

ELECTROCHEMISTRY

Concept of electrochemistry: The branch of science which deals with the relationship between electrical energy and chemical energy and their inter-conversion of one form to another is called electrochemistry.

Electrolysis: The changes in which electrical energy causes chemical reaction to occur.

Electro chemical cells: The changes in which electrical energy is produced as a result of chemical change.

Conductors: The substances which allow the passage of electric current are called conductors.

Eg. Metals like Cu, Ag, Sn etc.

Insulators: The substances which do not allow the electric current to pass through them are called non-conductors or insulators. Eg. Rubber, wood, wax, wool, glass etc.

Metallic conductors: These are the metallic substances which allow the electric current to pass through them without undergoing any chemical change. The flow of electric current in metallic conductors is due the flow of electrons in the metal atoms. Eg. Metals like Cu, Ag, Sn etc.

Electrolytes: These are the substances which allow the electric current to pass through them in their molten states or in the form of their aqueous solutions and undergo chemical decomposition. The flow of electric current through an electrolytic solution is called electrolytic conduction in which charge is carried by ions. These substances do not conduct electricity in the solid state but conduct electricity in the molten state or aqueous solutions due to movement of ions. Eg. Acids, bases and salts.

Non-electrolytes: The substances which do not conduct electricity either in their molten state or through their aqueous solutions are called non-electrolytes. Eg. Sugar, glucose, urea, ethyl alcohol etc.

Strong electrolytes: The electrolytes which are almost completely dissociated into ions in are called strong electrolytes. Eg: NaCl, KCl, HCl, NaOH, NH₄NO₃

Weak electrolytes: The electrolytes which do not ionize completely in solution are called weak electrolytes. Equilibrium is established between unionized electrolyte and the ions formed in the solution.

Summary

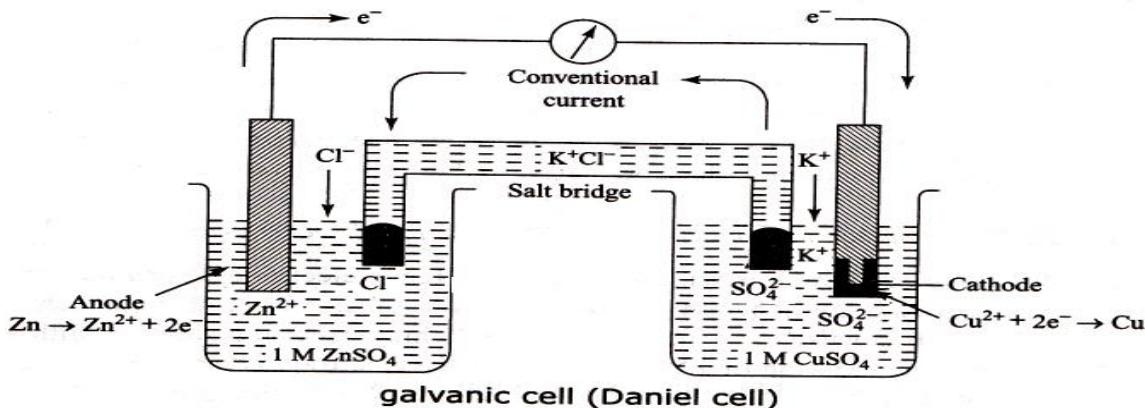
Sl.No.	Parameter	Notation	Formula	Units
1.	Resistance	R	$R = \rho \left(\frac{1}{a} \right)$	Ohms (Ω)
2.	Specific resistance	P	$\rho = R \left(\frac{a}{1} \right)$	Ohm.cm
3.	Conductance	C	$C = \frac{1}{R}$	Ohm ⁻¹
4.	Specific conductance	K	$\kappa = \frac{1}{R} \left(\frac{1}{a} \right)$	ohm ⁻¹ . cm ⁻¹ (or) S. cm ⁻¹
5.	Equivalent conductance	λ_v	$\lambda_v = \frac{\kappa \times 1000}{\text{Normality}}$	Ohm ⁻¹ . cm ² . equiv ⁻¹
6.	Molar conductance	λ_m	$\lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$	Ohm ⁻¹ . cm ² . mole ⁻¹
7.	Cell constant	X	l/a	cm ⁻¹

ELECTRO CHEMICAL CELLS

- An electrochemical cell is a device which converts chemical energy into electrical energy.
- The redox reaction is utilized for generation of electrical energy.
- The electrochemical cells are commonly referred as Voltaic or Galvanic cells.
- The electromotive force (EMF) of such cell is directly proportional to intensity of chemical reaction taking place in it.
- The electrochemical cell is divided into two half cells. The half cell electrode where oxidation (loss of electrons) occurs is called anode (negative electrode). The half cell electrode where reduction (gain of electrons) occurs is called cathode (positive electrode). An electrochemical cell is the coupling of these two half cells.

DANIEL CELL:

- The Daniel cell is a typical example of Galvanic cell.
- Daniel cell consists of a beaker containing copper rod dipped in CuSO_4 solution which is connected to another beaker containing zinc rod dipped in ZnSO_4 solution by a salt bridge.
- Salt bridge is an inverted U-tube containing saturated solution of some electrolyte such as KCl , KNO_3 , NH_4NO_3 which does not undergo chemical change during the process. The saturated solution is generally taken in agar-agar jelly or gelatin.
- The salt bridge allows the flow of ions to pass through it when the flow of electric current takes place. It completes the electrical circuit and maintains the electrical neutrality of two half cell solutions.

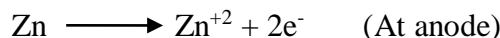


- When the circuit is completed, electric current flows through the external circuit as indicated by an ammeter. The following observations are made:
 1. Zinc rod gradually loses its weight.
 2. The concentration of $\text{Zn}^{2+}(aq)$ in the $\text{ZnSO}_4(aq)$ solution increases.
 3. Copper gets deposited on the electrode.
 4. The concentration of $\text{Cu}^{2+}(aq)$ in $\text{CuSO}_4(aq)$ solution decreases.
 5. The flow of electrons is from Zn-electrode (anode) to Cu-electrode (cathode).
 6. The flow of electric current is from Cu-electrode (cathode) to Zn-electrode (anode).

The above observations can be explained as follows:

UNIT-III

- Zn is oxidized to Zn^{+2} ions which go in the solution and therefore Zn rod gradually loses its weight (oxidation half cell).



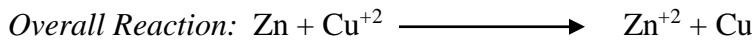
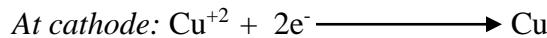
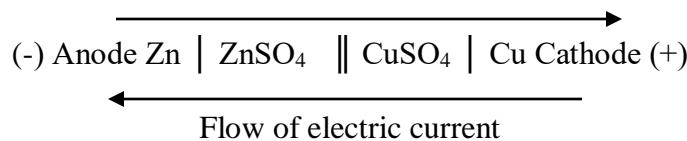
- The electrons released at the Zn electrode move towards Cu electrode through external circuit.
➤ These electrons are accepted by the Cu^{+2} ions in the solution and get reduced to copper which gets deposited on the Cu-electrode (reduction half cell).



- The oxidation of Zn occurs at anode (negative terminal) and reduction of Cu^{+2} occurs at cathode (positive terminal).

- The flow of electrons is from negative terminal (anode) to positive terminal (cathode).

Flow of electrons



TYPES OF ELECTRODES

Electrode potential (or) Single Electrode potential (E): It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

Standard Electrode potential (E°): It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of one molar concentration at $25^\circ C$.

Types of Electrodes: An electrochemical cell consists of two electrodes, positive and negative. Each electrode constitutes a half cell or a single electrode.

CONSTRUCTION AND FUNCTIONING OF SOME STANDARD ELECTRODES:

The single electrode potential is conveniently measured by combining the half cell with a standard electrode and measuring the total EMF of the cell.

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

$$E_{\text{cell}} = E_{\text{right}} - E^\circ \text{ (if standard electrode is anode)}$$

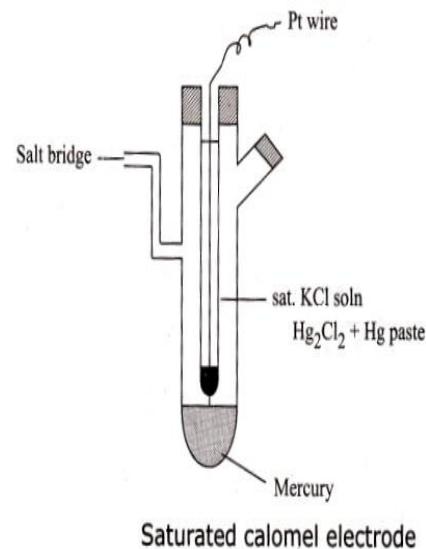
$$E_{\text{cell}} = E^\circ - E_{\text{left}} \text{ (if standard electrode is cathode)}$$

Where E° is the standard electrode potential.

Eg. Standard hydrogen electrode, Calomel electrode, Quinhydrone electrode

1. CALOMEL ELECTRODE

- It is a secondary reference electrode.
- It is a mercury-mercurous chloride ($Hg-Hg_2Cl_2$) electrode.
- The calomel electrode is used as only reducing electrode *i.e.* as cathode only.
- It consists of a glass tube having a side tube on each side. One side tube acts as salt bridge and other is used to fill KCl solution.
- The high purity mercury is placed at the tip of this tube and connected to the circuit by the means of Pt-wire, sealed in a glass tube.
- The surface of Hg is covered with a paste of mercurous chloride (calomel) and Hg in KCl solution.
- The electrolyte is the solution of KCl.
- The electrode is connected with the help of side tube on the left through salt bridge with the other electrode whose potential has to be determined.
- The potential of the calomel electrode depends upon the concentration of KCl.



Representation of calomel electrode: $Hg, Hg_2Cl_{(s)} \mid KCl$ (saturated solution)

2. ION SELECTIVE ELECTRODE- GLASS ELECTRODE

- They possess an ability to respond to only certain specific ions thereby developing a potential with respect to that species only in a given mixture and ignore all the other ions totally.
- The potential developed by ion selective electrode depends on the concentration of specific ion of interest.
- Eg. Glass electrode specific for H^+ ions and pressed pallet of $Ag_2S + AgCl$ specific for Cl^- ions.

GLASS ELECTRODE:

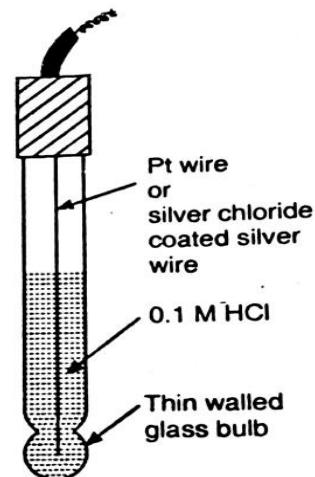
- When two solutions of different pH values are separated by a thin glass membrane, a potential difference develops between the two surfaces of the membrane.
- This potential difference developed is proportional to the difference in pH value.
- The glass membrane functions as ion-exchange resin.

UNIT-III

- An equilibrium is established between Na^+ ions of the glass and H^+ ions in the solution.
- The potential of the glass electrode is given by:

$$E_G = E^{\circ}_G + 0.0592 \text{ pH}$$

- Where pH range of the test solution is between 1-10.
- The glass electrode consists of a thin walled glass tube containing AgCl coated Ag-electrode or simply Pt-electrode in 0.1M HCl.



Cell representation of glass electrode is given by:



Glass electrode & determination of pH by glass electrode:

- HCl in the bulb furnishes constant H^+ ion concentration. Thus it is Ag-AgCl electrode reversible with respect to Cl^- ions.
- It is used as internal reference electrode for determining the pH of the solution especially the colored solution containing oxidizing or reducing agents.

Determination of pH of unknown solution by glass electrode:

- In order to determine the pH of the solution, the glass electrode is placed in the test solution. This half cell is coupled with saturated calomel electrode and the EMF of the cell is measured.

- **Cell representation:** $\text{Pt}, \text{HCl} (0.1\text{M}) \mid \text{Glass} \parallel \text{KCl}$
 $(\text{sat}) \text{Hg}_2\text{Cl}_{2(s)} \mid \text{Hg}$

$$E_{\text{Cell}} = E^{\circ}_{\text{Calomel}} - E^{\circ}_{\text{Glass}}$$

$$E_{\text{Cell}} = 0.2422 - [E^{\circ}_{\text{Glass}} + 0.0592 \text{ pH}]$$

$$E_{\text{Cell}} = \frac{0.2422 - E_{\text{Cell}} - E^{\circ}_{\text{Glass}}}{0.0592}$$

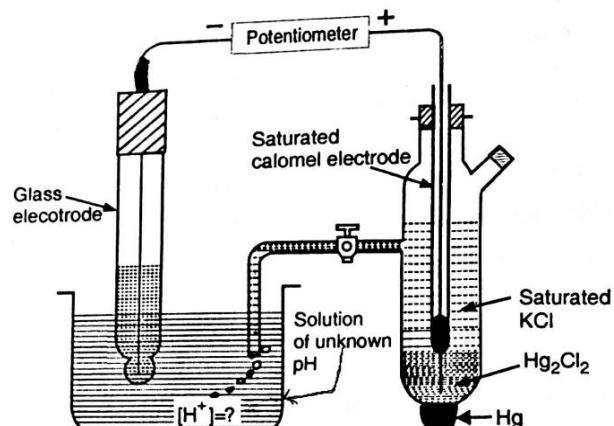
- Since the resistance is very high, a special electron tube voltmeter is used to measure the EMF of the above cell.

Advantages:

1. It is simple and can be easily used.
2. The results are accurate.
3. Equilibrium is rapidly reached.

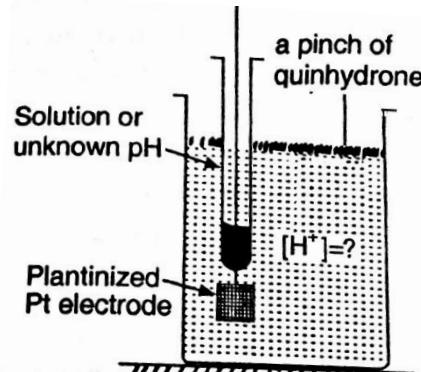
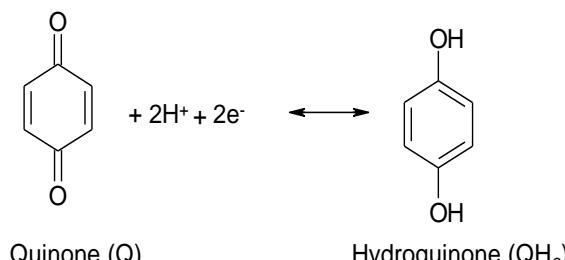
Limitations:

1. The range of solution pH is between 1 to 10.
2. The resistance of the membrane is very high.



3. QUINHYDRONE ELECTRODE

- It is a Quinone-hydroquinone system which forms a reversible redox system.
- When a Pt-electrode is immersed in this system, the potential E developed is given by



$$E_Q = E_{Q^\circ} - \frac{2.303RT}{nF} \log_{10} \frac{[\text{QH}_2]}{[\text{Q}][\text{H}^+]^2}$$

- When Quinone and Hydroquinone are maintained at equi molar ratios, then pH of an unknown solution can be determined using this electrode.
- The electrode potential of Quinhydrone electrode depends upon concentration of H^+ ions which can be used for the determination of pH of unknown solution.
- A pinch of quinhydrone powder which is sparingly soluble solid is added to the experimental solution with stirring until the solution is saturated.

Determination of pH of unknown solution by Quinhydrone electrode:

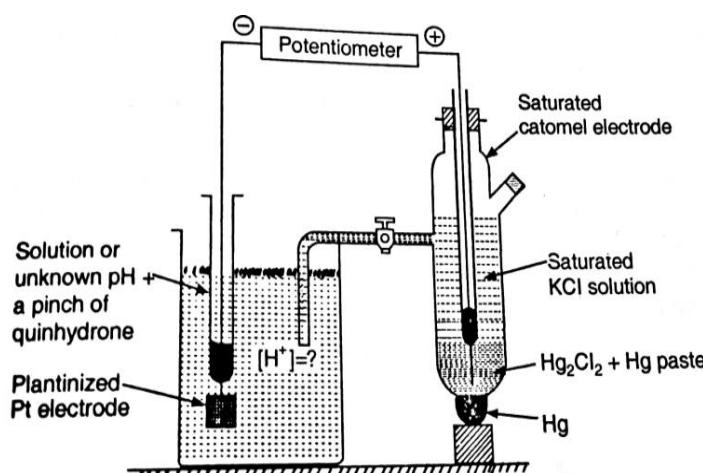
- **Cell representation:** $\text{Pt}, \text{QH}_2 \mid \text{Q}, \text{H}^+(\text{?}) \parallel \text{KCl (saturated)} \text{ Hg}_2\text{Cl}_2 \mid \text{Hg}$

- A Pt-electrode is inserted into the solution and a pinch of quinhydrone is added.
- This half cell is connected to a saturated electrode calomel electrode and the EMF of the solution is determined potentiometrically.

$$E_{\text{Cell}} = E_{\text{Calomel}} - E_{\text{Quinhydrone}}$$

$$E_{\text{Cell}} = 0.2422 - (0.6994 - 0.0592 \text{pH})$$

$$\text{pH} = \frac{E_{\text{Cell}} - 0.4572}{0.0592}$$



Advantages:

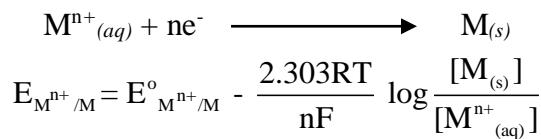
1. It is useful in acid-base titrations.
2. Equilibrium is rapidly attained.
3. It can be used for many metal ions which usually effect hydrogen electrode.

UNIT-III

NERNST EQUATION

Standard electrode potentials are measured at standard states i.e at 1M concentration of electrolyte, temperature at 298 K and 1atm pressure. However the electrode potentials depend upon concentration of electrolyte solutions and temperature. Nernst equation gives the relationship between electrode potentials and concentration of electrolytic solutions.

➤ For the general reduction reaction occurring at an electrode,



Where E° = Standard EMF of the cell for 1 M solution at 298 K;

R = Gas constant;

T = Kelvin temperature;

n = number of electrons involved in the cell reaction;

F = Faraday of electricity;

E = electrode potential of the metal;

[M] = activity of metal in the metal phase and is taken as unity;

[M^{n+}] = activity of metal ions in the solution is taken equal to their molarities;

But at STP conditions, R = 8.314JK⁻¹mol⁻¹; T = 298K; F = 96500 coulomb charge. Then the Nernst equation becomes

$$\text{E}_{\text{M}^{n+}/\text{M}} = \text{E}^{\circ}_{\text{M}^{n+}/\text{M}} - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{1}{[\text{M}^{n+}_{(aq)}]} \quad \text{considering } [\text{M}_{(s)}] = 1$$

$$\text{E}_{\text{M}^{n+}/\text{M}} = \text{E}^{\circ}_{\text{M}^{n+}/\text{M}} - \frac{0.0592}{n} \log \frac{1}{[\text{M}^{n+}_{(aq)}]}$$

$$\text{E}_{\text{M}^{n+}/\text{M}} = \text{E}^{\circ}_{\text{M}^{n+}/\text{M}} + \frac{0.0592}{n} \log [\text{M}^{n+}]$$

Nernst equation enables us to calculate the following:

1. Half cell potential or single electrode potential.
2. Cell potential or EMF of the cell.
3. Equilibrium constant for the cell reaction.

ELECTROCHEMICAL SERIES AND ITS APPLICATIONS

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

UNIT-III

(or)

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

Electrode	Electrode reaction	E° , volts	Nature
Li ⁺ /Li	$\text{Li}^+ + \text{e}^- \longleftrightarrow \text{Li}$	-3.01	Anodic ↑
Mg ²⁺ / Mg	$\text{Mg}^{2+} + 2\text{e}^- \longleftrightarrow \text{Mg}$	-2.37	
Zn ²⁺ / Zn	$\text{Zn}^{2+} + 2\text{e}^- \longleftrightarrow \text{Zn}$	-0.76	
Fe ²⁺ / Fe	$\text{Fe}^{2+} + 2\text{e}^- \longleftrightarrow \text{Fe}$	-0.44	
Sn ²⁺ / Sn	$\text{Sn}^{2+} + 2\text{e}^- \longleftrightarrow \text{Sn}$	-0.136	
Pb ²⁺ / Pb	$\text{Pb}^{2+} + 2\text{e}^- \longleftrightarrow \text{Pb}$	-0.13	
H ⁺ / H ₂	$2\text{H}^+ + 2\text{e}^- \longleftrightarrow \text{H}_2$	0.00	Pt-reference
Cu ²⁺ / Cu	$\text{Cu}^{2+} + 2\text{e}^- \longleftrightarrow \text{Cu}$	+0.34	↓ Cathodic
Ag ⁺ / Ag	$\text{Ag}^+ + \text{e}^- \longleftrightarrow \text{Ag}^+$	+0.80	
Au ⁺ / Au	$\text{Au}^+ + \text{e}^- \longleftrightarrow \text{Au}^+$	+1.50	
1/2F ₂ / F ⁻	$1/2\text{F}_2 + \text{e}^- \longleftrightarrow \text{F}^-$	+2.87	

Applications of electrochemical series:

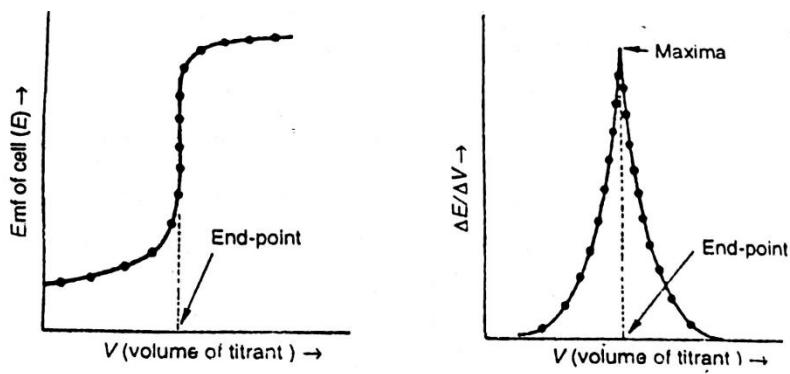
1. Calculation of standard EMF of the cell.
2. Relative ease of oxidation (or) Reduction.
3. Displacement of one element by the other.
4. Hydrogen displacement behavior.
5. Corrosion tendency of the elements.

POTENTIOMETRIC TITRATIONS

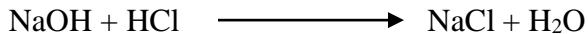
The titration in which the equivalent (or) end point of a reaction is determined with the help of measurement of the potentials of the reaction mixture is known as potentiometric titration.

1. Acid-Base Titrations:

The acid solution whose strength has to be determined is taken in a beaker and the hydrogen electrode and calomel electrode were dipped in the solution. The electrodes are connected to the potentiometer and the EMF is measured. A known volume of standard alkali solution is added from a burette, stirred thoroughly and the EMF of the cell is recorded. Like this 10-15 readings are recorded by repeating the procedure of the addition of alkali. The volume of alkali



added is plotted against EMF observed. The steepest portion of the curve indicates the equivalent point of the titration.



2. Redox titrations:

The EMF of the electrode is determined by the activity of ratio of the substance being oxidized or reduced. For example Fe^{+2} titrated against $\text{K}_2\text{Cr}_2\text{O}_7$. Ferrous iron solution is taken in the beaker and treated with dil. H_2SO_4 . Platinum electrode and calomel electrode are dipped into the solution and they are connected to the potentiometer. The EMF of the solution after the addition of $\text{K}_2\text{Cr}_2\text{O}_7$ from burette is recorded. A graph is plotted with EMF and volume of $\text{K}_2\text{Cr}_2\text{O}_7$. The steep rise is the end point of the titration.

3. Precipitation reactions:

The EMF of the electrode is determined by the precipitation of product. For example, titration of AgNO_3 with KCl where the later precipitates out. KCl is used along with calomel electrode. AgNO_3 is taken in the burette and KCl is taken in the beaker containing electrodes. The EMF of the cell is measured and plotted against volume of silver nitrate added. The steep rise in the curve shows the end point of the titration.



Advantages:

1. Colored solutions where the use of indicator is impossible are estimated by potentiometric titrations.
2. Solutions more than one halide can be analyzed in a single titration against silver nitrate.

BATTERIES

- The term battery is generally used for two or more galvanic cells connected in series. Thus a battery is a series of portable electrochemical cells which are capable of generating electrical energy.
- Batteries are of three types: (1) Primary cell (2) Secondary cell (3) Fuel cell.

Applications of batteries:

- The portability of electronic equipments in the form of handsets has been made possible by batteries.
- A variety of electronic gadgets with more reliability and service have been made more useful with the introduction of rechargeable storage batteries.

COMPARISON BETWEEN PRIMARY AND SECONDARY CELLS

Sl. No.	Primary cells	Secondary cells
1.	Cell reaction is irreversible	Cell reaction is reversible.
2.	Must be discarded after use.	May be recharged.
3.	Have relatively short shelf life.	Have long shelf life.
4.	Function only as galvanic cells.	Functions both galvanic Cell & as electrolytic cell.
5.	They cannot be used as storage devices	They can be used as energy storage devices (e.g. solar/ thermal energy converted to electrical energy)
6.	They cannot be recharged	They can be recharged.
7.	Eg. Dry cell, Alkaline cell and Li-battery.	Eg. Lead acid storage cell, Ni-Cd battery.

PRIMARY BATTERIES

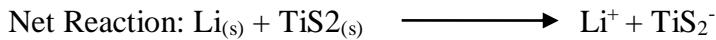
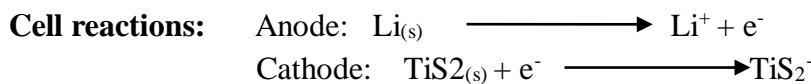
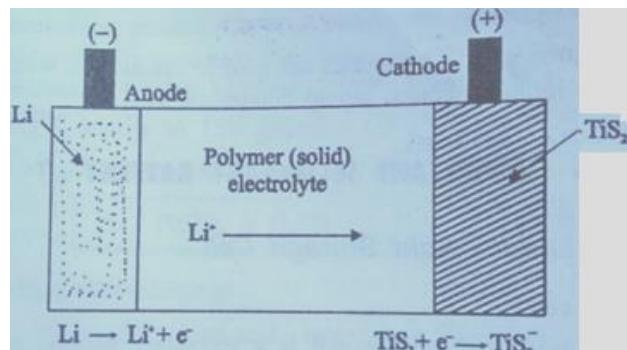
- The cell reaction is not reversible.
- No electricity is produced after complete conversion of the reactants to products and the cell becomes dead.
- These batteries are used as source of DC power.
- Eg. Lithium cell, Dry cell (Leclanche cell) and Alkaline cells

LITHIUM CELL - PRIMARY BATTERY

- Lithium cell is a primary cell, Lithium metal acts as anode.
- Metal oxide or TiS_2 acts as cathode.
- Solid polymer will act as an electrolyte; this polymer is packed in between the electrodes. The electrolyte permits the passage of ions but not that of electrons.

UNIT-III

- The EMF of the cell is 3.0V



Advantages:

1. In this cell voltage is high, 3.0V.
2. Lithium is a light weight metal (7gms).
3. Lithium has the most negative E° value.
4. In Lithium cell all constituents are in solid form so that there is no leakage.
4. The battery can be made in a variety of sizes and shapes.

Applications:

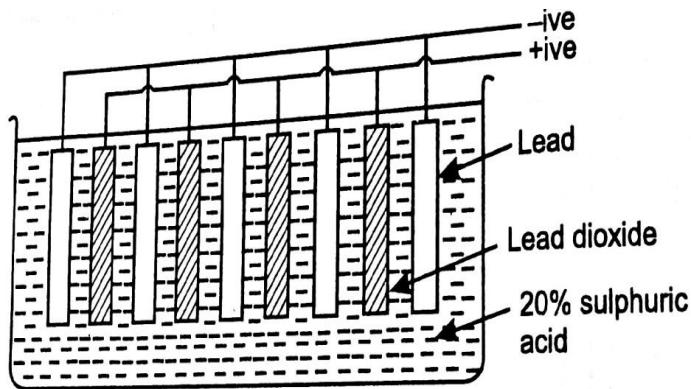
1. Button sized Lithium batteries are used in calculators, watches, cameras, mobile phones, laptop computers, etc.,

SECONDARY BATTERIES

- The cells in which the cell reaction is reversed by passing direct current in opposite direction i.e. it can operate both as a voltaic cell and as an electrolytic cell.
- The secondary batteries can be used through a large number of cycles of discharging and charging. They are used as a source of DC power.
Eg. Lead –acid storage cell, Lithium ion batteries and Ni-Cd battery.

1. LEAD ACID STORAGE CELL - SECONDARY BATTERY

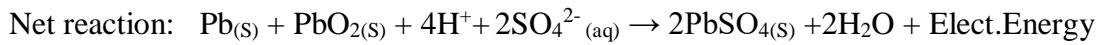
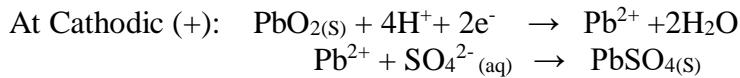
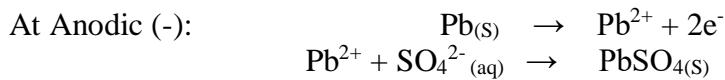
- It consists of lead –antimony alloy coated with lead dioxide (PbO₂) as cathode and spongy lead as anode. The electrolyte is a 20% solution of H₂SO₄.
- The storage cell can operate both as voltaic cell and electrolytic cell.
- It acts as voltaic cell when supplying energy and as a result eventually becomes rundown.
- The cell operates as electrolytic cell when being recharged.



➤ The cell consists of a series of Pb-plates (negative plates) and PbO₂ plates (positive plates) connected in parallel. The plates are separated from adjacent one by insulators like wood, rubber or glass fiber.

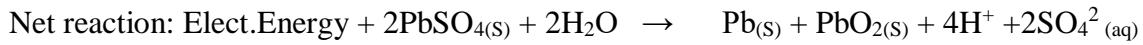
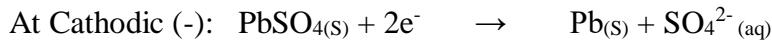
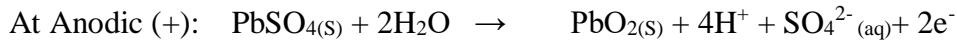
➤

➤ Cell reactions during discharging (voltaic cell):



During the discharging the battery, H₂SO₄ is consumed the density of H₂SO₄ falls to 1.20g/cm³, then battery needs recharging. In discharging, the cell acts as a voltaic cell where oxidation of lead occurs. In charging, the cell is operated like an electrolyte cell and electric energy is supplied to it.

➤ Cell reactions during recharging (electrolytic cell):



During this process, lead is deposited at the cathode, PbO₂, is formed at the anode and H₂SO₄ is regenerated in the cell.

Applications: The lead storage cells are used to supply current for electrical vehicles, gas engine ignition, telephone exchanges, electric trains, mines, laboratories, hospitals, broadcasting stations, automobiles and power station.

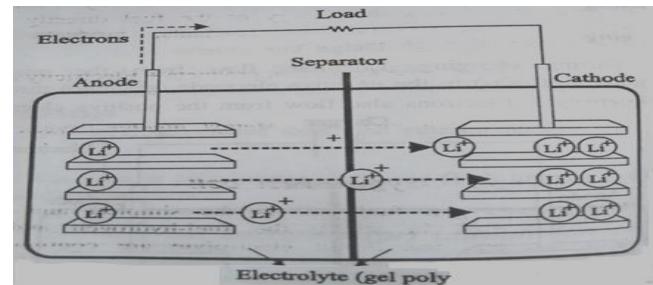
2. LITHIUM ION CELL - SECONDARY BATTERY

➤ It is rechargeable secondary cell. In lithium battery consists of a layers of porous carbon acts as anode and layers of lithium metal oxide acts as cathode.

➤ Electrolytes, generally a polymer gel, act as separator between the electrodes. The separator permits the passage of ions but not that of electrons.

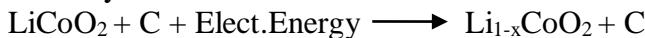
Cell reactions during discharging (voltaic cell): During discharging, the Li^+ ions flow back through the electrolyte from negative electrode to the positive electrode.

Electrons flow from the negative electrode to the positive electrode. The Li^+ ions and electrons combine at the positive electrode and deposit there as Li.



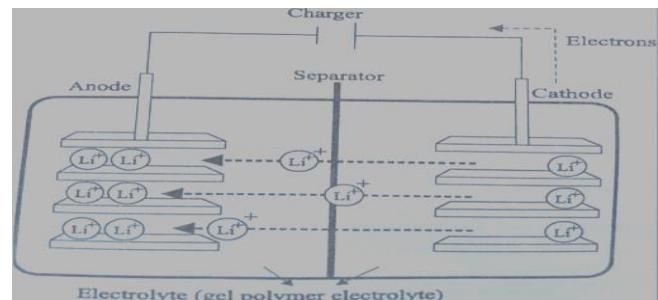
Cell reactions during charging (electrolytic cell):

During charging, the Li^+ ions flow from the positive electrode to negative electrode through electrolyte.



Advantages:

1. Lithium –ion batteries are high voltage and light weight batteries.
2. It is smaller in size.
3. It produces three times the voltage of Ni-Cd batteries.



Applications:

1. It is used in cell phone, note PC, portable LCD TV, semiconductor driven audios.

UNIT-III

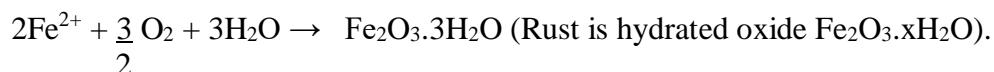
CORROSION AND ITS CONTROL.

Definition: Corrosion may be defined as the disintegration or eating away of a metallic material from its surface by chemical or electrochemical reaction with its environment.

Corrosion (Oxidation)

Metal $\xrightarrow{\text{Metallurgy (Reduction)}}$ Metallic compound + energy

Example: Rusting of iron when exposed to atmospheric conditions.



CAUSES OF CORROSION

In nature metals have a natural tendency to revert back to combined states. During this process mostly oxides are formed though in some cases sulphides, carbonates. Any process of deterioration and loss of solid metallic material by chemical or electrochemical attack by its environment is called corrosion. Corrosion is the reverse process of metallurgy.

Ore → Metal → Corrosion Product
 (Stable) (Unstable) (Stable)

EFFECT OF CORROSION

- Poor appearance
 - Maintenance and operating costs
 - Plant shutdowns
 - Contamination of product
 - Loss of valuable products due to leakage
 - Effects on safety and reliability in handling hazardous materials
 - Product liability
 - Valuable metallic properties such as conductivity, malleability, ductility, etc. are lost due to corrosion.

THEORIES OF CORROSION

There are two theories of corrosion

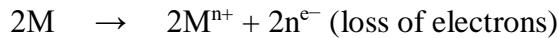
1. Dry/Chemical theory
2. Wet/Electrochemical/galvanic theory

1. Dry (or) chemical Corrosion: According to this theory type of corrosion occurs mainly through the direct chemical action of atmospheric gasses (O_2 , H_2S , SO_2 , and N_2) with metal.

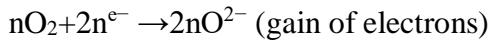
There are three main types of dry Corrosion:

- i. Oxidation corrosion
- ii. Corrosion of the other gases
- iii. Liquid metal corrosion.

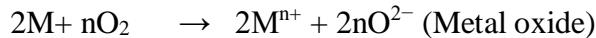
i. Oxidation corrosion: This is carried out by the direct action of oxygen low or high temperatures on metals in absence of moisture at ordinary temperature metals are very slightly attacked. The exceptions are Alkali metals and Alkaline earth metals. At high temperature all metals are oxidized. The exception is Ag, Au and Pt.



(Metal ion)



(Oxide ion)



Mechanism: During oxidation of a metal, metal oxide is formed as a thin film on the metallic surface which protects the metal from further corrosion. If diffusion of either oxygen or metal is across this layer, further corrosion is possible. Oxides of Pb, Al, Sn are stable, and hence inhibit further corrosion.

ii. Corrosion of the other gases: Cl_2 , SO_2 , H_2S , NO_x gases react with metal and form corrosion products which may be protective or non-protective. Dry Cl_2 reacts with Ag and forms $AgCl$ which is a protective layer, while $SnCl_4$ is volatile in petroleum industries at high temperatures, H_2S attacks steel forming FeS scale which is porous and interferes with normal operations.

iii. Liquid metal corrosion: In several industries, molten metals pass through metallic pipes and causes corrosion due to dilution or due to internal penetration.

Example: Coolant (sodium metal) causes cadmium corrosion in nuclear reactor. Liquid metal mercury dissolves most metals by forming amalgams, thereby clogging them.

2. Wet (or) Electrochemical Corrosion:

This type of Corrosion occurs where a conducting liquid is in contact with the metal (or) when two dissimilar metals (or) alloys are dipped partially in a solution. This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution. At anodic area, oxidation reaction occurs thereby destroying the anodic metal either by dissolution (or) formation of compounds. Hence corrosion always occurs at anodic parts. M^{n+} dissolution formation of compound at cathodic part, reduction reaction (electro nation) occurs. It does not affect the cathode, since most metals cannot be further reduced. At cathodic part, the dissolved constituents in the conducting medium accept the electrons forming ions (OH^- , O^{2-}). The metallic ions formed at anodic part and the ions formed at cathodic part diffuse towards each other through conducting medium and form a corrosion product somewhere between anode and cathode.

Mechanism: Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.

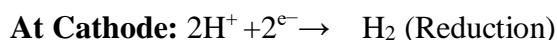


The cathodic reaction consumes electrons with either *evolution of hydrogen* or *absorption of oxygen* which depends on the nature of corrosive environment.

i. Evolution of hydrogen: This type of corrosion occurs in acidic medium.

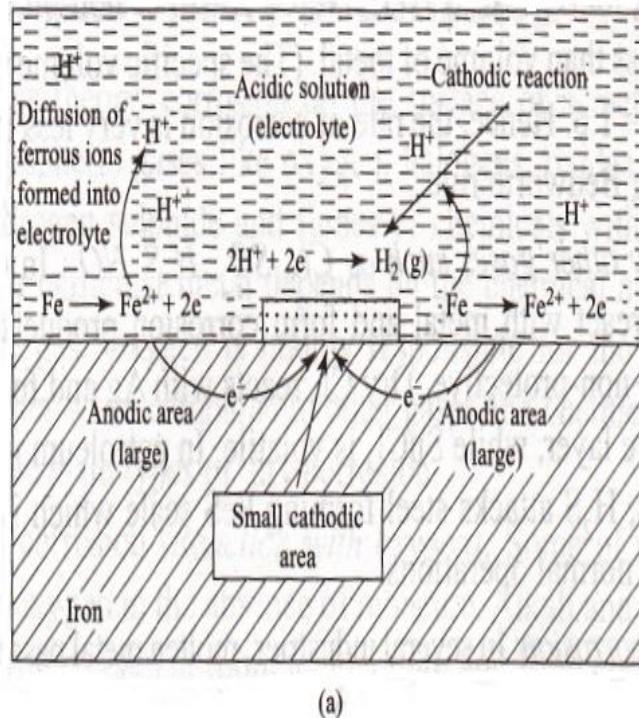
Ex: Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.

The electrons released flow through the metal from anode to cathode, whereas H^+ ions of acidic solution are eliminated as hydrogen gas.



This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H_2 gas.

The anodes are large areas, whereas cathodes are small areas.



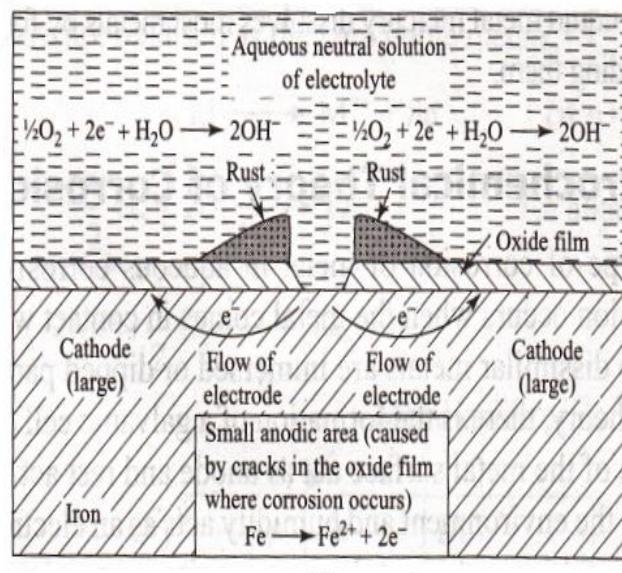
(a)

ii. Absorption of oxygen:

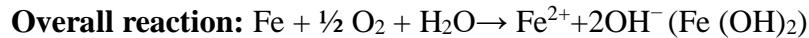
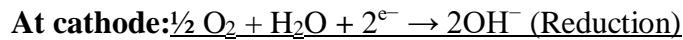
This type of corrosion occurs in neutral (or) basic medium.

Ex: Rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen.

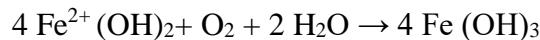
Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large cathodes.



(b)



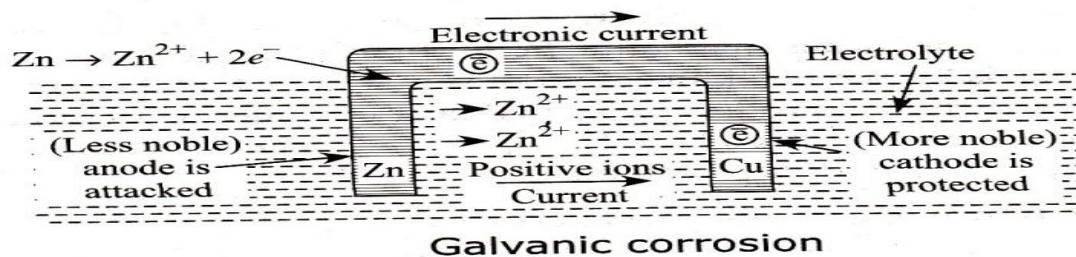
If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.



The product called yellow rust corresponds to $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

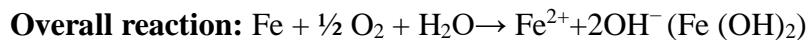
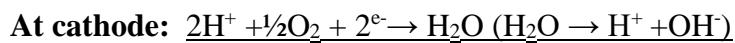
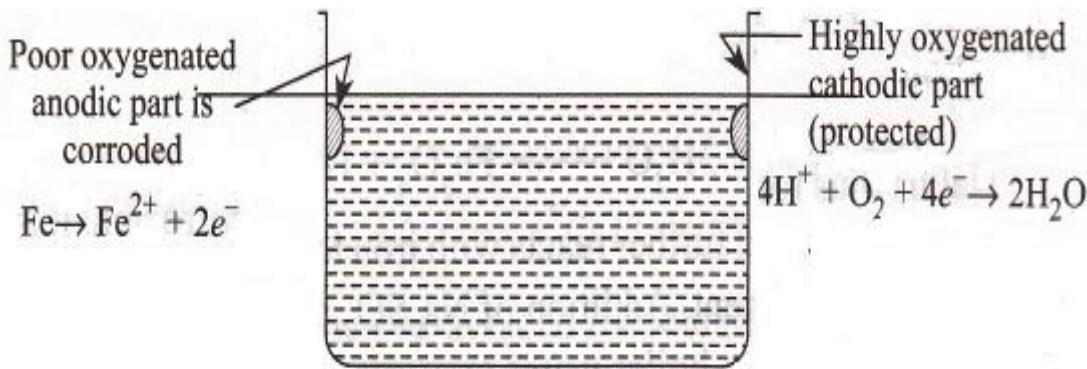
TYPES OF CORROSION

1. Galvanic Corrosion: When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called galvanic corrosion.



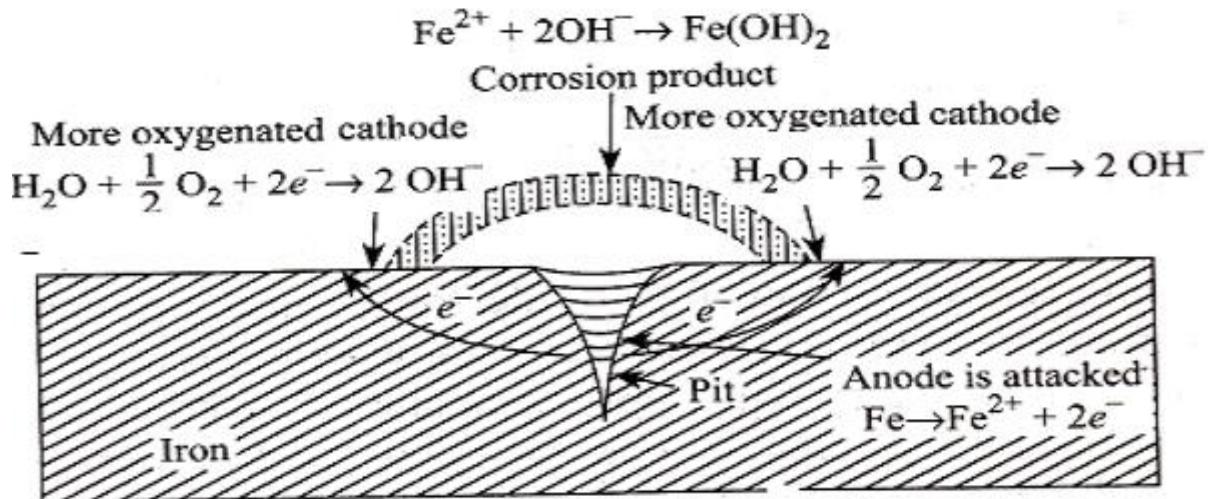
Galvanic corrosion can be avoided by coupling metals close to the electrochemical series, fixing insulating material between two metals, by using larger anodic metal and smaller cathodic metal.

2. Waterline Corrosion: This is also known as *differential oxygen concentration corrosion*. It has been observed in the case of iron tank containing water, that the portion of iron tank just below the water level undergoes corrosion. It is due to the difference in oxygen concentration.



The area above the waterline (highly oxygenated) acts as cathodic and is not affected by corrosion. However, if the water is relatively free from acidity, little corrosion occurs. This type of corrosion is prevented to a great extent by painting the sides of the ships by antifouling paints.

3. Pitting corrosion: Pitting corrosion is due to crack on the surface of a metal, there is a formation of a “*local galvanic cell*” (Pinholes, pits and cavities) in the metal.



Pitting is usually the result of the breakdown or cracking of the protective film on a metal at specific points. This gives rise to the formation of small anodic and large cathodic areas. In the corrosive environment this produces corrosion current.

FACTORS AFFECTING OF CORROSION

The rate and extent of corrosion depends on the nature of the metal and nature of corroding environment.

Those are **1. Effect of metal**

2. Effect of environment

1. Effect of metal: Different properties of a metal are responsible for corrosion. These properties are given below.

a. Position of metal in galvanic series
c. Nature of surface/oxide film

b. Hydrogen over voltage
d. Volatility of corrosion product

a. Position of metal in galvanic series: It decides the corrosion rate. A metal having higher position in galvanic series undergoes corrosion when connected to another metal below it.

b. Hydrogen over voltage: In case of Zinc metal placed in a normal solution of H_2SO_4 , reaction takes place forming bubbles of hydrogen gas on zinc surface. The process is slow due to high overvoltage of zinc metal (0.7 V) which reduces the effective potential to a small value. In presence of $CuSO_4$ the corrosion rate of zinc is accelerated.

c. Nature of surface/oxide film: In aerated atmosphere, all metals get covered with a thin surface film of metal oxides. The ratio of the volumes of metal oxides to the metal is known as specific volume ratio. Greater is this value lesser is the oxidation corrosion rate. Specific volume ratios of Ni, Cr and W are 1.6, 2.0 and 3.6 respectively suggesting Tungsten has least corrosion. Further the corrosion depends on nature of oxide film. Metals like Al have a firm oxide film in comparison to Fe and hence Al in less corrosive means it follows **Pilling-Bed worth Rule**. The iron oxide is porous in nature and this leads to extension of corrosion to inner surface.

d. Volatility of corrosion products: If the corrosion product is volatile, then the underlying surface is exposed for further attack. This causes rapid and continuous corrosion. E.g. MoO_3 is volatile.

2. Effect of environment: Different properties of an environment are responsible for corrosion. These properties are given below.

a. Effect of pH
c. Humidity of air

b. Temperature

a. Effect of pH:

In the corrosion reaction described H^+ or OH^- are also involved. Therefore the effect of pH is obvious. It can be easily seen from the chemical equation for a reaction the direction in which it will shift by change in concentration of H^+ or OH^- . As a general rule, acids are more corrosive than neutral or alkaline solutions.

b. Temperature:

As the temperature of environment is increased the reaction rate is increased thereby accelerating corrosion. The effect of temperature on the corrosion rate is complicated because of the fact that it affects the various factors in different ways. The rate of chemical reaction increases, with rise in temperature but the solubility of gases, like oxygen which affect corrosion, decreases. The temperature may affect the protective coatings in different ways. In general, the rate of corrosion due to oxygen or oxidizing agents is decreased with rise in temperature but the rate of hydrogen type corrosion is increased.

c. Humidity of air:

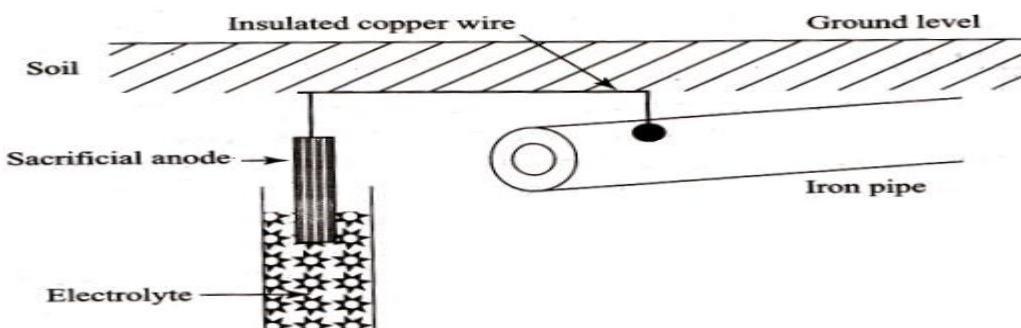
Corrosion of a metal is furnished in humid atmosphere because gases (CO_2 , O_2) and vapours present in atmosphere furnish water to the electrolyte essential to establish an electrochemical corrosion cell. The oxide film on the metal surface has the property to absorb moisture. In presence of this absorbed moisture, corrosion rate is enhanced. Rain water may also wash away the oxide film from the metal surface. This leads to enhanced atmospheric attack. The exceptions are Cr, Al.

CORROSION CONTROL METHODS

1. Cathodic Protection: The cathodic protection of metals is used to control corrosion metals where it is impossibly to alter the nature of the corrosion medium. The principle involved in this method is to protect metals and alloys from corrosion by making them completely cathodic. Since there will not be any anodic area on the metal, therefore corrosion does not occur. The following are **two types** of cathodic protections.

a. Sacrificial anodic protection b. Impressed current cathodic protection

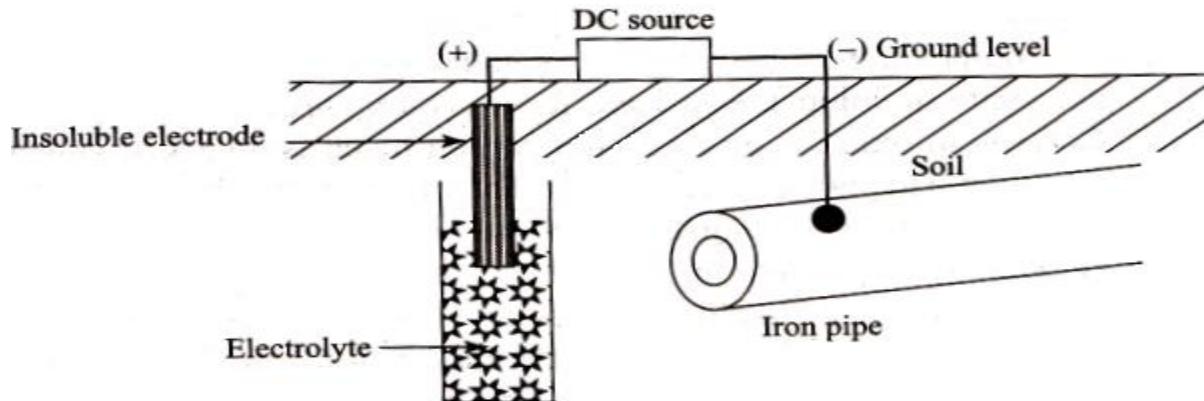
a. Sacrificial anodic protection: In this method, the metal structure can be protected from corrosion by connecting it with wire to a more anodic metal. As this more active metal is sacrificed in the process of saving metal from corrosion, it is known as sacrificial anode. The metals which are commonly used as sacrificial anodes are Mg, Zn, Al and their alloys.



The important applications of this method are:

- Protection of underground cables and pipelines from soil corrosion.
- Protection of ships and boat hulls from marine corrosion.
- Prevention of rusty water by inserting Mg sheets or rods into domestic water boilers or tanks.

b. Impressed current cathodic protection: As the name implies, an impressed current is applied to convert the corroding metal from anode to cathode. The applied current is in opposite direction since to nullify the corrosion current. This can be accomplished by applying sufficient amount of direct current source like battery or rectifier to an anode like graphite, high silica iron, stainless steel or platinum buried in the soil or immersed in the corrosion medium, and connected to the corroding metal structure which is to be protected as shown in the diagram below.



In impressed current cathodic protection, electrons are supplied from an external cell, so that the object itself becomes cathodic and not oxidized. This type of cathodic protection has been applied to buried structures such as tanks and pipelines, transmission line-towers, marine piers, laid-up ships etc. since, their operating and maintenance costs are less, they are well suited for large structures and long term operations.

2. Surface coatings/ Metallic coatings: These are produced by coating one metal on the surface of molten metal. The metal which is protected is called base metal and the metal which is coated on the surface of the base metal is called coating metal.

Methods of Application of Metallic coatings: Metallic coatings are done by the following methods:

- | | |
|--------------------------|---------------------------------|
| I: Hot dipping. | II: Electroplating. |
| III. Anodization. | IV. Electroless Plating. |

I. HOT DIPPING

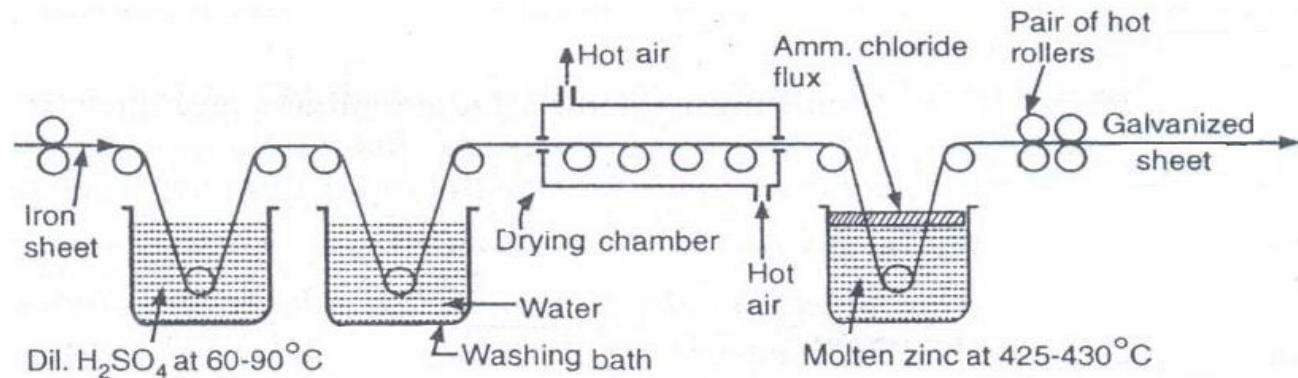
i. Hot-dipping: Hot dipping process is applicable to the metals having higher melting point than the coating metal. It consists of immersing well cleaned base metal in a bath containing molten coating metal, and a flux layer. The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal.

Examples: Coating of Zn, Sn, Pb, Al on iron, steel surfaces.

Most widely used hot dip process are:

- | | |
|---------------------------|------------------------|
| a. Galvanizing. | b. Tinning. |
| c. Metal Cladding. | d. Cementation. |

a. Galvanizing: Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc. At first iron or steel is cleaned by pickling with dilute H_2SO_4 at a temperature range of $60-90^{\circ}C$ for 15 to 20 minutes. Therefore, it removes scale, rust and other impurities present. Then after dipped molten zinc in the bath at $425-450^{\circ}C$, to prevent it from oxide formation, the surface of bath is covered with a flux (NH_4Cl).

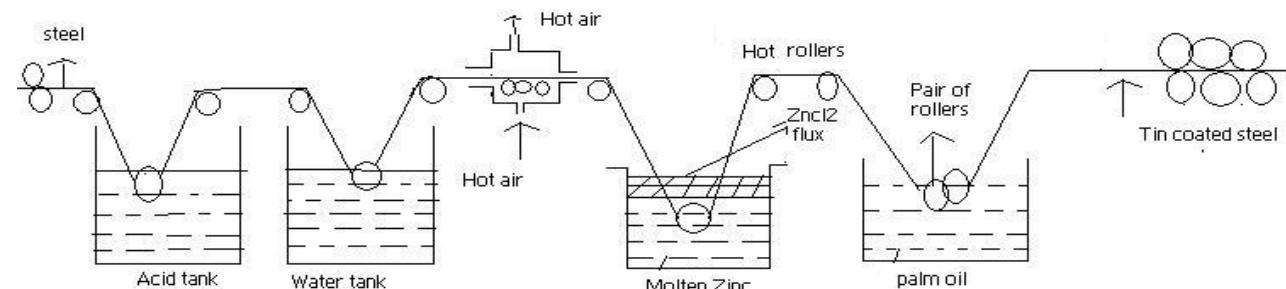


When the iron piece is taken out it is coated with a thin layer of zinc. And to remove excess zinc, it is passed through a pair of hot rollers; lastly, it is annealed at a temperature of $450^{\circ}C$ and then cooled slowly.

Applications of Galvanizing:

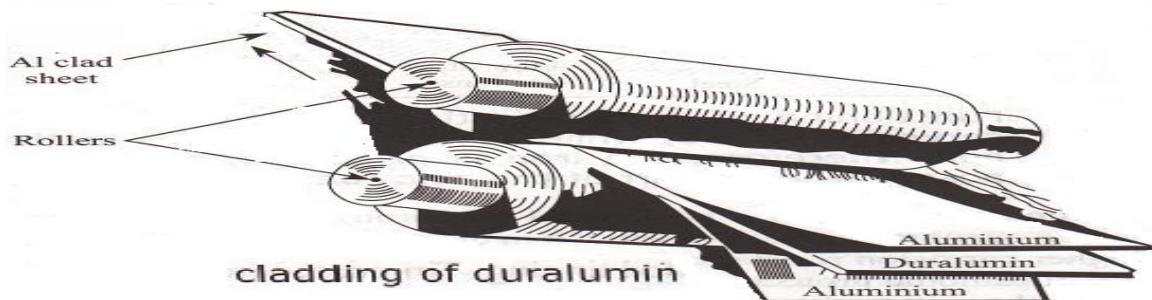
- It is widely used for protecting iron exposed to the atmosphere, as is the case with roofs, wire fences, pipes and articles fabricated from galvanized sheets like buckets, tubes.
- Galvanized ware is not used for keeping eatables because of the solubility of zinc.
- The popularity of galvanizing is due the low cost of zinc.
- Easy application and the anodic protection offered by the zinc.

b. Tinning: The process of coating tin over the iron or steel articles to protect it from corrosion is known as tinning. Tin is a nobler metal than iron, therefore, it is more resistance to chemical attack. In this process, at first Iron sheet is treated in dilute H_2SO_4 (pickling) to remove any oxide film if present.



A cleaned Iron sheet is passed through a bath molten flux. Like Zinc chloride, then through molten tin and finally through a suitable vegetable oil. Tinning of mild steel plates is done mostly for the requirements of the food stuff industry. A cleaned iron sheet is passed through a bath of molten flux, like zinc chloride, then through molten tin and finally through a suitable vegetable oil. Lastly it is passed between rolls to adjust the thickness of the tin layer, which may be about 0.002 mm thick.

c. Metal Cladding: The surface to be protected is sandwiched between two thin layers of coat metal and pressed between rollers. The finished product may be welded at the edges or riveted at some points. The coat metal has to be anodic to the base metal and only plain surfaces can be cladded. This method is used for coating Al, Cr, Ni, Duralumin, etc.



a coating of a thin homogeneous layer of a coating metal on a base metal a fused so that it strongly binds permanently either on one side or on both sides and passed through rollers under heat and pressure. All corrosion-resistant metals like Ni, Cu, Ag, Au & Pt, and alloys like steel nickel alloys can be used as cladding materials. Base metals on which cladding is done are mild steel, aluminum, copper, nickel and other alloys Duralumin is very light metal alloys used in aircrafts industry.

d. Cementation: This type of coatings is obtained by heating the base metal in a revolving drum containing powdered coating metal. The powdered metal forms a coat on the base metal and hence protects it from corrosion.

There are three important pack cementation processes, those are: Sherardising, Chromising and Calourising.

In Sherardising the base metal is heated with zinc powder in a metal drum. The drum is closed and heated to 350-370 °C with slow rotation for 2-3 hours. This results in formation of **Fe-Zn alloy** on the surface of the base metal. **It is used for protecting small steel parts such as nuts, bolts, etc.**

In chromising the base metal is heated with a powdered mixture of 55% Chromium and 45% alumina in a metal drum. The drum is closed and heated to 1300-1400 °C with slow rotation for 2-3 hours. This results in formation of **Chrome-alloy** on the surface of the base metal. **It is used to protect gas turbine blades.**

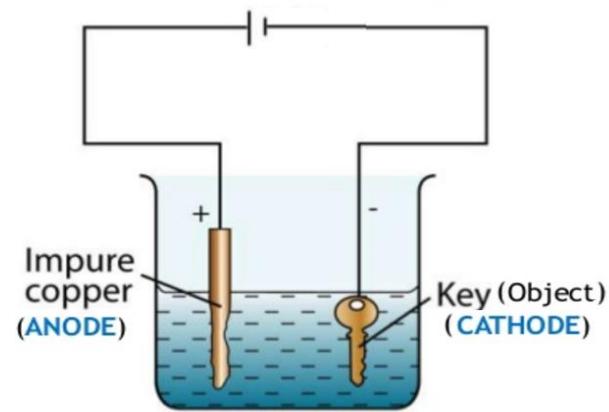
In calorising the base metal is heated with a powdered mixture of Aluminium and alumina in a metal drum. The drum is closed and heated to 840-950 °C with slow rotation for 4-6 hours. This results in formation of **Calorised steel**. **It is used to making of furnace parts.**

II. ELECTROPLATING

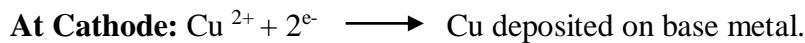
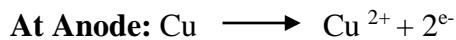
Electroplating is the process of coating metals and non-metals, to change their surface properties such as to improve the appearance, and corrosion or chemical attack. Electroplating is the electro-deposition of metal, by means electrolysis over surface of metals, alloys or non-metals.

Electro plating of copper over metal object:

The metal object, to be plated is first treated with dil.HCl or dil.H₂SO₄. The cleaned object is the made cathode of an electrolytic cell and pure copper plate as anode. CuSO₄ and dil.H₂SO₄ solutions are taken as electrolyte. When the current is passed from the battery through the solution copper dissolves in the electrolyte and deposits uniformly on the metal object.



Chemical reactions:



Conditions for Electro plating of copper over metal object:

Anode/coating metal: Pure copper plate

Cathode/Base metal: Metal object

Electrolyte: CuSO₄ and dil.H₂SO₄

Temperature: 40-45°C

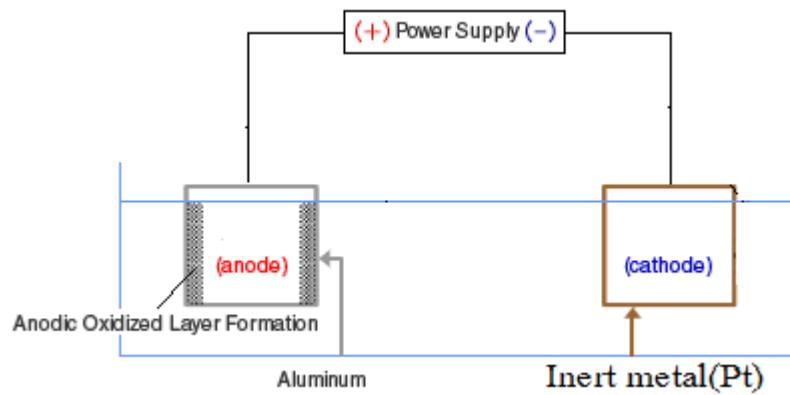
Current: 30-40 mA/cm²

Applications of electroplating are:

- This process is widely used in automobiles, aircrafts, etc.
- Plating for decoration.
- This process is also used in Refrigerators, jewellery, radios, cameras, type-writers, umbrellas, watches etc.
- Plating on non-metallic materials.

III. ANODIZATION (OR) ANODIZED COATING

Anodization is an electrolytic process in which a thick oxide coating is produced on the base metal. Anodised coatings are generally produced on nonferrous metals like Al, Zn, Mg and their alloys. Anodized coating on Aluminium is done by making Aluminium as an anode in an electrolytic bath containing H₂SO₄ (or) phosphoric acid at moderate temperature about 35 to 40 °C and the cathode is a plate of lead or stainless steel. On passing the current oxidation starts at anode and oxygen combine with an anodic metal to form the oxide. The oxide film initially will be very thin and grows from the metal surface outwards and increases in thickness as oxidation continues at aluminum anode. The oxide film is very porous and soft and this can be filled by immersing it in boiling water this treatment converts porous alumina into hydrated Alumina which occupies more volume thereby the pores are sealed.



Chemical reactions:

At Anode: $\text{Al} + \text{O}_2 \longrightarrow \text{Al}_2\text{O}_3$ (oxide film)
 $\text{Al}_2\text{O}_3 + \text{H}_2\text{O} \longrightarrow \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (hydrated Alumina)

Conditions for Anodization:

Anode/coating metal: Aluminium

Electrolyte: dil. H_2SO_4 , H_3PO_4

Current: 0.2-2 mA/cm²

Cathode/Base metal: Inert metal

Temperature: 40-50°C

Advantages of Anodization:

Very good resistance to corrosion and thicker oxide coating is more protective.

Applications of Anodization:

Anodised aluminium is used in automobile engine piston.

IV. ELECTROLESS PLATING COATING/ ELECTROLESS NICKEL PLATING

Electroless plating is a technique of depositing a noble metal (from its salt solution) on a catalytically active surface of the metal to be protected, by using a suitable reducing agent without using electrical energy.

The reducing agent reduces the metallic ions to metal, which gets plated was that catalytically activated surface giving a uniform thin coating.

Metal ions + Reducing agent \longrightarrow Metal (deposited) + oxidized products

IN ELECTRO LESS NICKEL PLATING HAVING THREE STEPS AS FOLLOWS:

Step I: Pretreatment and activation of the surface:

The surface to be plated is first degreased by using organic solvents or alkali followed by acid treatment.

Ex:

- The surface of the stainless steel is activated by dipping in hot solution of 50% dilute sulphuric acid.
- Metals and alloys like Al, Cu, Fe, Brass, etc., can be directly nickel-plated without activation.
- Non-metallic articles like plastics, glasses are activated by dipping them in the solution containing $\text{SnCl}_2 + \text{HCl}$, followed by dipping in PdCl_2 solution on drying a thin layer of freed is formed on the surface.

Step II: Plating bath: Plating bath consists of the following ingredients:

Coating solution: NiCl_2 .

Reducing agent: Sodium hypophosphate.

Complexing agent: Sodium succinate.

Buffer: Sodium acetate.

Optimum pH: 4.5

Optimum temperature: 93°C .

Step III: Procedure:

The pretreated object is immersed in the plating bath for the required time. During which of the following reducing another Nickel gets coated over the object.

**Applications of Electroless-plating:**

- Electroless Ni-plating is extensively used in electronic appliances.
- Electroless Ni-plating is used domestic as well as automatic fields.
- This application is used in making jewellery.
- Electroless Ni-coated Polymers are used in decorative and functional works.
- Electroless Copper and Nickel coated plastic cabinets are used in digital as well as electronic instruments.

Learning objectives:**After completion of this unit the student should be able to:**

- Electrode potential, standard electrode potential.
- Types of electrodes – calomel electrode, Quinhydrone.
- Types of electrodes – glass electrode, Nernst equation.
- Determination of pH of a solution by using quinhydrone electrode.
- Determination of pH of a solution by using glass electrode.

UNIT-III

- Electrochemical series and its applications.
- Numerical problems, Potentiometric titrations.
- Primary batteries (Lithium cell).
- Secondary batteries (Lead–acid battery and Lithium ion battery).
- Corrosion and its control: Causes and effects of corrosion.
- Theories of chemical and electrochemical corrosion.
- Mechanism of electrochemical corrosion.
- Types of corrosion: Galvanic, water-line and pitting corrosion.
- Factors affecting rate of corrosion.
- Corrosion control methods- Cathodic protection– Sacrificial anode.
- Corrosion control methods- Impressed current cathodic methods.
- Surface coatings – metallic coatings–methods of applications.

Short Answer Questions:

1. Explain the Standard electrode potential with example.
2. Explain Galvanic cell?
3. What are the applications of Nernst equation?
4. What is the Construction and functioning of Calomel electrode?
5. Differentiate Primary batteries and Secondary batteries.
6. What would result when a zinc road is placed in 0.1M-ZnSO₄ solutions at 298 K. write the electrode reaction and calculate the potential of the electrode. Zn = - 0.7 V?
7. Write cell reaction of primary Lithium cell.
8. Define electrochemical series?
9. What is meant by rusting of Iron?
10. What is galvanic corrosion?
11. What is the effect of P^H on the corrosion?
12. What is differential aeration corrosion?

Descriptive Questions:

1. Explain Construction & functioning of Glass electrode and calculate pH of unknown solution by using Glass electrode.
2. Explain Construction & functioning of Quinhydrone electrode and calculate pH of unknown solution by using Quinhydrone electrode.
3. Explain construction and functioning of Lead acid cell.
4. Describe construction and functioning of Lithium ion cell(Secondary Cell).
5. Explain the following? (a) Electroplating (b) Galvanizing (c) Tinning (d) Metal cladding.
6. Explain how corrosion control can be brought about by the following methods?
(a) Cathodic protection (b) Sacrificial anode.

Objective Questions:

1. What is potential of Saturated Calomel electrode is. []
a. 0.242V **b.** 0.280V
c. 0.333V **d.** 0.124V
2. A Voltaic cell converts. []
a. Electrical Energy in to chemical energy **b.** Chemical energy into electrical energy
c. Electrical energy into heat energy **d.** Chemical energy into heat energy
3. Calomel is. []
a. Mercuric sulfate **b.** Mercurous sulfate
c. Mercurous chloride **d.** Mercuric chloride
4. A galvanic cell converts. []
a. Electrical Energy in to chemical energy **b.** Chemical energy into electrical energy
c. Electrical energy into heat energy **d.** Chemical energy into heat energy
5. Corrosion is as an example of: [a]
(a) Oxidation (b) Reduction (c) Electrolysis (d) Erosion
6. When a buried pipeline is protected from corrosion by connecting to Mg block, it is called [c]
(a) Impressed voltage protection (b) Sacrificial cathodic protection
(c) Sacrificial anodic protection (d) Any of these

UNIT-III

7. The process of coating with tin on base metal is known as: [d]
(a) Galvanizing (b) Zincing (c) Sherardizing (d) Tinning
8. The rate of corrosion of iron in atmosphere depends upon: [a]
(a) The humidity of the atmosphere (b) The degree of pollution of the atmosphere
(c) The frequency of rain fall (d) All of these factors
9. In waterline corrosion the maximum amount of corrosion takes place [c]
(a) Along a line just above the level of the water meniscus
(b) Along a line at the level of the water meniscus
(c) Along a line just below the level of the water meniscus
(d) At the bottom of the vessel

Fill in the blanks:

1. The Electrolyte is used in Lead-Acid storage battery is -----.
2. The net EMF of the Galvanic Cell is -----.
3. A cell whose reaction is not reversible is called -----.
4. Nernst equation for electrode reaction is -----.
5. Corrosion is a gradual decay of metal by the attack of environment.
6. The rate of corrosion increases with decrease in pH.
7. Cathodic coatings are obtained by coating a noble metal than the base metal.
8. An example of cathodic coating is tinning.
9. Impurities in metal cause corrosion.