Electrochemical Energy Systems
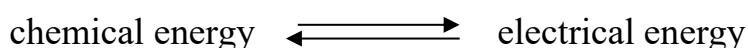
A. Electrode potential and Cells

Electrochemistry deals with the inter conversion of chemical energy and electrical energy.

There are two types of electrochemical cells:
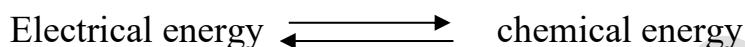
1. Galvanic cell:

It converts chemical energy to electrical energy.

chemical energy $\longleftrightarrow$ electrical energy
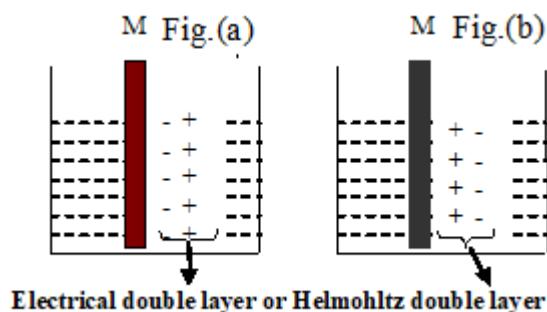
Ex: Batteries and fuel cells

2. **Electrolytic cell:** It converts electrical energy to chemical energy.

Electrical energy $\longleftrightarrow$ chemical energy

Ex: Electroplating and electro refining

Electrical double layer & its significance: When a metal is in contact with a solution of its own salt, the positive ions in the metal come into equilibrium with those in the solution; leaving behind an equivalent number of electrons on the metal. Thus, the metal acquires a negative charge, since it is now left with excess number of electrons and a number of positive metallic ions are formed in solution(fig a). Conversely, if the positive metallic ions from the solution enter the metallic lattices, then metal acquires a positive charge (fig b). Thus, following two reactions take place, when a metal is in contact with its salt solution:

Electrical double layer or Helmohltz double layer

1. Positive metallic ions passing into solution.

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

2. Positive ions depositing on the metal electrode

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

As the negative or positive charges developed on the metal attract the positively or negatively charged free ions in the solution, ultimately the dynamic equilibrium is established. Due to this attraction, the positive or negative ions remain quite close to the metal. Thus, a sort layer of positive ions (fig a) or negative ions (fig b) is formed all around the metal. This layer is called **Helmholtz electrical double layer**. A difference of potential is, consequently, set up between the metal and solution. This potential difference will persist as long as the charge is allowed to remain on the metal and this will prevent any further passing of the positive ions from or to the metal. At equilibrium, the potential difference between the metal and solution becomes a constant value. The equilibrium potential difference so established is called the electrode potential of the metal.

Definition: The electrical potential developed at the interface of the metal and its solution due to Helmholtz electrical double layer is called single electrode potential.

Standard electrode potential [Eº]: The potential of metal electrode when dipped into metallic salt solution of unit molar concentration at 25ºC 1 atmospheric Pressure [101.3k pa] is called standard electrode potential. The electrode potential is constant for the given electrode.

$$E^o{}_{Zn} = -0.76 \text{ V}$$
$$E^o{}_{Cu} = +0.34 \text{ V}$$

Free energy [ΔG]: It is measure of available energy which can be converted into useful work. It is defined mathematically $\Delta G = \Delta H - T \Delta S$

ΔH = enthalpy

ΔS = entropy

Standard free energy [ΔGº]: The free energy change of the reaction when all the reactants and products are in their standard states of 25ºC, 1 atmospheric Pressure,

Cell notation: To provide information about a cell a standard notation is followed:

- Anode half-cell is written first followed by cathode half cell.
- A pair of vertical lines represents salt bridge between anode and cathode.
- Within a half cell a single vertical line is used to represent phase boundary between solution and solid electrode. For solutions molar concentration is indicated in parenthesis.

Ex: In a Daniel cell, Zinc is anode and copper is cathode. If Zn^{2+} concentration is 1M & Cu^{2+} concentration is 1M the cell is represented by:

$$Zn(s)/Zn^{2+} (1M)//Cu^{2+} (1M) / Cu(s)$$

Emf of cell:

$$E_{cell} = E_{RHSE} – E_{LHSE} = E_{cathode} – E_{anode}$$

E_{cell} represents the driving force for the cell reaction to take place.

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

If reaction is spontaneous ΔG is negative, thus E_{CELL} should be positive.
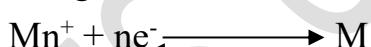
If reaction is non spontaneous ΔG is positive, thus E_{CELL} should be negative.

Derivation of Nerns't Equation-Equation for single electrode potential:

The electrical potential developed at the interface of the metal and its solution due to Helmholtz electrical double layer is called single electrode potential. Single electrode potential can be calculated from Nerns't equation. Nerns't equation can be derived on the thermodynamic consideration.

Consider a general redox reaction:

$$Mn^+ + ne^- \rightleftharpoons M$$

Oxidized form   reduced form

The reaction quotient for this reversible reaction, $Q= [M]/[M^{n+}]$

A thermodynamic equation which relates reaction quotient and decreases in free energy is given by,

$$\Delta G = \Delta G^o + RTlnQ$$

where Q is the reaction quotient.

$-\Delta G$ represents the maximum work that can be obtainable from the electrochemical reaction. $-\Delta G = W_{max}$

For an electrochemical cell, W_{max} depends on number of Coulombs, i.e., No. of moles of electrons exchanged in redox reaction (n), multiplied by no. of coulombs per mole of electrons. F(96,500 e/mol. E) = nF

Energy available per coulomb i.e., emf because volt = energy/Coulomb

Therefore $\Delta G = - nFE$

For a reversible reaction the relationship between the free energy change (ΔG) and equilibrium constant 'k' is given by Vant Hoff isotherm

$$\Delta G = \Delta G^o + RT \log_e \frac{[\text{Reduced form}]}{[\text{Oxidized form}]} \longrightarrow (1)$$

or $-\Delta G = -\Delta G^o - RT \log_e K$

$$\Delta G = \Delta G^o + RT \log_e \frac{[M]}{[M^{+n}]}$$

$$- nEF = - nE^o F + RT \log_e \frac{[M]}{[M^{+n}]}$$

$$-nEF = - nE^o F + RT \log_e \frac{1}{[M^{+n}]}$$

(The concentration of metal is Unit. i.e., M= 1)

$-nEF = - nE^o F - RT \log_e [M^{+n}]$

$nEF = nE^o F + RT \log_e [M^{+n}]$

Dividing by -nF

$E = E^o + \dfrac{RT}{nF} \log_e [M^{+n}]$

$E = E^o + \dfrac{RT}{nF} 2.303 \log_{10} [M^{+n}]$

Substituting R, T, F we get

$$\mathbf{E = E^o + \dfrac{0.059}{n} \log_{10} [M^{+n}]}$$

Where R= gas constant [$8.314 Jk^{-1}$ mol], T= lab temperature [298k]

[M^{n+}] = metal ion concentration
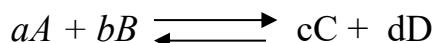
Concentration & Temperature dependency of single electrode potential:
Nerns't equation for single electrode potential is:

$E = E^o + \dfrac{RT}{nF} 2.303 \log_{10} [M^{+n}]$

From the above equation it is evident that Electrode potential increases as the Temperature & Concentration increases.

Nerns't equation can also be used to calculate the emf of a cell

$$aA + bB \rightleftharpoons cC + dD$$

The Nerns't equation for the emf of the cell is

$E_{cell} = E^0_{cell} - \dfrac{2.303}{nF} \log \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$
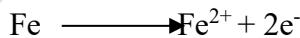
$E_{cell} = E^0_{cell} - \dfrac{0.0591}{n} \log \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ *at 298K*

Where n is the number of electrons transferred during the cell reaction and E^0_{cell} is the standard emf of the cell.
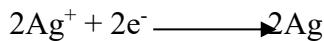
Numerical:

For the cell Fe/Fe^{2+} (0.05)//Ag$^+$ (0.1)/Ag write the cell reaction and calculate the emf of the cell at 298k if standard electrode potentials of Fe & Ag electrodes are –0.44 and 0.8V respectively.

Cell reaction: At anode: $Fe \longrightarrow Fe^{2+} + 2e^-$
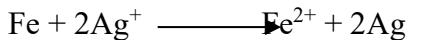
At Cathode: $2Ag^+ + 2e^- \longrightarrow 2Ag$

Overall reaction $Fe + 2Ag^+ \longrightarrow Fe^{2+} + 2Ag$

$E^o_{cell} = E^o_{Ag} - E^o_{Fe}$

$= 0.8 - (- 0.44) = 1.24$ V.

Ecell $= E^o_{cell} - \dfrac{0.0591}{n} \log \dfrac{[Fe^{2+}] [Ag]^2}{[Fe] [Ag^+]^2}$

$= 1.24 - \dfrac{0.0591}{2} \log \dfrac{[Fe^{2+}]}{[Ag^+]^2}$

$= 1.24 - \dfrac{0.0591}{2} \log \dfrac{0.05}{(0.1)^2}$

$= 1.24 - 0.0206$

$= 1.2194$ V

Types of electrodes

In order to form a cell, 2 half cells or 2 electrodes are required. Depending upon the purpose various types of electrodes are developed.

They are of following types

1. Metal-metal ion electrode:

It consists of metal in contact with a solution of its own ions.

Ex: Zn/Zn^{2+}, Cu/Cu^{2+}, Ag/Ag^{+} etc

Electrochemical reaction is, $M^{n+} + ne^{-} \rightleftharpoons M$.

- Nernst equation,

$$E_{M^{n+}/M} = E^{0}_{M^{n+}/M} + \frac{0.0591}{n}\log[M^{n+}]$$

2. Metal-Metal salt, ion electrode:

These electrodes consist of a metal in contact with a sparingly soluble salt of the same metal dipped in a solution of soluble salt of the same anion.

Ex : Calomel electrode $Hg/Hg_2Cl_2/KCl$ solution, $Ag/AgCl(s)/HCl$ solution

silver – silver chloride electrode consisting of silver, solid AgCl and a solution of soluble chloride such as KCl or HCl

- Electrochemical reaction is, $AgCl + e^{-} \rightleftharpoons Ag + Cl^{-}$

Nernst equation $E_{Ag/AgCl/Cl^{-}} = E^{0}_{Ag/AgCl/Cl^{-}} - 0.0591[Cl^{-}]$

3. Gas electrode:

It consists of gas bubbling about an inert metal foil, immersed in solution containing ions to which the gas is reversible. The metal provides electrical contact and facilitates the establishment of equilibrium between the gas and its ions
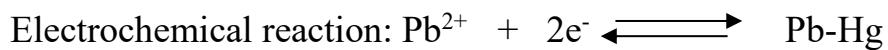
- Ex: Hydrogen electrode $Pt/H_2/H^{+}$ solution
- Chlorine electrode $Pt/Cl_2/Cl^{-}$ solution
- Electrochemical reaction is, $Cl_2 + 2e^{-} \rightleftharpoons 2Cl^{-}$
- Nernst equation:

$$E_{Pt/Cl_2/Cl^{-}} = E^{0}_{Pt/Cl_2/Cl^{-}} - \frac{0.0591}{2}\log[\frac{[Cl^{-}]}{p_{Cl_2}}]$$

4. Amalgam electrode:

It is similar to metal- metal ion electrode in which metal amalgam is in contact with a solution containing its own ions

Ex: Lead amalgam electrode $Pb-Hg/Pb^{2+}$

Electrochemical reaction: Pb^{2+} + $2e^-$ ⇌ $Pb-Hg$

Nernst equation:

$$E_{Pb^{2+}/Pb-Hg} = E^0_{Pb^{2+}/Pb-Hg} - \frac{0.0591}{2}\log[\frac{[Pb-Hg]}{[Pb^{2+}]}]$$

5. Oxidation - reduction electrode:

It involves an inert metal such as platinum immersed in a solution containing an appropriate oxidized and reduced form of redox system. The metal merely acts as electrical contact. The potential arises due to the tendency of one form to change in to other form.

- Ex: $Pt/Fe^{2+},Fe^{3+,}$ $Pt/Ce^{3+},Ce^{4+,}$ $Pt/Sn^{2+},Sn^{4+}$
- Electrochemical reaction: Sn^{4+} + $2e^-$ ⇌ Sn^{2+}

Nernst equation:

$$E_{Pt/Sn^{2+}/Sn^{2+}} = E^0_{Pt/Sn^{4+}/Sn^{2+}} - \frac{0.0591}{2}\log[\frac{[Sn^{2+}]}{[Sn^{4+}]}]$$

6. Ion selective electrode: (membrane electrode)

This electrode is more selective towards a particular type of ion in the mixture of ions and hence, it is specifically used to measure the concentration of that particular ion. It is an indicator electrode is not due to redox reaction but, it is due to ion exchange between membrane and the solution. Example glass pH electrode is more selective towards H^+ ion and used to find pH of a solution.

The potential of glass electrode is given by Nerns't equation.

- Ex: Glass electrode: selective to H^+, Na^+, K+ etc

$$E_G = E^0_G + \frac{0.0591}{n} \log_{10}[H^+]$$

Reference electrodes: The single electrode potential cannot be directly measured. Hence a standard electrode of known potential is used to measure the single electrode potential. The standard electrode whose potential is known is called reference electrode.

Types of Reference Electrodes:

Reference electrodes are classified into two types

1) Primary reference electrodes

Ex: Standard hydrogen electrode

2) Secondary reference electrodes

Ex: a) calomel electrode b) Ag – AgCl electrode   c) Ion selective electrodes

Limitations of primary reference electrode & the need for developing secondary reference electrodes:
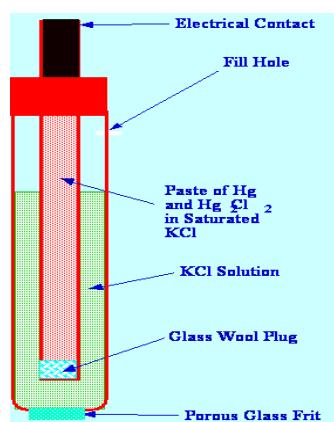
1. Standard hydrogen electrode requires hydrogen generating apparatus
2. It is difficult to maintain the pressure of hydrogen gas exactly at 1 atmospheric pressure throughout the experiment.
3. It is difficult to maintain the concentration of H^+ as unity throughout experiment.
4. This electrode cannot be used in the presence of oxidizing and reducing impurities.

Due to above (difficulties) limitations, it is difficult to set up the hydrogen electrode.   Hence secondary reference electrodes are commonly used in the laboratory because secondary reference electrodes are easy to set up and simple to operate.

Secondary Reference Electrodes:

a. Calomel electrode (Reversible); [Type: metal in contact with its insoluble salt]

Construction:

The calomel electrode consists of electrode vessel provided with a flat tube. Mercury is placed at the bottom of the electrode vessel. A bright platinum wire fused to glass tube is dipped into Hg to give electrical contact.
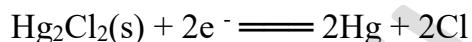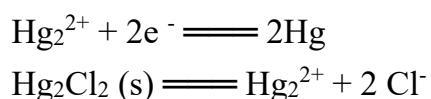
A paste of Mercurous chloride (calomel) is placed above the layer of mercury. Vessel including the side tube is completely filled with 1M KCl/0.1M KCl/ saturated solution of KCl.

The value of standard reduction potential of calomel depends upon the concentration of KCl. The standard reduction potential of calomel electrode is as follows:
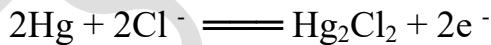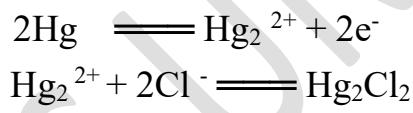
For saturated KCl = + 0.244 v.
For 1M KCl = + 0.280 v
For 0.1 M KCl = + 0.388 v

Electrode notation: The electrode is represented as Hg (l), Hg_2Cl_2 (s) /Cl$^-$

Electrode reactions: Calomel electrode is a reversible electrode. It behaves both as cathode and anode. When behaves as cathode (+ve electrode), the electrode reaction is represented as follows:
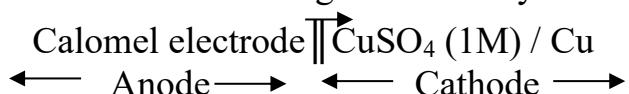
$$Hg_2^{2+} + 2e^- \rightleftharpoons 2Hg$$
$$Hg_2Cl_2 (s) \rightleftharpoons Hg_2^{2+} + 2 Cl^-$$

_____

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg + 2Cl$$

_____

When it behaves as anode (-ve electrode), the electrode reaction is represented as follows:

$$2Hg \rightleftharpoons Hg_2^{2+} + 2e^-$$
$$Hg_2^{2+} + 2Cl^- \rightleftharpoons Hg_2Cl_2$$

_____

$$2Hg + 2Cl^- \rightleftharpoons Hg_2Cl_2 + 2e^-$$

_____

Determination of standard electrode potential using calomel electrode: Copper electrode is constituted and it is coupled into calomel electrode internally by means of salt bridge and externally through potentiometer. The emf of the cell is determined experimentally and at the same time, the direction of flow of current. The voltmeter shows that the current flows from Cu to Zn electrode. Therefore Cu electrode acts as cathode and calomel electrode acts as anode. According to IUPAC system the cell is represented as follows:

Calomel electrode ‖ $CuSO_4$ (1M) / Cu
← Anode → ← Cathode →

$$\text{Emf} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$0.096 = E^{\circ}_{Cu} - E^{\circ}_{cal} \text{ (saturation)}$$

$$E^{\circ}_{Cu} = +0.34 \text{ v}$$

The standard electrode potential of the given electrode can be determined experimentally using hydrogen electrode/calomel.

Note: assigning the sign on the electrode.
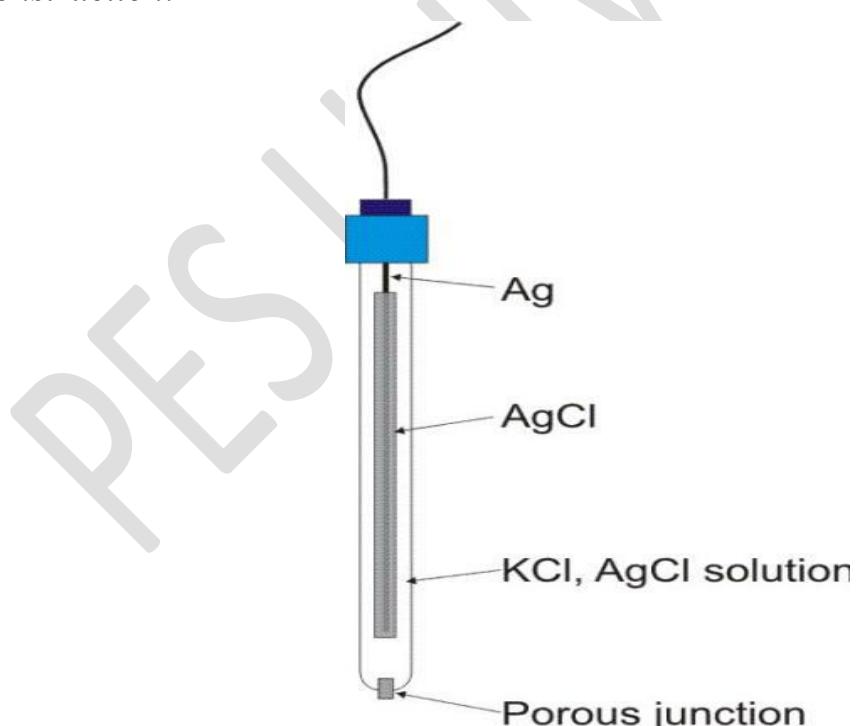
The anode and cathode of the cell can be identified by connecting the electrodes of the cell to a voltmeter. In any galvanic cell current flows from cathode and anode. Hence by observing the direction of deflection in the voltmeter the sign can be assigned to the given electrodes in the cell.

Advantages of calomel electrode:

a) It is very simple to construct and easy to operate.

b) The potential developed remains constant for long time.

c) The electrode potential does not vary with temperature.
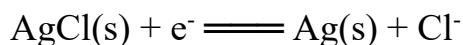
b. Ag – AgCl Electrode.

Construction:
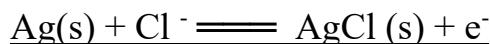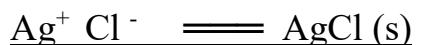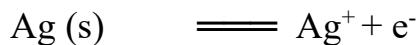
The electrode vessel is fitted with a silver wire coated with a fine deposit of AgCl which is dipped into a solution containing 1M KCl. A crystal of KCl fixed to the Agar bulb is placed at the bottom of the electrode. The reduction potential of Ag- AgCl electrode is found to be + 0.222v.

*Electrode reactions***:** This electrode behaves as reversible electrode. It behaves both as cathode and anode. When it behaves as cathode (+ve electrode) the electrode reaction is given by

$Ag^+ + e^- \Longrightarrow Ag(s)$

$\underline{AgCl\,(s) \Longrightarrow Ag^+ + Cl^-}$

$\underline{AgCl(s) + e^- \Longrightarrow Ag(s) + Cl^-}$

When it behaves as anode (-ve electrode), the electrode reaction is given by

$Ag\,(s) \Longrightarrow Ag^+ + e^-$

$\underline{Ag^+\ Cl^- \Longrightarrow AgCl\,(s)}$

$\underline{Ag(s) + Cl^- \Longrightarrow AgCl\,(s) + e^-}$

Applications:

1. as a secondary reference electrode.

2. in determining whether the potential distribution is uniform or not in ship hulls and old pipe lines protected by cathodic protection.

Ion selective electrodes:

Concept: The principle of concentration cell is used in the construction of Ion selective electrodes. The electrodes which have the ability to develop potential for a certain specific ions without causing interference from other ions present in the mixtures are called **ION SELECTIVE ELECTRODES.** The following membranes are used in ion selective electrodes

i) Glass membrane:

Eg: Glass electrode

The glass electrode is selective only for the measurement of H^+ ion concentration

ii) Solid state membrane:

Eg: a) For F^- ions: Lanthanum trifluoride (LaF_3) crystal mounted on Europium difluoride (EuF_2) is used.

b) For Cl^- ions: Pellet of Ag_2S and AgCl is used.

iii) Liquid membrane:-

Liquid state membrane is usually obtained by adsorbing active organic molecules like monocyclic crown ethane and phosphate di-esters on inert porous polymers.

Working principle of ion selective electrode:

The working principle of ion selective electrode is based on the construction of concentration cells.

Reference electrode / Test solution (c_1) ‖ internal standard (c_2) / identical reference electrode

Emf of the above concentration cell is given by

$$EMF = \frac{0.059}{n} \log_{10} c_2 - \frac{0.059}{n} \log_{10} c_1$$

$$E_{cell} = constant - \frac{0.059}{n} \log_{10} c_1$$

By measuring the emf of above concentration cell, the concentration of the ion selective ions can be calculated.

Applications:

a. Ion selective electrode like glass electrode is used in the determination of pH of solution.

b. Ion selective electrodes are used in the determinations of concentration cation Na^+, K^+, Cd^{2+}, Ca^{2+}, Pb^+, Hg^{2+}, Al^{3+} etc., is industrial effluents, pharmaceutical, polluted water etc.,

c. Ion selective electrode are used in the determination of concentration of anions F^-, Cl^-, NO_3^-, CN^-, S^{2-} etc.,

d. Ion selective electrode also used in the determination of concentration of gases using gas sensing electrodes.
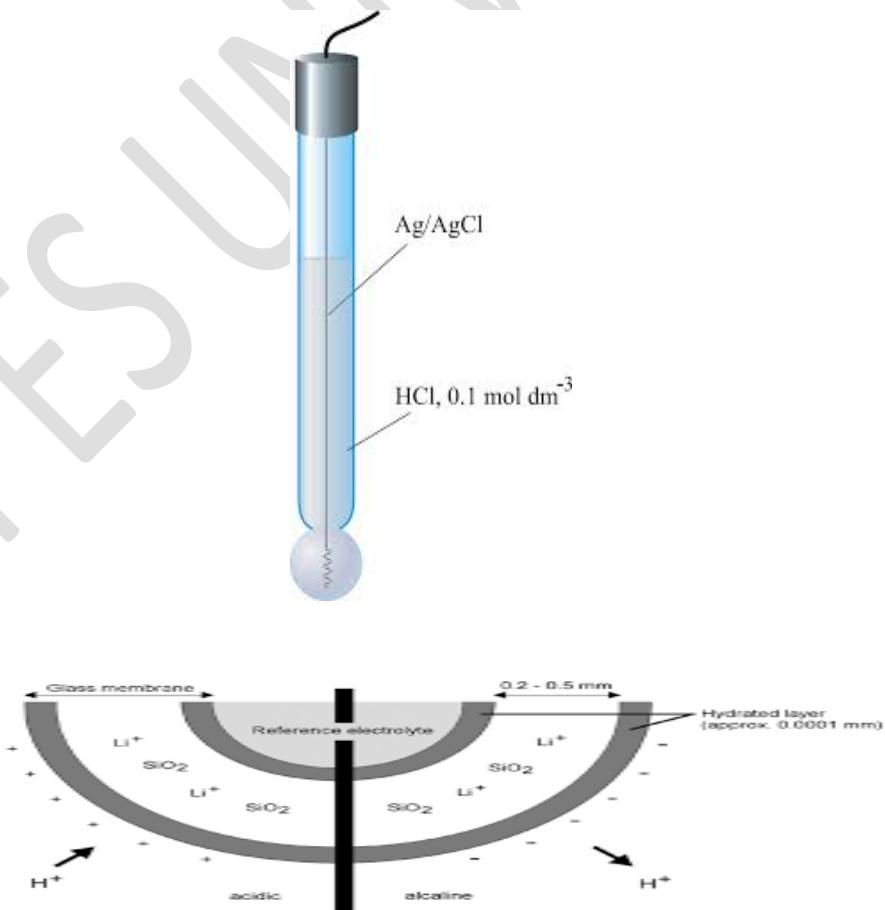
Example: Glass electrode

Concept: Whenever a thin glass membrane is in contact with two solutions of different H+ ion concentration, a potential arises across the membrane (glass), the potential developed depends upon the H^+ ion concentration of the test solution. The potential of glass electrode is given by Nerns't equation.

$$E_G = E°_G + \frac{0.059}{n} \log_{10}[H^+]$$
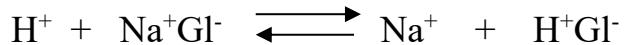
Where $E°_G$ is standard electrode potential of glass electrode and it is constant for the given electrode. Its value is + 0.456 v at 25° C.

Construction: A glass electrode consists of a long glass tube with a thin walled bulb at one end. Special glass containing 22% Na_2O, 6% CaO & 72% SiO_2 of low melting point and high electrical conductance is used for the purpose. This glass can specially sense hydrogen ions. The bulb containing 0.1M HCl and an Ag-AgCl electrode is immersed into a solution. The platinum wire is provided for external contact. The electrode is represented as Ag/AgCl/0.1MHCl/glass.

The hydrated glass membrane brings about ion exchange reaction between singly charged cations in the interstices of glass lattice and protons from the solution.

Electrode reactions: The electrode reaction is as follows:

$$H^+ + Na^+Gl^- \rightleftharpoons Na^+ + H^+Gl^-$$

Determination of membrane potential:

- It may be represented as

Analyte solution $\|$ Reference solution (0.1M HCl)/AgCl/Ag

Membrane

➢ The boundary potential arises due to the exchange of ions by the inner and outer boundaries of glass membrane.

➢ If E_1 and E_2 are potentials associated with inner and outer boundaries, then

$E_b = E_1 - E_2$

$$E_b = \frac{2.303RT}{nF} \log\left(\frac{C_1}{C_2}\right)$$

➢ C_2 = concentration of H^+ ions inside glass bulb which is constant

➢ At 298K, $E_b = K + 0.0591 \log C_1$,   For H^+, $n = 1$

➢ The overall potential of glass electrode E_G has 3 components,

1. The boundary potential
2. The potential of internal reference electrode
3. A small asymmetric potential

$E_G = E_b + E_{ref} + E_{asymmetric}$

➢ Asymmetric potential arises due to difference in responses of inner and outer surfaces of the glass bulb, due to differing conditions of stress on two glass surfaces.

➢ It varies with time and hence glass electrode has to be standardized by placing in a solution of known pH before use.

$E_G = E_b + E_{ref} + E_{asymmetric}$

$\quad = E^0_G + 0.0591 \log C_1$ Where $E^0_G = K + E_{ref} + E_{asymmtric}$

$E_G = E^0_G - 0.0591 pH$

➢ This equation is used in the determination of pH
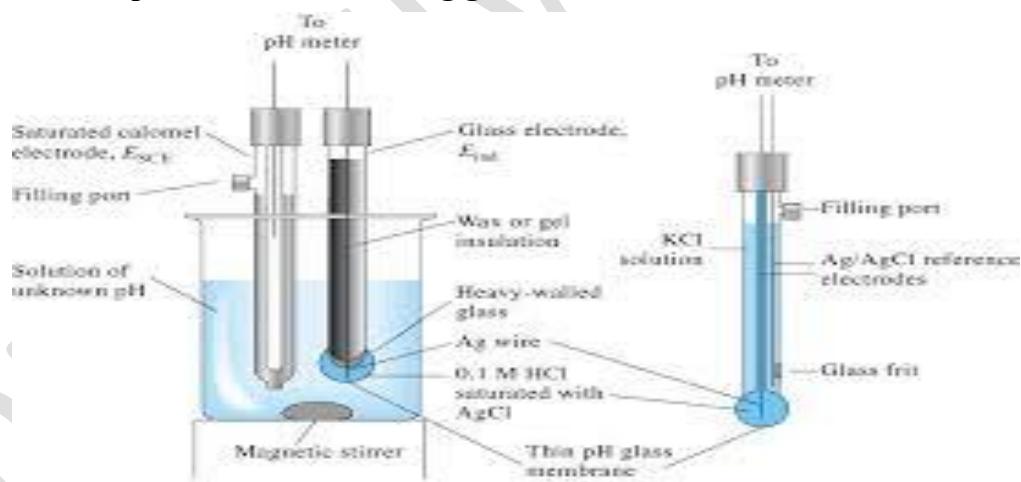
Advantages of glass electrode:
a) It is very easy to construct and simple to operate.
b) The potential developed remains constant for long time.
c) This electrode can be used with very small amount of the test solution.
d) This electrode can be used even in the presence of oxidized impurities, reducing impurities, poison molecules etc.,
e) The wide pH range from 0 to 14 can be measured using glass electrode.

Disadvantages:
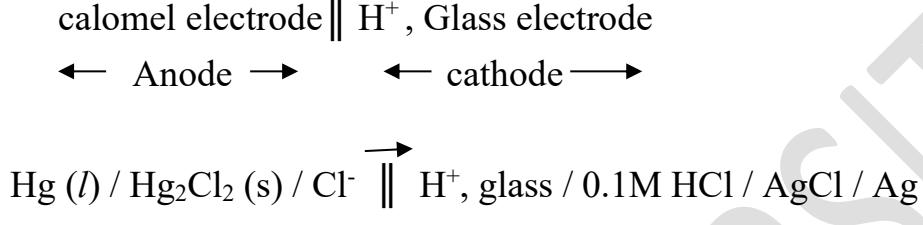
➢ Because of high resistance of glass, a simple potentiometer cannot be used. It requires sensitive potentiometer for emf measurements.

➢ Alkaline error: It is a phenomenon that occurs at very high pH levels usually pH 9 or over. This is observed when the Sodium ion level is relatively so high that some of the H^+ ions in the gel layer around the sensitive electrode membrane are replaced by Na^+ ions. The electrode may eventually respond to Sodium ions instead of H^+ ions, giving a falsely lower pH value than the real result.

Determination of pH of the solution using glass electrode:

The glass electrode consists of a glass tube having a thin walled bulb at the bottom which contains 0.1M HC*l*. A platinum wire is dipped into the acid solution to give electrical contact. This bulb is dipped into the test solution whose pH is to be determined.

The resulting glass electrode is combined with the calomel electrode internally through a salt bridge and externally through a potentiometer. The emf of the cell is determined experimentally and at the same time the direction of flow of current is noted. It was found that current flows from glass electrode into calomel electrode so that calomel electrode acts as anode and glass electrode acts as cathode. The cell is represented as follows.

calomel electrode $\|$ H^+, Glass electrode
← Anode → ← cathode →

Hg (l) / Hg_2Cl_2 (s) / Cl^- $\|$ H^+, glass / 0.1M HCl / AgCl / Ag
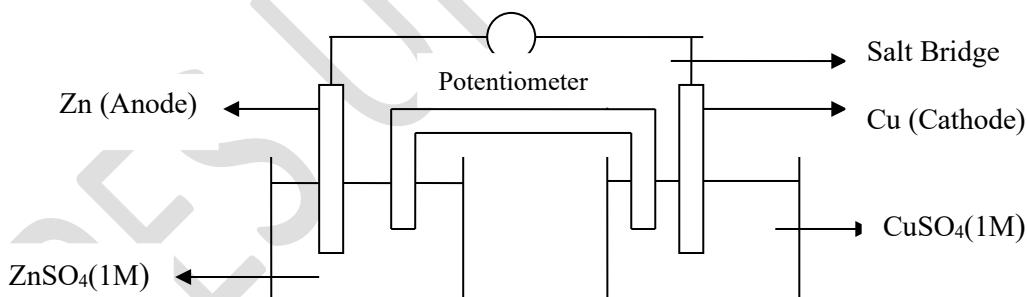
Emf of the cell is given by Emf = E_{Glass} − $E_{Calomel}$

$$E_{cell} = E_{Glass} - E_{Calomel}$$
$$= E^0_G + 0.0591 \log[H] - E_{Calomel}$$
$$= E^0_G - 0.0591 \, pH - E_{Calomel}$$
$$pH = \frac{E^0_G - E_{Calomel} - E_{cell}}{0.0591}$$
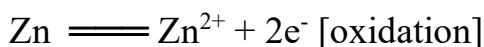
Formation of a cell: **Example:** Construction of Galvanic cell

Galvanic cell is a device used to produce electrical energy from chemical energy and it can be constructed as follows:

When Zn rod is dipped into $ZnSO_4$, Zn being more active undergoes oxidation.

Zn dissolves forming Zn^{++} ions and a negative layer of electrons remains on the metal rod.

$Zn \rightleftharpoons Zn^{2+} + 2e^-$ [oxidation]

Zn^{2+} ions present in the solution are attracted by a negative layer of electrons. Due to this electrical double layer, a potential is developed. The potential thus developed is called electrode potential/single electrode potential. Zn rod undergoes oxidation. Hence it acts as anode. Due to the negative layer of electrons on the Zinc rod, it develops a negative potential.

Cu rod is dipped into $CuSO_4$ solution. Copper is less active metal. Cu^{2+} ions present in the solution accept an electron from the metal rod and Cu is deposited on the metal rod. Hence copper rod becomes positively charged, and attracts the negatively charged SO_4^{2-} ions from the solution. Thus an electrical double layer is created and a potential at the interface of Cu rod and $CuSO_4$ solution.

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ [reduction]

Copper undergoes reduction and acts as cathode and develops a positive potential. When these two electrodes are connected internally by means of a salt bridge containing KCl solution and externally by copper wire through voltmeter, the resulting arrangement is known Galvanic cell. The cell is represented is as follows.

$$Zn / ZnSO_4 \ (1 \ M) \ \| \ CuSO_4 \ (1M) / Cu$$
$$\text{Anode} \qquad\qquad \text{cathode}$$

The net cell reaction of the galvanic cell is represented as follows:

$Zn \rightleftharpoons Zn^{2+} + 2e^-$: oxidation half cell

$Cu^{2+} + 2e^- \rightleftharpoons Cu$: reduction half cell

$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu$: net cell reaction
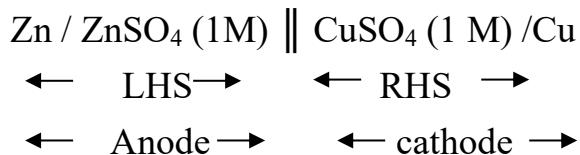
In the above cell, the current flows in the outer circuit from Cu electrode (cathode) to Zn electrode (anode). Hence the EMF of the cell is defined as the potential difference between cathode and anode.

$EMF = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{right}} - E_{\text{left}}.$

Notations & Conventions :(IUPAC rules to represent a galvanic cell):

A galvanic cell is a combination of two half cells called oxidation half-cell and reduction half-cell. The following convention is used to represent the galvanic cell.

$$Zn / ZnSO_4 \text{ (1M) } \| \text{ } CuSO_4 \text{ (1 M) } /Cu$$

$$\leftarrow \quad LHS \rightarrow \quad \leftarrow RHS \rightarrow$$
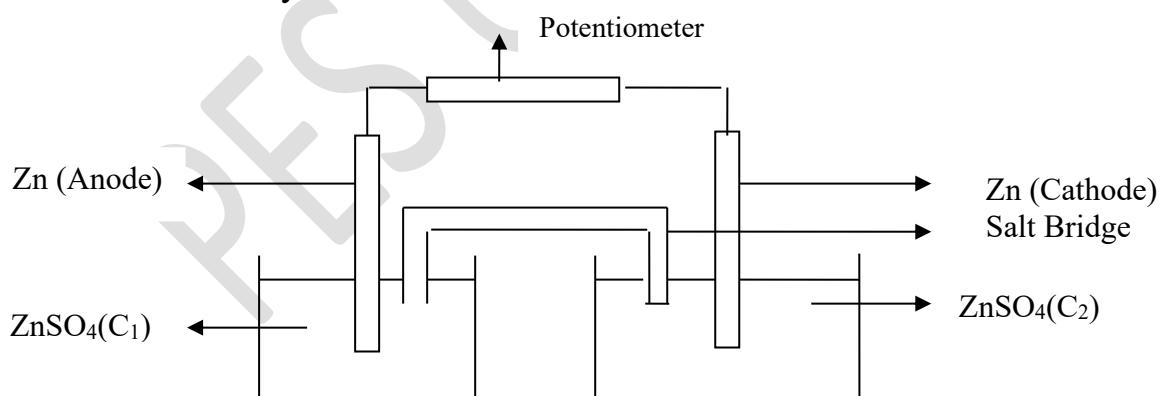
$$\leftarrow \quad Anode \rightarrow \quad \leftarrow cathode \rightarrow$$

a) The half-cell at which oxidation occurs. i.e. anode is always written on the LHS and half-cell at which reduction occurs i.e., cathode is always written on the RHS.

b) The salt bridge is indicated by writing two vertical lines between two half cells.

c) The arrow on the salt bridge indicates the direction of flow of electrons in the external circuit.

d) The term electrode potential is always referred as reduction potential.
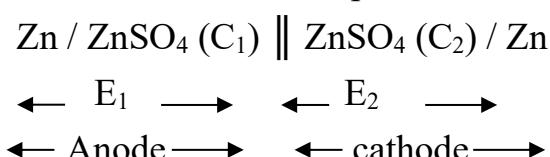
Classification of galvanic cells:

1. **Primary cells -** Electrode reactions are irreversible
2. **Secondary cells -** Electrode reactions are reversible
3. **Concentration cells -** Same electrodes but of different electrolyte concentrations.
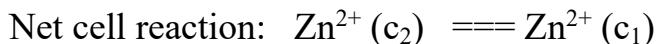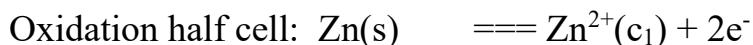
Concentration cell formed by the combination of same electrode dipped into same electrolyte of different concentration.
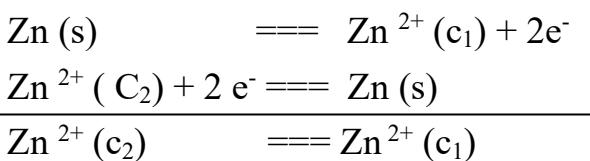
The concentration cell is represented as follows:

$$Zn / ZnSO_4 \text{ } (C_1) \| \text{ } ZnSO_4 \text{ } (C_2) / Zn$$

$$\leftarrow \quad E_1 \quad \longrightarrow \quad \leftarrow \quad E_2 \quad \longrightarrow$$

$$\leftarrow \quad Anode \rightarrow \quad \leftarrow cathode \longrightarrow$$

Suppose $c_2 > c_1$, cell reaction, is represented as

Oxidation half cell: $Zn(s) \quad === Zn^{2+}(c_1) + 2e^-$

Reduction half cell $\underline{Zn^{2+}(c_2) \quad === Zn(s)}$

Net cell reaction: $Zn^{2+}(c_2) \quad === Zn^{2+}(c_1)$

The above reaction, shows that there is no net chemical reaction but involves only transparence of Zn^{2+} ions from solution of higher concentration c_2 to solution of lower concentration c_1.

$$Zn (s) \quad === \quad Zn^{2+}(c_1) + 2e^-$$
$$\underline{Zn^{2+}(C_2) + 2e^- === Zn(s)}$$
$$\underline{Zn^{2+}(c_2) \quad === Zn^{2+}(c_1)}$$

Consider the above cell; the electrode potential is given by Nerns't equation

$$Zn / ZnSO_4 \parallel ZnSO_4 (C_2) / Zn$$

$$\leftarrow \quad E_1 \longrightarrow \quad \leftarrow \quad E_2 \longrightarrow$$

$$E_1 = E^o + \frac{0.059}{n} \log_{10} c_1$$

$$E_2 = E^o + \frac{0.059}{n} \log_{10} c_2$$

$$E_2 - E_1 = \frac{0.059}{n} \log_{10} \left(\frac{c_2}{c_1} \right)$$

$$EMF = 0.059 \log_{10} \left(\frac{c}{} \right)$$

From this expression, the EMF of the concentration cell can be calculated.

Applications:

a) concentration cells are used in the determination of valency of complex ions

b) concentration cells are used in the determination of solubility of sparingly soluble salt like $AgCl$, $PbSO_4$, $BaSO_4$ etc.,

CORROSION

Corrosion is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means.

Example: When iron metal is exposed to the moist environment, the metal forms a hydrated Ferric oxide called rust which is a reddish or yellowish-brown flaky coating of iron oxide.

(ii) When copper vessel is exposed to air in rainy season, the metal reacts with gases and moisture and atmospheric gases (oxygen & carbon dioxide) to form a mixture of copper carbonate and copper hydroxide. This gives a green color to the surface of copper metal.

During corrosion reaction a metal transfers electrons to the environment and undergoes valence change from zero to positive values resulting in the formation of thermodynamically more stable compounds by reacting with the corrosive environment.

There is no single figure for loss to the nation due to corrosion. It can be a minimum of 3.5% of the nation's GDP. Losses due to corrosion could be around Rs. 2.0 lakh crores per annum in India. Corrosion costs manifest in the form of premature deterioration or failure necessitating maintenance, repairs and replacement of damaged parts. Other than material loss, corrosion interferes with human safety, disrupts industrial operations and poses danger to environment. Awareness to corrosion and adaptation of timely and appropriate control measures hold the key in the abatement of corrosion failures.

Corrosion can be classified in different ways, such as

- Chemical and electrochemical
- High temperature and low temperature
- Wet corrosion and dry corrosion.

However, the two most important types are -

Based on the mechanism of corrosion
1) Chemical corrosion: By the direct chemical attack of the corrosion medium on the metal. Example: alkali and alkaline earth metal react vigorously with oxygen to form oxides at low temperature.
2) Electrochemical corrosion: By the electrochemical reaction of the metal in the corrosion medium. Example: Rusting of iron in ambient atmosphere.

**Based on the presence/absence of moisture (electrolyte)**
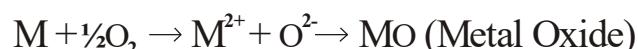
Dry Corrosion- This type of corrosion occurs through direct chemical action of dry gases (or) corrodents such as oxygen, halogen, H_2S, SO_2, etc. Since this is observed in the absence of moisture or conducting electrolyte, it is called dry corrosion.

This can be further classified as follows

Corrosion by oxygen (Oxidation corrosion)

Oxygen present in the atmosphere attacks metal surface resulting in the formation of metal oxide which is known as corrosion product and this process is known as oxidation corrosion.
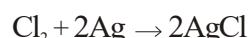
Metal ions combine with oxygen ions forms the metal oxide film

$$M + ½O_2 \rightarrow M^{2+} + O^{2-} \rightarrow MO \text{ (Metal Oxide)}$$

Corrosion by other gases

Other gases present in the atmosphere like SO2, CO2, Cl2, H2S etc. can also attack the metals. Example: Chlorine attacks on silver forms protective layer it protects silver from undergoing further corrosion as it act as a protective barrier.
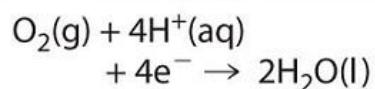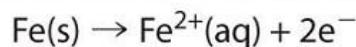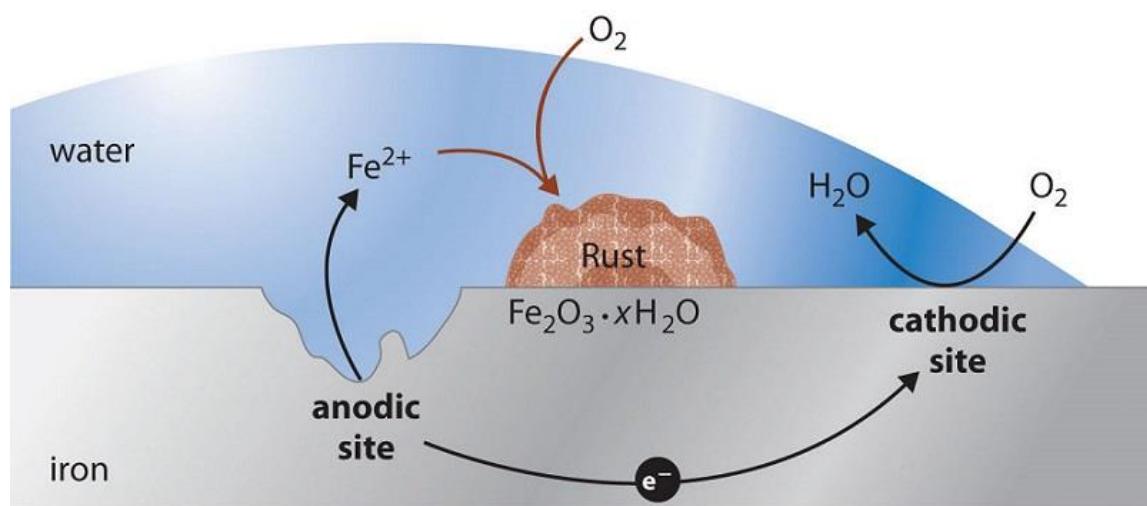
$$Cl_2 + 2Ag \rightarrow 2AgCl$$

Wet Corrosion - If the corrosion of the metal takes place through the ionic reactions in the presence of moisture or electrolytes it is called wet corrosion. Example: rusting of iron in ambient atmosphere.

$$Fe + ½O_2 + H_2O \rightarrow Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \text{ (corrosion product)}$$
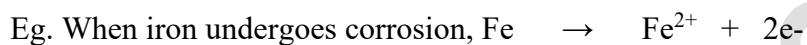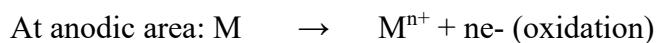
Theory of electrochemical corrosion: (Theory of rusting of iron)

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$$

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$$

According to this theory corrosion of the metal takes place through the formation of tiny anodic or cathodic regions within the same metal surface in the presence of conducting medium. The oxidation and reduction steps occur at separate locations on the same metal. This is possible because metals are conducting, so the electrons can flow through the metal from the anodic to the cathodic regions. The presence of water is necessary in order to transport ions to and from the metal, but a thin film of adsorbed moisture can be sufficient.

Corrosion reactions:
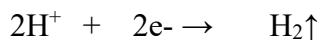
Anodic reaction (i.e. at the anodic area) involves the dissolution of metal as corresponding metallic ions with the liberation of free electrons.

At anodic area: $M \rightarrow M^{n+} + ne-$ (oxidation)

Eg. When iron undergoes corrosion, $Fe \rightarrow Fe^{2+} + 2e-$
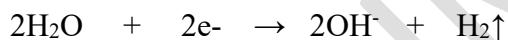
Cathodic reaction: Consumes electrons either by evolution of hydrogen or absorption of oxygen depending on the nature of corrosive environment.

(i) Evolution of hydrogen takes place in the absence of oxygen.

(a) In acidic medium and in the absence of oxygen, the cathodic reaction is,

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

(b) In neutral or alkaline medium and in the absence of oxygen, hydroxide ions are formed with simultaneous liberation of hydrogen

$2H_2O + 2e- \rightarrow 2OH^- + H_2\uparrow$

(ii) Absorption of oxygen takes place in the presence of oxygen

a) In acidic medium and in the presence of oxygen

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

(b) In neutral or alkaline medium and in the presence of oxygen, hydroxide ions are formed by the following reaction.

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

Corrosion of iron produces Fe^{2+} ions and OH^- ions at the anode and cathode sites respectively. These ions diffuse towards each other. Since smaller Fe^{2+} ions diffuse more rapidly than OH^- ions, their combination occurs more commonly near the cathodic region to produce insoluble $Fe(OH)_2$.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

In an oxidizing environment, it is oxidized to ferric oxide and the yellow rust is hydrated ferric oxide.

$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow Fe_2O_3.3H_2O.$

In the presence of limited oxygen, ferrous hydroxide is converted into magnetic oxide of iron (Fe_3O_4) and is known as black rust.

$3Fe(OH)_2 + \frac{1}{2}O2 \rightarrow Fe_3O_4.3H_2O.$
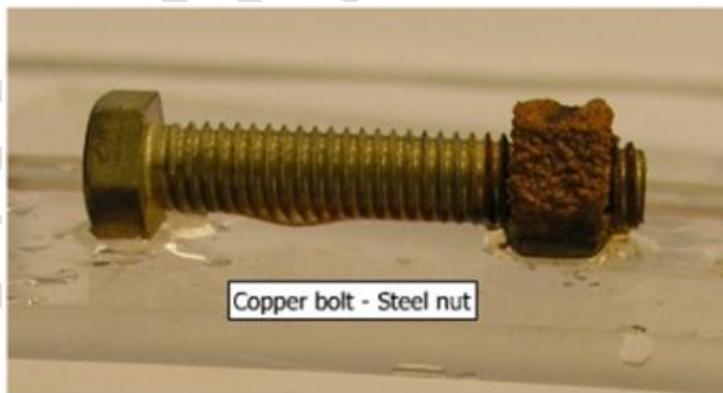
Types of corrosion:

1. Galvanic corrosion (differential metal corrosion):
- This occurs when two dissimilar metals are in contact with each other in corrosive medium.
- The potential difference between the two electrodes is the driving force for corrosion.
- The more active metal i.e. metal with lower electrode potential (higher in electrochemical series) acts as anode hence undergoes corrosion. (e.g. metals like Zn, Mg)
- The less active metal i.e. metal with higher electrode potential (lower in electrochemical series) acts as cathode.
- The anodic metal undergoes corrosion and the cathodic metal generally unattacked. EXAMPLES
- Steel pipe connected to copper plumbing,
- Copper containing precipitates in aluminium alloys.
- Impurities such as iron and copper in metallic zinc.

Copper bolt - Steel nut

In the above fig it is seen that that anodic nut made of steel has undergone corrosion whereas the Cu bolt stays unaffected.
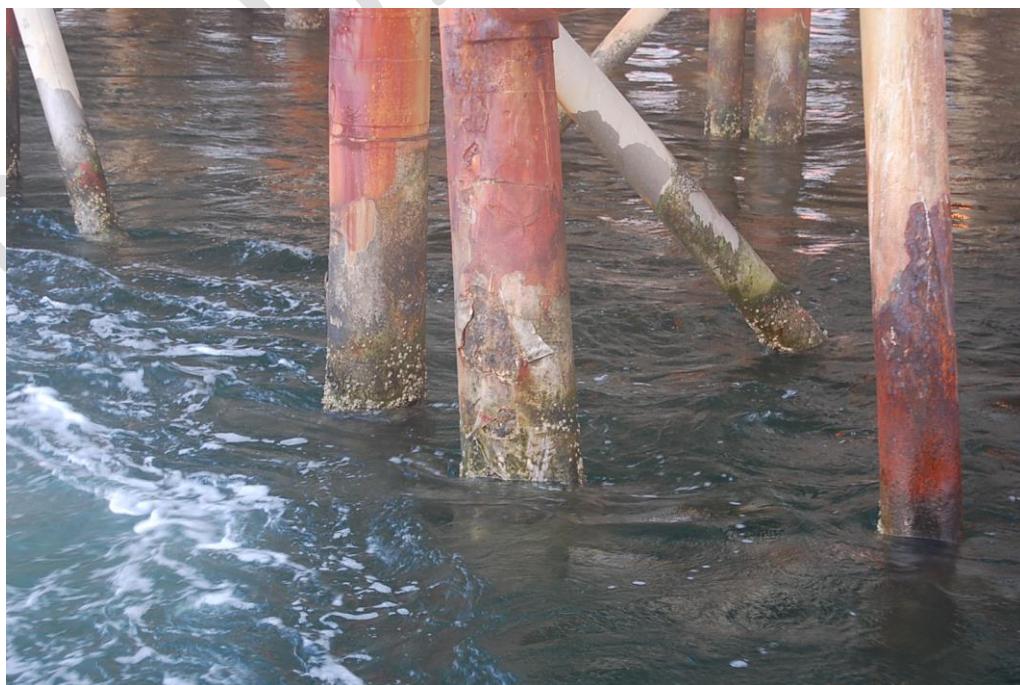
2. Differential aeration corrosion: (concentration cell corrosion):
- This type of corrosion occurs when metal is exposed to different concentrations of air or oxygen.
- This constitutes oxygen concentration cell due to which corrosion occurs.
- Portion of the metal which is less oxygenated acts as anode hence undergoes corrosion.

- More oxygenated part acts as cathode hence it is unattacked. Ex: In partially buried pipeline, the area below the soil is less oxygenated acts as anode hence undergoes corrosion whereas exposed region is more oxygenated is free from corrosion as it acts as cathode.

- At the anode (less O2 concentration), $M \rightarrow M^{n+} + ne$

  At the cathode (more O2 concentration), $H_2O + \frac{1}{2} O_2 + 2e- \rightarrow 2OH-$

- Net reaction – $M + H_2O + \frac{1}{2} O_2 \rightarrow M(OH)_2$

- The examples of differential aeration corrosion include: half immersed iron plate in aqueous solution, steel pipe carrying any liquid exposed to atmosphere, steel storage tanks   etc.

Waterline corrosion:
- It is a case of differential aeration corrosion.
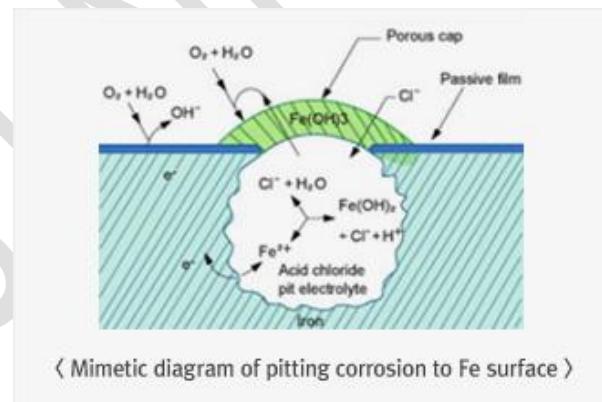
- Ocean going ships and water storage steel tanks undergo this type of corrosion.

- The metal portion which is just below the waterline (less oxygenated) is more anodic to portion above the waterline (more oxygenated).

- Therefore area below Water is corroded and area above water is protected.

- Hence a distinct brown line is formed below the water line due to corrosion.

It is interesting that ships sunk under water for several years do not undergo corrosion . The sunk ship is exposed to almost uniform concentration of air and thus does not undergo differential aeration corrosion.

3. Pitting corrosion:
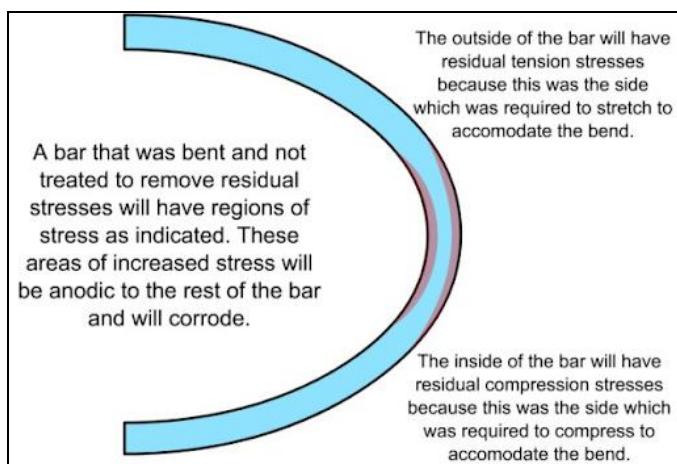
- It is form of extremely localized attack, the corrosion is initiated when a small portion of the metallic surface is occupied by dust/scale/sand/water etc. or when there is a breakage in the protective layer on the metal surface.

- The area of the metal below the deposit is exposed to less oxygen concentration hence acts as anode whereas the uncovered region acts as cathode. So the area below the deposit undergoes corrosion leading to small pinholes.

- It is one of the most destructive and menacing forms of corrosion. It causes the equipment to fail due to perforation with a small percent weight loss of the entire structure. Pits generally grow in the direction of gravity.

- At the anode (less O2 concentration), $M \rightarrow M^{n+} + ne^-$

  At the cathode (more O2 concentration), $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$

- Net reaction – $M + H_2O + \frac{1}{2} O_2 \rightarrow M(OH)_2$

⟨ Mimetic diagram of pitting corrosion to Fe surface ⟩

Because of small anodic and large cathodic area corrosion occurs at a brisk rate.

4. Stress corrosion cracking:

- It is a cracking of a metal due to combined effect of i) stressed metallic areas ii) corrosive environment.

- It is also highly localized and destructive form of corrosion.

A bar that was bent and not treated to remove residual stresses will have regions of stress as indicated. These areas of increased stress will be anodic to the rest of the bar and will corrode.

The outside of the bar will have residual tension stresses because this was the side which was required to stretch to accomodate the bend.

The inside of the bar will have residual compression stresses because this was the side which was required to compress to accomodate the bend.

- During manufacture of the metallic articles, they are subjected to processes like, bending pressing rolling, quenching etc. which leaves stress on the certain areas of metal.

- The stressed regions of the metal have higher energy, is more reactive and therefore acts as anode and the stress-free part acts as cathode

- In the presence of continuously acting stress and corrosion medium, the crack propagates through the metal.
  e.g. Season cracking of brass, Hydrogen embrittlement, Caustic embrittlement of steel boilers

**Caustic embrittlement**
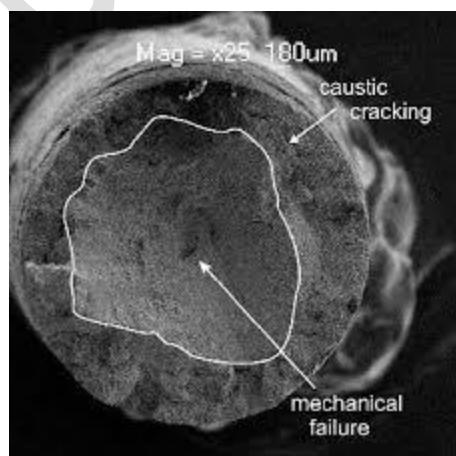
fig – link.springer.com

- It is a form of stress corrosion that occurs in boilers at high pressure leading to the failure of the boiler.

- This is initiated at stressed parts like, crevices, cracks, joints, bends etc.

- In case of high-pressure boilers, excess of sodium carbonate is added during the process of removal of hardness of water. As a result, the boiler feed water is slightly alkaline, which at high pressure decomposes to give sodium hydroxide.
  Na_2CO_3 + H_2O → $2NaOH$ + CO_2

- This sodium hydroxide enters into crevices under the rivet on the boiler walls. Water evaporates and concentration of sodium hydroxide increases.

- Thus, a galvanic cell is set up between the iron under stress and the iron in the main body. The cell can be represented as follows

- Iron (under stress) |Conc NaOH(cracks)|Dil NaOH (in boiling water) |Iron (main Body)

- The concentrated sodium hydroxide dissolves iron forming sodium ferrate (Na_2FeO_2). which decomposes forming magnetite as follows.
  $3Na_2FeO_2$ + $4H_2O$ → Fe_3O_4 + $6NaOH$ + H_2

- Thus sodium hydroxide is regenerated, which continues to corrode further. The continuous corrosion leads to deposition of magnetite on the wall, which makes it brittle.

- The continuous embrittlement of boiler parts results in failure of the boiler or boiler explosion.

- Caustic embrittlement can be prevented by the addition of compounds like sodium sulphite, tannin, lignin, phosphates etc. which blocks the crevices and cracks thereby preventing the infiltration of alkali.

Factors affecting rate of corrosion:
Nature of the metals:

- Metals with higher electrode potentials do not corrode easily. They are noble metals like, gold, platinum. Whereas metals with lower electrode potentials, readily undergo corrosion. E.g. metals like, zinc, magnesium, aluminium.

- When two metals are in contact with each other, higher the difference in electrode potentials greater is the corrosion.

- For e.g. the potential difference between iron and copper is 0.78V which is more than that between iron and tin (0.3V).

- Therefore, iron corrodes faster when in contact with copper than that with tin.

- On this account, the use of dissimilar metals should be avoided wherever possible.
- For example, bolt and nut or screw and washer should be made of the same metal (or alloy) to avoid galvanic corrosion.

Galvanic series

- One generally tends to assume that the standard electrode potential values are indicative of a metal's reactivity and hence of its tendency to undergo corrosion.
- But this is not always true. Although standard electrode potential of aluminium is lower than that of iron, aluminium resistant to corrosion than iron. This is due to formation of a passivating layer of aluminium oxide on aluminium.
- Therefore another series called **galvanic series** is introduced.
- The corroding tendency of various metals and alloys is studied in various environments. These metals and alloys are arranged in the order of their corroding tendency and such a series is called galvanic series.
- Such a list is useful for predicting galvanic corrosion situations. Galvanic series relationships are useful as a guide for selecting metals to be joined. In general, the further apart the materials are in the galvanic series, the higher the risk of galvanic corrosion, which should be prevented by design.
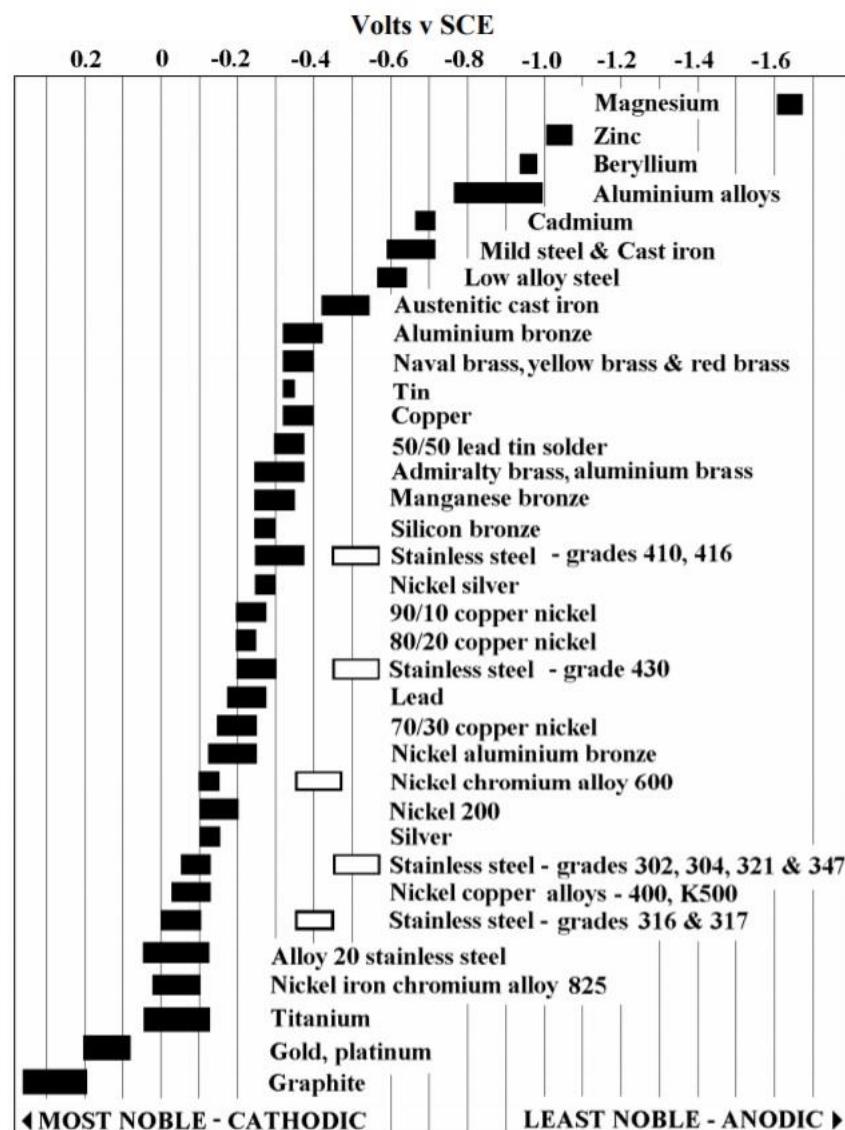
Fig – corrosionpedia.com

Ratio of cathodic to anodic region:

- The rate of corrosion is influenced by relative size of cathodic to anodic area.

- If the metal has small anode and large cathodic region, corrosion rate is very high. As the ratio decreases corrosion rate further increases. This is because at anode electrons are liberated which are consumed at cathodic region.

- When two dissimilar metals are in contact, Corrosion is more rapid and severe, if the anodic area is small and cathodic area is large (e.g., a small steel pipe fitted in a large copper tank).

- If during plating of tin on iron, some areas are not covered or some pin holes are left, there results a small anode and large cathode. An intense localized corrosion occurs at the exposed small anodic surface.

- On the other hand, zinc plating on iron gives an anodic coating to iron since zinc is above Fe in the electrochemical series. Even if zinc plating peels off at some points intense corrosion of iron would not occur. This is because of formation of large anodic and small cathodic areas.

Nature of the corrosion product:

- The corrosion product formed like metal oxide may act as protective film, if it is stable, insoluble, and non porous.
- If it acts as protective film it prevents further corrosion by acting as barrier between metal surface and corrosion medium.
- E.g. In oxidizing environments, metals like aluminium, chromium, titanium, etc., are highly passive as their oxides (corrosion products) form protective films on the metal surface, preventing further corrosion.
- On the other hand if corrosion product is unstable, porous, and soluble, it further enhances corrosion.
- Metals such as iron, zinc, magnesium etc., do not form any protective film and are highly susceptible for continuous corrosion, when exposed to oxidizing environments.

pH of the medium:

- In general rate of corrosion is higher in acidic pH than in neutral and alkaline pH.
- In acidic medium intense corrosion takes place with evolution of hydrogen.
- The corrosion product formed also gets dissolved in acidic media thereby exposing the underlying layers of metal to the corrosive media and accelerating corrosion reactions.
- Some exceptions are amphoteric metals like Zn & Al which undergo greater corrosion in alkaline medium as the metal hydroxide layer gets dissolved in alkaline medium at a pH above 12.

Temperature:

- Rate of corrosion increases with increase in temperature.
- This is due to the increase in conductance of the medium with increase in temperature and hence an increase in the diffusion rate. As a consequence, corrosion progresses faster at higher temperatures.

- With an increase in temperature polarisation effects of the system also decreases thereby increasing corrosion.

- In some cases, rise in temperature causes the passive protective layer to break thereby preventing corrosion.

Hydrogen over voltage:

- This factor comes into play when the cathodic reaction involves elimination of hydrogen. On the surface of some metals evolution of hydrogen is easier compared to others

- Since, at lower hydrogen over voltage, liberation of hydrogen gas is easy. Therefore cathodic reaction is very fast, which in turn makes anodic reaction very fast.

- Thus results in increased rate of corrosion. Higher the hydrogen over voltage lesser is the corrosion.

- Hydrogen evolution is a multistep process with the rate determining step being desorption of hydrogen from the surface of the metal. Thus different metals have different rates of evolution of hydrogen. Pt has the least hydrogen overvoltage of all metals

Polarization at anodic and cathodic region:

During corrosion polarization at anode and cathode decreases the corrosion rate substantially.

Anodic polarization:

Tendency of anodic metal surface to undergo corrosion decreases due to Anodic polarization. Polarization of anode may be due to,

- **Concentration polarization:** due to increase in concentration of metal ions in the vicinity of the electrode due to slow migration of the ions

- **Anodic passivity**: due to formation of passive film.

Anodic polarization reduces the rate of anodic reaction and hence the rate of corrosion rate. The presence of depolarizers reduces the polarization effect. Anodic depolarizers reduce polarization at anode and hence increase the rate of corrosion.

Ex: presence of complexing agent can chelate the metal ions completely and reduce anodic polarization.

Cathodic polarization retards the rate of cathodic reaction.

Polarization of cathode may be due to,

- Hindered combination of cathode reactant with the electron at cathode.

- Retarded movement of cathodic reactant to the cathode surface.

- Retarded removal of cathodic reaction product from the surface of cathode.

  Cathodic depolariser: These reduce polarisation at cathode and hence increase the rate of corrosion.

  - Ex: Presence of oxidising agents absorbs electrons from cathodic surface, oxygen itself acts as cathodic depolariser.
  - Ex: presence of ferric and cupric ions in mine water stimulates corrosion of water drainage equipment

Conductance of the medium-

- As the conductance of the medium increases diffusions of ions become faster and hence corrosion increases. e.g. Sea water is more corrosive than normal water. Mineralized soil is more conducting than sandy soil and therefore more corrosive

Corrosion control:

There are various ways by which corrosion can be controlled. They are,

i) Metallic coatings:

In this method protective metal is coated on the surface of the metal which can be done by electroplating, flame spray, hot dipping etc. They can be anodic coating or cathodic coatings.

a) Anodic coating:

In this base metal is coated with more active or metal with lower electrode potential which are anodic to the base metal. The coated metal undergoes corrosion, where as the base metal is protected. Thus anodic coating protects the underlying base metal sacrifically. The one of the important characteristics of anodic coating is that, even if the coating is ruptured, the base metal does not undergo corrosion. The exposed surface of the metal is cathodic with respect to the coating metal and the coating metal preferentially undergoes corrosion. The protection is ensured as long as the anodic coating metal is still present on the surface. Therefore, anodic coating is also known as sacrificial coating. Galvanization is a familiar example for anodic coating and is extensively used to protect iron and steel objects.

Galvanization:

The process of coating base metal like steel, copper etc. with zinc is called galvanization. It consists of following steps:
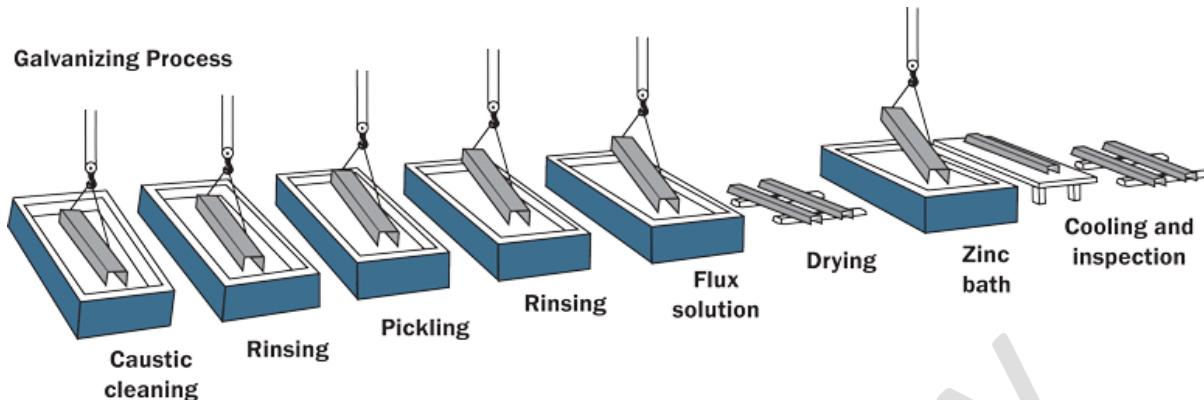
Fig – galvanizeit.org

1. Firstly, the fabrication to be galvanized is immersed in a hot caustic solution to remove any organic materials on the surface. This is followed by a rinsing in water.

2. Then dipped in dilute sulphuric acid to remove any rust and scale followed by a rinsing in water.

3. Then dipped in solution of zinc chloride and ammonium chloride which acts as a flux to have firm coating and prevent oxidation of molten zinc.

4. Then dipped in molten zinc at 430 ºC

5. Excess of zinc is removed by rolling over rollers.

Uses: It is most widely used for protection of iron from atmospheric corrosion in the form of roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes etc. It may be pointed here that zinc gets dissolved in dilute acids, to form highly toxic (or poisonous) compounds. Hence, galvanized utensils cannot be used for preparation and storing foodstuffs, especially acidic ones.

ii)   Inorganic   coating   (chemical   conversion   coating)

In this protective coating, the surface metal atoms are converted to inorganic metallic compound by suitable chemical reaction, which prevents the metal from corrosion by acting as barrier between the underlying metal surface and corrosive environment. Such coatings are particularly used as an excellent base for paints, lacquers oils and enamels.
.
1) Anodized oxide coatings: (ANODOSATION)
- Anodizing is a process for producing decorative and protective films on articles made of Aluminum and its alloys and metals like Ti, Co etc.
- In this type metals like Al, Ti, Co etc are made to develop protective metal oxide coating artificially on their surfaces.
- It is carried out by making base metal anode and inert metal like lead is made cathode.

- The electrolytic bath containing sulphuric acid, phosphoric acid, chromic acid, or boric acid is taken, temp is about 35^0C
- Anodic current density is 10-20mA/cm^2
- On passing current the oxide film is formed on the base metal. The thickness of the oxide layer is about 2-8 μm
- These oxide coatings prevent the corrosion of the base metal. Then it is subjected to sealing because the anodized surface is porous.

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e-$$

Sealing

Sealing is the process in which the pores at the surface of the oxide layer are closed off. It is done by placing the anodized object in boiling water for a 15 - 20-minute period. During this time water reacts with the aluminum oxide to produce $Al_2O_3.H_2O$ layer on metal surface.

Colorings

The clear anodized aluminum with its unsealed porous film is immersed in a bath containing organic dyes or inorganic pigments. The colorant is absorbed into the pores of the film and subsequently sealed in. Metal ions are deposited electrochemically in the anodized layer to have better color properties. Anodized articles are used as soap boxes, utensils, tiffin carriers, window frames, etc.

Colored anodized articles fig- fischer technology

2) Phosphate coatings (Phosphating):
- Phosphating is the process of converting a metal surface to metal phosphate. This is mostly used as a pre-treatment method.
- Such phosphating systems are predominantly applied to iron and steel, as well as zinc surfaces whereas other metals which can be phosphated, e.g., aluminium, magnesium, are less commonly processed by this method.
- The final surface is a layer of very fine phosphate crystals adhering to the surface of the metal. This is done by dipping base metal in electrolytic bath containing an aqueous

solution of phosphoric acid. The modern phosphate bath contains metal phosphate and phosphoric acid. The addition of metal phosphates increases the adherence and decreases the porosity of the coat.

- accelerators used are nitrates & nitrites
- pH is 1.8 – 3.2

Applications

- Phosphate coatings are used as primer coat for painting of automobiles, other equipment's like fridge, washing machine etc.

- One important application is the Phosphating of galvanized iron which is otherwise difficult to paint.

- It is coated over metal parts like nuts, bolts of machines which cannot be readily plated.

Phosphated steel tube Fig – flomax.ie

Corrosion inhibitors:

These are the substances added in optimum amounts to the corrosive medium to decrease the corrosion rate. They provide corrosion protection by retarding either cathodic or anodic reactions. On this basis they are classified as:

1) **Anodic corrosion inhibitors:**

These are the substances which decrease the corrosion rate by decreasing the rate of anodic reaction. During corrosion oxidation occurs at anode. These electrons are taken up by cathodic regions. Ex: When inhibitors like chromate, molybdate and tungstate are added, these anions will combine with metal ions formed at anode forming sparingly soluble salt. These deposit at anode as thin film which acts as a protective barrier between base metal and corrosive medium thereby decreasing the rate of corrosion.

Anodic inhibitors prevent corrosion by covering the anode area from corrosive environment. Therefore these should be added in sufficient quantity; otherwise it leads to aggressive corrosion by the formation small anodic and large cathodic regions. It would be more disastrous than not adding it at all.

2) **Cathodic inhibitors:**

These are the substances which decrease the corrosion rate by decreasing the rate of anodic reaction. Cathodic inhibitors can inhibit corrosion either by retarding the rate of,

a) Hydrogen evolution

b) Oxygen evolution

Hydrogen evolution
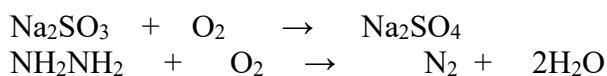
If the cathodic reaction is hydrogen evolution type, then inhibitors like, amines, urea, thiourea, mercaptans and heterocyclic nitrogen compounds are added. These are adsorbed at cathodic surface and prevent diffusion of hydrogen ions towards cathodic surface.

Hydrogen evolution can also be retarded by increasing the hydrogen overvoltage at cathode. This can be done by the addition of oxides of arsenic, antimony or salts like sodium meta arsenite etc which get reduced and deposited as adherent metallic film on the cathode surface and hence increase the hydrogen overvoltage of cathode surface because these metals have high hydrogen overvoltage.

Oxygen evolution

a). Oxygen scavengers

If reaction is oxygen absorption type, addition of sodium sulphite, hydrazine removes oxygen from aqueous solution by formation of salts.

$$Na_2SO_3 + O_2 \rightarrow Na_2SO_4$$
$$NH_2NH_2 + O_2 \rightarrow N_2 + 2H_2O$$

b) Sulphates of Magnesium, Zinc etc. can also be added as cathodic inhibitors, since they combine with OH^- ions at the cathode and form insoluble metallic hydroxides which deposits on cathode. These reactions prevent diffusion of oxygen to cathode.

$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2$

Limitations:
- Contamination of the environment
- Many inhibitors are toxic to environment
- Can be used only with close systems

Cathodic protection:

It is a technique of protecting a metal from corrosion by converting it to cathode. It is based on the principle that cathode always stays unaffected during corrosion reacton. Two types of cathodic protection techniques are-

i) sacrificial anodic method:
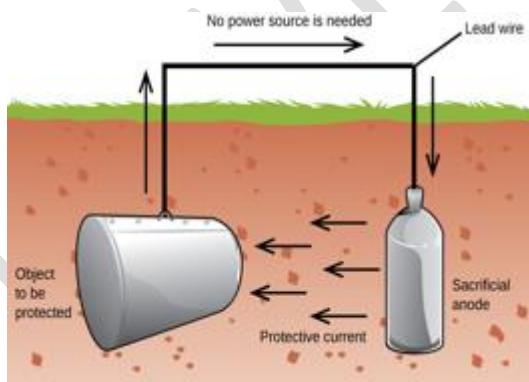
Fig- research

- In this metal to be protected is converted into cathode by connecting it to more active metal.
- The active metal acts as auxillary anode. The more active metal itself gets corroded slowly; while the parent structure (cathodic) is protected.
- Metals like Zn & Mg generally used as auxillary anodes.
- A metallic block of zinc or Mg is connected to metallic structure of iron to be protected.
- Anode being more reactive undergoes corrosion, where as the metallic structure is unaffected. Since anode is sacrificed to prevent the corrosion of anode, it is called sacrificial anode method.
- Ex: When Magnesium blocks are connected to the sides of the ship, it acts as anode, prevents ship from corrosion. Magnesium blocks connected to buried pipelines prevents structure from corrosion, by acting as anode.

Advantages: The method is simple, low installation cost, minimum maintenance and no power supply required.

Disadvantages: Periodic maintenance is required to ensure sacrificial anodes are replaced or else protection will not be ensured.

ii) Impressed current method:

In this method electrons are supplied from external source to the metallic structure to be protected. Metal to be protected is connected to the negative terminal of D.C source. A rod made up of inert graphite or palladium is converted to positive terminal. The electrons are released from anode prevents the basic structure from corrosion.
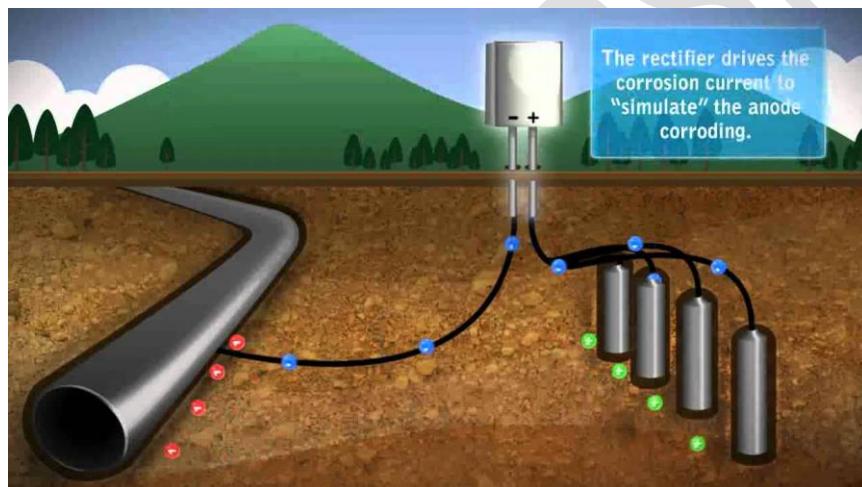

fig- Impressed current method (YouTube upload)

Advantages: Low maintenance cost

Disadvantages:

1. Rather expensive, since high current is used.
2. On large objects current density may not be uniform throughout, hence may lead to localized corrosion.
3. Hydrogen evolution at cathode can lead to entrapment of hydrogen which may cause hydrogen embrittlement.

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