic water

Na_2HPO_4 – Disodium hydrogen Phosphate – Used for slightly acidic water

NaH_2PO_4 – Sodium di hydrogen phosphate – Used for alkaline water

c) Calgon conditioning:

Calgon is the trade name of sodium hexa meta phosphate- $Na_2[Na_4(PO_3)_6]$.

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

$2CaSO_4 + Na_2[Na_4(PO_3)_6] \longrightarrow Na_2[Ca_2(PO_3)_6] + 2\,Na_2SO_4$

EXTERNAL TREATMENT METHOD:

Ion exchange method (Demineralisation)

Working:

1. Here all the cations and anions are completely removed . It uses twp cylinders pf cation exchange cylinder and anion exchange cylinder filled with resins.
2. Resins are linear, insoluble, cross linked , organic polyers. There are 2 types.
   a)Cation exchange resins – RH_2 (e.g) Sulphonated coals , RSO_3H
   b)Anion exchange resins . $R'(OH)_2$ (e.g)Urea-formaldehyde resin,Amines $R\text{-}NH_2$

3. The water is fed into cylinder –I where all the cations are replaced by RH_2 Resins.

$$RH_2 + CaCl_2 \longrightarrow RCa + 2\,HCl$$

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

$$R'(OH)_2 + 2\,HCl \longrightarrow R'Cl_2 + 2H_2O$$

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 H^+ orOH^- ions to exchange the unwanted ions. So, they have to be regenerated.

Cation resins are regenerated by HCl and anion resins by NaOH.

$$RCa + 2\,HCl \longrightarrow RH_2 + CaCl_2$$

$$R'Cl_2 + 2NaOH \longrightarrow R'(OH)_2 + 2NaCl$$

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) Fe, Mn cannot be removed as they form complexes with resins
iii) Cannot be used for turbid water as they clog the resins.

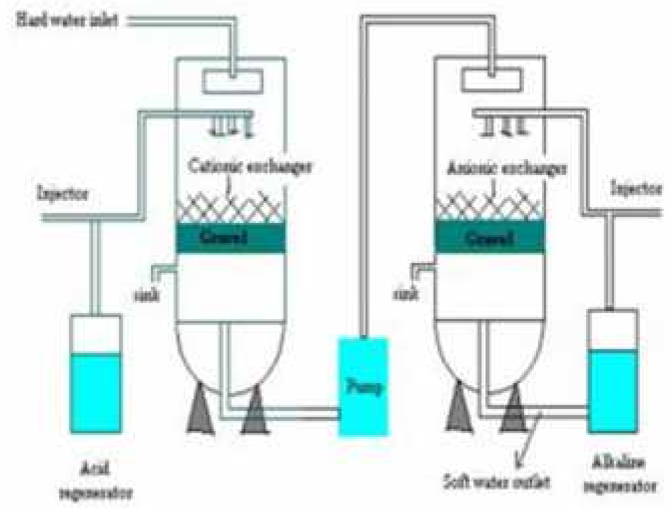


Fig.4.10. Demineralization process

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.

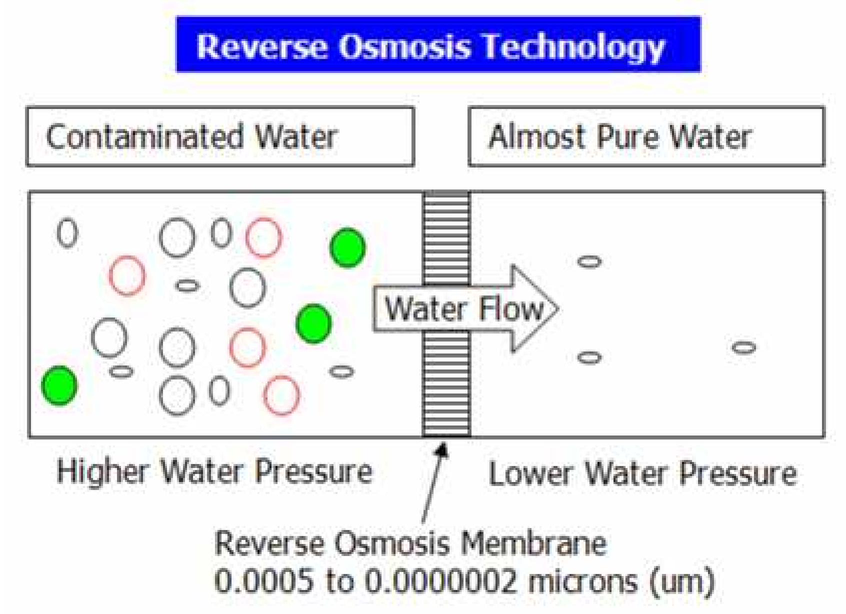
3.But when we apply an excess and opposite Hydrostatic pressure to overcome the osmotic pressure, then higher concentrated solvent will flow to the lower one. This is known as reverse osmosis.

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 madeup 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: CH_3COOH , NH_4OH , $CaCO_3$ **,** *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 □Zn^{2+}

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-}$$

Reduction

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

$$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu\ (s)$$

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,

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-}\ \text{(oxidation)}$$

$$Cu^{2+}_{(aq)} + 2e^{-} \longrightarrow Cu_{(s)}\ \text{(reduction)}$$

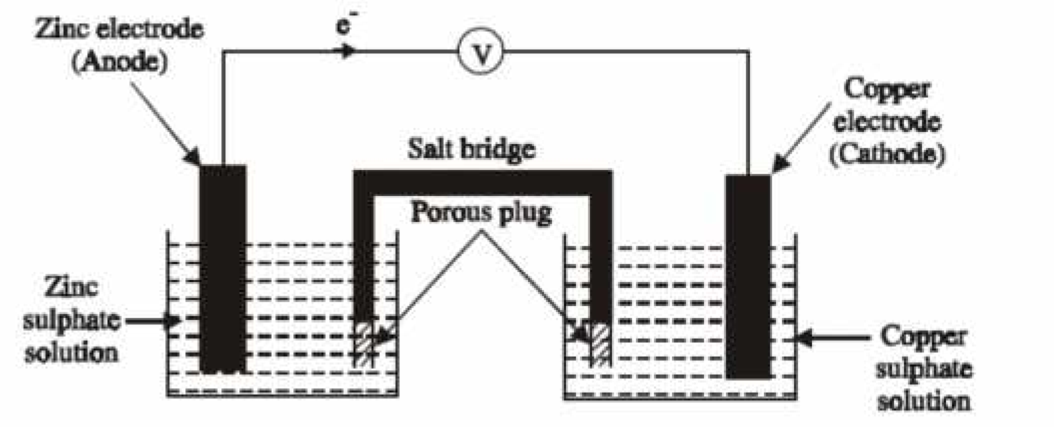
$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}\ \text{(redox)}$$

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 ZnSO4 solution and a copper electrode dipped in 1MCuSO4 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.

$Zn \longrightarrow Zn^{2+} + 2e^-$ (at anode)
$Cu^{2+} + 2e^- \longrightarrow Cu$ (at cathode)
$Cu^{2+} + Zn$ ----- > $Zn^{2+} + Cu$ (net cell reaction)

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 NH4NO3 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 reproductive.

(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) Zn/Zn$^{2+ (}$or) Zn/ZnSO4 (or) Zn; Zn^{2+}

(b) Standard hydrogen electrode

Pt, H_2 (1 atm); H^+ (1 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:

Cu$^{2+/}$Cu (or) $CuSO_4$/Cu (or) Cu^{2+}; 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.

Zn / $ZnSO_4$ (1 M) // $CuSO_4$ (1 M) / Cu
(or) Zn / Zn$^{2+ (}$1 M) // Cu^{2+} (1 M) / Cu
(or) Zn; Zn^{2+} (1 M) // Cu^{2+} (1 M); Cu

ELECTRODE POTENTIAL

Origin of Electrode Potential

A metal (M) consists of metal ions Mn+) with valence electrons. When the metal (M) is placed in a solution of its mown salt, any one of the following reactions will occur.

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

$$M \longrightarrow M^{n+} + ne^- \text{ (oxidation)}$$

(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 ZnSO4 solution***

When Zn electrode is dipped in ZnSO4 solution, Zn goes into the solution as Zn2□ ions due to oxidation.

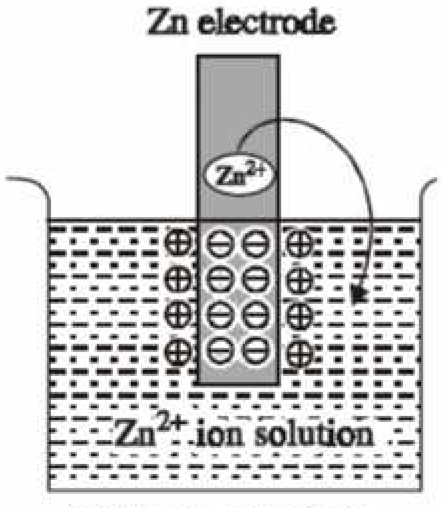
$$Zn \longrightarrow Zn^{2+} + 2e^-$$

Now, the Zn electrode attains a negative charge, due to the accumulation of valence electrons on themetal. 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.

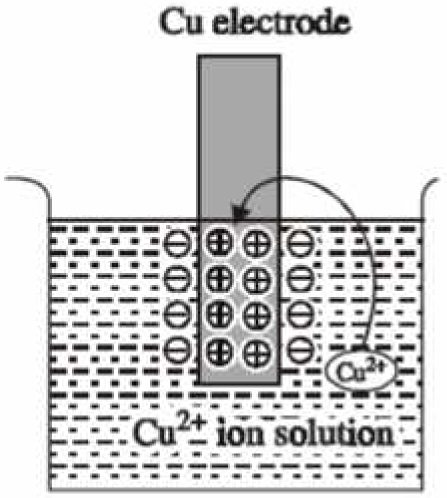
Example -2 Cu electrode dipped in CuSO4 solution

When Cu electrode is dipped in CuSO4 solution, Cu2□ ions from the solution deposit over the metal due to reduction.

$Cu^{2+} + 2e^{-}$ –––––> Cu



(a) Zn electrode in $ZnSO_4$ solution



(b) Cu electrode in $CuSO_4$ solution

Now, the Cu electrode attains a positive charge, due to the accumulation of Cu2□ 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.

$$Zn \text{ –––––> } Zn^{2+} + 2e^-$$

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

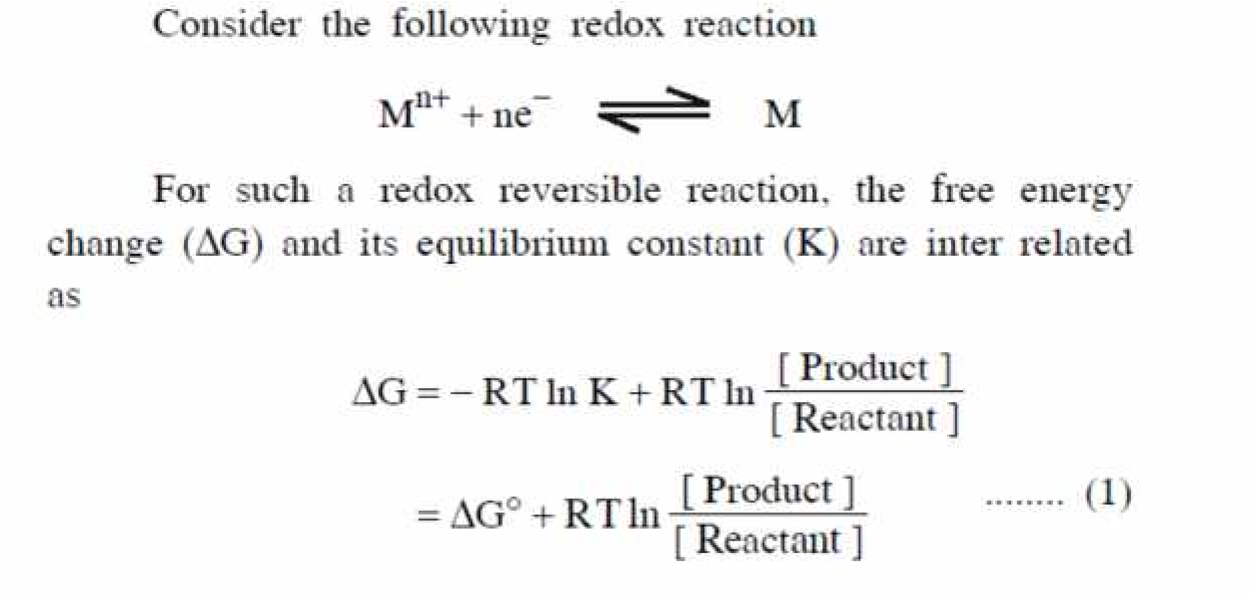
Reduction potential

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

$$Cu^{2+} + 2e^- \text{ –––––> } Cu$$

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

NERNST EQUATION FOR ELECTRODE POTENTIAL



Consider the following redox reaction

$$M^{n+} + ne^- \rightleftharpoons M$$

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

$$\Delta G = -RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$= \Delta G^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \text{........ (1)}$$

where,

ΔG° = 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

$$-\Delta G = nEF$$

(or)

$$-\Delta G^\circ = nE^\circ F \qquad \ldots\ldots\ldots (2)$$

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

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

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

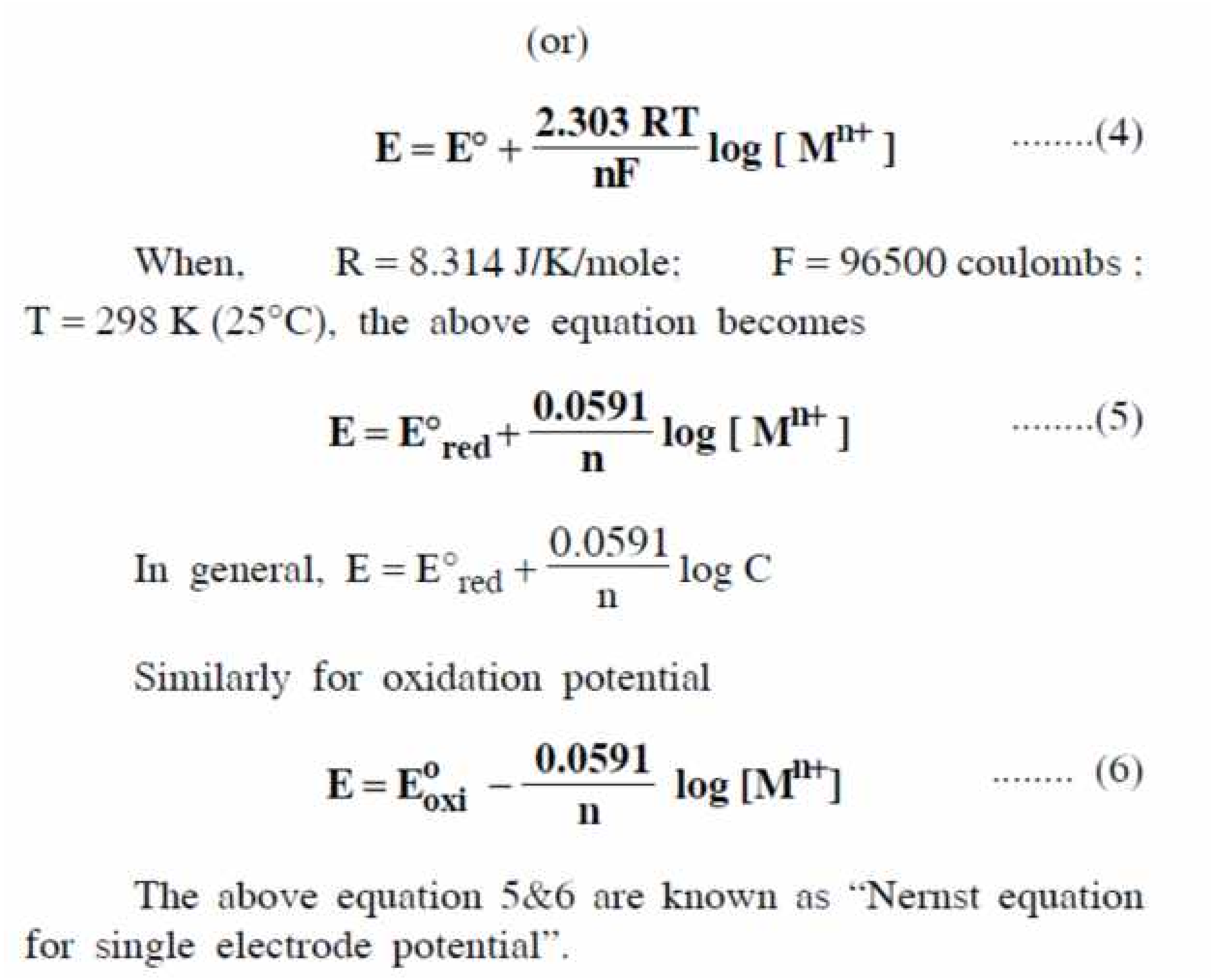
[$\because$ the activity of solid metal [M] = 1]

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

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)

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

When, R = 8.314 J/K/mole: F = 96500 coulombs : T = 298 K (25°C), the above equation becomes

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

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

Similarly for oxidation potential

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

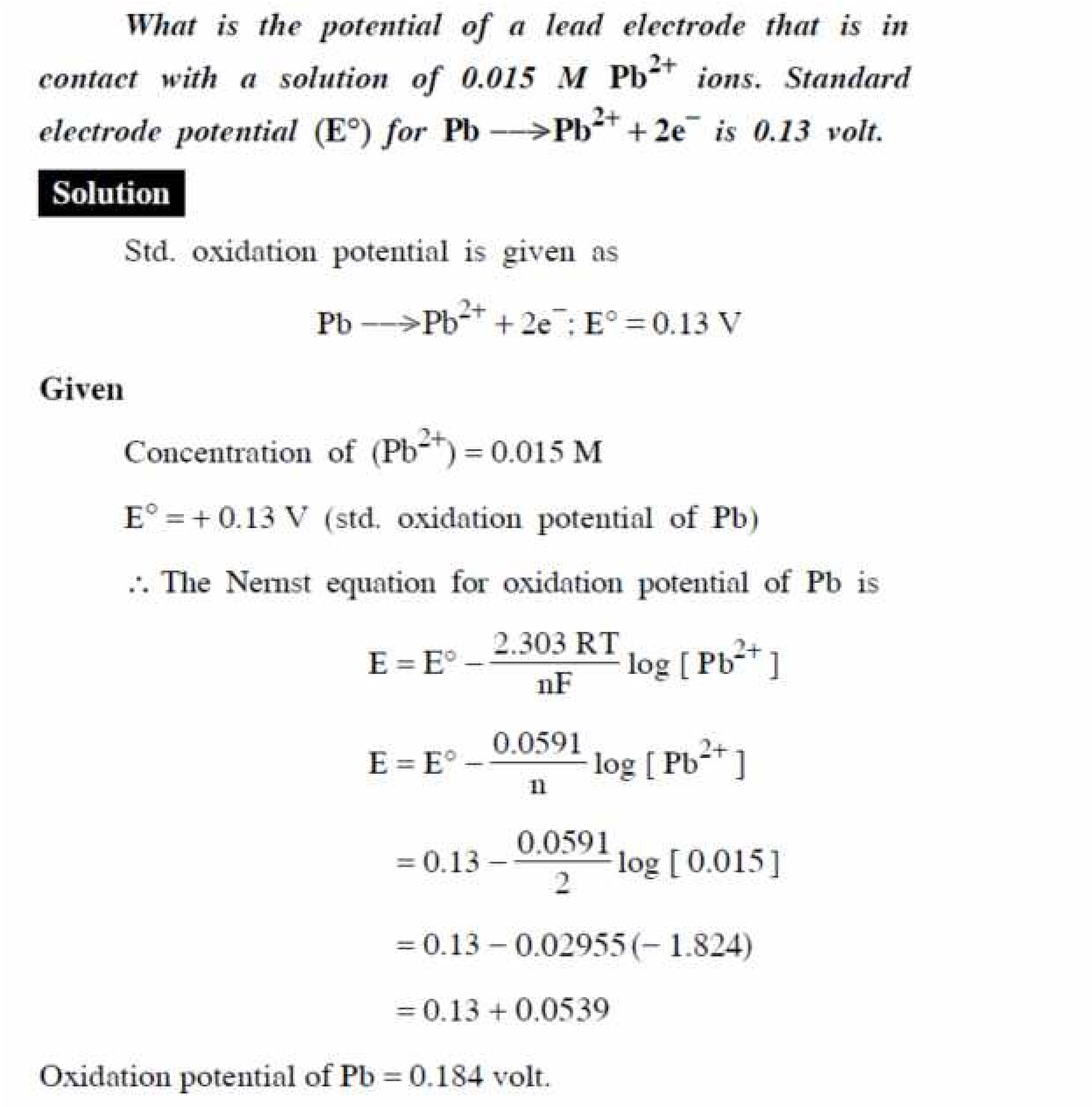
The above equation 5&6 are known as "Nernst equation for single electrode potential".

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 Pb^{2+} ions. Standard electrode potential ($E°$) for $Pb \longrightarrow Pb^{2+} + 2e^-$ is 0.13 volt.

Solution

Std. oxidation potential is given as

$$Pb \longrightarrow Pb^{2+} + 2e^-;\ E° = 0.13\ V$$

Given

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

$E° = + 0.13$ V (std. oxidation potential of Pb)

∴ The Nernst equation for oxidation potential of Pb is

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

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

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

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

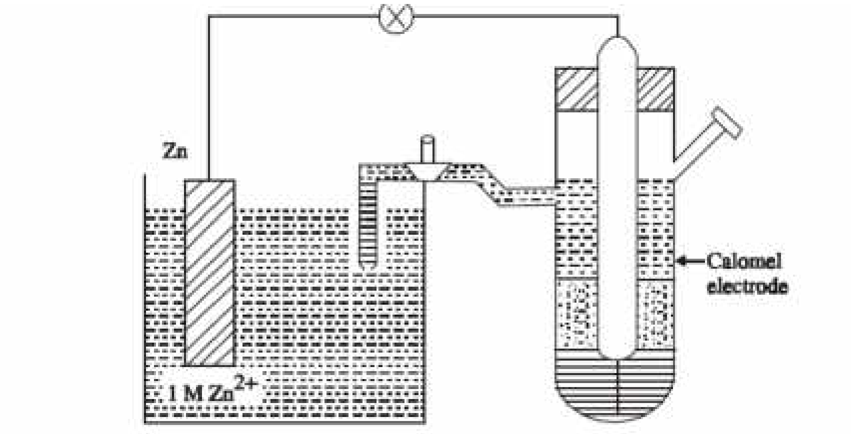
$$= 0.13 + 0.0539$$

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.

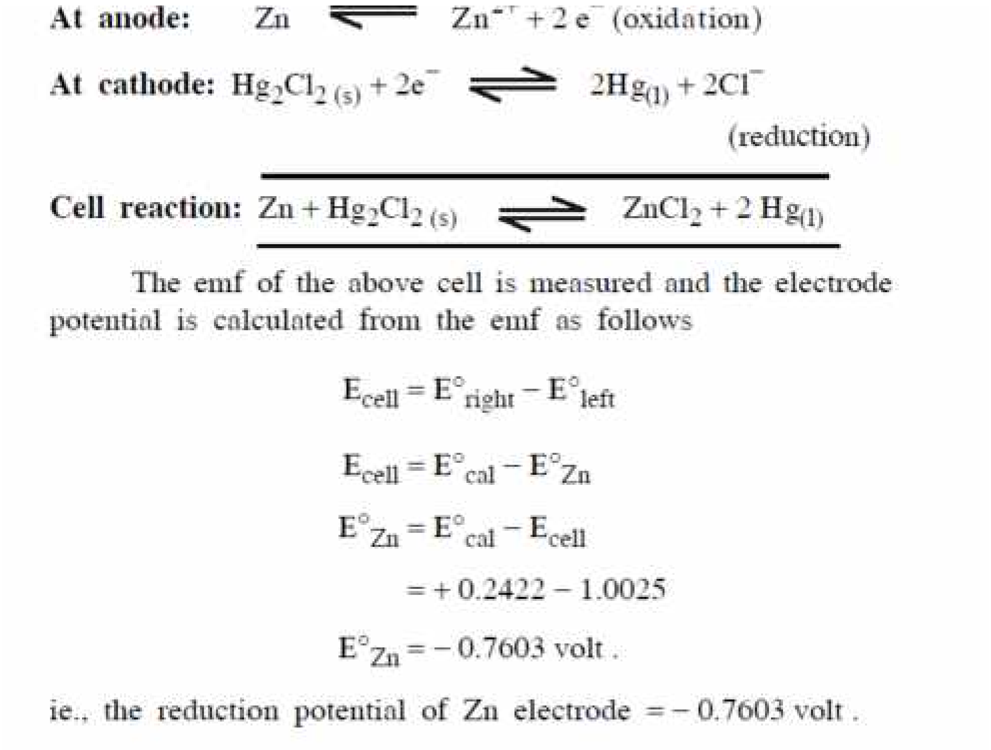
It is very difficult to set up a hydrogen electrode. So other electrodes called secondary reference electrodes like calomel electrodes are used.



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 □□ 0.2422 V□, the calomel electrode will act as cathode and zinc electrode will act as cathode.

The following cell reaction will occur in the above cell



At anode: $Zn \rightleftharpoons Zn^{2+} + 2e^-$ (oxidation)

At cathode: $Hg_2Cl_{2\,(s)} + 2e^- \rightleftharpoons 2Hg_{(l)} + 2Cl^-$ (reduction)

Cell reaction: $Zn + Hg_2Cl_{2\,(s)} \rightleftharpoons ZnCl_2 + 2\,Hg_{(l)}$

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

$$E_{cell} = E^\circ_{right} - E^\circ_{left}$$

$$E_{cell} = E^\circ_{cal} - E^\circ_{Zn}$$

$$E^\circ_{Zn} = E^\circ_{cal} - E_{cell}$$

$$= +0.2422 - 1.0025$$

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

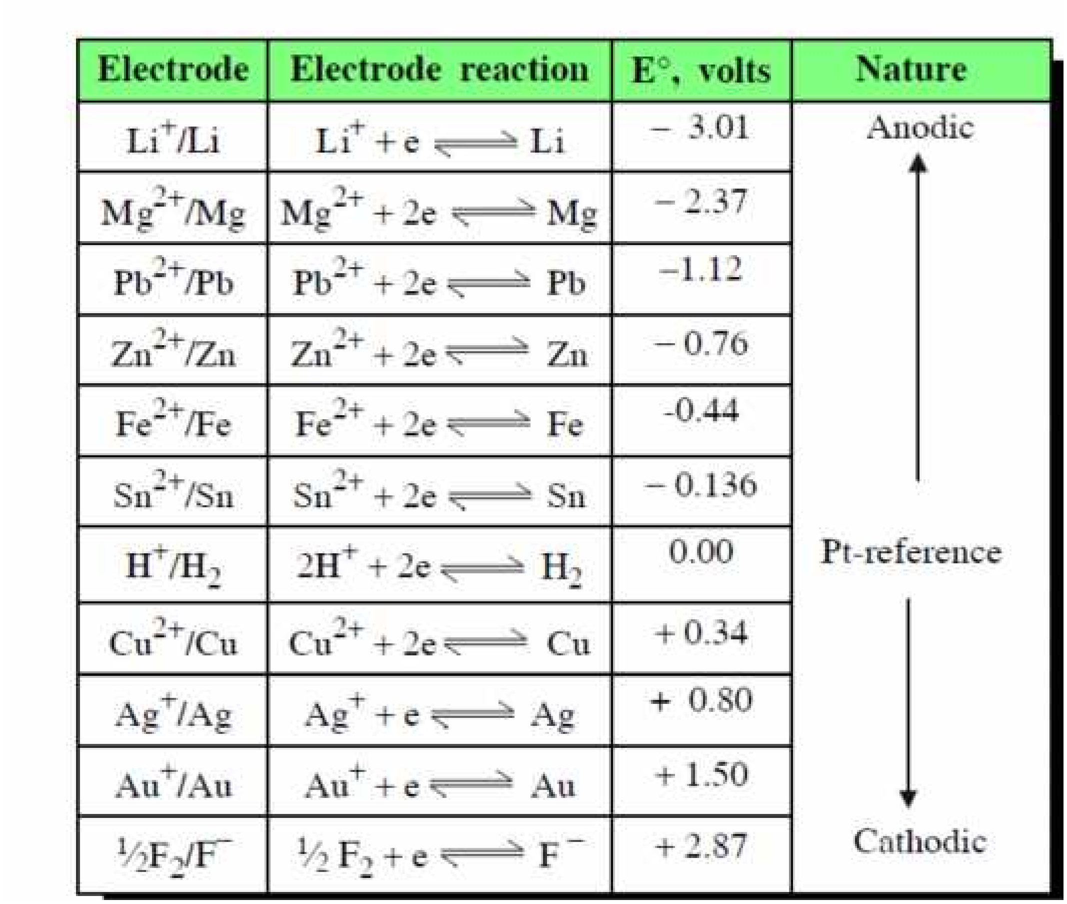
ie., the reduction potential of Zn electrode $= -0.7603$ volt .

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°, volts	Nature
Li^+/Li	$Li^+ + e \rightleftharpoons Li$	− 3.01	Anodic
Mg^{2+}/Mg	$Mg^{2+} + 2e \rightleftharpoons Mg$	− 2.37	
Pb^{2+}/Pb	$Pb^{2+} + 2e \rightleftharpoons Pb$	−1.12	
Zn^{2+}/Zn	$Zn^{2+} + 2e \rightleftharpoons Zn$	− 0.76	
Fe^{2+}/Fe	$Fe^{2+} + 2e \rightleftharpoons Fe$	-0.44	
Sn^{2+}/Sn	$Sn^{2+} + 2e \rightleftharpoons Sn$	− 0.136	
H^+/H_2	$2H^+ + 2e \rightleftharpoons H_2$	0.00	Pt-reference
Cu^{2+}/Cu	$Cu^{2+} + 2e \rightleftharpoons Cu$	+ 0.34	
Ag^+/Ag	$Ag^+ + e \rightleftharpoons Ag$	+ 0.80	
Au^+/Au	$Au^+ + e \rightleftharpoons Au$	+ 1.50	
$½F_2/F^-$	$½ F_2 + e \rightleftharpoons F^-$	+ 2.87	Cathodic

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.

$$E^\circ_{cell} = E^\circ_{R.H.E} - E^\circ_{L.H.E}$$

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 V□), and shows higher tendency towards reduction.

(b) The lithium has highest negative value(-3.01 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., $E^\circ_{Cu^{2+}/Cu} = +0.34$ V and $E^\circ_{Zn^{2+}/Zn} = -0.76$ V.
So, Cu^{2+} has a great tendency to acquire Cu form, thanZn^{2+} has for acquiring Zn form.

4. Determination of standard free energy change ΔG and equilibrium constant for the reaction

Standard electrode potential can also be used to determine the standard free energy change ΔG andequilibrium constant □K□ for the reaction. We know that

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

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

$$= \frac{nFE^\circ}{2.303\,RT} \qquad [\therefore -\Delta G^\circ = nFE^\circ]$$

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 H2 in the emf series) will displace the hydrogen from an acid solution.

Example:

Zinc reacts with dil H_2SO_4 to give H_2 but Ag does not, why?

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$$

$E°_{Zn} = -0.76$ volt

The metal with positive reduction potential (ie., the metals placed below H_2 in the emf series) will not displace the hydrogen from an acid solution.

$$Ag + H_2SO_4 \longrightarrow \text{No reaction}$$

$E°_{Ag} = +0.80$ volt

Predicting Spontaneity (or) feasibility of Redox Reactions

Spontaneity of redox reaction can be predicted from the emf □ value of the complete cell reactio $(\Delta G = -nFE°)$.

(i) If E^0 of the cell is positive, the reaction is spontaneous (or) feasible

(ii) If E^0 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, 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,

$Pt, H_2\ (1\ atm)/H^+\ (1\ M);\ E° = 0\ V$

Anode reaction

$H_2(g) \longrightarrow 2H^+ + 2e^-$

Cathode reaction

$2H^+ + 2e^- \longrightarrow H_2(g)$

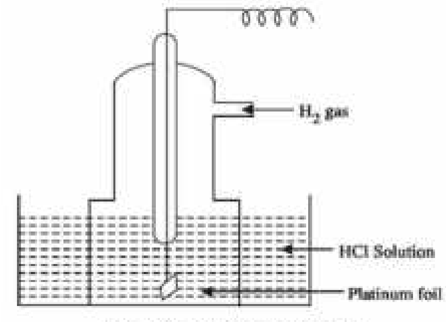


Fig. 1.2 Hydrogen electrode

Limitations

i. It requires hydrogen gas and is difficult to set up and transport.
ii. It requires considerable volume of test solution.
iii. 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

Hg, Hg_2Cl_2, KCL(Saturated Solution); $E^0 = 0.2422$

If the electrode acts as anode the reaction is

$$2Hg_{(l)} \longrightarrow Hg_2^{2+} + 2e$$
$$Hg_2^{2+} + 2Cl^- \longrightarrow Hg_2Cl_2\,_{(s)}$$
$$2Hg_{(l)} + 2Cl^- \text{-------} Hg_2Cl_2\,_{(s)} + 2e^-$$

If the electrode acts as cathode the reaction is

$$Hg_2\,Cl_2\,(s) \longrightarrow Hg_2^{2+} + 2Cl^-$$
$$Hg_2^{2+} + 2e^- \longrightarrow 2Hg_{(l)}$$
$$Hg_2Cl_2\,_{(s)} + 2e^- \text{------------} 2Hg_{(l)} + 2Cl^{-`}$$

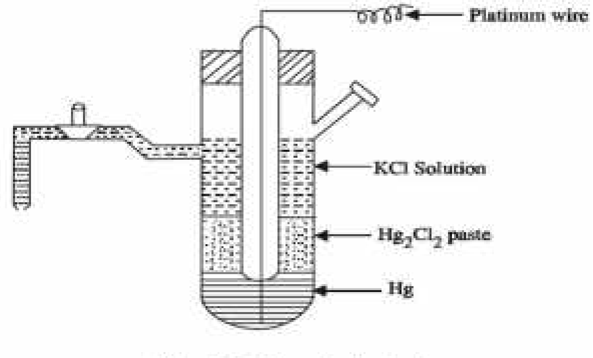


Fig. 1.3 Calomel electrode

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.

Measurement of single electrode potential of Zn using calomel electrode

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

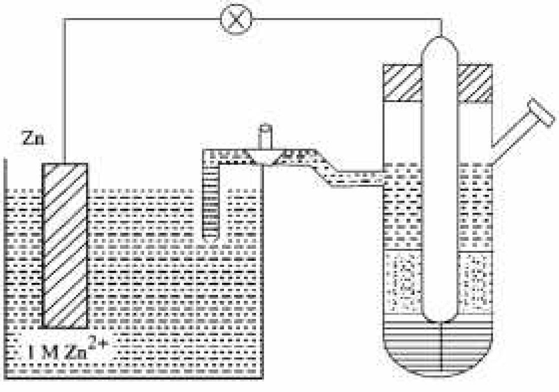


Fig. 1.4 Measurement of electrode potential (Zn)

$E_{cell} = E°_{right} - E°_{left}$

$E_{cell} = E°_{cal} - E°_{Zn}$

$E°_{Zn} = E°_{cal} - E_{cell}$

$= + 0.2422 - 1.0025$

$E°_{Zn} = - 0.7603$ volt .

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 Na+ ions of glass and H+ ions in solution
- The potential difference vary with H+ ion concentration and EMF

$$E_G = E^0_G + 0.0592\ P^H$$

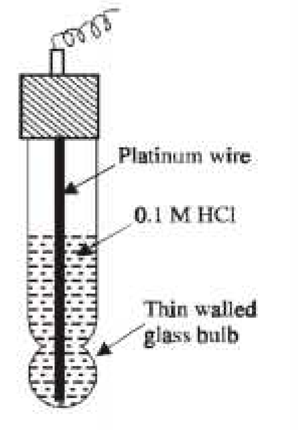


Fig. 1.5 Glass electrode

Determination of pH of a Solution using Glass Electrode

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

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

$E_{cell} = E_{cal} - E_G$

$= E_{cal} - (E°_G + 0.0592\ pH)$

$= E_{cal} - E°_G - 0.0592\ pH$

$pH = E_{cal} - E°_G - E_{cell}$

$\therefore\ E_{cal} = 0.2422\ V$

0.0592

$$\therefore\ pH = \frac{0.2422 - E^o_G - E_{cell}}{0.0592}$$

Advantages of Glass Electrode

i. It can be easily constructed
ii. The results are accurate.
iii. It is not easily poisoned.
iv. Equilibrium is rapidly achieved.

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

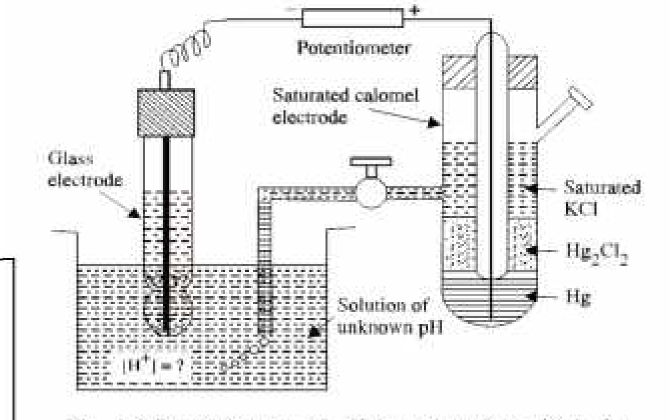


Fig. 1.6 Determination of pH by using glass electrode

Applications of ISE

Used for determining the concentration of cations like H+,Na+,K+ etc
Used for the detemination of hardness of Ca2+ and mg2+
Used for determining the concentration of anions like CN – NO3-, S2- 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.

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

1.8.1 Measurement of EMF of a cell

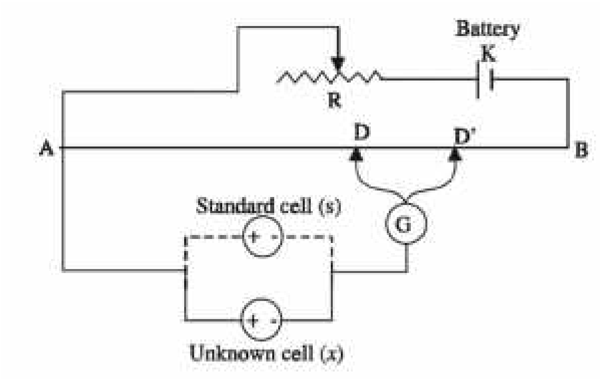
The potential difference or emf of a cell can be measured on the basis of poggendorff's compensation principle.

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 rheostatR
- 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 directionaly proportional to distance AD
- Then the unkown cell is replaced by a standard cell.the distance is Ad'.

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

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



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. $E = \frac{-2.303RT}{nF}pH$
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 obey the following three conditions of thermodynamic reversibility is called 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, small amount of current flows from the cell and 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

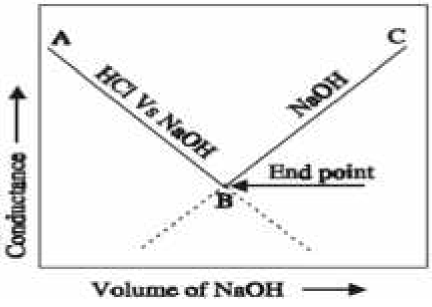
Cells which do not obey the conditions of thermodynamic reversibility are called irreversible cells. Zinc-Silver cell is an example for a irreversible cell. It is represented as

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

(a) Acid-Base titrations.
(b) Precipitation titrations.
(c) Redox (oxidation-reduction) titrations.
(d) 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.
- Initialy 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 addtion of NaoH will increase the fast moving OH – ions

$$H^+Cl^- + Na^+OH^- \text{------}\rightarrow Na^+Cl^- + H_2O$$

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

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

1.10.4 Disadvantages of Conductometric Titration

(i) Only limited number of redox titration can be carried out.
(ii) 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.

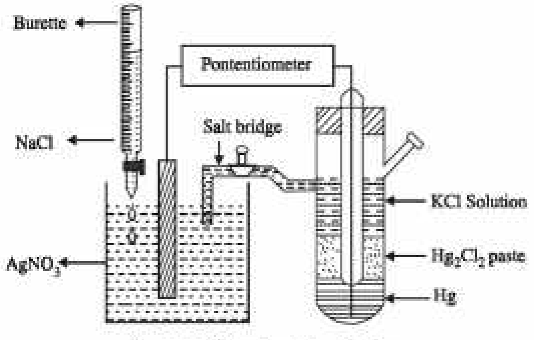


Fig. 1.12 Potentiometric titration

1.11.1 Types of potentiometric Titration

1. Precipitation titration ($AgNO_3$ Vs NaCl)

- $AgNo_3$ 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 Ecell is determined.
- When $AgNo_3$ is titrated against to the Nacl the emf will be decreasing to the Ag+ concentration decreases

$$\mathbf{AgNO_3 + NaCl \text{ ---> } AgCl\downarrow + NaNO_3.}$$

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

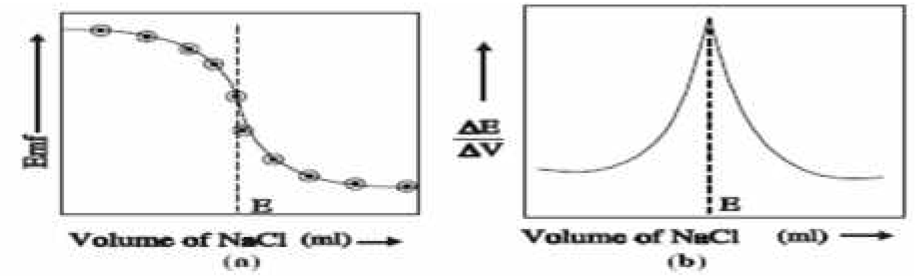


Fig. 1.13 E_{cell} Vs Vol. of NaCl

- When the emf is plotted against the volume of 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 Nacl is plotted as above to get the accurate end point.

2. Redox titration ($FeSO_4$ Vs $K_2Cr_2O_7$)

- $FeSO_4$ 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 Ecell is determined.
- When $FeSO_4$ is titrated against to the $K_2Cr_2O_7$ the emf will be increasing to the Fe^{3+}concentration increases

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

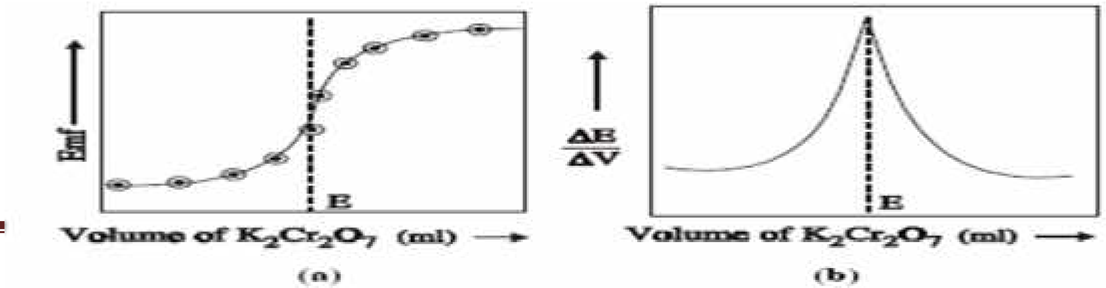


Fig. 1.14 E_{cell} Vs Vol. of $K_2Cr_2O_7$

-
- 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 an 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 spontanenity 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, napthalenes and aromatics.
(iii) Gaseous fuels: The gaseous fuels of engineering importance are natural gas,coalgas.propducer 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±20˚C for 7 minutes in a muffle furnace. The loss in weight of the sample is found 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˚±50˚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-% 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 in to CO_2 and H_2O.The gaseous products of combustion are absorbed in KOH and $CaCl_2$ of known weights respectively. The increase in weights of these tubes are then determined.

$C+O_2 \longrightarrow CO_2$
12 44
$H_2+1/2O_2 \longrightarrow H_2O$
2 18
$2KOH+CO_2 \longrightarrow K_2CO_3+H_2O$
$CaCl_2+ 7H_2O \longrightarrow CaCl_2.7H_2O$

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

$$\text{Percentage of hydrogen: } \frac{\text{Increase in weight of weight of } CaCl_2 \text{ tube} \times 2 \times 100}{\text{Weight of coal taken} \times 18}$$

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: Volume of acid used x normality/ 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.

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

Ash

Its determination is carried out as in proximate analysis

Oxygen

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

Percentage of oxygen=100-% 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

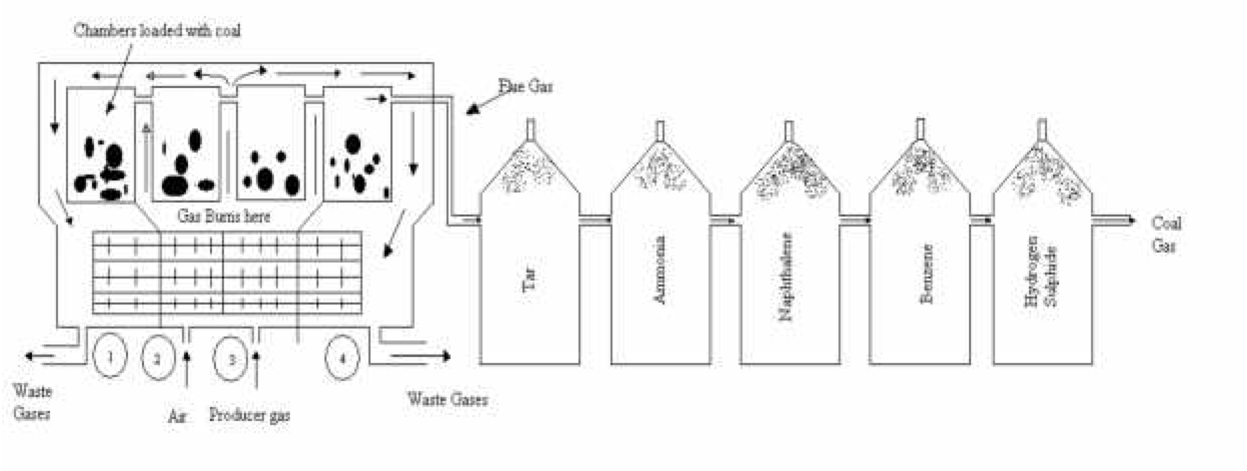
There are so many types of ovens are used for the manufacture of metallurgical coke. But the important one is Otto-Hoffman’s by-product oven method.

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 2nd and 3rd for regenerators. Hot flue gases produced during the carbonization are allowed to pass through 1st and 4th regenerators until the temperature has been raised to 1000 degree Celsius. While 1st and 4th regenerators are heated by hot flue gases. The 2nd and 3rd 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_2S 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_4OH.
(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_2S**: The remaining gases are then passed through a purifier, packed with moist Fe_2O_3. Here H_2S 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) napthalenes, 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.

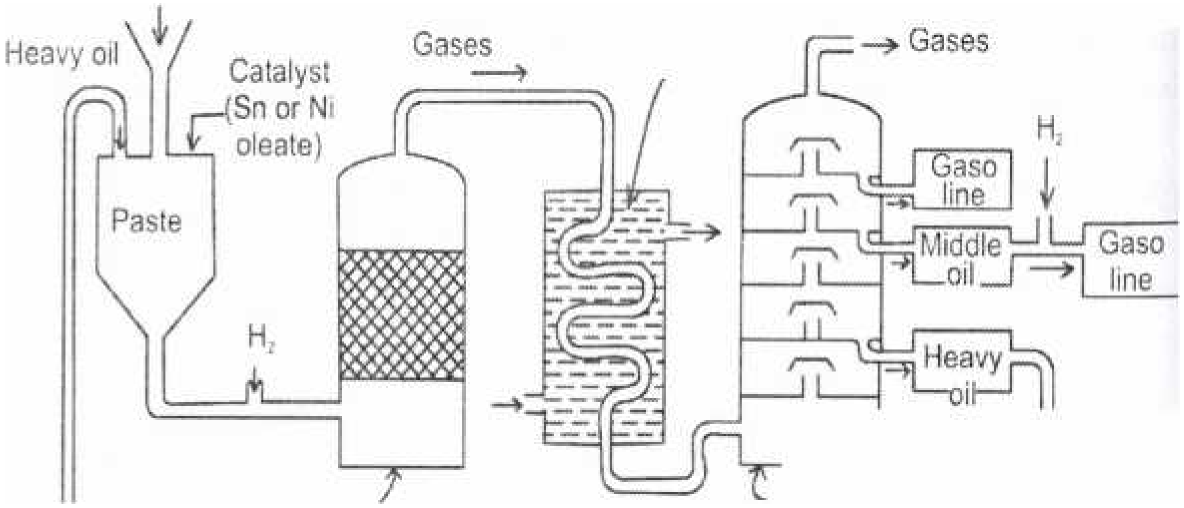
Petrol synthesized either by polymerization of low molecular mass olefins and alkanes (or) from finely powdered coal and heavy oil is called synthetic petrol.

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°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 fractioned 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 (CO+I-h), produced by passing steam over heated coke, is mixed with hydrogen.

1. The gas is purified by passing through $Fe_{2}0J$ to remove H_2S and then into a mixture of Fe20J.Na2C03 to remove organic sulphur compounds.

2. The purified gas is compressed to 5 - 25 atm and then led through a converter maintained at about 200- 300°C.
3. A mixture of saturated and unsaturated hydrocarbons results
4. The reaction is exothermic, so out coming gaseous mixture is led to a cooler, where a liquid resembling crude oil is obtained
5. The crude oil thus obtained is then fractioned to yield (i) gasoline and (ii) high-boiling heavy oil.
6. 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 plum bite with controlled addition of sulphur. This refining process converts sulphur compounds into disulphides.

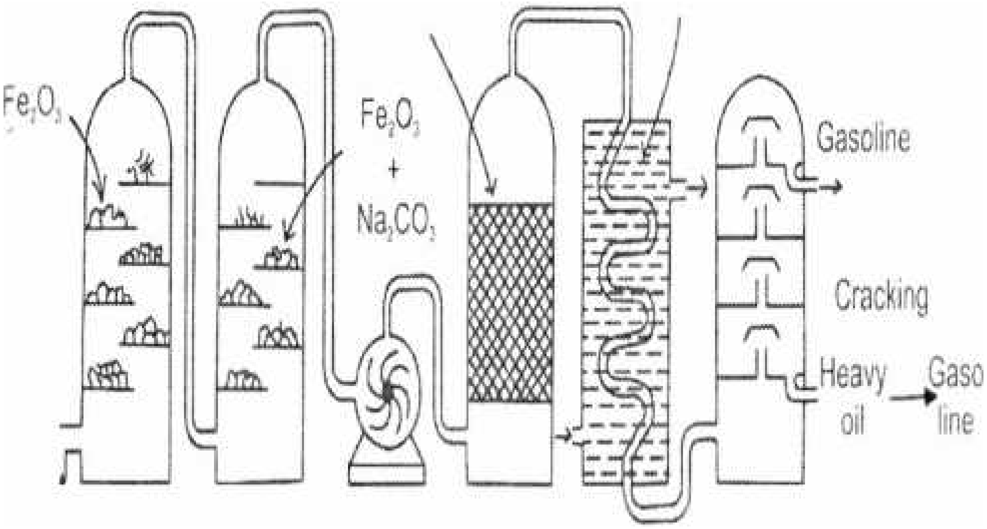
$2RSH + Na_2Pb0_2 \sim Pb(SR)_2 + 2NaOH$

$Pb(SR)_2 + S \sim PbS + RSSR$ (Disulphide)

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 efficency,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 possesss 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 $CH_3CH_2\ CH_2\ CH_2\ CH_2CH_3$ knocks very badly and hence ,its antiknock value has been given zero. On the other hand, so octane (2, 2,4-trimethylpentane) $(CH_3)_3CCH_2CH(CH_3)_2$

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) , (c2h5)4 Pb or diethyl telluride, (c2h5)2 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,(TEL,$(CH_3)_4Pb$ has been found better then 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 shoud 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 ehyl nitrte, isoamyl nitrite , acetone peroxide.

GASEOUS FUELS

a. **Water Gas:**

It is a mixture of CO and H with small amount of N2.The Average Composistion of water gas is as follows

Constituents	**Percentage (%)**
CO	41
H2	51
N2	4
Co2+Ch4	rest

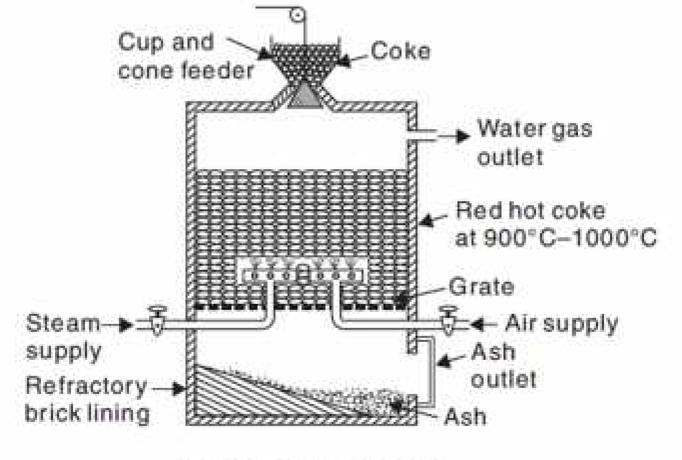
Its calorific value is about 2800 kcal/m3

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 seam 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



Water gas production

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 & H2 gases are produced. The reaction is endothermic. Hence, the temperature of the coke bed falls.

$$C + H_2O \longrightarrow CO + H_2; \text{ endothermic}$$

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

$$C + O_2 \longrightarrow CO_2; \text{ exothermic}$$

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

Uses

1. It is used for the production of h2 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^3 or 20000 Iitres 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_2.

Composition:

The composition of producer gas is
CO = 22 - 30%
N_2 = 52 - 55%
H_2 ＝ 8-12%
CO_2 = 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 C02. The temperature of this zone is about 11 OODC.

$$C + O_2 \sim CO_2 + 97 \text{ kcal}$$

$$C + 1/202 \sim CO + 29.5 \text{ kcal}$$

Reduction zone:

It is the upper zone in which CO_2 and steam combines with red hot coke to liberate H_2 and CO. .

Calorific value:

The calorific value of producer gas is l300 Kcal/m '.

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 (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 (H2O). 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

$$=1/100\ [8,080C + 34,500(H-0/8)+ 2,240S]\ \text{Kcal/Kg}$$

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

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

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

This is based on the fact that 1 part of H by mass gives 9 parts of H_2O 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 -0/8)+ 2,240S] Kcal/Kg

=1/100 [(8,080 x 85) + 34,500(8 – $\underline{O/8}$+ (2,240x1)]kcal/kg

= 1/100[965,040] Kcal/Kg = 9,650.4 Kcal/Kg

Net calorific value (NCV)

= (GCV - 0.09H x 587) Kcal/Kg

= [9,650.4 - (0.09 x 8 x 587)] Kcal/Kg

= 9,227.8 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:

Lower calorific value (LCV) = (HCV - 0.09H x 587) Kcal/Kg

(i.e.) 8,490.5 Kcal/Kg = (HCV - 0.09H x 587) Kcal/Kg

(i.e.) HCV= (8,490.5 + 52.8H) Kcal/Kg ……………1

Higher calorific value (HCV)

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

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

= [7,272 + 345H - 129.4 +11.2] KcallKg

HCV = [7,153.8 + 345H] KcallKg ………………………………….2

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

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

(or) 292.2H = 8,490.5 -7,153.8

292.2H = 1,336.7

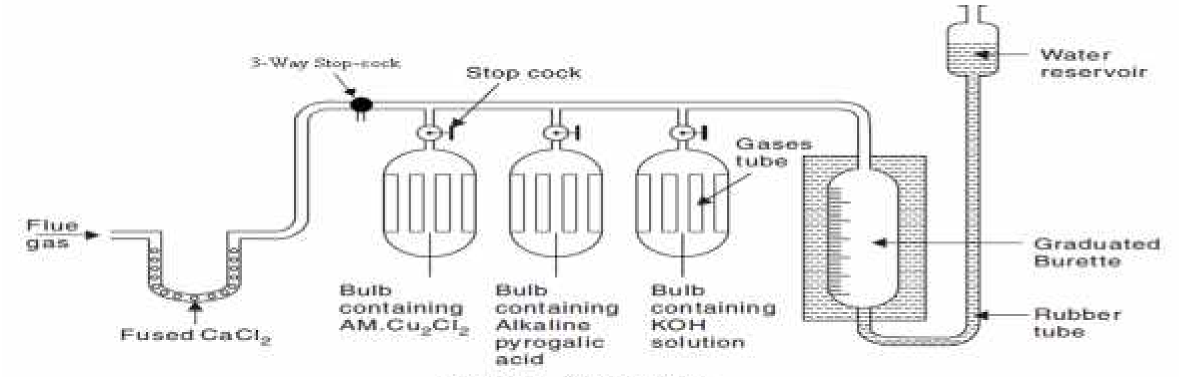
$$\% \text{ of H} = \frac{1336.7}{292.2} = 4.575\%$$

Flue Gas Analysis (ORSAT METHOD)

The mixture of gases like (CO_2, O_2, 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 CaCl2 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.



Orsat's Apparatus

The horizontal tube is also connected with three different absorption bulbs I, II, and III for absorbing CO2, O2, CO.

I-Bulb contains 'potassium hydroxide' solution, and it absorbs only CO2

II-Bulb contains 'alkaline pyrogallol' solution, and it absorbs CO2 and O2.

III-Bulb contains 'ammoniacal cuprous chloride solution' and it absorbs CO2, O2 and 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 CO_2

The stopper of the absorption bulb-I, containing 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 CO2 present in the flue gas is absorbed by KOH

The gas is again sent to the burette. This process is repeated several times to ensure the complete absorption of CO2. The decrease volume of flue gas in the burette indicated the volume of CO2 in 100 cc flue gas

(b)Absorption of 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 O2 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 O2.

(c)Absorption of CO

Now stop-cock of bulb-II is closed and the stop-cock of bulb-II is opened. The remaining gases sent into the absorption bulb-III, where 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 CO, The remaining gas in the burette after the absorption of Co2, O2, &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 CO, it indicates that incomplete combustion is occurring and it also indicates that the short supply of O2

3, If the flue gases contains considerable amount of O2,it indicates that complete combustion is occurring and also it indicates that the excess of O2 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 tropsch 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:

$$\underset{\text{Metal}}{M} \longrightarrow \underset{\text{Metal ion}}{M^{2+}} + \underset{\text{Electron}}{2e^-} \text{ (loss of electron, Oxidation)}$$

$$H_2O_2 + 2e^- \longrightarrow \underset{\text{Oxide ion}}{O^{2-}} \text{ (Gain of electron, reduction)}$$

$$M + H_2O_2 \longrightarrow \underset{\text{Metal Oxide}}{M^{2+} + O^{2-}}$$

Mechanism

Usually, oxidation first occurs at the surface of the metal and resulting metal oxide scale forms a barrier that ends 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

Metal + Oxygen ---------------→ 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.

Metal oxide → Metal + 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 STABLE

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 (MoO_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_2, CO_2, Cl_2, H_2 and H_2S 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 ($SnCl_4$) 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_2S to liberate atomic hydrogen.

$$Fe + H_2S \xrightarrow{\quad} FeS + \underset{\text{Atomic Hydrogen}}{2H}$$

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

$$H + H \xrightarrow{\quad} H_2$$

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.

H_2 ------------→ H + H

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:

$$\underset{\text{Metal}}{M} \text{ -------------}\rightarrow \underset{\text{Metal ion}}{M^{n+}} + ne^- \text{ (oxidation)}$$

M^{n+} -------------→ Dissolves in solution

↓

Metal ion-----------→ Forms compounds such as oxide.

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.

At anodic area: $\underset{\text{Metal}}{M} \xrightarrow{\hspace{2cm}} \underset{\text{Metal ion}}{M^{n+}} + ne^-$ (oxidation)

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.

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad \text{(oxidation)}$$

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

$$2H^+ + 2e^- \longrightarrow H_2\uparrow \quad \text{(Reduction)}$$

- The overall reaction is $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2\uparrow$
- 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.

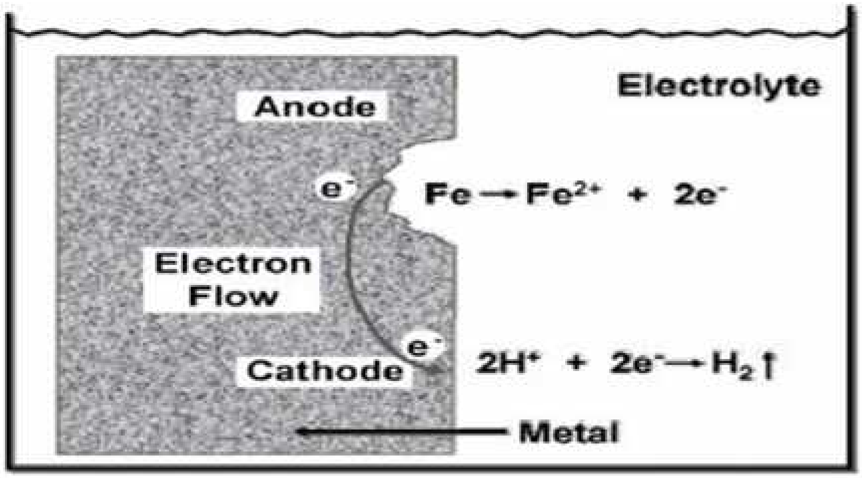


Fig 3. Mechanism of evolution of hydrogen type corrosion

(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.

  $Fe \text{ --------------}\rightarrow Fe^{2+} + 2e^-$ (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

  $\frac{1}{2}O_2+H_2O+2e^- \text{ ----------}\rightarrow 2OH^-$ (Reduction)
- The Fe^{2+} ions at anode and OH^- ions at cathode diffuse and when they meet, ferrous hydroxide is precipitated.

  $Fe^{2+} + OH^- \text{ ----------}\rightarrow Fe\,(\overset{\downarrow}{O}H)_2$
- If enough oxygen is present, ferrous hydroxide is easily oxidised to ferric hydroxide and this product is called yellow rust which actually corresponds to $2[Fe_2O_3.3H_2O]$.

$4Fe(OH)_2 + O_2 + 2H_2O$ -------------→ $4Fe(OH)_3$

$4Fe(OH)_3$ ------------→ $2[Fe_2O_3.3H_2O]$

Yellow Rust

- If limited supply of oxygen is present, the corrosion product is black anhydrous magnetite, Fe_3O_4.

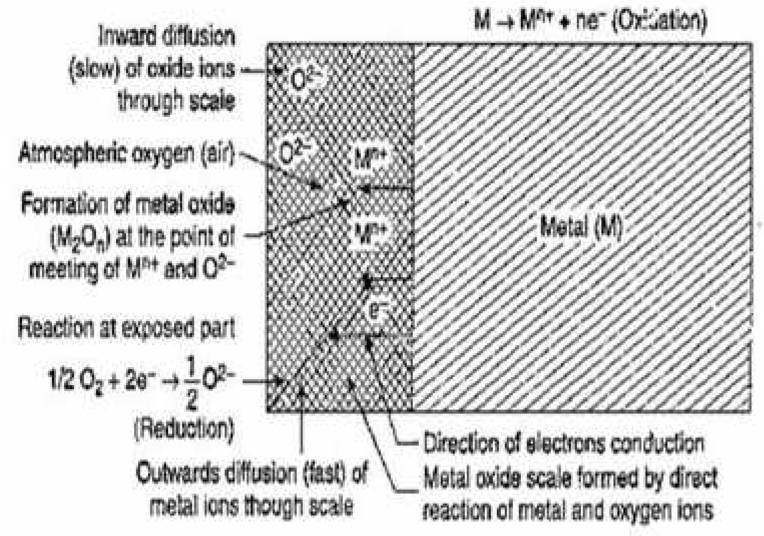


Fig . 4. Mechanism of absorption of oxygen type corrosion

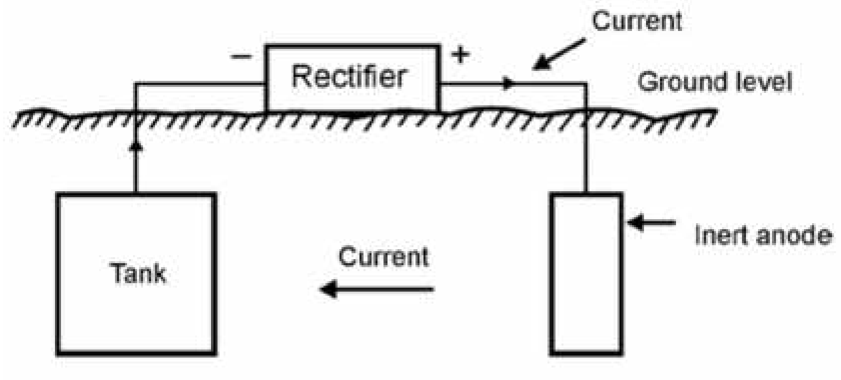
CATHODIC PROTECTION

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

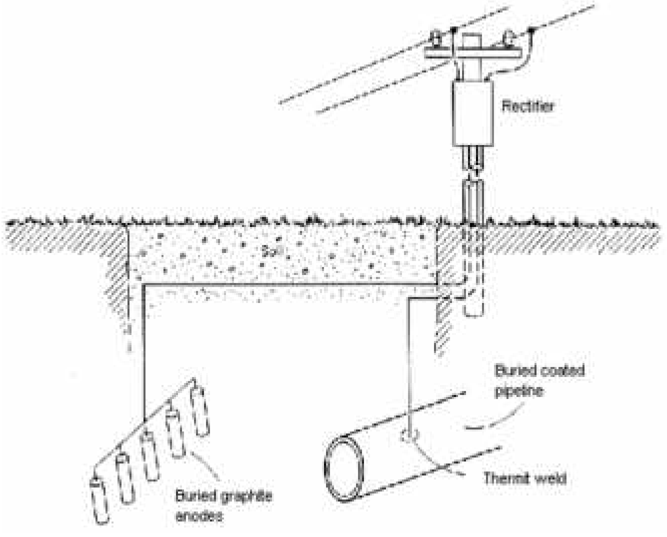
- To protect underground pipelines, cables etc., from soil corrosion
- To prevent the corrosion of ship hulls and other marine devices
- Insertion of Mg sheets into domestic water boilers to prevent the formation of rust.



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 ($2PbCO_3Pb(OH)_2$)
  Lithophone (75% $BaSO_4$ + 25% Zn S)
- Red pigment: Venetian red (Fe_2O_3 and $CaSO_4$)
  Indian red (Fe_2O_3)
- Green pigment: Chromium oxide
- Blue pigment: Prussian blue $Fe_4(Fe(CN)_6)_3$

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:* Lincseed 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 he 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_2SO_4. The cleaned object is then made cathode and gold foil as the anode. $AuCl_3$ 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

$AuCl_3 \quad Au^{3+} + 3Cl^- \longrightarrow$

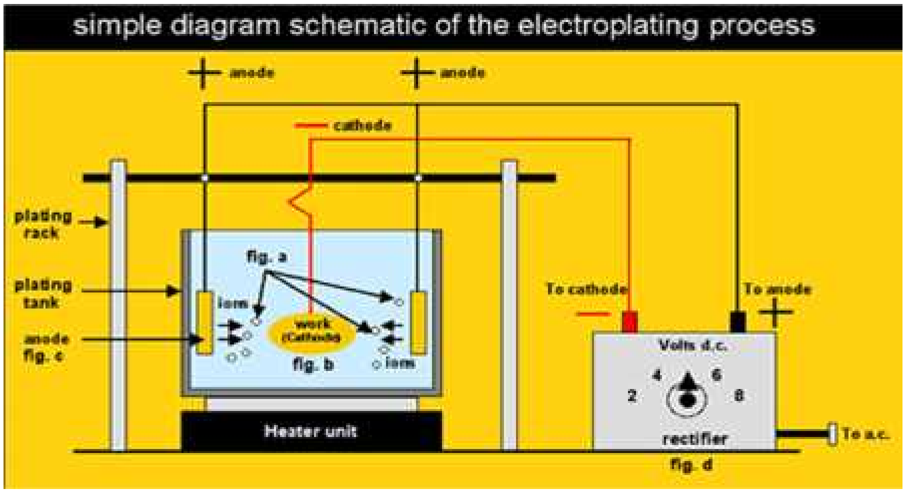
at cathode : On passing current , Au^{3+} ions move to the cathode and get deposited there as Au metal

$Au^{3+} + 3e^- \quad Au \longrightarrow$

at anode: The free chloride ions migrate to the gold anode and dissolves an equivalent amount of Au to form $AuCl_3$

$Au + 3Cl^- \quad Au^{3+} + 3e^- \longrightarrow$

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 (60ºC), optimum current density (1-10 Ma/cm^2) 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 µm (.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 370ºC (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 µm to 25 µm (100 µin to 1000 µin) can be coated on most aluminums. Thick coatings from 25 to 75 µm (1000 to 3000 µin) 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.

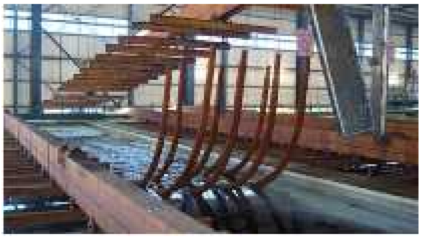
Hot Dip Galvanizing

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

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_3, Cl_2, etc.) are adsorbed more easily than the permanent gases (like H_2, N_2, O_2, etc.).
- The ease of liquefaction of a gas depends upon its critical temperature
- The higher the critical temperature (T_c), 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., adsorping 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 (solutes) 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 NH_4OH 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

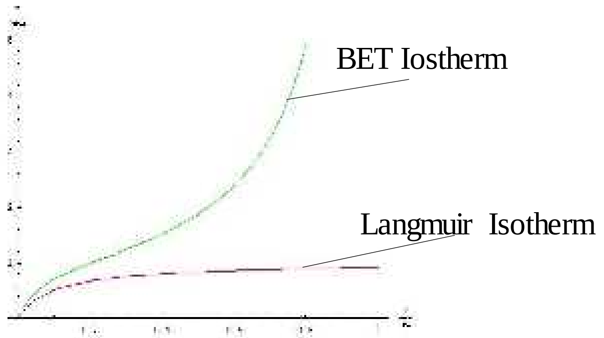
ADSORPTION ISOTHERMS

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
- Furthur 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_2 on Pt at -195 C
- e.g., Adsorption of Br_2 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_2O 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 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 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 $P_{1/n}$ 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:

(i) Purely empirical basis
(ii) Valid upto certain pressure and invalid at high pressure
(iii) Fails when concentration of adsorbate is very high
(iv)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. T he residual valency force on the surface of adsorbent is effective only up to a small distance (about 2 × 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 atound on the surface.

Langmuir's adsorption equation.

$w = bP/1+aP$ ……………… (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/x 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:

$w= bP =bP^1$ ……………… (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

$w= bP/aP = b/aP^0 = \text{constant}$ ……………… (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

$w=b/aP^{1/n}$

$= \text{constant } P^{1/n}$……………… (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 iostherm

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 ce measured (BET method)

(10) Water Conservation

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

(11) Ore Dressing

- Froath floation process: Low grade sulphide ores are freed earthy impurities

UNIT V

PHASE RULE

INTRODUCTION

All chemical reactions are broadly classified into 2 types:

1) Irreversible Reactions : $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\uparrow$
2) Reversible reactions:
   (a) Homogeneous reversible reactions
   Eg: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   (b) Heterogeneous reversible reactions
   Eg: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

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 O_2, H_2, N_2, 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 $CaCO_3$*

$$\mathbf{CaCO_3(s) \rightleftharpoons CaO\ (s) + CO_2(g)}$$

It involves 3 phases namely solid $CaCO_3$, solid CaO and gaseous CO_2

OTHER EXAMPLES:

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

$$\textbf{Ice(s)} \rightleftharpoons \textbf{Water(l)} \rightleftharpoons \textbf{Vapour(g)}$$

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

4) **$MgCO_3$ (s) $\rightleftharpoons$ MgO (s) + CO_2 (g)**

It involves 3 phases, solid $MgCO_3$, solid MgO and gaseous CO_2.

5) Rhombic sulphur (s) −−−−> Monoclinic sulphur (s). It forms 2 phases.

6) Consider the following heterogeneous system.

$CuSO_4$(s) + $5H_2O$ (l) $\rightleftharpoons$ $CuSO_4 . 5H_2O$ (s)

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.

$$\textbf{Ice(s)} \rightleftharpoons \textbf{Water(l)} \rightleftharpoons \textbf{Vapour(g)}$$

The chemical composition of all the three phases is H2O. 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 $CaCO_3$

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

The system has 3 phases namely, solid $CaCO_3$, solid CaO and gaseous $CO_2$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 $CaCO_3$and CaO are considered as components, the chemical equations are:

Phase	Components
$CaCO_3$	$CaCO_3 + 0CaO$
CaO	$0CaCO_3 + CaO$
CO_2	$CaCO_3 - CaO$

(d) **$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$**

This system has 3 phases and 2 components namely, PCl_3 and Cl_2.

(e) An aqueous solution of NaCl is a two component system. The constituents are NaCl and H_2O.

(f) **$CuSO_4 . 5H_2O(s) \rightleftharpoons CuSO_4 . 3H_2O(s) + 2H_2O(g)$**

It is also a two component system as components are $CuSO_4.3H_2O$ and H_2O.

(g) In the dissociation of NH_4Cl , the following equilibrium occurs.

$$NH_4Cl\ (s) \rightleftharpoons NH_3\ (g) + HCl\ (g)$$

The system consists of 2 phases namely solid NH_4Cl and the gaseous mixture containing NH_3 + HCl. When $NH_3$and HCl are present in equivalent quantities the composition of both the phases can be represented by NH_4Cl 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

$$\text{Ice(s)} \rightleftharpoons \text{Water(l)} \rightleftharpoons \text{Vapour(g)}$$

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

$$\text{Liquid Water(l)} \rightleftharpoons \text{Water- vapour(g)}$$

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 N_2 and 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

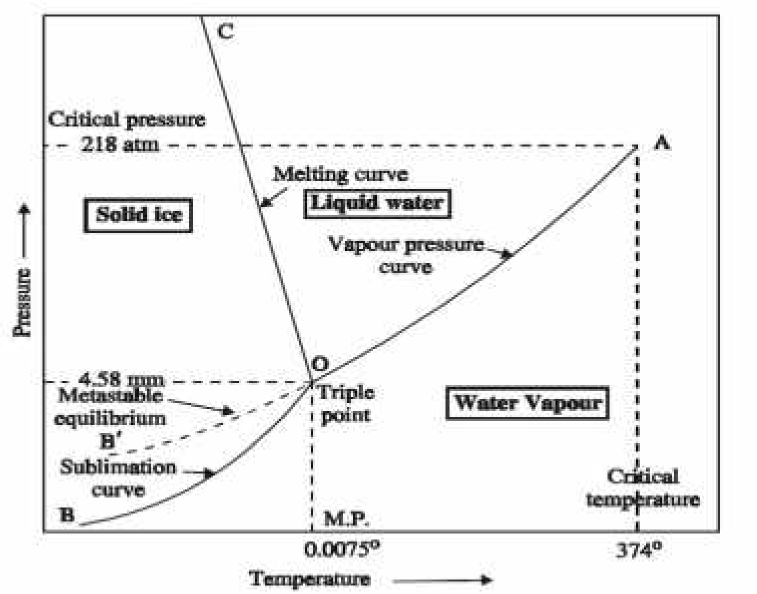
The Water System

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.

Solid Ice $\rightleftharpoons$ **Liquid Water**

Liquid Water $\rightleftharpoons$ **Water- vapour**

Solid Ice $\rightleftharpoons$ **Water- vapour**



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.

Liquid Water $\rightleftharpoons$ **Water- vapour**

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.

$$\textbf{Solid Ice} \rightleftharpoons \textbf{Water- vapour}$$

This equilibrium (i.e.line OB) will extend up to the absolute zero (− 273°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.

$$\textbf{Solid Ice} \rightleftharpoons \textbf{Liquid Water}$$

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.

$$\textbf{Super- cooled water} \rightleftharpoons \textbf{Water- vapour}$$

Sometimes water can be cooled below it‟s freezing point (0°C) without the formation of ice, this water is called super-cooled water.

Super cooled water is unstable and it can be converted into solid 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:

$$\mathbf{F = C - P + 2;\ F = 1 - 2 + 2;\ F = 1}$$

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

$$\textbf{Ice(s)} \rightleftharpoons \textbf{Water(l)} \rightleftharpoons \textbf{Vapour(g)}$$

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%.

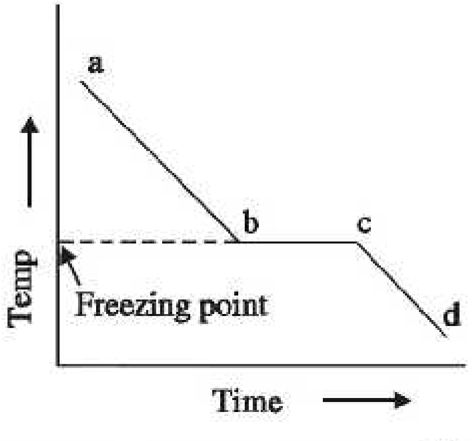
EXPERIMENTAL METHOD OF CONSTRUCTION OF A SIMPLE EUTECTIC PHASE DIAGRAM

Thermal Analysis (or) Cooling Curves

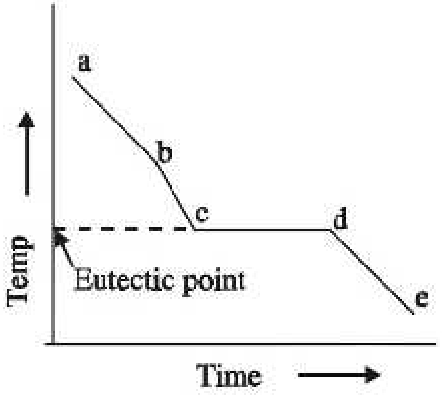
Thermal analysis is a method of studying the cooling curves of various compositions of a system during solidification. The shapes of the freezing point curves for any system (involving metals) can be determined by thermal analysis. The form of cooling curves indicates the composition of the solid.

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.

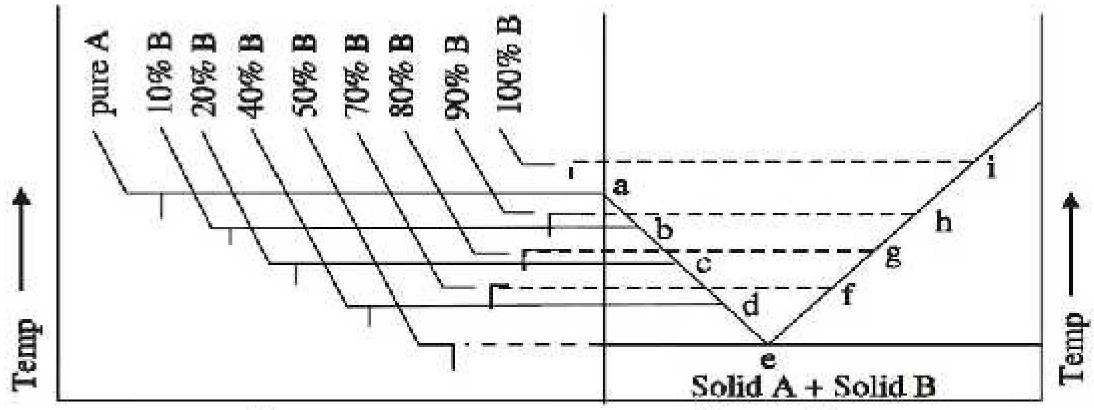
Example 2:

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.



Cooling curve of various compositions of two solids

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.

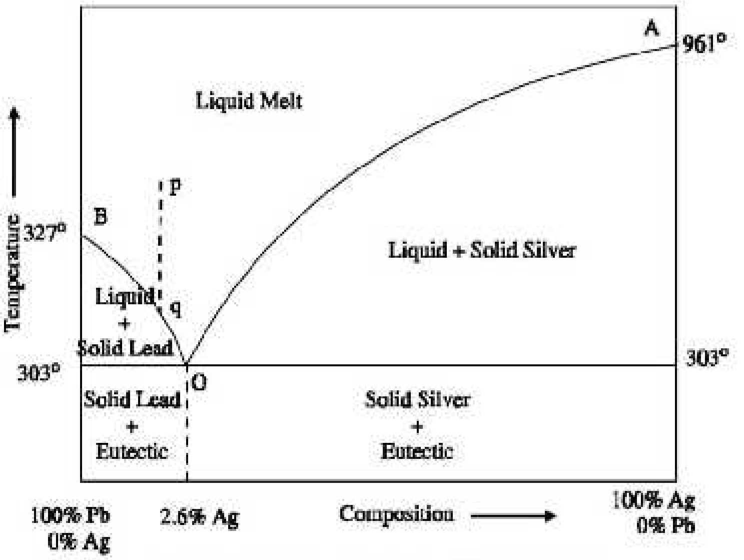
BINARY ALLOY SYSTEM (OR) THE SIMPLE EUTECTIC SYSTEM

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.



Phase diagram of Lead - Silver system

(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.

Solid Ag $\rightleftharpoons$ Liquid Melt

(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.

Solid Pb $\rightleftharpoons$ Liquid Melt

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’(Eutecticpoint)

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.

Solid Ag + Solid Pb $\rightleftharpoons$ Liquid Melt

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'sprocessforthedesilverisationofArgentiferouslead

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‟sprocess.

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.

$$\textbf{Solid A} \rightleftharpoons \textbf{Liquid A}$$

2. Eutectic Point: It is the temperature at which two solids and a liquid phase are in equilibrium

$$\textbf{Solid A + Solid B} \rightleftharpoons \textbf{Liquid}$$

3. Triple Point

It is the temperature at which three phases are in equilibrium.

$$\textbf{Solid} \rightleftharpoons \textbf{Liquid} \rightleftharpoons \textbf{Vapour}$$

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

Questions	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 Ca(HCO3)2 present in water forms	CaCO3, CO2 & H2O	CaCO3 & H2O	CaO & CO2	CaCO3 & CO2	**CaCO3, CO2 & H2O**
Which of the calcium salts contributes to non-carbonate / permanent hardness?	Bicarbonate	Sulphate	Carbonate	Hydroxide	**Sulphate**

Unit of hardness is equivalent of -	CaCl2	CaSO4	CaCO3	CaO	**CaCO3**
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	AgNO3 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	CuSO4	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	CaSO4	CaCO3	Mg(HCO3)2	Ca(HCO3)2	**CaSO4**

Sludge formation is due to	MgCO3	Mg(OH)2 and CaCO3	MgCl2 and CO2	MgCO3 and CO2	**Mg(OH)2 and CaCO3**
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 N2	Dissolved H2	Dissolved SO2	Dissolved O2	**Dissolved O2**
Corrosion due to CO2 is removed by adding	NH_4OH	Na2SO4	N2H4	NH3	**NH_4OH**
Corrosion due to O2 is removed by adding	Na3PO4	Na2SO4	N2H4	NH3	**N2H4**
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	Na3PO4	Na4P2O7	Na2 [Na4P6O18]	Na4 [Na2P6O18]	**Na2 [Na4P6O18]**

In phosphate conditioning the residual hardness is converted into – (*Ca/Mg phosphate*)	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?	Na3PO4	Na2HPO4	NaH2PO4	NaPO3	**NaH2PO4**
If boiler feed water is acidic, then which ortho phosphate is used for internal treatment	Na3PO4	Na2HPO4	NaH2PO4	NaPO3	**Na3PO4**
Water free of all ions is obtained by	deionizaton 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	RH+	ROH-	R CH_3	C_6H_5R	**RH+**
The functional group of anion exchange resin is	RH+	ROH-	R CH_3	C_6H_5R	**ROH-**
Regeneration of Anion exchange resin is done by	dil Na2SO4	dil HCl	dil NaOH	10 %NaCl	**dil 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 highconcentrated 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 guage	**Hydrostatic pressure**
The life of semipermeable membrane used in RO is	1 year	2 years	3 years	8 years	**1 year**
The Bureau of Indian Standards (BIS) has specified drinking water	Quality	quantity	acidity	alkalinity	**quality**

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	$E_{CELL}= E^0_{Zn}- E^0_{Cu}$	$E_{CELL}= E^0_{Cu}- E^0_{Zn}$	$E_{CELL}= E^0_{Pb}- E^0_{Cu}$	$E_{CELL}= E^0_{Cu}- E^0_{Pb}$	$\mathbf{E_{CELL}= E^0_{Zn}- E^0_{Cu}}$
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 H2 with dil H2SO4	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	Poggendroff compensation principle	Heisen burg principke	Pauli exclusion principle	Aufbau principle	**Poggendroff compensation principle**
The metal present in bottom of calomel electrode	Ag	Hg	Au	Zn to Cu outside the cell	**Hg**
The emf value ----------- whenFe2+/K2Cr2O7	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	Fe2+/K2Cr2O7	AgCl/NaOH	HCl/NaOH	NaCl/NaOH	**Fe2+/K2CR2O7**
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	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_2	Zn	Cd	**PbO_2**

UNIT III - FUELS AND COMBUSTIONS

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^3.	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_2	CO & N_2	CO_2 & H_2	CH_4 & H_2	**CO & H_2**

A good metallurgical coke should have very low	porosity	sulphur & phosphorous content	fusion point of its ash	hardness & strength	**hardness & strength**
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_4 (upto 90%)	C_2H_6	C_3H_8	H_2	**CH_4 (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.**

$CaCl_2$ is used to absorb ___________ in the Ultimate analysis	H_2O	CO_2	O_2	CO	**H_2O**
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 metallergical coke	to reduce knocking	**Produce synthetic petrol**
Highest ranked coal is	Antharacite	Lignite	Peat	Bitumeanous coal	**Antharacite**
To remove moisture coal is heated to	105-110 ^{o}C	925-950 ^{o}C	750-800 ^{o}C	400-450 ^{o}C	**105-110 ^{o}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 ^{o}C	925-950 ^{o}C	750 ^{o}C	50 ^{o}C	**925-950 ^{o}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_2	KOH	$CaCl_2$	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 ^{o}C	700^{o}C	1000^{o}C	1500^{o}C	**1000^{o}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 ^{o}C	300-400 ^{o}C	100-200 ^{o}C	400-500 ^{o}C	**200-300 ^{o}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 _______________ ^{o}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_2 & CO	N_2 & CO_2	CO & CO_2	CO & H_2	**N2 & CO**
Blue gas consists large % of	CO & H_2	N_2 & CO_2	H_2 & N_2	H_2 & CO_2	**CO & H_2**
Which form of energy source yields only water?	H_2	Biogas	Methane	O_2	**H_2**
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 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	Platium	Calcium	**Aluminium**
Electrochemical corrosion can occurs 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 parts	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+ 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 SO2	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	**Anodizing**
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_2O_3	Fe_3O_4	MoO_3	**MoO_3**
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_2O_3	Fe_3O_4	$Fe_2O_3.XH_2O$	**$Fe_2O_3.XH_2O$**

Which of the following gases accelerates rusting of iron?	SO_2	NO_2	CO_2	All the above	**All the above**
Standard electrode potential of Fe^{2+}/Fe is,	+ 1.44 V	- 1.44 V	+ 0.44 V	- 0.44 V	**- 0.44 V**
Which of the following metal does not resists 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 acts as	Anodic	Cathodic	Corroded	None	**Cathodic**
Paints which are used to restrict corrosion are known as	Antifouling paints	Anticorrosion paints	Marine paints	Special paints	**Antifouling paints**
Caustic embrittlement, a type of stress corrosion contains deposition of corrosion products,	Fe_3O_4	$NaFeO_2$	Na_2FeO_2	K_2FeO_2	**Na_2FeO_2**
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 AND PHASE RULE

Questions	opt1	opt2	opt3	opt4	Answer
The Phenomenon of the assimilation of higher concentration of any molecular species at the surface of a solid as compared to that present in the bulk of the material is known as	adsorption	desorption	absorption	sorption	**adsorption**
The solid on whose surface gas is adsorbed is called	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 of adsorption with pressure at a given constant temperature ?	Adsorption is not affected by pressure	Adsorption decreases with pressure	Adsorption increases with pressure	Adsorption first increases then decreases with	**Adsorption increases with pressure**
Physisorption	is irreversible in nature	has highly specific nature	has high heat of adsorption	is generally multilayered	**is generally multilayered**
Freundlich adsorption isotherm can be represented as	$x/m=(k_1k_2p)/(1+K_1P)$	$x/m=(kp^{1/2})$	$x/m=(k_1k_2p)$	$x/m=(1+K_1P)$	$\boldsymbol{x/m=(kp^{1/2})}$
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**
The extent of adsorption of solutes from solution by solids	is usually greater for low molecular weight solutes	is usually grater for high molecular weight solutes.	increases with rise in temperature	decrease with rise in temperature	**is usually grater for high molecular weight solutes.**
The process in which both absorption and adsorption take place is called as	desorption	sorption	adsorbent	adsorbate	**sorption**
Chemisorption is callled as	activated adsorption	adsorption	negative adsorption	positive adsorption	**activated adsorption**

Physisorption is also known as	adsorption	vander waals adsorption	activated adsorption	multilayer adsorption	**vander waals adsorption**
Adsorption of gases on the surface of a solid is also referred to as	occlusion	collision	dissimilation	digestion	**occlusion**
The variation of adsorption with pressure at a given constant temperature is called an	Chemisorption	Physisorption	adsorption isotherm	absortiom isotherm	**adsorption isotherm**
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 desorption when	Temperature increases	Temperature decreases	Pressure increases	Concentration increases	**Temperature decreases**
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 mathametical formula of phase rule is	F = C-P+2	F = P-C-2	P = C-P+2	F = P-C+2	**F = C-P+2**
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	**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	**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**

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 absorbate is held on a surface by weak Vander Waal's forces, the absorption 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	**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	Adsorption produces heat which increases	**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 regarding physisorption	Enthalpy of adsorption ($\Delta H_{adsorption}$) is low and positive	It occurs because of van der Walls forces	It occurs because of van der Walls forces	Under high pressure it results into	**Enthalpy of adsorption ($\Delta H_{adsorption}$) is low and positive**
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 using the assumption	The adsorbed molecules interact with each other	The adsorption takes place in multilayers	The adsorption sites are equivalent in their ability to adsorb the	The heat of adsorption varies with	**The adsorption sites are equivalent in their ability to adsorb the**
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	the mass of gas striking a given area of surface is independent of the	the rate of dissociation of adsorbed	**the mass of gas striking a given area of surface is proportional to the**
The extent of adsorption of a gas on a solid depends on	temperature of the gas	adsorption of the gas	absorbtion of the gas	multilayer adsorption of gas	**temperature of the gas**
ldentify 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	in the process of adsorption, the activation energy of the	adsorption lowers the activation	**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	**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	**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**

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 –vely 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**
Water system has three phases - ice, water and vapours. The number of components in the system is	zero	two	one	three	**one**
For one component system the phase rule is	F = 3 – P	F = 2 – P	F = 1 – P	none of these	**F = 3 – P**
The Ag-Pb system component is	one	two	zero	three	**two**
For a two component system in a single phase, the degree of freedom is	zero	one	two	three	**three**
At a triple point	three phases co-exist in equilibrium	the vapour pressure is equal to the atmospheric pressure	there are three components in equilibrium	there are three degrees of freedom	**three phases co-exist in equilibrium**

The phase rule was first discovered by	Nernst	Gibbs	Arrhenius	Le Chatelier	**Gibbs**
The reduced phase rule for a condensed system is	$F = C - P + 2$	$F' = C - P + 1$	$F' = C - P$	$F = C - P + 3$	$\mathbf{F' = C - P + 1}$