UNIT II - ELECTROCHEMISTRY & CORROSION

- Electrochemistry is a branch of chemistry which deals with interconversion of electrical energy to chemical energy and vice versa.

  For ex:

  i) In a battery, chemical energy is converted to electrical energy

  ii) In electroplating / electrolysis electrical energy is converted to chemical energy

- Electric current is a flow of electrons. Substances that allow electric current to pass through them are known as conductors.

  For ex: the metals, graphite, fused salts, aqueous solution of acids, bases & salts.

- While insulator or non-conductor is a substance which does not allow electric current to pass through it.

  For ex: wood, plastic;

Q1) What are conductors? How are they classified? Differentiate metallic conductors from electrolytic conductors.

Conductors are of two types:

  Metallic conductors: These are substances which conduct electricity by electrons.

  For eg: all metals, graphite etc; Na, K, alkaline earth metals Cu, Ag, Au and other transition metals.

  Electrolytic conductors: Are the substances which in aqueous solution (or) in fused state liberate ions & conduct electricity through these ions, there by resulting in chemical decomposition:

  For eg: Acids, bases & salt solution. etc.

Conductance:

Reciprocal of resistance is called conductance. C = 1/R.

- For metallic conductors, resistance is the characteristic property. Whereas electrolytes are characterized by conductance rather than by resistance.

- The resistance of a conductor [metallic] is directly proportional to its length & inversely proportional to its cross sectional area[ohm's law]

  R = Resistance in ohms

i.e; $R = \rho \dfrac{l}{A}$ ρ = specific resistance

        l = Length in cm.

        A = area of cross section in cm^2

Thus, when l = 1cm & A = $1cm^2$ then R = ρ

Thus, the specific resistance is defined as the resistance of a 1 centimeter cube.

Q2) Define following terms and explain their relationship.

  a) Specific conductance, b) Equivalent conductance and c) Molar conductance.

Specific conductivity: (κ) is the reciprocal of specific resistance of an electrolytic solution.

$$\text{i.e, } \kappa = \frac{1}{\rho} = \frac{1}{AR}$$

Hence specific conductivity is the conductance of $1cm^3$ of a solution.

Units: $\kappa = \dfrac{1}{AR} = \dfrac{cm}{cm^2 \Omega} = cm^{-1} \Omega^{-1}$ (or) $ohm^{-1} cm^{-1}$ (or) Scm^{-1}

Where, $Ohm^{-1} = S$

Equivalent conductivity: [Λ_{eq}] is the conductance of all the ions liberated by 1 gram equivalent of the electrolyte at v dilution. If 1gm equivalent of electrolyte is present in v ml, then

    $\Lambda_{eq} = v \times \kappa$ (Specific conductivity)

     $= v \times \kappa$ (volume 'v' contains of 1gram equivalent of electrolyte)

     Otherwise, if the normality of electrolytic solution is N then

    $v = \dfrac{1}{N} L$ (N = concentration)

     $= \dfrac{1000}{N}$ ml $= \dfrac{1000}{N} cm^3$

    .: $\Lambda_{eq} = \dfrac{1000}{N} \times \kappa$

Units : $\Lambda_{eq} = v \times \kappa = cm^3 \times ohm^{-1} cm^{-1} eq^{-1}$

     $= ohm^{-1} cm^2 eq^{-1}$ (or) $S cm^2 eq^{-1}$

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Molar conductivity: (Λ_m) is defined as the conductance of all the ions produced by 1 mole of an electrolyte at "v" dilution.

Suppose 1 mole of electrolyte is present in v ml of solution, then

$\Lambda_m = v \times \kappa$ (where v contains 1 mole of the electrolyte)

Whereas M is molar concentration in mol l^{-1}

Then $\quad \Lambda_m = \dfrac{1000}{M} \times \kappa$

Units: ohm^{-1} cm^2 mol^{-1} (or) S cm^2 mol^{-1}.

Q3. What are conductometric titrations. Explain the conductometric titration of strong acid vs strong base.

Conductometric titration- (strong acid vs strong base):

Conductometric titration is the volumetric analysis based upon the measurement of the conductance during the course of titration. The number of free ions and mobility of the ions affects the conductance of an aqueous solution. When one electrolyte is added to another electrolyte, the change in number of free ions causes a change in the conductance. For eg: when a strong acid (HCl) is titrated against a strong base(NaOH), before NaOH solution is added from the burette, the acid solution has high conductivity due to highly mobile H^+ ions. When NaOH is added to the acid, the conductivity of the acid solution decreases due to the neutralization of highly mobile H^+ ions of the acid with OH^- ions of the base.

$$H^+ \, Cl^- \; + \; Na^+ \, OH^- \quad \rightarrow \quad Na^+ \, Cl^- \; + \; H_2O$$

Thus the conductance of the solution continues to decrease until the equilibrium point is reached. Further addition of NaOH solution will increase the conductance by highly mobile hydroxyl (OH^-) ions. The point of intersection of the graph plotted between conductance of the solution on y-axis and volume of alkali added on x-axis corresponds to the end point of titration.

*Measurement of the conductivity of the solution:*

Pipette out 40 ml of the HCl solution into a 100ml beaker. Dip the conductivity cell in HCl solution after rinsing the conductivity cell with distilled water and HCl solution. Connect the conductivity cell to the conductometer. Set the function switch to check position. Display must read 1000, if not set it to 1000 with control knob at the back panel. Put the function switch to cell constant position and set the value of cell constant as determined previously. Set the temperature control knob to the actual temperature of the solution. Set the function switch to conductivity position and read the conductivity. This is the exact conductivity of the solution. Add 0.5 – 1 ml

of NaOH (0.01N) solution taken in the burette to HCl solution and stir well. Note the conductivity of the solution after the addition of NaOH solution. Repeat the procedure by addition of 0.5 – 1 ml NaOH (0.01N) solution every time and noting the conductivity readings of the resulting solution. Take $15 - 20$ readings and note the readings in the given table. Then the following graph will be obtained. The point where it coincides with X-axis corresponds to equivalence point or called as end point.
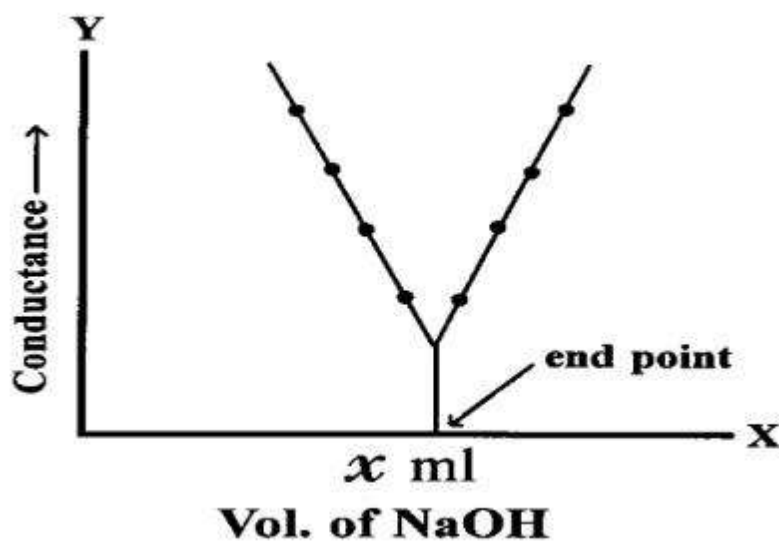
Q6. Explain the conductometric titration of weak acid vs strong base.

Conductometric titration of weak acid vs strong base:

$$CH_3COOH + NaOH \longrightarrow CH_3COO^- Na^+ + H_2O$$
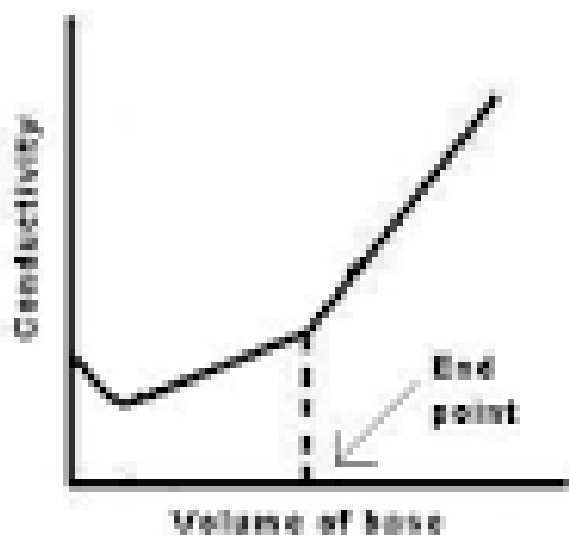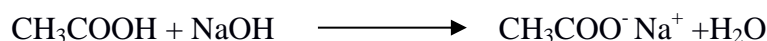
Acetic acid has low conductivity (being weak acid), when NaOH is added poorly conducting acid is converted into highly ionized salt, CH_3COONa. As a result by doing the similar titration like above the following graph will be obtained.

The conductivity increases very slowly upon addition of NaOH. When the acid get neutralized further addition of NaOH causes a sharp rise in conductance. The intersection point gives the end point.

Q7.what is meant by electrochemical cell. Explain the functioning of Daniel cell?

Electrochemical cell: The devices used for converting chemical energy to electrical energy & electrical energy into chemical energy are known as electrochemical cells they contain two electrodes in contact with an electrolyte, they are mainly of two types.

1) Galvanic cells, 2) Electrolytic cells.

1) *Galvanic cells:* It is an electrochemical cell in which the free energy of chemical reaction is converted into electrical energy i.e. electricity is produced from a spontaneous chemical reaction.
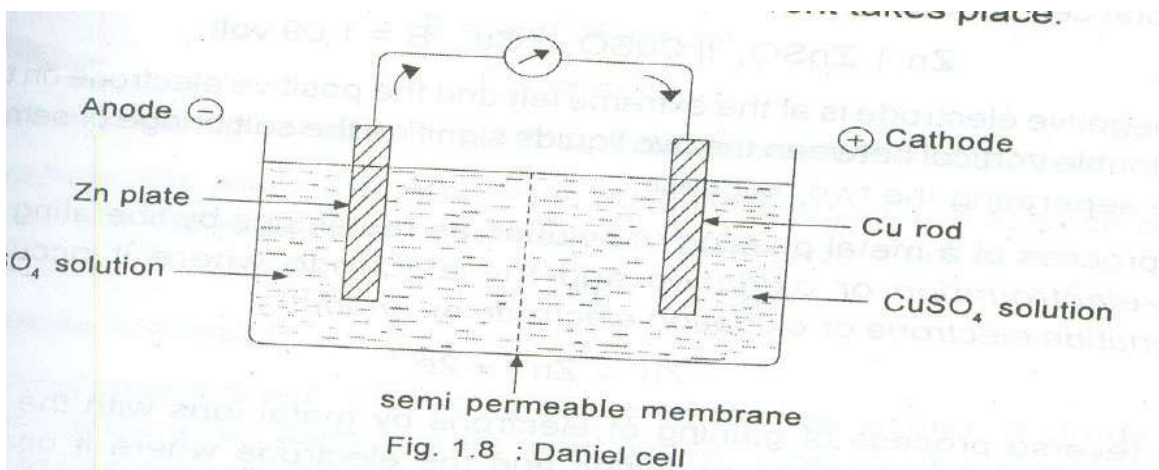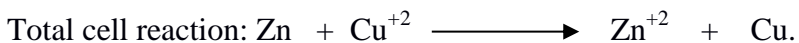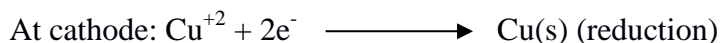
2) *Electrolytic cell:* It is an electrochemical cell in which external electrical energy is used to carry out a non- spontaneous chemical reaction.

Daniel cell

o It is an example of galvanic cell.

o It consists of Zn rod and Cu rod; Zn rod and Cu rod dipped in $ZnSO_4$ solution and $CuSO_4$ solution respectively.

o Each electrode in its electrolytic solution is known as half-cell.

o The two solutions are connected by a salt bridge, and thus two electrolytic solutions are in contact with each other, in order to complete the circuit.

Cell reactions:

The electrode reactions of Daniel Cell are :

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

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

$$\text{Total cell reaction: } Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu.$$

Fig. 1.8 : Daniel cell

Cell representation:

An electrochemical cell or galvanic cell is obtained by coupling two half cells. For example, Daniel cell obtained by coupling Zn half-cell and copper half-cell through a salt bridge

Zn | ZnSO₄ (aq) || CuSO₄(aq) | Cu

(-ve electrode)   (+ve electrode)

Oxidation takes place   Reduction takes place
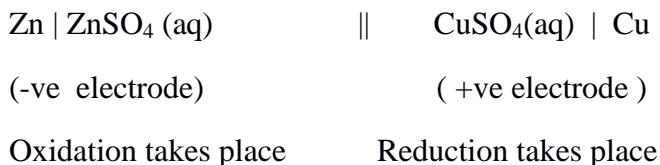
Cell is generally written with the negative electrode on the left hand side and the positive electrode on the right side

[|] single line represents phase separation

[‖] double lines represents salt bridge

When reduction potentials of electrodes are known then the emf of the cell is represented as

$$E = E^0 - \frac{2.303 \times R \times T}{nF} \log c$$

$$E = E^0 - \frac{0.0591}{n} \log c$$

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

E_{cell} = EMF of the cell.

E_{right} = Reduction potential of right electrode.

+ve value of E_{cell} indicates, the cell reactions feasible

-ve value of E_{cell} indicates, that the cell reaction is not feasible. In such case electrodes are to be reversed in order to bring about the chemical reaction.

Q7. What are electrolytic cells. Write the difference between electrochemical cells and electrolytic cells.
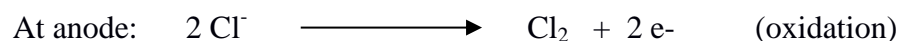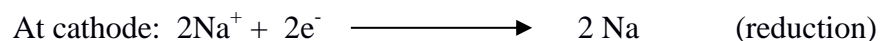
*Electrolytic Cells***:** Those cells which convert electrical energy to chemical energy.
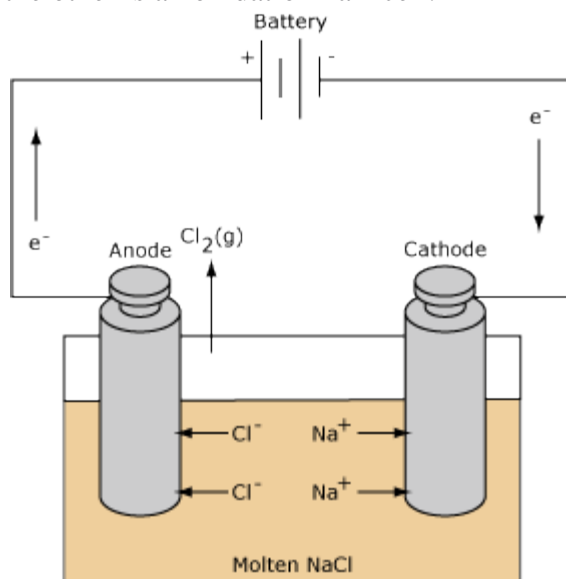
Eg: Electrolysis of fused NaCl & aq NaCl.

Description: They contain two inert electrodes like Pt. These two are dipped in fused NaCl electrolyte. The two electrodes are connected to an energy source like battery. The electrode which is connected to negative terminal of the battery is **cathode** and the electrode which is connected to positive terminal of battery is **anode**. (or) The

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electrode towards which Na+ ions start moving towards is called as cathode and Cl⁻ ions start moving towards is called the anode.

Working: When electricity is passed in to the cell , Na+ ions start moving towards the cathode and Cl⁻ ions towards the anode. Then

$$\text{At cathode: } 2Na^+ + 2e^- \longrightarrow 2\,Na \qquad \text{(reduction)}$$

$$\text{At anode: } 2\,Cl^- \longrightarrow Cl_2 + 2\,e\text{-} \qquad \text{(oxidation)}$$

Electrolytic cells, like galvanic cells, are composed of two half-cells--one is a reduction half-cell, the other is an oxidation half-cell.

Though the direction of electron flow in electrolytic cells is in reverse direction from that of spontaneous electron flow in galvanic cells, the definition of both cathode and anode remain the same as reduction takes place at the cathode and oxidation occurs at the anode.

When comparing a galvanic cell to its electrolytic counterpart, as is done in, occurs on the right-hand half-cell. Because the directions of both half-reactions have been reversed, the sign, but not the magnitude, of the cell potential has been reversed.

Electrolytic Cell

S.No	Galvanic cells	Electrolytic cells
1.	convert chemical energy to electrical energy	Convert an electrical energy to chemical energy
2.	The anode is negative terminal while cathode is positive terminal	The anode is positive terminal while cathode is negative terminal
3.	Galvanic cell has no battery, it is for spontaneous reactions	Electrolytic cell has a battery to act as a source of energy for non-spontaneous reactions to occur.
4.	Salt bridge is required.	Salt bridge is not required.

Q8) What do you understand by electrochemical series? How is it useful in determination of corrosion of metals?

Electrochemical series

When elements are arranged in increasing order (downwards) of their standard electrode potentials that arrangement is called as electrochemical series.

Metal ion ------------ Standard Reduction Potential (eV).

$Li^+ + e^- \longrightarrow Li$ --------------- -3.05

$K^+ + e^- \longrightarrow K$ --------------- -2.93

$Ca^+ + 2e^- \longrightarrow Ca$ --------------- -2.90

$Na^+ + e^- \longrightarrow Na$ --------------- -2.71

$Mg^+ + 2e^- \longrightarrow Mg$ --------------- -2.37

$Al^{+3} + 3e^- \longrightarrow Al$ --------------- -1.66

$Zn^{+2} + 2e^- \longrightarrow Zn$ --------------- -0.76

$Cr^{+3} + 3e^- \longrightarrow Cr$ --------------- -0.74

$Ni^{+2} + 2e^- \longrightarrow Ni$ --------------- -0.23

$Sn^{+2} + 2e^- \longrightarrow Sn$ --------------- -0.14

$Pb^{+2} + 2e^- \longrightarrow Pb$ --------------- -0.73

$Fe^{+3} + 3e^- \longrightarrow Fe$ --------------- -0.04

$H^+ + e^- \longrightarrow \frac{1}{2} H$ --------------- 0.00

$Cu^{+2} + 2e^- \longrightarrow cu$ --------------- +0.34

$Ag^+ + e^- \longrightarrow Ag$ --------------- +0.80

$pb^{+4} + 4e^- \longrightarrow Pb$ --------------- +0.86

$Au^+ + e^- \longrightarrow Au$ --------------- +1.69

$\frac{1}{2} F_2 + e^- \longrightarrow F^-$ --------------- +2.87

Features of electrochemical series: In these series a system with high reduction potential has a great tendency to undergo reduction , where as a system with a low reduction potential tend to

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oxidize more easily. For eg standard reduction potential of F_2 / F^- is the highest, so F_2 is easily reduced to F^-. On the other hand standard reduction potential of Li^+ / Li is least, so Li^+ is reduced with great difficulty to Li.

Replacement tendency: In electrochemical series the metals which are placed on top displace the metals below them, from their salt solution.

For eg : Zn will displace Cu from the solution of Cu^{2+}

$$Zn \ + \ Cu^{+2} \longrightarrow Zn^{+2} \ + Cu.$$
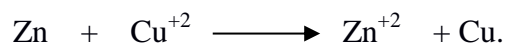
Predicting spontaneity: If emf is positive then the reaction is spontaneous, if emf is negative reaction is non-spontaneous. An element with lower reduction potential can displace another element having higher reduction potential spontaneously.

Q9. What are concentration cells? Explain how emf of a concentration cell can be calculated.
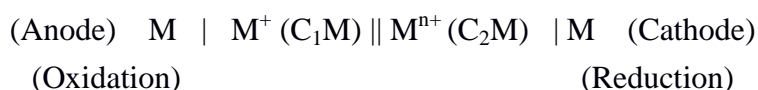
Concentration cells:

In concentration cells, the emf arises due to the change in the concentration of either the electrolytes or the electrodes. This is in contrast to galvanic cell where the emf arises from the decrease in the free energy of the chemical reaction taking place in the cell. However in a concentration cell, there is no net chemical reaction. The electrical energy in a concentration cell arises from the transfer of a substance from the solution of lower concentration (around the other electrode) a concentration cell is made up of two half cells having identical electrodes, except that the concentration of the reactive ions at the two electrodes are different. The half cells may be joined by a salt bridge.

Ag | $AgNO_3$ (C_1) ‖ $AgNO_3$ (C_2) | Ag

Dilute   Concentrated

Theory: when a metal(M) electrode is dipped in a solution containing its own ions (M^{n+}) , then a potential (E) is developed at the electrode, the value of which varies with the concentration(C) of the ions in accordance with the Nernst's equation.

$$E = E^0 + \frac{2.303 \times R \times T}{nF} \log c$$

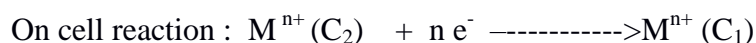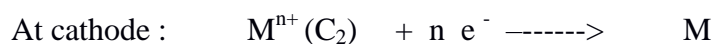let us consider a general concentration cell represented as

(Anode)   M | M^+ (C_1M) ‖ M^{n+} (C_2M) | M   (Cathode)

(Oxidation)   (Reduction)
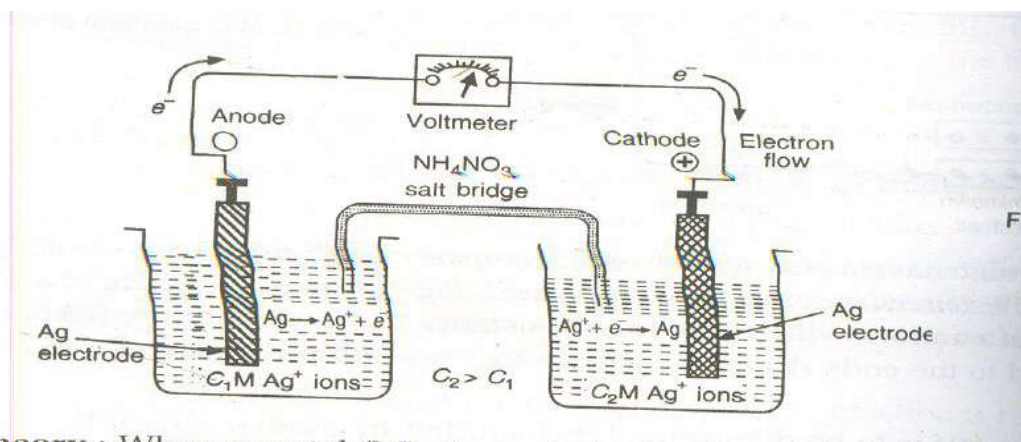
C_1 and C_2 are the concentrations of the active metal ions (M^{n+}) in contact with the 2 electrodes respectively and $C_2 > C_1$ emf of cell is

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

$$= E^0 + \frac{0.0591}{n} \log c_2 - E^0 + \frac{0.0591}{n} \log c_1$$

(or)

$$E_{cell} = \frac{0.0591}{n} \log (C_2 / C_1) \quad \text{at } 25^0 C$$

And at any temp., the general equation is

$$E_{cell} = \frac{2.303 \times R \times T}{nF} \log (C_2 / C_1)$$

At anode : M --------> $M_{(C1)}$ + n e$^-$

At cathode : $M^{n+}(C_2)$ + n e$^-$ -------> M

On cell reaction : $M^{n+}(C_2)$ + n e$^-$ ------------> $M^{n+}(C_1)$

Evidently the emf so developed is due to the more transference of metal ions from the soln. of higher concentration (C_2) to the solution of lower concentration (C_1).

Batteries: Battery can be defined as a device which contains two or more electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltage. They are mainly of 2 types.

(1) **Primary cells (or) primary batteries:** The cells in which the cell reaction is not reversible i.e, when the cell reaction is completed or all the reactants are exhausted, then no more electricity is produced and the battery becomes dead. Primary cells can't be recharged.

(2) **Secondary cells (or) secondary batteries:** Cells in which the cell reaction can be reversed by passing direct electric current in opposite direction. Thus a secondary battery may be used through a large number of cycles of discharging and charging.

Q10. What are primary batteries? Explain the functioning of lithium cells.

Primary batteries (non-rechargeable): They are non-rechargeable and are less expensive and are often used in ordinary gadgets like torch lights, watches and toys. Commercially many kinds of primary batteries are available, and the important ones are leclanche cell, alkaline cell and lithium cell.

Lithium cells: - The cells having Li anodes are called Li cells. These are classified into two types.

1. Lithium cells with solid cathode.   2. Lithium cells with liquid cathode.

1. **Lithium cells with solid cathode:**

Anode: lithium

Cathode: MnO_2

Electrolyte: mixture of propylene carbonate and 1,2-dimethoxyethane.

Li - MnO_2 is emerging as most widely used 3 volt solid cathode lithium primary battery. Cathode MnO_2 should be heated to $>300^o$ C to remove water before incorporating it in cathode.

Anodic reaction: Li --------> $Li^+ + e^-$

Cathodic reaction: $Li^+ + e^- + MnO_2$ ---------> $LiMnO_2$

Net reaction: $Li + MnO_2$ ------------> $LiMnO_2$

Applications:

Cylindrical cells are used in fully automatic cameras.

Coin cells are widely used in electronic devices such as calculators and watches.

2. **Lithium cells with liquid cathode.**

Anode: lithium

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Cathode: $SOCl_2$

Anodic reaction: $4 Li \text{--------}> 4 Li^+ + 4 e^-$

Cathodic reaction: $4 Li^+ + 4 e^- + 2 SOCl_2 \text{------->} 4 LiCl + SO_2 + S$

 Net reaction: $4 Li + 2 SOCl_2 \text{-------} > 4 LiCl + SO_2 + S$

Due to the nature of Li - $SOCl_2$ cells possess very high energy density. Further the SO_2 liberated as product is liquid under the internal pressure of the cell. No co solvent is required for the solution as thionyl chloride is a liquid having moderate vapour pressure. The discharging voltage is 3.3 – 3.5 volts.

Applications:

These cells are used for military and space applications

These cells are used in medical devices such as neuro-stimulators and drug delivery systems.

These cells are used on electronic circuit boards for supplying fixed voltage for memory protection.

Q11. Explain composition, application and advantages of lead acid cell.

Secondary Cells: - These cells are rechargeable and reversible

Lead – acid cells:

Anode   :   sponge metallic lead

Cathode   :   Lead dioxide

Electrolyte: dil. H_2SO_4

Construction: A number of lead plates (- ve plates) are connected in parallel and a number of lead dioxide plates (+ve plates) are also connected in parallel. The lead plates are fit in between lead dioxide plates various plates are separated from adjacent plates by insulators like wood strips, rubber or glass fibre. The entire combination is immersed in approximately 20 – 21 % dil. H_2SO_4 of density 1.2 to 1.3.
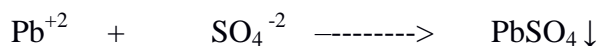
Discharging: -   when the strong cell is operating as voltaic cell, it is said to be discharging, he lead electrode loses e^- s which flow through the wire. Thus at anode oxidation of lead takes place

    At anode :   Pb $\text{--------}> Pb^{+2} + 2e^-$

Then it combines with SO_4^{-2} ions

$$Pb^{+2} \quad + \quad So_4^{-2} \quad \text{-------}> \quad PbSO_4$$

The electrons flow to the cathode. Here PbO_2 gains electrons and undergoes reduction from +4 to +2 and thus combines with SO_4^{-2} .

$$PbO_2 \quad + 4H^+ \; + 2e^- \quad \text{-------}> \quad Pb^{+2} + 2H_2O$$

$$Pb^{+2} \quad + \quad SO_4^{-2} \quad \text{--------}> \quad PbSO_4 \downarrow$$

So, the net reactions during use is

$$Pb + PbO_2 + 4H^+ + 2SO_4^{-2} \quad \text{------}> 2PbSO_{4\,+}\,2H_2 \quad + energy$$

Used in automobiles is a combination of six cells in series to form a battery with an e.m.f of 12 volts. (each cell is about 2 volts).
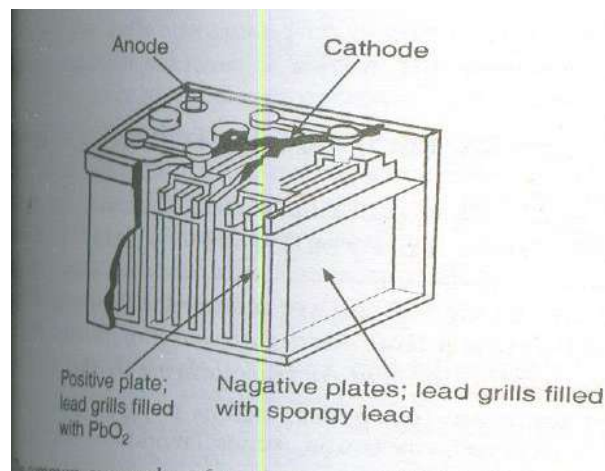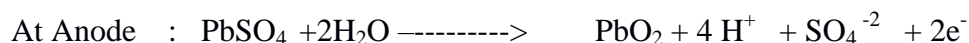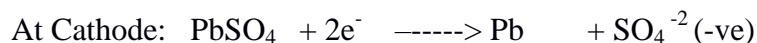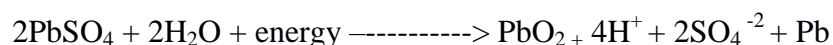

Fig. 26. A lead accumulator for car consists of six lead-acid storage cells in series and it is capable of delivering 12 V.

Charging: - when both anode and cathode become concert with $PbSo_4$, the cell stops to function as voltaic cell to recharge it, the reactions taking place during charging are reversed by passing an external e.m.f greater than 2 volts from a generation and following reactions take place at the respective electrodes

At Cathode: $PbSO_4 \; + 2e^- \quad \text{------}> Pb \quad + SO_4^{-2}$ (-ve)

At Anode   : $PbSO_4 + 2H_2O \text{----------}> \quad PbO_2 + 4\,H^+ \; + SO_4^{-2} \; + 2e^-$

The Net reaction during charging is :

$$2PbSO_4 + 2H_2O + energy \text{-----------}> PbO_{2\,+}\,4H^+ + 2SO_4^{-2} + Pb$$

During charging, the lead acid strong cell acts as electrolytic cell.

During discharging, concentration of H_2SO_4 decreases while during charging, its concentration increases.

*Applications:* Automobile and construction equipment, stand by backup systems.

Advantages: Low cost, ability to withstand mistreatment and also perform well in high and low temperatures.

Disadvantages: They have low cycle life a quick self-discharge and low energy densities.

Q12) What are fuel cells? Explain the hydrogen-oxygen fuel cell and its advantages.

Fuel cells: In a fuel cell, electrical energy is obtained without combustion from oxygen and a fuel gas that can be oxidized (like H_2 gas). Hence a fuel cell converts the chemical energy of the fuels directly to electricity.

The essential process in a fuel cell is

Fuel $+ O_2$ ----------> oxidation products + electricity.
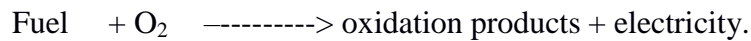
In a fuel cell one or both of the reactants are not permanently contained in the cell, but are continuously supplied from a source external to the cell and the reaction products are continuously removed.

One of the most successful and simplest fuel cell is hydrogen oxygen fuel cell.
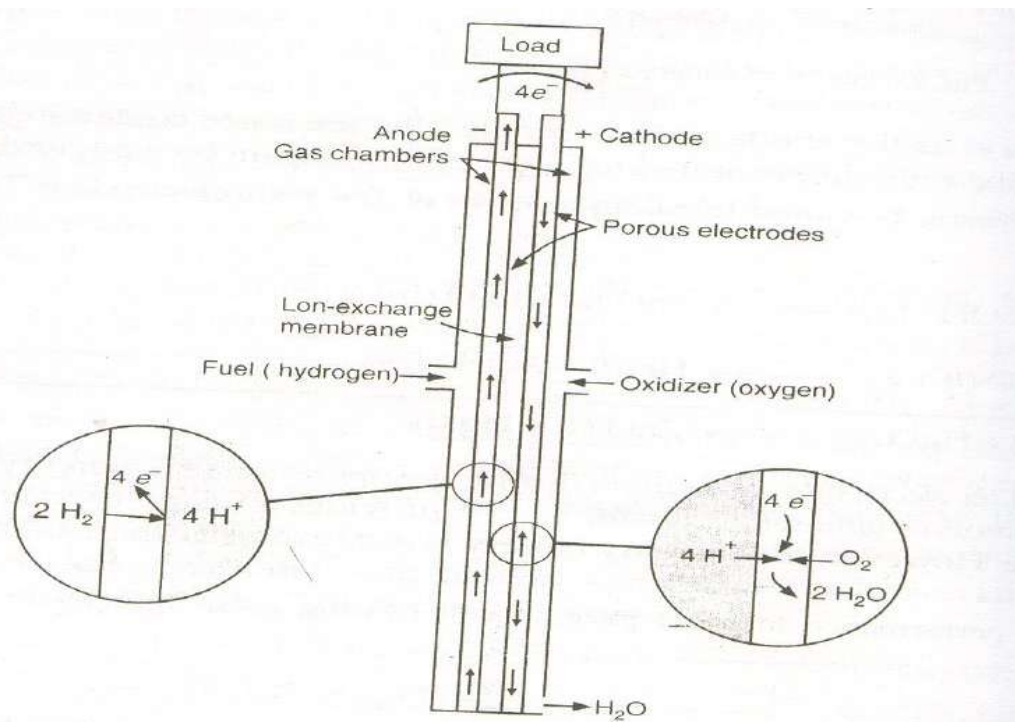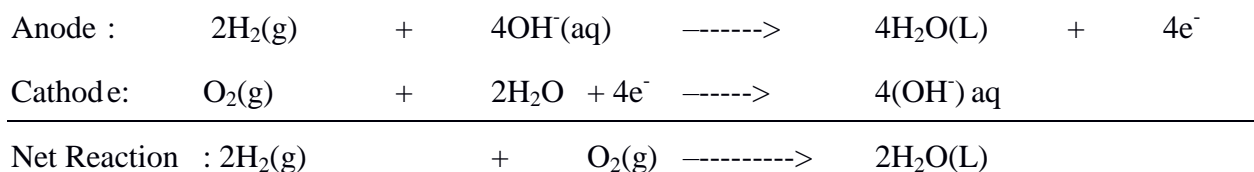

Figure: Schematic diagram of hydrogen oxygen fuel cell

It consists of an electrolytic solution such as 25% KOH and two inert porous electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartment respectively where the following reaction takes place.

Anode : $2H_2(g)$ + $4OH^-(aq)$ -------> $4H_2O(L)$ + $4e^-$

Cathode: $O_2(g)$ + $2H_2O + 4e^-$ -----> $4(OH^-) aq$

Net Reaction : $2H_2(g)$ + $O_2(g)$ ----------> $2H_2O(L)$

It may be noticed the only product that is discharged is H_2O.

Usually, large members of these cells are stacked together in series to make a battery, called fuel all battery or fuel battery.

Advantages of fuel cells:

1. No emission of toxic gases. Chemical wastes are in safe limits. The reactants and products are environmental friendly.

2. High efficiency of conversion of chemical energy to electrical energy. So can be used as an excellent renewable energy resource.

3. No noise pollution like generators.

4. Low maintenance and fuel transportation costs.

5. Unlike nuclear energy, fuel energy is economical and safe.

6. Fuel cells are operable up to 200^0C and so find applications in high temperature systems.

Limitations of fuel cells:

1. The main limitation of fuel cells lie in high initial costs associated with electrode material and design costs.

2. Large weight and volume of H_2 gas fuel storage system.

3. High cost of H_2 gas.

4. Lack of infrastructure for distributions and marketing of hydrogen gas.

5. Most alkaline fuel cells suffer from leakage of gases.

CORROSION AND ITS CONTROL

Introduction: - Many metals exist in nature in combined form as their oxides, carbonates, sulphides, chlorides and silicates (except noble metals) such as Au (gold), Pt (Platinum) etc. During extraction process these are reduced to their metallic state from their ores and during extraction of ores considerable amount of energy is required.

Compounds are in lower energy state than the metals. Hence when metals are put into use in various forms, they get exposed to environment such as dry gases, moisture, liquids etc. and slowly the exposed metal surface begin to decay by conversion into a compound.

Definition: - Any process of deterioration or destruction and consequent loss of a solid metallic material through an unwanted chemical or electrochemical attack by its environment at its surface is called corrosion. Thus corrosion is a reverse process of extraction of metals.

Examples:-

i) Rusting of iron – when iron is exposed to the atmospheric conditions, a layer of reddish scale and powder of Fe_3O_4 is formed.

ii) Formation of green film of basic carbonate- $[CuCO_3 + Cu(OH)_2]$ on the surface of copper when exposed to moist air containing CO_2.

Disadvantages of corrosion: The process of corrosion is slow and occurs only at surface of metals but the losses incurred are enormous. Destruction of machines, equipment, building materials and different types of metallic products, structures etc. Thus the losses incurred are very huge and it is estimated that the losses due to corrosion are approximately 2 to 2.5 billion dollars per annum all over the world.

Theories of corrosion: - Corrosion can be explained by the following two theories .

1. Dry or chemical corrosion.
2. Wet or electrochemical corrosion.

Q1. Explain dry corrosion in detail.

Dry or Chemical corrosion: -

This type of corrosion occurs mainly by the direct chemical action of the environment i.e., by the direct attack of atmospheric gases such as O_2, halogens, H_2S, SO_2, N_2 or anhydrous inorganic liquids on the metal surface with which they are in contact. There are 3 main types of chemical corrosion.
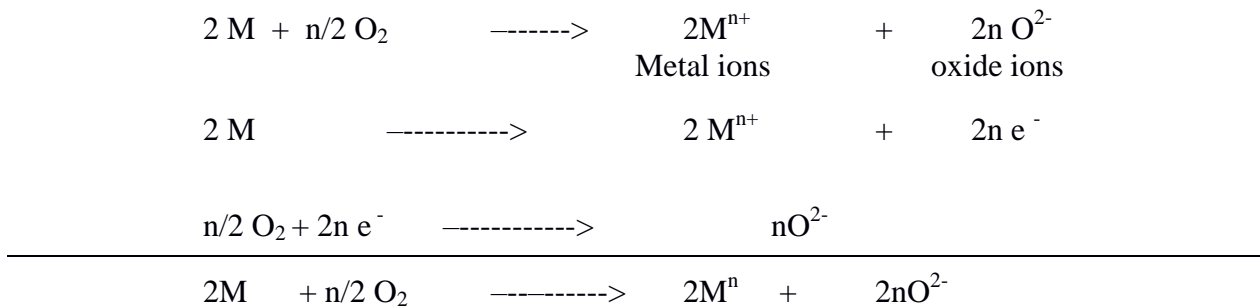
1) Corrosion by oxygen (or) oxidation corrosion.

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2) Corrosion by other gases like SO_2, CO_2, H_2S and F_2 etc.

3) Liquid metal corrosion.

Oxidation corrosion:-

o It is brought about by direct action of oxygen at low (or) high temperatures, usually in the absence of moisture.

o At high temperatures all metals are attacked by oxygen and are oxidized – except noble metals like Ag, Au, and Pt.

o At ordinary temp generally all the metals are slightly attacked. However alkali metals – Li, Na, K, Rb etc. and alkaline earth metals – Be, Ca, Sr etc. are attacked very rapidly and get oxidized readily.

The reactions in the oxidation corrosion are

$$2\,M + n/2\,O_2 \quad \text{------>} \quad \underset{\text{Metal ions}}{2M^{n+}} \quad + \quad \underset{\text{oxide ions}}{2n\,O^{2-}}$$

$$2\,M \quad \text{---------->} \quad 2\,M^{n+} \quad + \quad 2n\,e^-$$

$$n/2\,O_2 + 2n\,e^- \quad \text{----------->} \quad nO^{2-}$$

$$2M + n/2\,O_2 \quad \text{----------->} \quad 2M^n + 2nO^{2-}$$

Mechanism of oxidation corrosion: - Oxidation occurs first at the surface of the metal and a scale of metal oxide is formed on the surface of the metal and it tends to act as a barrier for further oxidation.

Therefore, for oxidation to continue either the metal must diffuse outwards through the scale to the surface or the oxygen must diffuse inwards through the scale to the underlying metal. Both transfers occur, but the outward diffusion of the metal is generally much more rapid than the inward diffusion of oxygen. Since the metal ion is appreciably smaller than the oxide ion, therefore the metal ion has much higher mobility.

Fig. 1. Oxidation mechanism of metals.
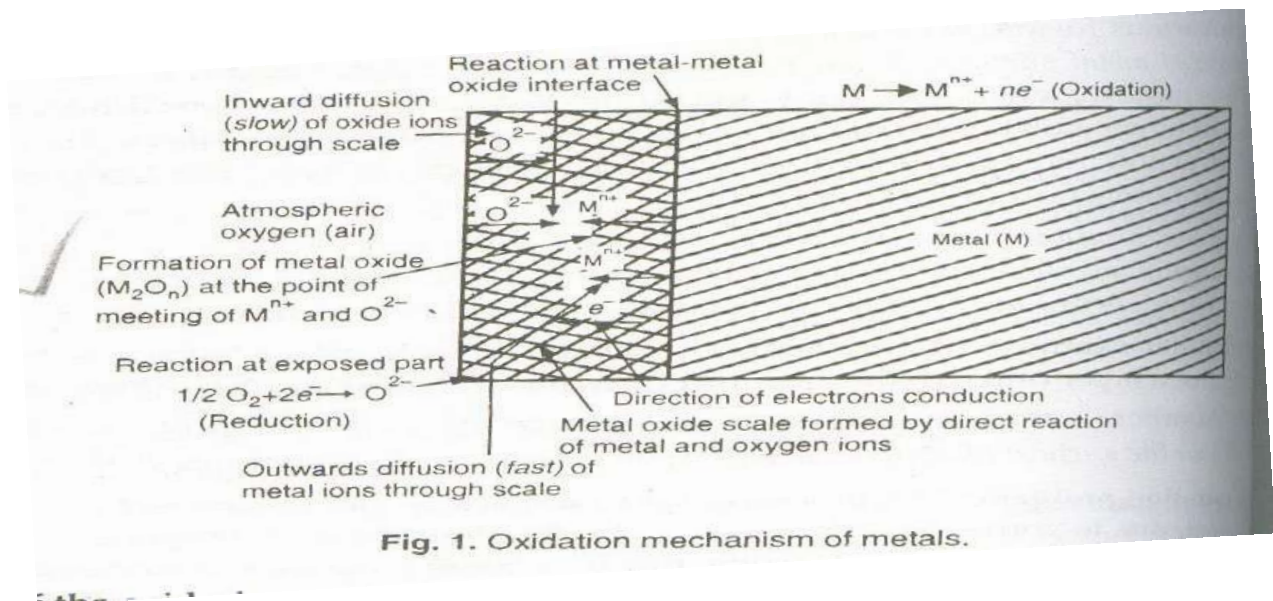
Nature of the oxide formed: - It plays an important role in further oxidation corrosion process.

Metal + oxygen $\longrightarrow$ metal oxide (corrosion product)

When the oxide film formed is

i) *Stable layer*: - A stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Such a layer will be impervious in nature and hence behaves as protective coating, thereby shielding the metal surface. Consequently further oxidation corrosion is prevented.

E.g.: Al, Sn. Pb, Cu, etc. form stable oxide layers on surface thus preventing further oxidation.

ii) *Unstable Layer*: - The oxide layer formed decomposes back into metal and oxygen

Metal oxide $\longrightarrow$ metal + oxygen
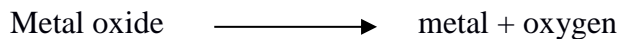
Consequently oxidation corrosion is not possible in such cases.

Eg: Ag, Au and Pt do not undergo oxidation corrosion.


Fig. 2. Unstable oxide layer.

iii) *Volatile Layer:*   The oxide layer formed is volatile in nature and evaporates as soon as it is formed.   There by leaving the under lying metal surface exposed for further attack. This causes rapid continuous corrosion, leading to excessive corrosion eg: Mo- molybdenum forms volatile MoO_3 layer.

Fig. 3. Volatile oxide layer.

iv) *Porous Layer*: Contains pores and cracks. In such a case the atmospheric oxygen has access to the underlying surface of the metal through the pores or cracks of the layer, there by corrosion continues until the entire metal is converted to its oxide.

Eg: Iron when attacked by H_2S at high temperature forms porous FeS layer.

Fig. 4. Porous oxide layer.
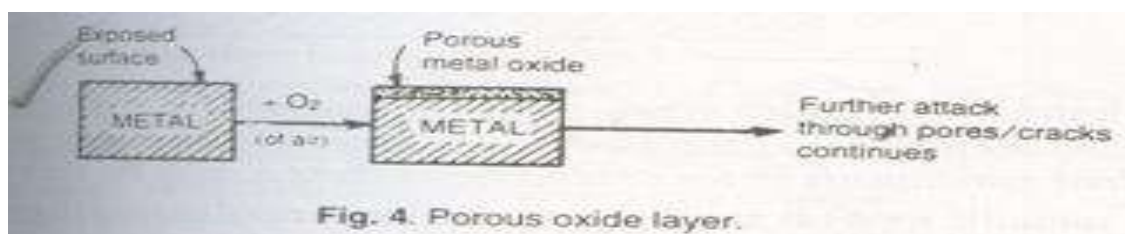
Pilling – Bedworth rule: The oxide layer acts as a protective or non–porous barrier, if the volume of the oxide is at least as great as the volume of the metal from which it is formed .

On the other hand -if the volume of the oxide layer is less than the volume of metal, the oxide layer is porous and hence non-protective. Because it cannot prevent the access of oxygen to the fresh metal surface below. If the specific volume ratio is small, then rate of corrosion is large.

For eg: alkali and alkaline earth metals like Li, Na, K, Mg forms oxides of volume less than volume of metals.

 These layers are porous and non-protective. Hence these undergo corrosion more rapidly.

 On the other hand metals like Al forms oxide whose volume is greater than the volume of the metal. Therefore Al forms a tightly – adhering non-porous protective layer.

Q2. Explain the principle involved in wet corrosion.

Wet (or) electrochemical corrosion:-

        This type of corrosion is observed when

➢ A conducting liquid is in contact with a metal (or)

➢ When two dissimilar metals (or) alloys are either immersed (or) dipped partially in a solution.

➢ The corrosion occurs due to the existence of separate anodic and cathodic areas or parts between which current flows through the conduction soln.

➢ In the anodic area oxidation reaction takes place so anodic metal is destroyed by dissolving (or) forming a compound such as an oxide.

➢ Hence corrosion always occurs at anodic areas

.: At Anode

$$M \quad \text{--------->} \quad M^{n+} \quad + \quad ne^-$$

.: At cathode

$$M^{n+} \quad +ne^- \quad \text{--------->} M$$

➢ In cathodic area, reduction reaction (gain of e^-s) takes place. The metal which is acting as cathode is in its reduced form only. Therefore it cannot be further reduced. Therefore cathodic reactions do not affect the cathode.

➢ So at cathodic part dissolved constituents in the conducting medium accept the electrons to form some ions like OH^-, O_2^- etc.

➢ The metallic ions from anodic part and non- metallic ions from cathodic part diffuse towards each other through conducting medium and form a corrosion product somewhere between anode and cathode.

➢ The e^-s which are set free at anodic part flow through the metal and are finally consumed in the cathodic region.

➢ Thus we may sum up that electrochemical corrosion involves:

i)   The formation of anodic and cathodic areas.

ii)   Electrical contact between the cathodic and anodic parts to enable the conduction of electrons.

iii) An electrolyte through which the ions can diffuse or migrate this is usually provided by moisture.

iv)   Corrosion of anode only

v)   Formation of corrosion product is somewhere in between cathode and anode.

Q3. What is electrochemical corrosion and how does it take place? Describe the mechanism.

Mechanism of wet or electrochemical corrosion:-

In wet corrosion the anodic reaction involves- the dissolution of metal as corresponding metal ions with the liberation of free electrons:

$$M \text{ --------> } M^{n+} \quad + \quad ne^-$$

Whereas the cathodic reaction consumes e⁻s either by a) evolution of hydrogen b)or by absorption of oxygen depending on the nature of the corrosive environment.

Q4. Define metallic corrosion. Explain the electrochemical theory of corrosion by Hydrogen evolution and oxygen absorption.
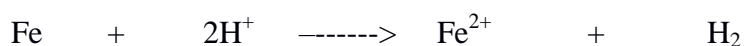
Evolution of hydrogen: occurs

> ➢ In acidic environments.

> ➢ For eg in the corrosion of iron metal the anodic reaction is dissolution of Fe as ferrous ions with liberation of e⁻s.
>
> $$Fe \quad \text{-----> } Fe^{+2} \quad + \quad 2e^- \qquad \text{oxidation.}$$

> ➢ These electrons flow through the metal from anode to cathode (acidic region) where H^+ ions are eliminated as H_2 gas.
>
> $$2H^+ \quad + \quad 2e^- \quad \text{------> } \quad H_2 \qquad \text{reduction.}$$

> ➢ The overall reaction is
>
> $$Fe \quad + \quad 2H^+ \quad \text{------> } \quad Fe^{2+} \quad + \quad H_2$$

> ➢ This type of corrosion causes "displacement of hydrogen ions from the acidic solution by metal ions.

> ➢ In hydrogen evolution type corrosion, the anodes are very large areas, where as cathodes are small areas.

> ➢ All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.
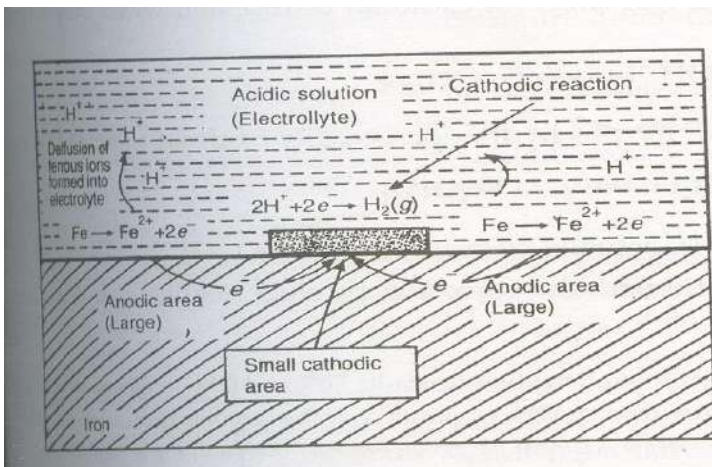
Fig. 5. Mechanism of wet corrosion by hydrogen evolution.

Q5. Explain the corrosion of iron by dilute mineral acids.

Absorption of oxygen type corrosion: Rusting of Fe in neutral aqueous solution of electrolytes like NaCl in the presence of atmospheric oxygen is a common example of this type of corrosion.
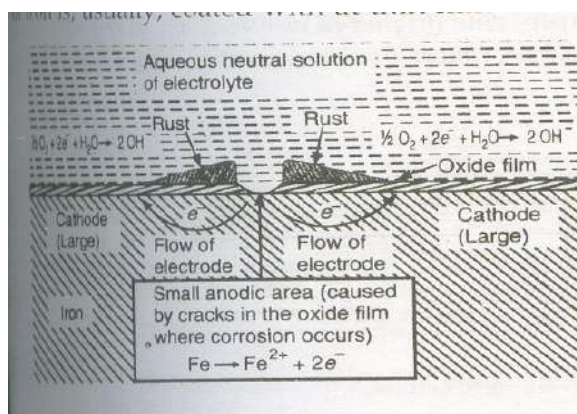

Fig. 6. Mechanism of wet corrosion by oxygen absorption.

➢ The surface of iron will be usually coated with a thin film of iron oxide. However if this oxide film develops some cracks, anodic areas are created on the surface.

➢ While pure metal parts act as cathode.

➢ Thus anodic areas are very small surface parts.

➢ The rest of the surface of the metal forms cathodes.

➢ Thus at the anodic part iron metal dissolves as Fe^{+2} ions with the liberation of e^- s.

$$Fe \quad ------> Fe^{+2} \quad + \quad 2e^-$$

➢ The liberated e^- s flow from anodic to cathodic areas through iron metal during which they interact with dissolved oxygen and moisture.

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$$\tfrac{1}{2}\,O_2 \;+ H_2O + \quad 2e^- \quad \rightarrow \quad 2OH^-$$
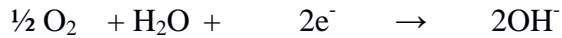
- The Fe^{+2} ions and OH^- ions diffuse and form ferrous hydroxide precipitate when they meet with each other

$$Fe^{+2} \quad + 2OH^- \quad \text{------->} \quad Fe(OH)_2$$

- If enough O_2 is present $Fe(OH)_2$ is easily oxidized to $Fe(OH)_3$ (ferric hydroxide)

$$4\,Fe(OH)_2 \quad + O_2 \quad + \quad 2H_2O \;\text{------>}\; 4Fe(OH)_3$$

The product called yellow rust actually corresponds to $Fe(OH)_3.H_2O$.

- If the supply of O_2 is limited, the corrosion product may be even black anhydrous magnetite Fe_3O_4.

Q6. Explain the factors which influence the rate of corrosion?

Factors influencing corrosion:

i)   Nature of metals

ii)   Nature of the corroding environment.

Nature of metals:

1) ***Position in galvanic series:***-The metal higher in series is more active and suffers corrosion. The rate and extent of corrosion is directly proportional to electrode potential difference between them.

2) ***Over voltage:*** - when a metal, which occupies a high position in galvanic series (say Zinc), is placed in H_2SO_4 , it undergoes corrosion forming a film and hydrogen gas.

The initial rate of reaction is quite slow, because of high over voltage (0.70 V) of the zinc metal, which reduces the effective electrode potential to a small value. However, if few drops of copper sulphate ($CuSO_4$) are added, the corrosion rate of zinc is accelerated, because some copper gets deposited on the zinc metal forming minute cathodes, where the hydrogen over voltage is only 0.33 V, thus, reduction in over voltage of the corroding metal/ alloy accelerates the corrosion rate.

Zn has over hydrogen voltage due to which the rate of corrosion of Zn is very slow (Zn rod dipped in $ZnSO_4$). But when $CuSO_4$ solution is added to H_2SO_4 Cu gets deposited on Zn rod and acts as small cathode. For Cu higher over hydrogen voltage value is less. Hence rate of corrosion of Zn in presence of cu becomes more. Thus metals for which over voltages are more get corrode slowly, where as those which have higher over voltages, the rate of corrosion is high.

Ex: corrosion of Zn rod dipped in H_2SO_4 is very slow. When small amount of $CuSO_4$ solution is added to H_2SO_4 , Cu gets deposited on the Zn rod and acts as cathode and the rate of corrosion of Zn increases.

(Over voltage of Zn metal is 0.73)

3) **Purity of metal**: - Impurity of a metal generally causes heterogeneity and form minute electrochemical cells and the anodic part gets corroded. For eg: Zn metal containing impurity such as Pb (or) Fe undergoes corrosion .

The rate and extent of corrosion increases with extent of impurities.

4) **Nature of the surface film**: - when metals are exposed to atmosphere, practically all metals get covered with a thin surface film of metal oxide. The ratio of the volume of metal oxide to the metal is known as specific volume ratio. Greater the specific volume ratio, lesser is the oxidation corrosion rate. For eg: the specific volume ratio of Ni, Cr, W are 1.6, 2.0 and 3.6 respectively. Consequently the rate of oxidation corrosion is least for (w) tungsten.

5) **Nature of the corrosion product:-** a) Solubility of corrosion products : If the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate otherwise if it is insoluble, corrosion will be suppressed e.g: $PbSO_4$ formation in case of Pb in H_2SO_4.

b)Volatility of corrosion products : -   If the corrosion product is volatile , it evaporates as soon as it is formed, there by leaving the underlying metal surface exposed for further attack.

This causes rapid and continuous corrosion.

For eg: Mo forms MoO_3 volatile oxide.

Nature of the corroding environment:-

i) *Temperature:* With increase of temperature, the corrosion rate also increases because the reaction as well as diffusion rate of ions in the corrosion medium increases.

ii) *Humidity***:** The higher the humidity of the atmosphere the greater is rate and extent of corrosion because the moisture acts as medium for O_2 in air and behaves as an electrolyte.

For eg: atmospheric corrosion of iron is slow in dry air compound to moist air. Iron combines with O_2 and water to form ferrous hydroxide which combines with atmospheric CO_2 to form ferrous bicarbonate.

$2Fe + O_2 + 2H_2O$ --------> $2Fe(OH)_2$

$Fe(OH)_2 + CO_2$ ------->$Fe(HCO_3)_2$
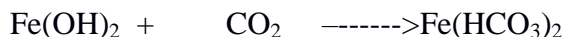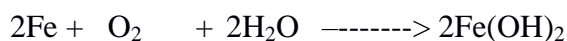
iii) *Effect of pH: -* Generally acidic media are more corrosive than alkaline and neutral media. Hence metals may be virtually classified according to pH range in which they will be affected (or) resistant. However atmospheric metals like Al, Pb etc. are corroded in alkaline medium and the corrosion rate of iron in O_2 free water is slow, until the pH is below Zn is rapidly corroded in weakly acidic solutions.

CORROSION CONTROL

Q7. What is sacrificial anode? Mention its role in control.

1) **Cathodic protection** : The principle involved in this method is to force the metal to be protected to behave like a cathode thereby corrosion doesn't occur. There are two types of cathodic protection.

i) **Sacrificial anodic protection method**: - In this method the metallic structure to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal implies the more active metal itself gets corroded slowly. While the parent structure which is cathodic is protected .The more active metal so employed is called "sacrificial anodic" whenever the sacrificial anode is consumed completely. It is replaced by a fresh one. Metal commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys. Sacrificial anodes are used for the protection of buried pipe lines underground cables, marine structures, ship hulls, water tanks etc.
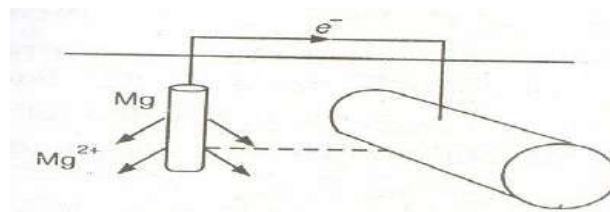
Q8. What is the principle of cathodic protection? Explain impressed current method of protection. (0r) How are metals protected by impressed current method?

Impressed current – cathodic protection: - In this method an impressed current is applied in opposite direction to nullify the corrosion current and current the corroding metal from anode to cathode. Usually the impressed current is derived from a direct current source (like battery or rectifier on ac line) with an insoluble anode, like graphite, high silica iron, scrap iron, stainless steel or platinum. Usually a sufficient d.c is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected.

Fig. 2.21: Protection given to underground pipeline by impressed current cathodic protecti-

EXT BOOK OF ENGINE-
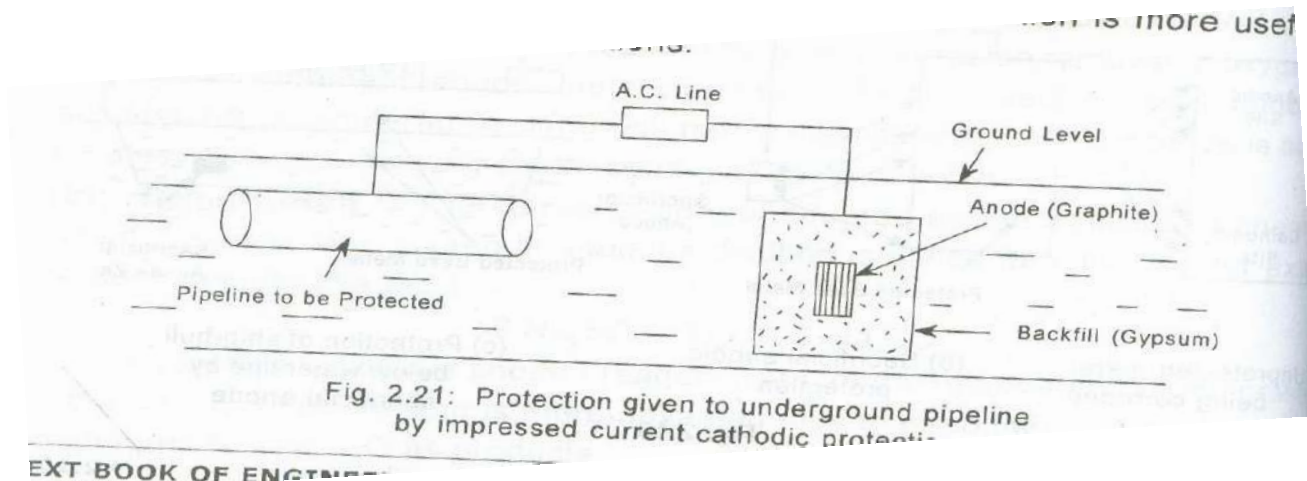
The anode is buried is a backfill such as coke breeze or gypsum to increase the electrical contact between itself and the surrounding soil.

Applications:- This type of protections is used in buried structures such as tanks and pipelines, transmission line towers, marine piers, laid up ships etc.,

Advantages: - They can be automatically controlled which reduce maintenance and operational costs.

Q9. What are metallic coatings? Explain the galvanization process? 0r Explain the process of hot dipping to prevent from corrosion?

Metallic coatings:

Anodic coatings (galvanization):

Galvanizing is the process of coating iron or steel sheets with a thin coat of zinc to prevent them from rusting. For carrying out galvanizing firstly the iron or steel article such as sheet, pipe or wire is cleaned by pickling with dil H_2SO_4 solution for 15-20 mts at 60-90^{0}C. In pickling any scale, dirt, oil, grease or rust and any other impurities are removed from the metal surface. The article is washed well and then dried. It is then dipped in bath of molten zinc maintained at 425-430°C. The surface of bath is kept covered with ammonium chloride – flux to prevent oxide formation. The article is covered with a thin layer of zinc when it is taken out of bath. It is then passed through a pair of hot rollers, which removes any excess of zinc and produces a thin film of uniform thickness then it is annealed and finally collected slowly.

Fig. 24. Galvanizing of sheet steel.
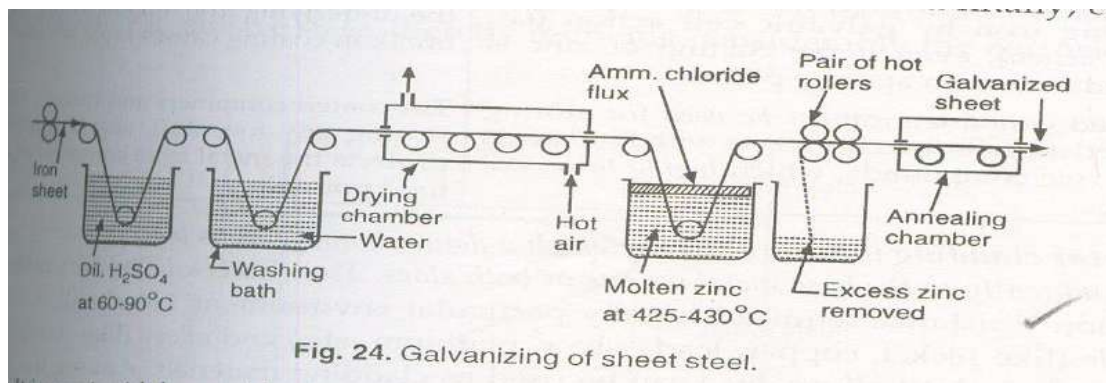
Uses: - Roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes etc. which are made of iron are protected from atmospheric corrosion by galvanizing them. But galvanized utensils cannot be used for preparing and storing food stuffs, especially acidic ores since zinc gets dissolved in all acids forming highly toxic compounds.

**Q10. Write a brief note on cementation.**

Cementation (sheradising):

Developed by sherad cowpercoles in 1980. It is the process of cementation ,using zinc powder as coating material. The iron article to be coated is cleaned by acid pickling process and rotated for 2 to 3 hours in a drum containing zinc dust at 350-370°C. During this process zinc diffuses into iron forming Fe-Zn alloy at the junction of base metal and coating metal and a thin layer of zinc is deposited on the surface of iron. Sheradising is used for coating small steel articles like bolts, screws, nuts and valves etc. The advantage of sheradizing is that the metal coating is uniform and there is no change in the dimension of article.

Q11. What are metallic coatings? Describe the electroplating method with the help of neat diagram.

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

Theory of electroplating:- suppose the anode is made up of coating metal (M) itself, during electrolysis the concentration of the electrolytic bath remains unaltered since the metal ions deposited from the bath are replenished continuously by the reaction of the free anions of the electrolyte with the anode metal. Thus for e.g. if $CuSO_4$ solution is used as an electrolyte it ionizes as

$$CuSO_4 \quad \text{--------->} \quad Cu^{+2} + SO_4^{-2}$$
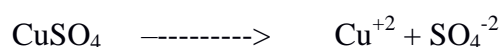
On passing current Cu^{+2} ions go to the cathode (the article to be plated) and get deposited there.

$Cu^{+2} + 2e^{-}$ ------> Cu (at cathode)
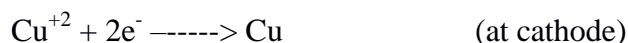
The free sulphate ions migrate to the Cu anode and dissolve an equivalent amount of the Cu to form $CuSO_4$

$Cu + SO_4^{-2}$ --------> $CuSO_4 + 2e^{-}$ (at anode)

The $CuSO_4$ thus formed dissolves in the electrolyte thus there is continuous replenishment of electrolytic salt during electrolysis.

Procedure:- The article to be electroplated is first treated with organic solvent like tetrachloro ethylene to remove oil, grease etc. then it is treated with dil Hcl or H_2SO_4 to remove surface scales, oxides etc. For Ni and Cu Hcl is used while for Cr plating H_2SO_4 is used. The cleared article is then made as cathode of an electrolytic cell. The anode is either the coating metal itself or an inert material of good electrical conductivity like graphite. The electrolyte is a solution of a soluble salt of the coating metal. When direct current is passed coating metal ions migrate to the cathode and get deposited there. Thus a thin layer of coating metal is obtained on the article made as cathode. For brighter and smooth deposits, favorable conditions such as low temp, medium current density and low metal ion concentrations are used.

Fig. 2.27 : Electroplating
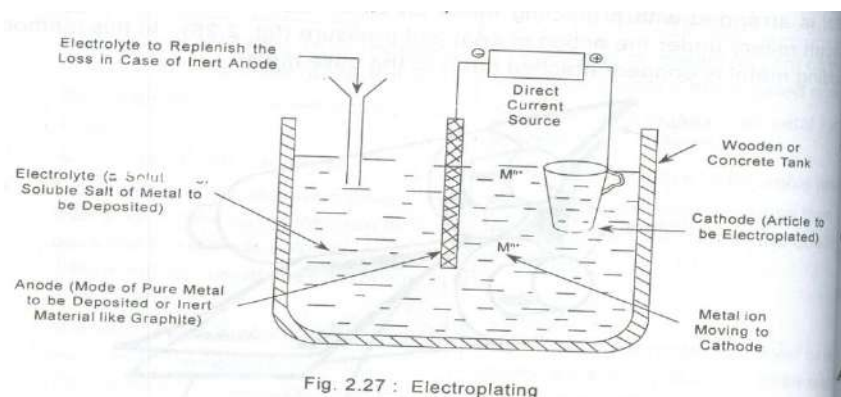
Organic coatings:-

Organic coatings are inert organic barriers like paints, varnishes, lacquers and enamels applied on metallic surfaces and other constructional materials for both corrosion protection and decoration. A good organic coating should process the following qualities.

i) Should be chemically inert to the corrosive environment.

ii) Should have good surface adhesion.

iii) Should be impermeable to water, salts and gases.

iv) Should possess good spreading capability.

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Q12. What are paints? What are their constituents and uses?

Paints:-

Paint is a mechanical dispersion mixture of one or more pigments in a vehicle. The vehicle is a liquid consisting of non-volatile film forming material, drying oil and a highly volatile solvent thinner, when paint is applied to a metal surface the thinner evaporates, while the drying oil slowly oxidizes forming a dry pigmented film.

Constituents of paints:-

i) *Pigment*: It is a solid substance which is an essential constituent of paint it provides

i) Capacity to paints ii) Strength to paint iii) desired color to paint iv) Esthetic appeal to the paint film. (v) Protection to the paint film by reflecting harmful ultra violet light (vi) Resistance to paint film against abrasion/wear (vii) impermeability of paint film to moisture (viii) increases the weather resistance of the film.

Important pigments used are i) whites – such as white lead, Zinc Oxide, litho phone, titanium oxide.

Red colored – red lead, ferric oxide, Venetian red, chrome red etc.

Green colored: - Chromium Oxide

Blue colored: - Prussian blue

Black colored: - Carbon black

Brown colored: - Brown umber etc.

Vehicle or Drying Oil: is a film forming constituent of the paint. These are glyceryl esters of high molecular-weight fatty acids generally present in animal and vegetable oils. The most widely used drying oils are linseed oil, soya bean oil and castor oil.
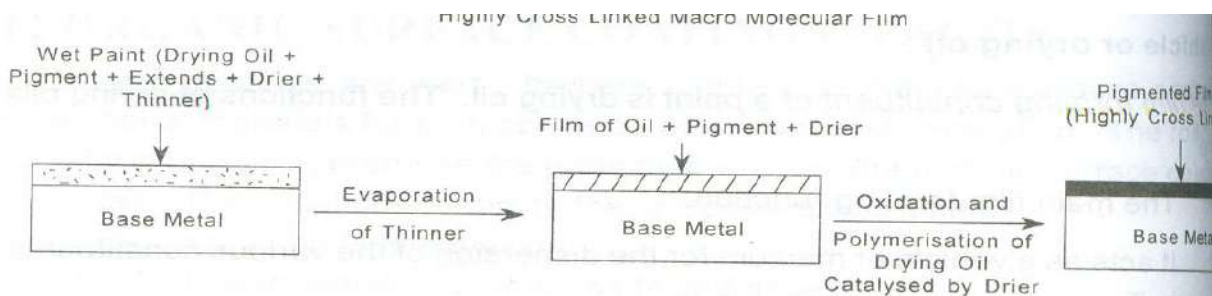

Fig. 2.28 : Drying of paint film

Functions of drying oil: Drying oil supplies i) Main Film-forming constituent ii)Vehicle or medium iii)Toughness iv)adhesion V)Durability and Vi)water proof.

Thinners *:* i) Reduce the viscosity of the paint to suitable consistency, so that it can easily be handled and applied.

ii) Dissolves the vehicle and the additions increases the penetration power of the vehicle

iii) Helps the drying of the paint film, as they evaporate.

Common thinners are turpentine, benzene, dipentene, naptha, kerosene etc…

Driers: are oxygen carrier catalysts, they accelerate the drying of the oil film through oxidation, polymerization and condensation. Thus they improve the drying quality of the oil film.

The most effective driers are resonates, lenoleates, tungstates of Co, Mn, Pb and Zinc.

Extenders or fillers *:* They are added in limited quantities to the oil paints for adjusting the working quantities of the paint they help to present the setting of heavier pigments.

i) They also increase the mechanical strength of the paint film.

ii) They reduce the cost of the paint examples are aluminium silicate, barium carbonate, barium sulphate.

Plasticizers *:* sometimes plasticizes are added to the paint. They do not evaporate like thinners and they permanently remain in paints.

i) They improve flexibility and elasticity of the paint film.

ii) They minimize its cracking

Eg. High molecular weight esters like triphenyl phosphate tributyl phosphate, tricresyl phosphate etc.

Anti-Skinning agents *:* They are sometimes added to paints to prevent gelling and skinning of the paint film.

Eg. poly hydroxy phenols.