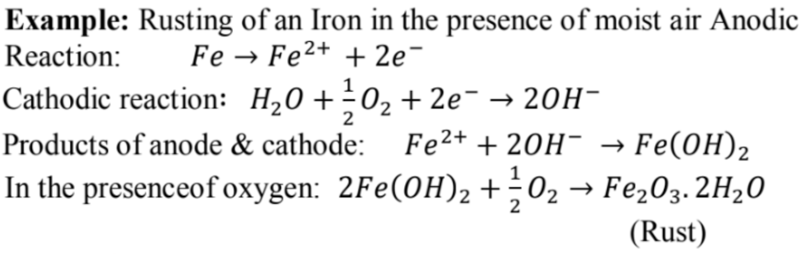
Define metallic corrosion. Describe the electrochemical theory of corrosion taking iron as an example.

- When a metal is in contact with an electrolyte (moist air or solution), electrochemical cells are formed. These cells have an anode and a cathode area on the metal surface.
- The metal undergoes oxidation (loses electrons) at the anode, while reduction (gain of electrons) of species present in the electrolyte occurs at the cathode.
- The anodic part of the metal undergoes corrosion, while the cathodic part is protected from corrosion due to the reduction reaction that occurs there.
- The electrons are transferred through the metal from the anode to the cathode via an external circuit.
- During corrosion, the following reactions take place:
  - Anode: $M \rightarrow Mn^+ + ne^-$ (oxidation reaction)
  - Cathode: $H^+ + ne^- \rightarrow ½ H_2$ (reduction reaction)



Example: Rusting of an Iron in the presence of moist air Anodic Reaction: $Fe \rightarrow Fe^{2+} + 2e^-$

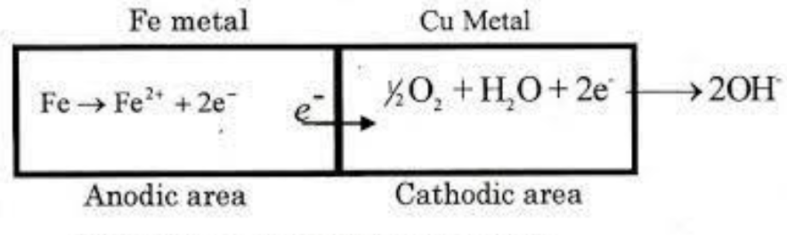
Cathodic reaction: $H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2OH^-$

Products of anode & cathode: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

In the presenceof oxygen: $2Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow Fe_2O_3.2H_2O$ (Rust)

Discuss the following types of Corrosion:
a. Differential Metal Corrosion b. Differential aeration Corrosion

- Differential metal corrosion occurs when two dissimilar metals are in contact with each other in a corrosive conductive medium, such as a saltwater solution.
- The two metals have different tendencies to undergo oxidation or reduction.
- The metal with the lower electrode potential or more active metal acts as the anode and undergoes oxidation.
- The metal with the higher electrode potential acts as the cathode and undergoes reduction.
- The potential difference between the two metals is the main factor for corrosion to take place.
- In the case of iron and copper, iron has a lower electrode potential and acts as the anode, undergoing oxidation, while copper with a higher electrode potential acts as the cathode and remains unaffected.


Fe metal
Cu Metal
$Fe \rightarrow Fe^{2+} + 2e^-$
e^-
$½O_2 + H_2O + 2e^- \rightarrow 2OH^-$
Anodic area
Cathodic area

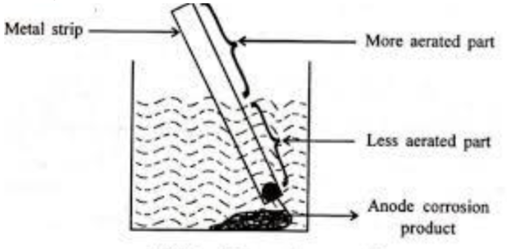
Differential metal corrosion

- Differential aeration corrosion occurs when a metal surface is exposed to varying levels of air or oxygen concentration.
- The metal exposed to lower oxygen concentration acts as the anode, and the part exposed to higher oxygen concentration acts as the cathode.
- The cathodic reaction requires oxygen, and hence the cathodic area tends to concentrate near the water line.
- The bottom portion of the metal strip acts as the anode, where corrosion starts due to the differential concentration of oxygen.

- At the anode, iron is oxidized to Fe2+ ions, and at the cathode near the water line, oxygen, water, and electrons react to form hydroxide ions

At anode: $\mathbf{Fe} \longrightarrow \mathbf{Fe^{2+} + 2e^-}$

At cathode (near water line): $\mathbf{O_2 + 2H_20 + 4e^-} \longrightarrow \mathbf{4OH^-}$

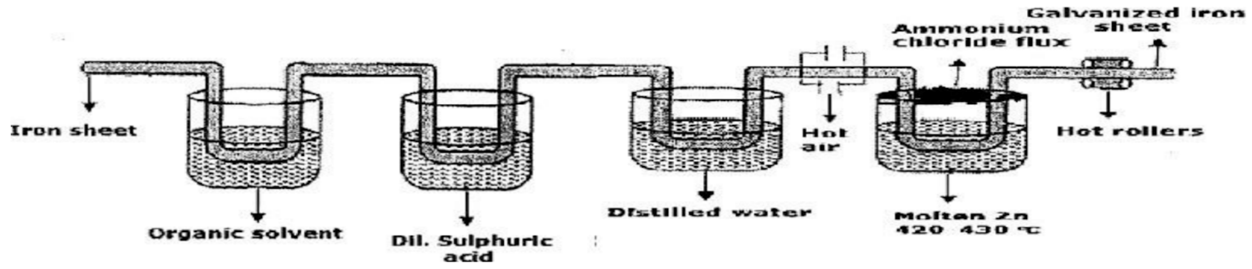

Metal strip
More aerated part
Less aerated part
Anode corrosion product

Differential aeration corrosion

What is cathodic protection? Describe sacrificial anode technique and mention the advantages and disadvantages.

- Sacrificial anodic protection is a technique used to protect a metal from corrosion by connecting it to a more anodic metal using a metallic wire.
- The more active metal, known as the sacrificial anode, corrodes instead of the parent structure and protects it from corrosion.
- Metals commonly used as sacrificial anodes include magnesium, zinc, and aluminum.
- The sacrificial anodes need to be replaced with fresh ones when they become depleted.
- For example, a steel pipe can be protected from corrosion by connecting it to a block of zinc. In this case, steel acts as the cathode and is protected from corrosion, while zinc acts as the anode and undergoes sacrificial corrosion.
- This technique is widely used in the marine industry to protect ships, offshore platforms, and other submerged structures from corrosion.

Define galvanizing. Describe galvanizing of Iron and mention its applications.


Iron sheet
Organic solvent
Dil. Sulphuric acid
Distilled water
Hot air
Ammonium chloride flux
Galvanized iron sheet
Hot rollers
Molten Zn 420 430 °C

- The iron sheet is subjected to pretreatment by degreasing with organic solvent.
- The sheet is passed through dilute H2SO4 to remove any rust.
- Washed with distilled water and dried by supplying hotair.
- Then the iron sheet is dipped in a molten bath of Zn at 419°C and the surface is covered with NH4Cl flux which prevents the oxidation of Zn metal.
- The excess of coated metal is removed by passing through a pair of hot rollers and cooled gradually.

Galvanized articles are mainly used in roofing sheets, fencing wire, buckets, bolts nuts, pipes and tubes etc. but galvanized articles are not used for preparing and storing food stuffs. Since zinc dissolves in dil. Acids become toxic.

What is anodizing of aluminum? Describe anodizing of Aluminium and mention its applications.

- Anodizing is the electrolytic oxidation of the outer layer of metal to form a protective metal oxide layer.
- Aluminum is used as the anode and copper or steel is used as the cathode.
- An electrolyte consisting of 5-10% chromic acid is used, and the temperature is maintained at 30-40 °C.
- A potential of 0-40 V is applied, which oxidizes the outer layer of aluminum to form Al2O3, which gets deposited over the metal.
- Anodizing is used for surface treatment and protection of aluminum parts in industries such as aerospace, automotive, construction, and electronics.

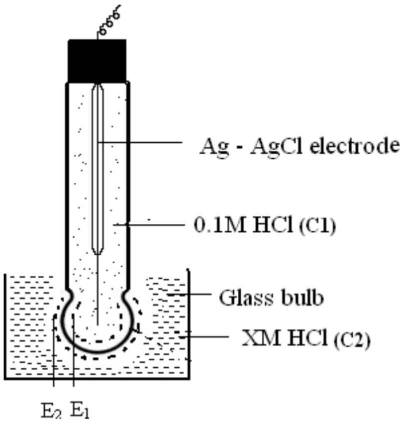
$$At\ Anode: 2Al(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 6H^+ + 6e^-$$
$$At\ Cathode: 6H^+ + 6e^- \rightarrow 3H_2(g)$$

$$Over\ all\ reaction: 2Al(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 3H_2(g)$$

Discuss the different types of electrodes with examples

- Metal-metal ion exchange: A metal immersed in the ionic solution of its own salts, e.g. Cu/Cu2+.
- Redox electrode: Ions of a chemical species in two different oxidation states in contact, e.g. Pt.
- Gas electrode: An inert metal like platinum in contact with gas molecules, e.g. Standard Hydrogen electrode.
- Metal-insoluble salt electrode: Metal in contact with its insoluble salt, e.g. Calomel electrode.
- Amalgam electrode: A known concentration of metal dissolved in liquid mercury in contact with ionic solution of the metal, e.g. Pb(Hg).
- Ion selective electrode: More selective towards a particular type of ion in the mixture, e.g. Glass electrode.

Glass electrode and Ion selective Electrode



Construction

- A glass electrode consists of a long glass tube with a thin-walled glass bulb containing 0.1 M HCl [C1].
- An Ag/AgCl electrode is placed inside the solution to provide electrical contact.
- The glass electrode is dipped in an unknown solution of concentration C2.
- The potential developed across the membrane by the exchange of ions with the composition of glass is known as the boundary potential Eb (E2– E1).
- Even when C1=C2, E≠ 0, a small potential is developed across the membrane, which is called the asymmetric potential (Easy).

Working

Cell representation: Ag / AgCl / HCl (0.1M) / unknown solution/ Glass

Working:

E_1& E_2 is the potential developed at outer and inner membrane respectively the boundary potential is, $E_b = E_2 - E_1$

$$E_b = E^0 + \frac{0.0591}{n}\log[C2] - \left\{E^0 + \frac{0.0591}{n}\log[C1]\right\}$$

$$E_b = \frac{0.0591}{n}\log[C2] - \frac{0.0591}{n}\log[C1]$$

$$E_b = \frac{0.0591}{n}\log[C2] + \frac{0.0591}{n}log\frac{1}{[C1]}$$

Where $L = \frac{0.0591}{n}log\frac{1}{[C1]}$

Therefore

$$E_b = L + \frac{0.0591}{n}\log[C2]$$

Here n=1, [C2] = [H^+] ions in outer membrane, Then

$$E_b = L + 0.0591\log[H^+]$$

$E_b = L - 0.0591p^H$ (pH= -log[H^+])

The Glass electrode potential is given by

$$E_G = E_b + E_{Ag/AgCl} + E_{Asy}$$

Substitute the value of E_b

$$E_G = L - 0.0591p^H + E_{Ag/AgCl} + E_{Asy}$$

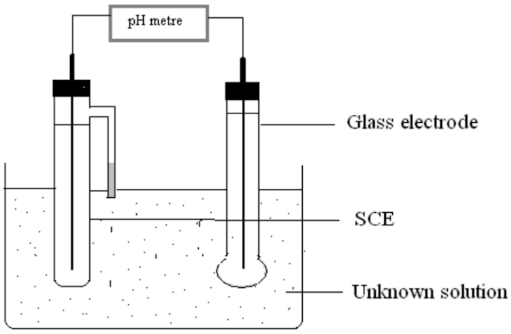
Consider $L_1 = L + E_{Ag/AgCl} + E_{Asy}$, Therefore

$$E_G = L_1 - 0.0591p^H$$

Determination of pH of a Solution using Glass Electrode

The potential of a glass electrode depends on the concentration of H^+ ions. Hence, pH of a solution can be determined by using glass electrode and calomel electrode assembly. The cell assembly is represented as

$Hg/Hg_2Cl_2/Cl^-$ // solution of unknown pH / glass/0.1 M HCl / AgCl / Ag



The emf of a cell is determined by using voltmeter.

E_{cell} is the difference b/w glass electrode potential E_G and the calomel electrode potential E_{SCE}

$$E_{cell} = E_G - E_{SCE}$$

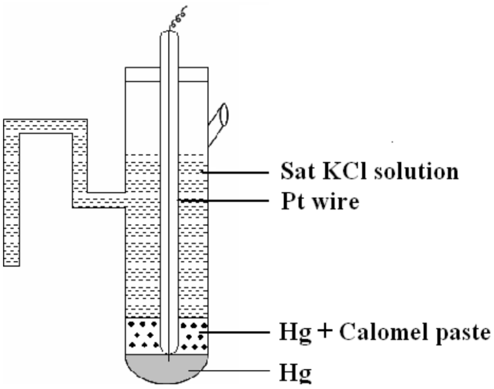
$$= L_1 - 0.0591pH - E_{SCE}$$

$$pH = \frac{L_1 - E_{SCE} - E_{cell}}{0.0591} \quad [K = L_1 - E_{SCE}]$$

$$\boxed{pH = \frac{K - E_{cell}}{0.0591}}$$

Calomel Electrode

Construction



- Calomel electrode consists of a long glass tube with two side tubes.
- Mercury is placed at the bottom of the tube, covered with a layer of Hg and Hg2Cl2 paste.
- The remaining portion of the tube is filled with saturated KCl solution.
- One of the side tubes is used to fill the tube with saturated KCl solution, and the other side tube is connected to the salt bridge.
- A platinum wire is inserted into the mercury and is used to provide external electrical contact.
- The calomel electrode is represented as $Cl^- \mid Hg_2Cl_2 \mid Hg$

Working

Calomel electrode behaves as anode or cathode depending upon the nature of another electrode.
The half-cell reaction when it acts as an anode is

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

The half-cell reaction when it acts as a cathode is

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

The electrode reaction is,

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

Applying Nernst equation,

$$E = E^0 + \frac{0.0591}{n} log \frac{[Reactants]}{[Products]}$$

$$E = E^0 + \frac{0.0591}{n} log \frac{[Hg_2Cl_2]}{[Hg]^2[Cl]^{2-}}$$

Since $[Hg_2Cl_2] = [Hg]^2 = 1$, the above equation becomes

$$E = E^0 + \frac{0.0591}{2} \log \frac{1}{[Cl^-]}$$

The calomel electrode potential is depending on the concentration of chloride ions in KCl. If the Concentration of chloride ions increases, the potential decreases and vice versa. (The potential of calomel is inversely proportional to the concentration of chloride ions)
The potential of calomel electrode is measured with respect to SHE and it depends on concentration of KCl solution used.

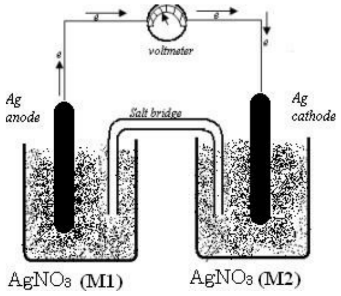
Conc. KCl	0.1N	1N	Saturated KCl
Potential (V)	0.334V	0.281V	0.242V

Application

- The calomel electrode is commonly used as a reference electrode in all potentiometric determinations.
- It is used to determine the potential of other electrodes.

Concentration Cell

- The concentration cell consists of two identical electrodes.
- The electrodes are in contact with the same electrolyte solution but of different concentrations.
- The cell generates a potential difference between the two electrodes due to the difference in ion concentrations.
- The electrode in the more dilute solution acts as the anode, while the electrode in the more concentrated solution acts as the cathode.
- The potential difference can be measured with a voltmeter.



$At\ Anode: Ag \rightarrow Ag^{+}(M1) + e^{-}$
$At\ Cathode: Ag^{+}(M2) + e^{-} \rightarrow Ag$
$Net\ Cell\ Reaction: Ag^{+}(M2) \leftrightarrow\ Ag^{+}(M1)$

Apply Nernst equation for the cell reaction,

$$E = E^{0} + \frac{0.0591}{n} log \frac{[Reactants]}{[Products]}$$

$$E^{0} = E^{0}{}_{Cathode} - E^{0}{}_{Anode}$$

Since both anode & cathode is made up of same metal, $E^{0} = 0$

$$E = 0 + \frac{0.0591}{n} log \frac{[M2]}{[M1]} \quad or\ E = \frac{0.0591}{n} log \frac{[M2]}{[M1]}$$

Potentiometry

Principle:

The principle behind the estimation of iron by potentiometry is based on the redox reaction between iron and cerium ions. The reduction potential of cerium ions is measured against a reference electrode, and the endpoint is determined by the sudden change in potential when all the iron is reduced to the ferrous state.

Procedure:

The iron sample is dissolved in an acidic solution and the pH is adjusted to 2-3. A standard cerium solution is prepared and added to the iron solution. The mixture is then titrated against a standard ferrous solution using a platinum indicator electrode and a calomel reference electrode. The endpoint is detected by the sudden change in potential when all the iron is reduced to the ferrous state.

Instrumentation:

- A potentiometer consists of an indicator electrode (e.g., platinum), a standard reference electrode (e.g., calomel electrode), and a potentiometer to read the values directly as a change in potential.
- The potential difference between the indicator and reference electrodes is measured using the potentiometer.
- The concentration of the unknown solution can be determined by comparing the potential difference to that of known concentrations.

Applications:

- Potentiometry is used to titrate colored solutions.
- It can be used for acid-base titration and oxidation-reduction titration.
- Precipitation reactions can also be carried out potentiometrically.
- It gives more accurate and precise results compared to other titration techniques.