B.Tech I-Year Unit–3 ELECTROCHEMISTRY

Batteries; Classification and applications of Primary Cells (Dry Cell) and Secondary Cells (Lead Acid battery). *Corrosion:* Introduction to corrosion, Types of corrosion, Cause of corrosion, Corrosion prevention and control, Corrosion issues in specific industries (Power generation, Chemical processing industry, Oil & gas industry and Pulp & paper industries).

Chemistry of Engineering Materials:

Cement; Constituents, manufacturing, hardening and setting, deterioration of cement, Plaster of Paris (POP).

Questions:-

Q1. Differentiate between Electrochemical cell and Electrolytic cell.

It is a branch of chemistry which deals with the transformation of chemical energy to electrical energy and vice versa.

<u>Cell</u>: A device which converts chemical energy to electrical energy and vice versa is known as cell.

Electrochemical cell or Voltaic Cell	Electrolytic cell
Cell which converts chemical energy to electrical energy.	Cell which converts electrical energy to chemical energy.
Redox reaction takes place which is spontaneous and it is responsible for the production of electrical energy.	Redox reaction is non spontaneous and electrical energyis supplied so that the reaction may take place.
Electrodes used are of dissimilar material.	Electrodes used may be of similar or different material.
Each electrode is dipped in electrolytic solution of its own ions.	Both electrodes are dipped in same electrolytic solution.
Salt bridge is used.	Salt bridge is not used.
Anode is negative and cathode is positive.	Anode is positive and cathode is negative.
Electrons move from anode to cathode in external circuit.	Electrons are supplied by battery and enter through cathode and come out through anode.
Ex: galvanic cell.	Ex: lead acid storage battery.

Cells are of two types: Electrochemical cell and Electrolytic cells

ELECTRODE POTENTIAL

Q1. What is Electrode potential? Give its type.

"<u>Electrode potential</u> is the measure of the tendency of metallic electrode to lose or gain electrons, when it is in contact with its own salt solution."

"<u>Standard electrode potential</u> is the potential difference set up between the metal and its own salt solution of 1M concentration at 25^oC at equilibrium."

Electrode potential is of two types:

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1. **Oxidation potential**: It is the measure of tendency of an electrode to lose electrons or toget oxidised is called its oxidation potential.

 $M(s)M^{n+}(aq) + ne^{-} \longrightarrow$

2. **Reduction potential**: It is the measure of tendency of an electrode to gain an electron orto get reduced is called its reduction potential.

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

Electrode potential depends on:

- 1. Nature of metal and its ions
- 2. Temperature
- 3. Concentration of ions in the solution

EMF (ELECTROMOTIVE FORCE OR CELLPOTENTIAL)

EMF is the potential difference between the two electrodes of the cell when either no or negligible current is allowed to flow in the circuit.

E.M.F = Reduction Potential of cathode – Oxidation Potential of anode

 $E^{0}_{cell} = E^{0}_{cathode} - E^{0}_{anode}$

 $E^{0}_{cell} = E^{0}_{right} - E^{0}_{left}$

The cell reaction is feasible only when E_{cell} is positive.

STANDARD HYDROGEN ELECTRODE (SHE) OR NORMAL HYDROGEN ELECTRODE (NHE)

Since half cell in an electrolytic cell can work only when combined with other half cell, so it's impossible to determine the absolute electrode potential of a single electrode. Thus, to determine the electrode potential of a half-cell, the electrode is connected to a reference electrode whose potential is fixed to 0.0V. This reference electrode is known as SHE/NHE.

NERNST EQUATION

We know that, $\Delta G = -nFE$ $\Delta G^{\circ} = -nFE^{\circ}$

Also, $\Delta G = \Delta G^{\circ} + RT \ln Q$ So, $-nFE_{cell} = -nFE_{cell}^{\circ} = E_{cell}^{+} RT - nFR_{cell} P + nFR_{cell$

At standard temperature T = 298 K, R = 8.314 J/K mol, F=96500 C

 $E_{cell} = E_{cell}^{\circ} - \underline{.0592}_{n} \log_{10} Q \quad - Eq. 1$

At equilibrium: $Q = K_{eq}$ and $\Delta G = 0$, Therefore, E = 0, Equation 1 will become

 $E^{\circ}_{cell = \underline{.0592}} \log_{10} K_{eq}$ For a cell reaction: $aA + bB \longrightarrow cC + dD$

$$\mathbf{Q} = \mathbf{K}_{eq} = \frac{[\mathbf{C}]^{c}[\mathbf{D}]^{d}}{[\mathbf{A}]^{a}[\mathbf{B}]^{b}}$$

Here, Equation 1 will be written as:

$$E_{cell} = E_{cell}^{\circ} - \underline{.0592}_{nF} \log_{10} [C]^{c} [D]^{d}$$

$$nF [A]^{a} [B]^{b}$$

$$E_{cell} = E_{cell}^{\circ} - \underline{.0592}_{cell} \log_{10} \underline{Product}$$

$$n \quad Reactant$$

OR Nernst Equation

$$E_{cell} = E_{cell}^{\circ} + \underline{.0592} \log_{10} \underline{Reactant}$$

n Product

Electrochemical series: The arrangement of elements in order of increasing reduction potential values is called electrochemical series. With the help of this series we can:

a) When two metals are in contact we can predict which metal will act as anode and which willact as cathode. (The one with lower reduction potential act as anode and is corroded).

b) Feasibility of the reaction: If the EMF of cell is positive, then only the reaction is feasible.

c) Replacement tendency of metals: The metal placed higher in series can replace the metal placed below it in electrochemical series.

d) Evolution of hydrogen: All the metals placed above hydrogen in series can evolve hydrogen.

<u>Galvanic Series</u>: In this series the metals and their alloys are placed according to their corroding tendency. As we move down the series the corroding tendency of metals increases.

<u>Passivity</u>: Some metals do not corrode according to their position in galvanic series and resist corrosion. This property of metals is called passivity and such metals are called passive metals.

This happens because they form a protective, self-healing and strong metal oxide layer on their surface which protects them from further corrosion.

GALVANIC CELL or VOLTAIC CELL



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At Anode: $Zn \longrightarrow Zn^{+2} + 2e^{-}$ At Cathode: $Cu^{2+} + 2e^{-} \longrightarrow Cu$ Overall reaction: $Zn + Cu^{+2} \longrightarrow Zn^{2+} + Cu$

Cell Representation: $Zn(s) \mid ZnSO_4 (sol) \parallel CuSO_4 (sol) \mid Cu(s)$

OR $Zn | Zn^{2+} || Cu^{2+} | Cu$

Q1. What are Secondary batteries? Discuss the various reactions involve during the charging and discharging of lead storage battery. [2018-2019]

Q2. Define the term batteries. Explain the construction of Lead acid battery. Write all the chemical reactions taking place during charging and discharging of lead acid battery.[2021-2022]

Answer:

LEAD ACID STORAGE CELL

- It is both a voltaic cell and an electrolytic cell.
- It is a secondary storage battery, as it can be recharged.
- It is called lead acid because it contains acid as an electrolyte and plates are made up of lead.

Construction:

- **Anode**: Made of lead grid filled with spongy lead.
- <u>**Cathode**</u>: Made of a lead grid filled with PbO₂
- **Electrolyte:**28-30% solution of H₂SO₄ (d=1.31 g/cm³; 38% by mass) in a hard rubber or plastic container (ebonite case).
- The battery consists of <u>6 such cells connected in series</u>: since each cell has an emf of about 2V, the overall <u>emf of the battery is 12V</u>.
- The cathode and anode plates are arranged alternatively, separated by thin perforated plastic or fibre glass.

Working:

During Discharging: When the battery supplies current or electrical energy,

Anode: $Pb + SO_4^{2^-} \rightarrow PbSO_4 + 2e^-$ Cathode: $PbO_2 + 4H^+ + SO_4^{2^-} + 2e^- \rightarrow PbSO_4 + 2H_2O + ENERGY$ Net reaction during discharging : $Pb + PbO_2 + 4H^+ + 2SO_4^{2^-} \rightarrow 2PbSO_4 + 2H_2O + ENERGY$

 H_2SO_4 is used up during discharging so level of acid falls. When the density falls below1.20 g/cm³ the battery needs recharging.

Also precipitate of lead sulphate is formed during discharging which completely covers both anode & cathode. As a result, cell stops working, Then, it needs to be recharged.

During recharging cell operates like an electrolytic cell. Lead sulphate formed is used up during recharging.

Recharging is done by passing an external emf greater than 2V. Electrode reactions are reverse of those during discharging.

The cell could be recharged because solid lead sulphate is formed during discharging which acts as a reactant in recharging.

During Recharging:

Cathode: $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ **Anode:** $PbSO_4 + 2H_2O + ENERGY \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$ **Net reaction:** $2PbSO_4 + 2H_2O + ENERGY \rightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$

The net cell reaction during charging and discharging process for a cycle:



Question: Define Corrosion by giving a suitable example. Answer:

CORROSION

Corrosion is a process of gradual destruction or deterioration of metals by chemical or electrochemical attack of environment. Ex: Rusting of iron, tarnishing of silver etc.

Units of Corrosion:

Mils per year (MPY) Milligram per decimetre square per day (MDD) 1 mil = 1/1000 inch

REASON / CAUSES OF CORROSION

ORES OR METAL COMPOUND	Extraction of metal (+energy		METAL (PURE)
Stable form with lower energy	Corrosion (- energy)	un	stable due to higher
energy			

FACTORS AFFECTING CORROSION:

Rate and extent of corrosion depends upon:

1 Nature of metal

2 Nature of environment

NATURE OF METAL:

1. Position of metals in galvanic series:

a) If two metals are in electrical contact, then the metal placed higher in galvanic series acts as anode and gets corroded.

b) Greater is the difference in the position of the metals in the galvanic series, faster is the rate of corrosion.

2. Relative areas of anode and cathode:

Rate of corrosion a cathodic area/ Anodic area

3. Purity of metal: The impurities present in metal results in setting up small electrochemical cells leading to corrosion.

4. Physical state of metal: Rate of corrosion α 1/ grain size of metal

5. Nature of oxide film: If the oxide film formed on metal surface is porous and loosely held, then the corrosion of the metal takes place very rapidly.

6. Solubility of corrosion products: If corrosion products are soluble then metal corrodes rapidly and continuously.

7. Volatility of corrosion products: If the corrosion products formed are volatile, then there is rapid and continuous corrosion.

NATURE OF CORRODING ENVIRONMENT:

1) Temperature: Rate of corrosion α Temperature

2) Moisture: Moisture acts as solvent for corrosion. So, Rate of corrosion α Moisture

3) **pH:** Generally acidic medium leads to more corrosion.

4) Nature of corroding medium: Nature of anions, cations and their conducting nature affects the rate of corrosion.

5) Presence of impurities and suspended particles in atmosphere: Corrosive gases, fumes of sulphuric acid and hydrochloric acid, suspended particles like NaCl, charcoal, etc. increases the rate of corrosion.

Corrosion law – Pilling Bed worth rule

Specific volume ratio = $\frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$

ELECTROCHEMICAL / WET THEORY OF CORROSION

Questions:-

- Q1. Describe electrochemical theory of corrosion. How corrosion can be prevented by sacrificial anodic protection and impressed current cathodic protection. [2019-2020]
- Q2. Discuss rusting of iron by Hydrogen evolution and Oxygen absorption mechanism. Briefly explain sacrificial cathodic protection and impressed current cathodic protection. [2018-2019]

Answers:

Electrochemical corrosion involves flow of electrons between anode and cathode.

Electrochemical theory of corrosion is explained by two mechanisms:

- 1. Oxygen absorption mechanism (in neutral and alkaline medium).
- 2. Hydrogen evolution mechanism (in acidic medium).

For Ex: Rusting of iron.

Mechanism of Corrosion:
OXYGEN ABSORPTION MECHANISM (in basic or neutral medium)
Reaction at ANODE (OXIDATION)
$Fe \rightarrow Fe^{2+} + 2e^{-}$
Reaction at CATHODE (REDUCTION)
$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$
OVERALL REACTION
$Fe + \frac{1}{2}O_2 + H_2O Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2(ferrous hydroxide)$

If enough O_2 is present: $Fe(OH)_2$ is oxidised to rust: $Fe_2O_3.xH_2O$ (Yellow rust) In limited supply of oxygen Black Magnetite is formed: $Fe_2O_3.FeO.6H_2O$ (Black magnetite)



Mechanism of wet corrosion by oxygen absorption mechanism

(Small anodic area and large cathodic area, so higher rate of corrosion)

HYDROGEN EVOLUTION MECHAINSM (In acidic medium):

All the metals placed above H_2 in electrochemical series, corrodes in acidic solution by hydrogen evolution mechanism.

Anodic reaction: Fe \rightarrow Fe⁺² + 2e⁻ Cathodic reaction: 2H⁺ + 2e⁻ \rightarrow H₂

Overall reaction: Fe + $2H^+$ \rightarrow $Fe^{2+} + H_2$



Mechanism of wet corrosion by hydrogen evolution mechanism

CHEMICAL CORROSION OR DRY CORROSION

Corrosion that takes place in the absence of electrolyte, due to direct attack of gases on metals is called dry corrosion. This type of corrosion takes place at elevated temperature and corrosion is uniform over metal surface.

E.g. attack of oxygen on iron.

Questions: What are corrosion inhibitors? Explain with example how anodic and cathodic inhibitor provides protection against corrosion.

Answer:

PREVENTION OF CORROSION

Corrosion can be prevented by the following methods:

1. PROPER DESIGN

- a) Avoid sharp bends and sharp corners.
- b) Avoid contact of dissimilar metals in presence of corroding medium.
- c) There should be proper drainage.
- d) When the two dissimilar metals are to be used in contact, anodic area should be large and cathodic area should be small.
- e) If two dissimilar metals have to be used in contact, their position in electrochemical series should as close as possible.
- f) If two metals have to be coupled use insulation between them.

2. MODIFICATION OF ENVIRONMENT

- 1) Removing moisture by using silica gel.
- 2) Removing oxygen by adding oxygen scavengers like hydrazine
- 3) By adjusting pH using pourbaix diagram.

3. BY USING INHIBITORS: The substances which are added from outside to inhibit the corrosion are known as inhibitors.

There are two types of inhibitors:

a) ANODIC INHIBITORS

They react with the metallic ions of anode and form insoluble precipitate which is adsorbed on metal surface forming a protective film/barrier. Ex: alkalis, phosphates, chromates, etc.

b) CATHODIC INHIBITORS

They decrease the rate of reaction thereby reducing rate of overall corrosion.

i) IN ACIDIC MEDIUM

Cathodic reaction:

 $2H^+ + 2e^- \longrightarrow H_2$

Cathodic inhibitors slow down the diffusion of H^+ ions through cathode and thus reduces corrosion rate.

Ex – Amines, Mercaptons, urea, thioureas, etc.

ii) IN NEUTRAL /ALKALINE MEDIUM

Cathodic reaction:

 $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

Cathodic inhibitors remove O_2 that is being used at cathode, thereby reducing corrosion. Ex: O_2 scavengers like Na_2SO_3 , N_2H_4 , etc.

4. CHANGINING THE OPERATING VARIABLES:

- By lowering the temperature
- By selecting suitable pH.

5. PROTECTIVE COATINGS

- (a) **Organic coating**: includes use of paints, varnishes, etc. which acts as organic barrier between metal and environment.
- (b) **Inorganic coating**: inorganic surface barriers produced by chemical/ electrochemical reactions at the surface of base metal coatings are used for paints. Ex phosphates, chromates, etc.

(c) **Metallic coatings:** In metallic coatings one metal is coated over another metal. There are two types of metallic coatings: anodic coating and cathodic coating.

ANODIC COATING or SACRIFICIAL COATING:

- 1. Base metal is coated with a metal which is more reactive.
- 2. Protects the underlying base metal sacrificially.

3. Known as anodic coating as the reduction potential of coated metal is less than that of base metal.

4. If there are pores, cracks, or breaks in such a coating base metal is not corroded till all the coated metal is consumed.

5. Zn, Cd, Al are generally used as sacrificial coatings.

6. Ex: galvanised iron (coating of Zn on Fe)

CATHODIC COATING or NOBLE COATING:

1. Base metal is coated with a metal which is less reactive (more noble) in its comparison.

2. Protects the base metal due to its noble character.

3. Also known as Cathodic coating as reduction potential of coated metal is more than that of base metal.

4. If there are pores, break, etc. corrosion takes place because of small anodic area and large cathodic area.

5. Ni, Ag, Cr, Pb, etc. are used generally for noble coating.

6. Ex: coating of Sn on Fe.

6. Modification of metal

Metal can be modified by annealing, refining and alloying.

Questions:-

Q.1 Explain sacrificial anodic and impressed cathodic protection method for prevention of corrosion. [2021-2022] OR

How can anodic and cathodic metallic coating help in protection against corrosion? Q2. Define the term corrosion. Describe the mechanism of electrochemical corrosion with the help of hydrogen evolution and oxygen absorption reactions. How it can be prevented using sacrificial anodic protection? [2021-2022]

7. CATHODIC PROTECTION

The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection.

There are two types of cathodic protection

- (a) Sacrificial anodic protection.
- (b) Impressed current method.

SACRIFICIAL ANODIC PROTECTION

Base metal is connected by a wire to a more reactive metal so that the base metal becomes cathode and more reactive metal becomes anode.



The anodic metal gets corroded slowly, while the base metal (cathodic) is protected. The more active metal is called sacrificial anode and is replaced by a fresh one, when it is completely consumed. Mg, Zn, Al and their alloys are generally used as sacrificial anodes.

Ex: 1. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

2. The underground water pipelines and water tanks are also protected by sacrificial anode method.



IMPRESSED CURRENT CATHODIC PROTECTION:

In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.

The impressed current is slightly higher than the corrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.

The impressed current is taken from a battery or rectified on A.C. line. The impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers etc.



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Cement

Concrete is widely used as a non-metallic material in construction of buildings, dams, bridges, high ways etc. In concrete, cement is a building material that possesses cohesive and adhesive properties and capable of bonding with stones, bricks, building blocks etc.

Portland cement

The name Portland cement is used because this powder on mixing with water gives a hard, stone like mass which resembles Portland rock (Leeds city UK). It is widely used as a non-metallic material in construction. It is a composition of calcium silicates, calcium aluminates and small amount of gypsum.

Composition of Portland cement:-

A sample of Portland cement contain following composition:

S.No.	Component	Percentage range by mass
1.	Calcium Oxide or lime(CaO)	50-60%
2.	Silica (SiO ₂)	20-25%
3.	Alumina (Al ₂ O ₃)	5-10%
4.	Magnesia (MgO)	2-3%
5.	Fe ₂ O ₃	1-2%
6.	Sulphur trioxide(SO ₃)	1-2%

Manufacture of Portland Cement:

The steps involve in the manufacturing process are as follows:

- 1) Mixing
- 2) Burning
- 3) Grinding
- 4) Packing

(1) Mixing:

Mixing of raw materials can be done either by (a) dry process (b) wet process

S.No.	Dry Process	Wet Process
1.	It is adopted when the raw materials are quite hard.	It can be used for any type of raw materials.
2.	Fuel consumption is low.	Fuel consumption is high.
3.	Process is slow.	Process is comparatively faster.
4.	Cement produced is of inferior quality.	Cement produced is of superior quality.
5.	Cost of production of cement is less.	Cost of production of cement is somewhat higher.
6.	On the whole, the process is costly.	On the whole, the process is cheaper.

2) Burning:

The burning process is done in Rotary Kiln. The Rotary Kiln possesses three different temperature zone like drying zone, calcinations zone and Clinkering zone.



Rotary Kiln

(a) Drying zone:

It is the upper part of Rotary Kiln having temperature around 400°C, most of the water from the slurry gets evaporated.

(b) Calcinations zone:

It is middle portion of Rotary Kiln where the temperature is around 1000°C. In this region lime stone undergoes decomposition to form quick lime and carbon dioxide (escape out).

(c) Clinkering zone:

It is the lower part of Rotary Kiln, the temperature is between 1500 to 1700°C where quick lime and clay undergo chemical interaction or fusion, yielding calcium silicate and aluminates.

$2CaO + SiO_2$	→ Ca ₂ SiO ₄	
	Tricalcium sil	icate(C ₂ S)
$3CaO + SiO_2$	→ Ca ₃ S	iO ₅
	Tricalcium silicate	(C ₃ S)
$3CaO + Al_2O_3$	→ Ca ₃ A	l_2O_6
	Tricalcium al	uminate (C ₃ A)
$4\text{CaO} + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	>	$Ca_4Al_2Fe_2O_{10}$
		Tetracalciumaluminoferrite (C ₄ AF)

The aluminates and silicates then fuse together to form stone like structure known as clinkers.

3) Grinding:

The cooled clinkers are ground to a fine powder in ball mill. At this time 2-3% of gypsum is added to prevent the early setting of cement.

(4) **Packing**

The ground cement is stored and then fed to automatic packing machine.

Setting and hardening of cement

When water mixed with Cement, forms a plastic paste, hydration reaction begin, resulting in the formation of gel and crystalline products.

Setting: It is defined as stiffening of the original plastic mass, due to initial gel formation.

Hardening: It is the development of strength, due to crystallization.

Initial setting:

The initial setting of the cement is mainly due to the hydration of tricalcium aluminate (C_3A) and gel formation of tetracalcium aluminoferric.

 $3CaO.Al_2O_3+6H_2O \rightarrow 3CaO.Al_2O_3.6H_2O+Heat$ $2(2CaO.SiO_2)+4H_2O\rightarrow 3CaO.2SiO_2.6H_2O+Ca(OH)_2+Heat$

 $4CaO.Al_2O_3.Fe_2O_3+7H_2O {\longrightarrow} Ca_3Al_2O_6.6H_2O + CaO.Fe_2O_3.H_2O + Heat$

Final setting and hardening:

It is due to the formation of tobermonite gel plus crystallization of calcium hydroxide and hydrated tricalcium aluminate.

 $2(2CaO.SiO_2) + 6H_2O \longrightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2 + Heat$

Function of gypsum in cement:

Tricalcium aluminate combines with water very rapidly with the evolution of large amount of heat.

 $3CaO.Al_2O_3+ 6H_2O \longrightarrow 3CaO.Al_2O_3.6H_2O + Heat$

After the initial setting the paste becomes somewhat stiff. However, the added gypsum retards the dissolution of Tricalcium aluminate by forming insoluble calcium sulpho-aluminate:

 $3CaO.Al_2O_3 + xCaSO_4.2H_2O \longrightarrow 3CaO.Al_2O_3.xCaSO_4.7H_2O$

Chemical reactions taking place during setting and hardening of cement



Decay of Concrete

Cement concrete is mechanically strong, yet it is highly prone to chemical attack, because concrete contains some free lime (CaO). In acidic water, lime of concrete dissolves, thereby making it weak, pH of most natural waters is slightly greater than 7, consequently, such waters do not have any marked effect on the strength of concrete. However, as the acidity increases, the deterioration of concrete enhances.

Lime is more soluble in soft water than hard water. Consequently, deterioration of concrete is quicker, when in contact with soft water. The most serious type of damage to concrete takes place in the presence of sulphates. The sulphates combine with tricalcium aluminate to form sulpho-aluminates, which occupies more volume.

Protection of concrete:

(1) By giving a coating of bituminous material. This prevents direct contact between concrete and water.

(2) By coating the surface with silicon fluoride in a soluble form together with oxides of Zn, Mg or Al. The precipitate of calcium fluoride so-formed in the capillaries prevents dissolution of lime.

Plaster of Paris (POP)

It is a hemihydrates of calcium sulphate. Its molecular formula is $2CaSO_4$. H_2O or $CaSO_4$. $1/2H_2O$.

Preparation:

It is obtained when gypsum, CaSO₄·2H₂O, is heated to 393 K. $2(CaSO_4.2H_2O) \rightarrow 2(CaSO_4).H_2O + 3H_2O$ Gypsum Plaster of Paris

Above 393 K, no water of crystallization is left and anhydrous calcium sulphate, CaSO₄ is formed. This is known as 'dead burnt plaster'.

Properties:

i) When plaster of Paris reacts with water, large amount of heat is release. It absorbed water and convert into gypsum. This process is known as setting of plaster of Paris.

ii) Plaster of Paris is a fine white powder. When heated at 200°C it first convert into *Gamma-CaSO4* and on further heating at 600°C it changes into *beta*-CaSO₄.

When *beta*-CaSO₄ is heated about 1100°C, then it converted into quicklime (CaO) and SO₃. The quick lime is used in formation of cement.

Uses of Plaster of Paris:

- i) It is used in making casting and in surgical bandage.
- ii) Used in making plaster wall and for making plaster boards
- iii) Used in making statue, toy, models etc.
- iv) Used in formation of gypsum and cement.

v) Used in the formation of calcium sulphate.

Numerical Problems

Question: Calculate the cell potential of the given cell at 25°C. ($R = 8.31 JL^{-1} mol^{-1}$, F=96500Cmol⁻¹).[2018-2019]

```
Ni(s)|Ni<sup>+2</sup>(0.01M)||Cu<sup>+2</sup>(0.1M)|Cu(s)
Given E^{\circ}_{Cu+2/Cu}=+0.34V;E^{\circ}_{Ni+2/Ni}=-0.25V
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Solution:



Question: Calculate the EMF of the following cell and also write the cell reactions: Z_{1}/Z_{2}^{++} (0.00110) ((A + (0.110)) (A

 $Zn / Zn^{++} (0.001M) // Ag^{+} (0.1M) / Ag$ The standard potential of Ag / Ag⁺ half-cell is 0.80 V and Zn / Zn⁺⁺ is -0.76 V.

Solution:

At Anodis:

$$2n \rightarrow 2n^{2+} + 2e^{\Theta}$$
At Cethodi:

$$2Ag^{+} + 2e^{\Theta} \rightarrow 2Ag$$

$$2n + 2Ag^{+} \rightarrow 2n^{2+} + 2Ag$$
Eall = Eall - 0.0592 log [flooduct]

$$r = 1.56 - 0.0592 log [0.00]$$

$$= 1.56 - 0.0592 log [10^{-3}]$$

$$= 1.56 - 0.0592 log [10^{-3}]$$

$$= 1.56 - 0.0592 log [10^{-1}]^{2}$$

$$= 1.56 - 0.0592 log [10^{-1}]$$

$$= 1.56 - 0.0592 log [10^{-1}]$$

$$= 1.56 - 0.0592 log [10^{-1}]$$

$$= 1.56 + 0.0592$$

$$= 1.56 + 0.0592$$

$$= 1.56 + 0.0592$$

$$= 1.56 + 0.0592$$

Question: Give significance of Nernst equation.

Consider a cell reaction: $Zn / Zn^{2+}[0.1M] \parallel Cu^{2+}[0.2M] / Cu$ Standard reduction potential of Zn^{2+} and Cu^{2+} are -0.76V and 0.34V respectively. Write half-cell reactions, complete cell reaction and calculate EMF of the cell. [2020-2021] Solution:

At Anode: 7 Zn2++2e Ø Calhodes cu2++2e0 -> Cu 2++Cu overall 2+_ Zn+cu >zh 501] -0.0592 100 Ecre = Eratisde - Eanode [012] 2 = 0:34+0.76 = 11 - 0.0296 (-0.693) = 11 V = 11 + 0:0205 = 11205 V

Question: Al^{3+} (1.2 M)+ Fe \longrightarrow Al +Fe₃ (2.5 M) [2021-2022] Calculate E_{cell} for the reaction if E^o_{cell} = -1.62 V.

Solution:

Question: How much rust (Fe₂O₃.3H₂O) can be produced by 3g of iron? [2020-2021]

Question: What is Nernst equation? The emf of a cell measured by means of a hydrogen electrode against a saturated calomel electrode at 298K is 0.4188 V. If the pressure of the Ht(g) was maintained at1 atm, calculate the pH of the unknown solution, given potential of reference calomel electrode is 0.2415X*. **[2019-2020].**