Lecture : 20

Electrochemistry: It is a branch of chemistry which deals with the conversion of chemical energy to electrical energy and vice-versa.

- **Cell**: It is the device which converts chemical energy to electrical energy and vice versa. There are two types of cells – Electrolytic cells and Daniel or Voltaic cell.

Voltaic cell	Electrolytic cell
1. converts chemical energy to electrical energy.	1. converts electrical energy to chemical energy.
2. Electrodes are of dissimilar metals and are dipped in electrolytic solutions of their own ions.	2. Both electrodes are dipped in same electrolytic solution.
3. Salt bridge is used.	3. Salt bridge is not used.
4. Anode is negative & cathode is positive	4. Anode is positive and cathode is negative
5. Electrons move from anode to cathode in external circuit.	5. Electrons are supplied by battery, enter through cathode and come out through anode
6. Eg- Galvanic cell	6. Eg- leadacid storage battery

- **Oxidation**: Addition of O_2 or loss of electrons is known as oxidation. There occurs an increase in oxidation number.
- **Reduction**: Removal of O_2 or gain of electrons is called reduction. There occurs decrease in oxidation number.
- **Standard Hydrogen electrode or Normal Hydrogen electrode**
  To determine the electrode potential of a half cell, the electrode is connected to a referance electrode, whose potential is fixed to 0.0V. This referance electrode is known as Standard Hydrogen electrode. (SHE/NHE)

Q1. Define electrode potential and E.M.F. How m types of electrode potential is there?

Ans. Electrode potential is defined as the potential diff developed between electrode and its own electr When this potential difference is measu at 1M concentration of electrolyte and 25°C a equilibrium, it is known as standard electr potential. It is of two types:

Oxidation Potential: It is the measure of the tendency any electrode to lose electrons or to get oxidised.

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

Reduction Potential: It is the measure of tendency of electrode to gain electrons or to get reduced.

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

Electrode potential depends on:

a) Nature of metal and its ions
b) Temperature
c) Concentration of ions in the solution

EMF or Electromotive force: It is the potential differ between the two electrodes of the cell when either no or negligible current is allowed to flow in the circuit.

$$\boxed{\text{EMF} = \text{Reduction Potential of cathode} - \text{Reduction Potential of anode}}$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

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

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

Q2. What is Electrochemical series? What are its applicatio

Ans. The arrangement of elements in order of increasing reduct potential value is called electrochemical series. The applications of this series are as follows:

a) When two metals are in contact, we can predict which metal will act as anode & which one will act as cathode [The metal with lower reduction potential acts as anode]

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

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

d) Evolution of hydrogen : All the metals placed above H_2 in series can evolve hydrogen.

Q3. Imp Discuss the principle and working of a galvanic cell. (2016-17).

Ans. Principle of Galvanic cell : Galvanic cell or voltaic cell is an electrochemical cell which converts chemical energy of spontaneous redox reactions into electrical energy.

The working principle of voltaic cell is based on the fact that, the electric work is done by a galvanic cell due to the Gibbs free energy of spontaneous redox reactions in the galvanic cell.

Construction of Galvanic cell : It consist of two half cells and a salt bridge. Each half cell has a metallic electrode dipped in an electrolyte. The two half cells are connected to a voltameter with the help of connecting wires.

- cathode : Made of copper. It is positive terminal of cell and reduction occurs at this electrode. It is dipped in $CuSO_4$ solution.
- Anode : Made of zinc. It is negative terminal of cell and oxidation occurs at this electrode. It is dipped in $ZnSO_4$ solution.
- Salt bridge : It is a U shaped glass tube filled with an electrolyte which do not take part in cell reactions eg:- KNO_3, KCl, in Agar-Agar gel.

External circuit : Through this flow of electrons takes place between the electrodes.

Working : Following reactions takes place :-

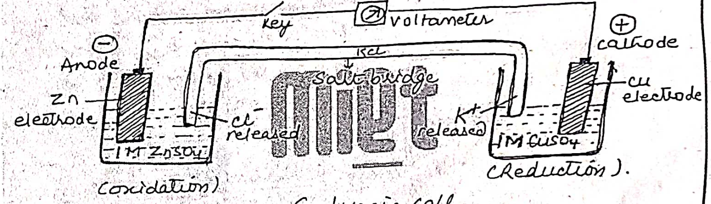
At anode : $Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$ (oxidation)

At cathode : $Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ (Reduction)

overall reac^n : $Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$

Cell Representation : $Zn_{(s)} / ZnSO_{4\,(aq)} // CuSO_{4\,(aq)} / Cu_{(s)}$

When the cell operates, electrons flow through the external circuit from zinc electrode to copper electrode.



Galvanic cell

M. Imp

Q4. Derive Nernst equation (2018-19), (2020-21)

Ans. Derivation of Nernst equation : we know that -

$$\Delta G = -nFE_{cell}$$

under standard conditions : $\Delta G^\circ = -nFE^\circ_{cell}$

where, n = number electrons transferred)

Also, $\Delta G = \Delta G^\circ + 2.303 RT \log Q$

where, R = universal gas constant (8.314 J $K^{-1} mol^{-1}$)

F = Faraday constant (96500 C mol^{-1})

so, $-nFE_{cell} = -nFE^\circ_{cell} + 2.303 RT \log Q$

$$\boxed{E_{cell} = E^\circ_{cell} - 2.303 \frac{RT}{nF} \log_{10} \frac{[Product]}{[Reactant]}}$$

Imp

Q5. Calculate the cell potential of the given cell at 25°C.
$R = 8.31\ JK^{-1}mol^{-1}$, $F = 96500\ C\ mol^{-1}$ (2018-19)

$Ni_{(s)}/Ni^{2+}(0.01\,mol)\ //\ Cu^{+2}(0.1\,mol)\ /\ Cu^{+}(s)$

∴ Given: $E^0_{Cu^{+2}/Cu(s)} = 0.34\,V$; $E^0_{Ni^{+2}/Ni(s)} = -0.25\,V$

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

$= 0.34-(-0.25) = 0.59\,V$

$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log_{10}\frac{[Product]}{[Reactant]}$

$= 0.59 - \frac{0.0591}{2}\log_{10}\frac{[0.01]}{[0.1]}$

$= 0.59 - 0.295 = 0.61955\,V.$

Imp

Q6. Calculate the cell potential at 298 K for the cell reaction

$Al^{3+} + Fe(s) \longrightarrow Fe^{3+} + Al(s)$; $E^0_{cell} = 1.62V$

The concentration of Al^{3+} and Fe^{3+} are 1.2 M and 2.M respectively (2018-19)

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

$= 1.62\,V.$

$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log_{10}\frac{[Product]}{[Reactant]}$

$= 1.62 - \frac{0.0591}{3}\log_{10}\frac{[2.5]}{[1.2]}$

$= 1.62 - 0.00196 \times 0.3187$

$= 1.6293 - 0.00626 = 1.63556\,V$

Imp

Q7. Standard reduction potential of Zn^{+2} and Cu^{+2} are $-0.76V$ and $0.34V$ respectively. Write half cell reactions, complete cell reactions and calculate EMF of the cell (2020-21)

∴ $Zn(s)/Zn^{+2}[0.1M]\ //\ Cu^{2+}(0.2M]\ /\ Cu(s).$

Ans. At anode : $Zn(s) \longrightarrow Zn^{+2} + 2e^-$ (oxidation half)

At cathode : $Cu^{+2} + 2e^- \longrightarrow Cu(s)$ (Reduction half)

overall reaction: $Zn_{(s)} + Cu^{+2} \longrightarrow Zn^{+2} + Cu(s)$

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

$= 0.34-(-0.76).$

$= 1.1$ volts.

$E_{cell} = E^0_{cell} - \frac{0.059}{n}\log_{10}\frac{[Product]}{[Reactant]}$

$= 1.1 - \frac{0.059}{2}\log_{10}\frac{[0.1]}{[0.2]}$

$= 1.1 - 0.0295 \times (-0.301).$

$= 1.1 + 0.0088$

$= 1.1088\,V.$

Q8. Give the significance of Nernst equatio

Ans. Significance of Nernst equation :

It helps in the determination of cell potential non standard conditions.

It relates the measured cell potential to the of the reaction and allows the exact determina constants of equilibrium.

Q9. What is salt bridge? What are its uses?

Ans. Salt bridge is used in Voltaic cell or Ga cell. It is a U shaped tube connecting the electrolytes in which the electrodes (ano cathode) are dipped.

It is filled with an electrolyte which do interfere with the cell working eg- KCl etc

Uses of salt bridge

1. It completes the internal circuit of the ce
2. It maintains the electrical neutrality of cell.

Lecture - 21

Relation between emf of cell, ΔS and ΔH

From Gibbs Helmholtz equation, we have -

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \quad — ①$$

Also, $\Delta G = -nFE$ — ②

Differentiating eq^n ② with respect to temperature at constant pressure -

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -nF\left[\frac{\partial E}{\partial T}\right]_P \quad — ③$$

Substituting the value of $\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$ in eq^n ② -

$$\Delta G = \Delta H - nFT\left[\frac{\partial E}{\partial T}\right]_P \quad — ④$$

$$\boxed{\Delta H = nF\left[T\left(\frac{\partial E}{\partial T}\right)_P - E\right]}$$

Relation between ΔS and Ecell

Eq^n ④ can also be written as -

$$\Delta G = \Delta H + T\left[-nF\left(\frac{\partial E}{\partial T}\right)_P\right]$$

Also we know that $\Delta G = \Delta H - T\Delta S$

On comparing the above two equations we get -

$$\boxed{\Delta S = +nF\left[\frac{\partial E}{\partial T}\right]_P}$$

Here, ΔS = Entropy change (J/K)

$\left[\frac{\partial E}{\partial T}\right]_P$ = Temperature coefficient (V/K)

ΔH = Enthalpy change (Joules)

F = Faraday constant (96500 c/mole)

E = EMF in volts ; n = no. of electrons

$$E_{cell} = E^\circ_{cell} + 0.0591(-\log[H^+])$$

$$= E^\circ_{cell} + 0.0591\ p_H$$

M.Imp

Q8: The emf of the cell $Cd/CdCl_2, 2.5H_2O(sat)||AgCl_{(s)}/Ag$ involving following reaction:

$$Cd_{(s)} + 2AgCl_{(aq)} \longrightarrow CdCl_2.5H_2O(sat) + 2Ag_{(s)}$$

is 0.6753V and 0.6915V at 25°C and 0°C. Calculate ΔH, ΔG and ΔS at 25°C (2020-21)

Ans $E_1 = 0.6915$ at $T_1 = 0°C = 273K$

$E_2 = 0.6753$ at $T_2 = 25°C = 298K$

$$(\partial E/\partial T)_P = \left(\frac{E_2 - E_1}{T_2 - T_1}\right) = \left(\frac{0.6753 - 0.6915}{298 - 273}\right) = -0.00065\ V/K$$

$\Delta G = -nFE^\circ_{cell}$ (E°_{cell} is asked for 25°C)

$= 2 \times 96500 \times 0.6753$

$= -130332.9$ Joules.

$\Delta H = nF\left(T(\partial E/\partial T)_P - E\right)$

$= 2 \times 96500 \times [298(-0.00065) - 0.6753]$

$= -167717$ Joules.

$\Delta S = -nF[\partial E/\partial T]_P$

$= 2 \times 96500(-0.00065)$

$= -125.45$ J/K.

M. Imp

Q1. What is corrosion? Explain wet theory of corrosion or electrochemical theory of corrosion. (2014-15, 2015-16, 2016-17, 2017-18, 2018-19, 2019-20).

Ans. Electrochemical corrosion involves the formation of large number of galvanic cells on the surface of material. The reactions takes place in presence of electrolyte and there occurs flow of electrons from anode to cathode. corrosion products are formed towards cathode.

Eg: Rusting of Iron.

Electrochemical corrosion or wet corrosion can be explained by two mechanisms:

- Oxygen absorption mechanism (in alkaline / neutral medium)
- Hydrogen evolution mechanism (in acidic medium)

Mechanism:

★ Oxygen absorption mechanism (in basic or neutral medium):

Anode: $Fe \longrightarrow Fe^{+2} + 2e^-$ (oxidation)

cathode: $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$ (Reduction)

$$Fe + \frac{1}{2}O_2 + H_2O \longrightarrow \underbrace{Fe^{+2} + 2OH^-}_{Fe(OH)_2 \rightarrow \text{Ferrous hydroxide}}$$

If enough O_2 is present - $Fe(OH)_2$ is oxidised to rust. $Fe_2O_3 \cdot xH_2O$ (Yellow rust)

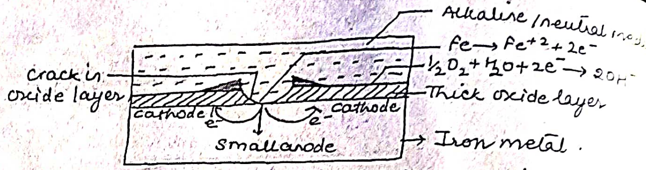
In limited supply of O_2 Black magnetite is formed: $Fe_2O_3 \cdot FeO \cdot 6H_2O$. (Black Magnetite)

★ Hydrogen evolution mechanism (in acidic medium)

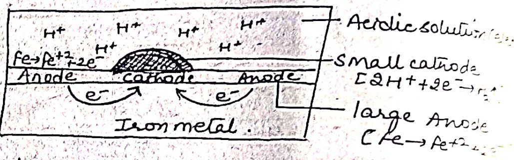
Anode: $Fe \longrightarrow Fe^{2+} + 2e^-$

cathode: $2H^+ + 2e^- \longrightarrow H_2\uparrow$

$$Fe + 2H^+ \longrightarrow Fe^{+2} + H_2\uparrow$$



oxygen absorption mechanism.



hydrogen evolution mechanism

★ Corrosion:- corrosion is defined as a process destruction or deterioration of materials by chemical electrochemical attack of environment. Example: of iron, tarnishing of silver etc.

M. Imp

Q2. Why do metals corrode? What are the fact affecting corrosion?

Ans. During extraction of metals from their ores, con amount of energy is required. consequently, isolat metals are at higher energy state (excited state) their corresponding ores. They have a natural tend to revert back to their combined state i.e form (more stable due to lower energy).

So, metals combine with different elements (m oxygen) in environment to attain stable state hence begin to corrode or decay.

$$\text{ORES or METAL COMPOUNDS} \underset{\text{corrosion}}{\overset{\text{Extraction of metal}}{\rightleftharpoons}} \text{METAL}$$

(Stable with lower energy) (unstable higher e

Factors affecting corrosion

Rate and extent of corrosion depends on:-

(1) Nature of metal
(2) Nature of environment.
(3) Nature of electrolyte

1) NATURE OF METAL :

i) Position of metals in galvanic series:

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

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

c) Metals placed higher in series has higher tendency to get corroded.

ii) Relative areas of anode and cathode:

$$\text{Rate of corrosion} \propto \frac{\text{cathodic area}}{\text{anodic area}}$$

As increased or greater area of cathode means more requirement of electrons from anode.

iii) Purity of metal : The impurities in metals results in setting up small electrochemical cells leading to corrosion.

iv) Physical state of metal :- Metallic materials with unevenly distributed stresses are easily corroded. The areas under stress acts as anode and gets corroded. caustic embrittlement takes part in stressed areas like bents, joints, rivets etc.

v) Nature of oxide film : The oxide layer formed on the surface of metal is protective or non protective in nature is determined by Pilling Bedworth rule.

It is given as:

$$\boxed{\text{Pilling Bedworth Ratio} = \frac{\text{volume of oxide layer formed.}}{\text{volume of metal consumed.}}}$$

According to this rule oxide layer is protective & non porous, if the volume of oxide is higher than the volume of metal from which it is formed.
If the volume of oxide is less than the volume of metal then the oxide layer is porous and hence non protective

2. Nature of Environment :

i) Temperature : Corrosion increases with increasing temp. due to increase in the rate of diffusion of ions.

ii) Humidity: Rate of corrosion increases rapidly in presence of moisture as moisture acts as solvent for O_2 in air to form electrolyte & setting up an electrochemical cell.

3. Nature of Electrolyte: If the electrolyte consists of silicate ions, they form insoluble silicates and prevent further corrosion.
chloride ions in electrolytes destroy the protective film and surface is exposed for further corrosion.

4. Effect of pH: Rate of corrosion is maximum when the corrosive environment is acidic.

LECTURE-24

- Corrosion can not be stopped altogether but it can be minimised using various protective methods or preventions.
- Following methods are used to minimise or prevent corrosion :-

① Proper designing
② Modification of environment
③ By using inhibitors
④ By changing the operating variables
⑤ By using protective coatings.
⑥ By modification of metal
⑦ Cathodic Protection.

- There are several types of corrosion like:

① **Galvanic corrosion**: It takes place when two different metals are kept in contact having sufficient difference in their potential and are exposed to electrolyte. The metal having lower reduction potential acts as anode and gets corroded.

② **Concentration cell corrosion**: It is due to varying concentrations of oxygen or varying aeration. It occurs when one part of metal is exposed to different supply of air as compared to other part. Due to this difference of potential is generated and the part having limited or less supply of air (O_2) act as anode & gets corroded.
eg :- water line corrosion

③ **Crevice Corrosion**: Intense corrosion is observed within crevices & other shielded areas on metal surfaces exposed to corrosive environment. It occurs due to

deposition of sand, dirt etc. Due to this O_2 supply gets reduced in crevices and that area starts acting as anode.

④ **Pitting corrosion**: It is localised corrosion. Due to this small holes are formed at the surface of the Mechanism involves setting up of differential aerati concentration cell. Metal area covered by a drop water, dust, sand, scale etc and hence it is less oxygenated as compared to uncovered area. This acts as anode. It has been found that when area of cathode is large as compared to anode then the is very intense and localised and results in formati of hole or pit.

⑤ **Stress corrosion**: It is due to crack formation on the metal surface.

⑥ **Erosion or abrasion corrosion**: It is due to the relati movements of corrosive fluid over a metallic material immersed in it. Here, metallic material is exposed to wear & tear, leading to clean surfaces which increa reactivity of metal.

Imp

Q1. How can corrosion be minimised by proper design? (2014-15), (2016-17)

Ans. Proper designing plays an important role in the control of corrosion of metallic equipments and structures. General guidelines for the design of material and components to control corrosion are:

1) Always use simple design and structure. Avoid sharp bends and corners.

2) Avoid contact of dissimilar metals in presence of electrolyte.

3) When two dissimilar metals are to be used together insulation should be used between them.

4) When two dissimilar metals are to be in contact, the anodic area must be as large as possible & cathodic area should be as small as possible.

5) As far as possible, crevices (gap or crack) should be avoided between adjacent parts of a structure.

6) Bolts and rivets should be replaced by proper welding.

7) Metal washers should be replaced by rubber or plastic washers as they do not absorb water. They also act as insulations.

8) If two different metals are to be used, they should be as close as possible in galvanic series to minimise the potential difference between them.

1. Imp

Q2. What are corrosion inhibitors? Explain with examples how anodic and cathodic inhibitors provides protection against corrosion (2015-16).

Ans. Corrosion inhibitors are the substances which are added from outside the inhibit or to decrease the rate of corrosion. Usually they are added in small amounts to the corrosive medium. Inhibitors are classified into anodic inhibitors, cathodic inhibitors and vapour phase inhibitors.

a) Anodic Inhibitors: They retard the corrosion of metals by reacting with the metallic ions of anode and

forming insoluble precipitate (which acts as a passive film or barrier) which is adsorbed on metal surface. Anodic inhibitors are used to repair crack of the oxide film over the metal surface. Example: chromate, phosphate, tungstate, nitrate, molybdate etc.

b) Cathodic Inhibitors: Depending on the nature of cathodic reaction, cathodic inhibitors are classified into:

i) In acidic solution: Main cathodic reaction is the liberation of hydrogen gas, the corrosion can be controlled by slowing down the diffusion of H^+ ions through the cathode. Eg- Amines, Mercaptans, Thiourea etc.

$$2H^+ + 2e^- \rightarrow H_2\uparrow$$

ii) In neutral / Alkaline medium: The cathodic reaction that occurs during corrosion is:-

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

Here, corrosion is controlled either by eliminating O_2 from the corroding medium or retarding its diffusion to cathodic area. This can be done by adding reducing agents like Na_2SO_3. The diffusion of O_2 can be controlled by adding inhibitors like Mg, Zn, Ni salts. Eg- N_2H_4, salts of Mg, Zn or Ni.

c) Vapour phase inhibitors: These are organic inhibitors which are readily vapourised a form a protective layer on metal surface. Example- benzotriazole, phenylthiourea etc.

M.Imp

Q3. How corrosion can be prevented by sacrificial anodic protection and impressed cathodic protection or Explain cathodic protection to prevent corrosion. (2015-16), (2016-17), (2017-18), (2018-19), (2019-20).

Ans. Since metal deterioration takes place at anode, corrosion of metal can be prevented by making metallic structure to act as cathode in the electrolytic cell. It is known as cathodic Protection.
As there will not be any anodic area on the metal, corrosion will not occur. There are two methods of

applying cathodic protection to metallic surfaces:

i) Sacrificial anodic protection (Galvanic protection)

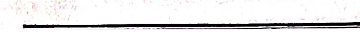
ii) Impressed current cathodic protection.

i) Sacrificial anodic Protection:

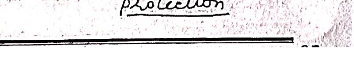
In this method, the metallic structure to be protected is made cathode by connecting it with more reactive metal which acts as anode. Hence, corrosion will occur only on the active metal. The main structure is thus protected. The more active metal used is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one. Metals commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys.

applications:-
- Protection for underground pipelines, underground cables etc.
- Protection from marine corrosion. (cables, ship hulls etc.)
- Insertion of Mg sheets into the domestic water boilers to prevent formation of rust.

ii) Impressed Current Cathodic Protection: In this method an impressed current is used in opposite direction to reverse the corrosion current and convert the corroding metal from anode to cathode. The impressed current is slightly higher than the corrosion current and is derived from a direct current sources (like battery or rectifier on AC lines). This type of protection technique is particularly useful for large structures for long term operations.



Sacrificial anodic protection



Impressed current cathodic protection

Q4. Explain why a pure metal rod half immersed verticaly water starts corroding at the bottom? (2017-18)

Ans. This happens due to differential aeration corrosion. The part of rod inside the water is poorly oxygenated in comp to the part above water. Due to differential aeration th poorly oxygenated part (under the water) acts as ano and it is corroded, the part above water acts as cathod

Imp Q5. Why is a block of magnesium attached through an insulated metallic wire to an underground iron pipe to the hull of the ship. (2017-18), (2016-17); (2014-15)

Ans. It is done to protect iron by cathodic protection beca the reduction potential of Mg is less than iron, so whe it is connected to iron through an insulated metallic wire, it start acting as anode and starts corroding. Iron acts as cathode and is saved from corrosion.

Q6. Why iron tank corrodes just beneath the water lin (2014-15).

Ans. Due to differential aeration, the part of tank just beneath the water becomes anodic, while the upper part (well oxygenated) becomes cathodic. Consequently a differential current starts flowing, whereby the anodic part is corroding.

Q7. comment on the use of Aluminium in place of Z for cathodic protection of iron from rusting (2018

Ans. The reduction potential of Al is even less than Zn. So, when iron and Aluminium are electrically connecte Al acts as anode and is corroded whereas iron ac as cathode and is saved from rusting.

Anode: $Al \longrightarrow Al^{3+} + 3e^-$

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

Imp Q8. why does a part of nail inside the wood undergoe corrosion easily? (2018-19)

Ans. Due to differential aeration, the nail inside the wood is not properly oxygenated, where as the remaining part is exposed to environment & is well oxygenated. Hence, the part of nail inside the wood acts as anode and starts corroding.

Q9. How much rust ($Fe_2O_3.6H_2O$) can be produced by 1 kg of of iron? (2016-17)

$$2Fe + \frac{3}{2}O_2 + 3H_2O \longrightarrow Fe_2O_3.6H_2O$$

$$2 \times 55.85 \qquad\qquad 267.7.$$

Atomic weight of Fe = 55.85

Molecular weight of rust formed $= 2 \times 55.85 + 3 \times 16 + 6 \times 18$
$= 267.7.$

As 2×55.85 g of iron forms 267.7 g rust.
or, 2×55.85 kg of iron forms 267.7 kg of rust.
Hence 1 kg iron forms $1 \times \frac{267.7}{2 \times 55.85}$ = [illegible] kg rust
2.408 kg

Imp
Q10 How does a cathodic metallic coating help in protection against corrosion? (2014-15).

Ans. Cathodic coating or noble coating: In this type of coating

1. Base metal is coated with a less reactive (more noble) metal.
2. Coated metal protects the base metal due to its noble character.
3. Reduction potential of coated metal is more than base metal.
4. Ni, Ag, Cr, Pb etc are used generally for noble coating example coating of Sn on Fe.

Imp
Q11. The standard reduction potential of three metallic cations X, Y and Z are 0.52, − 3.03 and 1.18 V respectively, arrange them in decreasing order in their reducing power. (2017-18).

Ans. Reducing power of metals ∝ Reduction potential of metals
Reducing power of metallic cations
So, decreasing order of reducing power of metallic cations will be Z > X > Y.

Corrosion issues in specific industries – Power generation, chemical processing industry, Oil and gas industry and Pulp & paper industries.

Sweet corrosion (CO_2 corrosion)

CO_2 is one of the main corroding agents in the oil and gas production systems. When CO_2 is dissolved in an aqueous phase through which it can promote an electrochemical reaction between steel and the contacting aqueous phase. CO_2 will mix with the water forming carbonic acid making the fluid acidic.

At elevated temperatures, iron carbide scale is formed on the oil and gas pipe as a protective scale and the metal starts to corrode under these conditions.

CO_2 corrosion can appear in two principal forms :-
pitting (localised attack that results in rapid penetration and removal of metal at a small discrete

area) and mesa attack (a form of localised CO_2 corrosion under medium-flow conditions).

All CO_2 corrosion process involve either carbonic acid or the bicarbonate ion formed on dissolution of CO_2 in water. The best known mechanism is as follows:-

$$H_2CO_3 + e^- \longrightarrow H + HCO_3^-$$

$$2H \longrightarrow H_2(g)$$

with steel reacting

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

and overall

$$CO_2 + H_2O + Fe \longrightarrow \underset{\text{(Iron carbonate)}}{Fe_2CO_3} + H_2$$

Sour Corrosion (H_2S corrosion)

The deterioration of metal due to contact with H_2S (hydrogen sulfide) and moisture is called sour corrosion. Hydrogen sulfide when dissolved in water is weak acid, therefore it is a source of hydrogen ions and is corrosive. The corrosion products are iron sulfides (FeS_x) and hydrogen. Iron sulfide forms a scale that at low temperature can act as a barrier to slow corrosion.

The forms of sour corrosion are uniform, pitting and stepwise cracking.

$$H_2S + Fe + H_2O \longrightarrow FeS_x + 2H + H_2O$$

Oxygen corrosion

Oxygen is a strong oxidant and reacts with metal very quickly. Oxygen dissolved in drilling fluids a major cause of drill pipe corrosion.

The presence of oxygen magnifies the corrosive effect of the acid gases (H_2S and CO_2).

The form of corrosion associated with oxygen are mainly uniform corrosion and pitting type corrosi

Galvanic corrosion

This type of corrosion occurs when two metallic materials with different electrode potential are in contact and are exposed to an electrolytic environm In such situation, the metal with the most negative reduction potential becomes the anode and starts corroding. These problem are most acute when the ratio of the cathode-to-anode area is large

Crevice Corrosion

Crevice Corrosion is a localised corrosion taking place in the narrow crevices in the metal. This is caused by concentration differences of corrodents over a metal surface. Oxygen dissolved in drilling fluid promotes crevice and pitting attack of metal in the shielded areas of drill string.

Erosion Corrosion

The erosion corrosion is the process of continous removal of passive layer corrosion products from the metal surface. The removal of passive layer take place due to high shear stress on the metal surface.

Microbiologically induced corrosion

This type of corrosion is caused by bactorial activities. The bacteria produce wase products like CO_2, H_2S and organic acids that corrode the pipes by increasing the toxicity in the medium of pipeline.

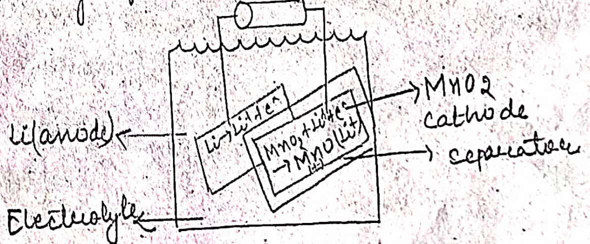
primary Cells :→

lithium Cells – lithium cells are primary cells in which lithium acts as anode and the cathode may differ. lithium metal is used as anode because of its light weight, high standard oxidation potential ($\geq 3V$) and good conductivity. As the reactivity of lithium in aqueous solution is more, lithium cells use non-aqueous solvents as electrolyte.

lithium cells are classified in two categories:

(a) lithium Cells with Solid Cathode :-

The electrolyte in this system is a solid electrolyte. The most widely used cell is lithium-manganese dioxide cell (3V), MnO_2 should be heated to over 300°C to remove water before keeping it in the cathode, thereby increasing the efficiency of the cell.



Anode lithium Metal
Cathode MnO_2 as an active material
Electrolyte $LiBF_4$ salt in a solution of propylene carbonate and dimethoxy ethane.

Reactions

Anode $Li \rightarrow Li^+ + e^-$
Cathode $e^- + MnO_2 \rightarrow MnO_2^-$
Net Reaction $Li + MnO_2 \rightarrow LiMnO_2$

Application -

1. The Coin type Cells are used in watches and Calculators.
2. Cylindrical Cells are used in fully automatic cameras.

(b) lithium Cell with liquid Cathode -

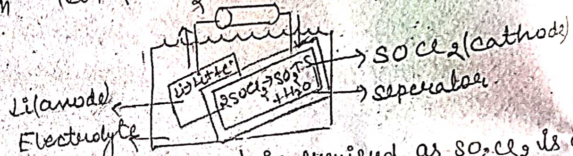
lithium - sulphur dioxide Cell is an example of Lithium - sulphur dioxide Cell is an example of liquid Cathode. The co-solvents used are acrylonitrile or propylene carbonate (or) mixture of two with SO_2 in 50% by volume.

Cell Reaction - $2Li + 2SO_2 \rightarrow Li_2S_2O_4$.

lithium thionyl Chloride cell is another example of liquid Cathode. It consists of high Surface area Carbon Cathode, a non-woven glass seperator. Thionyl Chloride acts as an electrolyte and as a cathode.

Cell Rxn -

At anode $Li \rightarrow Li^+ + e^-$
At cathode $4Li^+ + 4e^- + 2SOCl_2 \rightarrow 4LiCl + SO_2 + S$
Net Rxn $4Li + 2SOCl_2 \rightarrow 4LiCl + SO_2 + S$.



In this Cell no-cosolvent is required as SO_2Cl_2 is liquid with moderate vapour pressure. The Discharg voltage is 3.3 - 3.5 V.

USES →

1. They are used for military and space applications
2. In Medicinal devices such as neuro-stimul ato drug delivery System, lithium batteries are widely used.
3. They are also used in electric circuit boards for supplying fixed voltage for memory protection and

Advantages -

1. The Energy output of a lithium Cell is 2-4 times b than that of conventional zinc anode batteries
2. lithium batteries can work over temp. range of 40
3. They have higher voltages of about 4V when co to other primary cell with 1.5V only.

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 -

(i) Calcium oxide or lime (CaO) → 60-70%.

(ii) silica (SiO_2) → 20-24%.

(iii) Alumina (Al_2O_3) → 5-7.5%.

(iv) Mangnesia (MgO) → 2-3%.

(v) Ferric Oxide (Fe_2O_3) → 1-2.5%.

(vi). Sulphur trioxide (SO_3) → 1-1.5%.

(vii) Sulphur oxide (Na_2O) → 1%.

(viii) Potassium oxide (K_2O) → 1%.

Manufacture of portland Cement.

The steps involve in the manufacturing process are as follows -

(i) Crushing

(ii) Mixing

(iii) Burning

(iv) Grinding

(i) Crushing - In this step raw Material of portland Cement lime, Silica, Alumina, Magnesia, Ferric oxide, Sulphur trioxide, Sulphur Oxide, Potassium Oxide are crushed and ground to fine powder through ball mail.

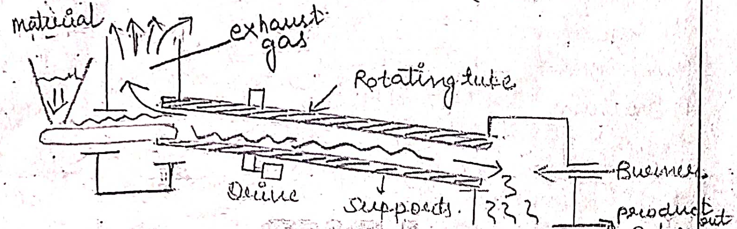
(ii) Mixing → In this step raw ingredients or fine powder are mixed in presence (wet process) or absence (dry process) of water to form slurry, then slurry is stored in storage tank.

(iii) Burning → The burning process is done in Rotary kiln. The rotary Kiln processes three different temperature zone like drying zone, Calcinations zone and Clinkering zone.

(iv) Drying zone - It is the upper part of Rotary Klin having temperature around 250°C where the water from the slurry evaporates.

Calcinations Zone-

It is middle portion of rotary kiln where temperature ranges from 700-1200°C. In this region limestone undergoes decomposition to form quick lime and carbon dioxide (escape out).



Clinkering Zone → It is the lower part of Rotary kiln where quick lime with clay to form calcium silicates, aluminates and ferrite.

$2CaO + SiO_2 \rightarrow Ca_2SiO_4 (Ca_2S)$
Dicalcium silicate

$3CaO + SiO_2 \rightarrow Ca_3SiO_5 (Ca_3S)$
Tricalcium silicate

$3CaO + Al_2O_3 \rightarrow Ca_3Al_2O_6 (Ca_3A)$
Tricalcium aluminate

$4CaO + Al_2O_3 + Fe_2O_3 \rightarrow 4CaO \cdot Al_2O_3 \cdot Fe_2O_3 (Ca_4AF)$
Tetracalcium alumino ferrite

The aluminates and silicates are mixed with CaO to form stone like structure, known as clinkers.

Grinding → The cooled clinkers are groun to fine powder in ball mill. At this tim 2-3% of gypsum is added to prevent the ea setting of cement.

Setting and hardening of cement.
When water mixed with cement form a plast paste. The past is subjected to hydration an gel and finally crystalline products are fo

$3CaO\,Al_2O_3 + 6H_2O \rightarrow 3CaO\,Al_2O_3 . 6H_2O + Heat$.

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

$4CaO.Al_2O_3Fe_2O_3 + 7H_2O \rightarrow Ca_3Al_2O_6.6H_2O + CaO.Fe_2O_3.H_2$
$+ Heat$

Tobermonite gel, calcium hydroxide crystallization and hydrated tricalcium aluminate are responsible for final setting and hardening of cement.

$2(2CaO.SiO_2) + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(O$
$+ Hea$

$3CaO\,Al_2O_3 + 6H_2O \rightarrow 3CaO\,Al_2O_3 . 6H_2O + Heat$

Role of gypsum → 2-3% of gypsum is add to prevent the early setting of cement.

$3CaO\,Al_2O_3 + xCaSO_4.2H_2O \rightarrow 3CaO.Al_2O_3.xCaSO_4.$

Plaster of Paris (POP) →

Plaster of paris is Calcium sulphate hemihydrates having molecular formula $2CaSO_4 . H_2O$ or $CaSO_4 . \frac{1}{2}H_2O$.

preparation

when gypsum is heated about at 150°c then plaster of paris is formed.

$$\underset{\text{Gypsum}}{CaSO_4 \cdot 2H_2O} \xrightarrow{150-160^\circ c} 2CaSO_4 \cdot H_2O + 3H_2O$$

properties →

1. 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.

$$\underset{\text{Plaster of Paris}}{2CaSO_4 . H_2O} + 3H_2O \rightarrow \underset{\text{Gypsum}}{CaSO_4 . 2H_2O}$$

2. 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

$$2CaSO_4 . H_2O \xrightarrow{200^\circ C} \text{gamma-}CaSO_4 \xrightarrow{600^\circ C} \text{beta}CaSO_4 \xrightarrow{1100^\circ C} CaO + SO_3$$

when beta $CaSO_4$ is heated about 1100°c, then it converted into quick lime (CaO) and SO_3.

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.

Meerut Institute of Engineering and Technology, Meerut

Topic-Wise Important Questions for AKTU End Semester Examinations

ode: BAS102		Subject Name : Engg. Chemistry	Taught In :	I Year / All B
Topics	Q. No.	Question (Statement) - As Appeared In AKTU	Year	Marks
IERNST EQUATION	19	Derive Nernst equation. Give its significance. Consider a cell reaction: Zn / Zn2+ (0.1M) ||Cu2+ (0.2M) / Cu Standard reduction potential of Zn2+ and Cu2+ are -0.76V and0.34V respectively. Write half-cell reactions, complete cell reaction and calculate EMF of the cell.	2021-2022 (Even)	2
	20	The voltage of the cell $Pb/PbSO_4/Na_2SO_4.10H_2O/Hg_2SO_4/Hg$ is 0.9647 V at 25°C. The temperature coefficient is 1.74×10^{-4} VK^{-1}. Calculate the values of ΔG, ΔS and ΔH	2018-2019	6
ECTROCHEMICAL CELL & GALVANIC SERIES	21	Explain why: a) Sheets of Zinc metal are hung around the ship hull of ocean-going ships. b) A block of magnesium attached through an insulated metallic wire to an underground iron pipeline.	2016-2017, 2017-2018	2, 2
CELL	22	Give the construction & working of Leclanché cell and Lithium cell		
	23	Give the reactions of Lead acid storage battery during discharging and recharging.	2017-2018, 2021-2022 (Odd)	6
CORROSION	24	Discuss the electrochemical theory of corrosion along with equations. How much rust $(Fe_2O_3.6H_2O)$ can be produced by 3gm of iron?	2021-2022 (Odd)	10
	25	Define corrosion. How corrosion can be minimised by:a) Proper designing b) Cathodic protection or sacrificial anodic protection and impressed cathodic protection.	2021-2022 (Odd)	10
	26	What are corrosion inhibitors? Explain with examples how anodic and cathodic inhibitor provides protection against corrosion.Explain Corrosion issues in different industries(Power generation, Chemical processing industry, Oil & gas Industry and Pulp & paper industries).		10
CEMENT	27	Explain the manufacturing process of cement. Give the chemical composition of Portland cement along with its setting and hardening.	2017-2018,2016-17	7