

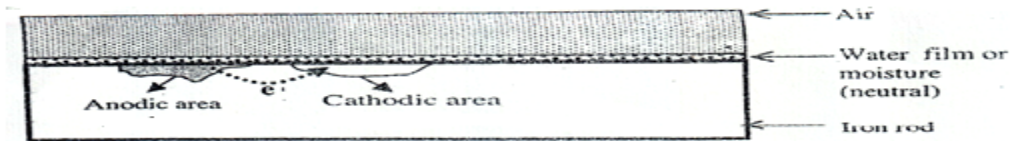
MODULE - 3

CORROSION AND ELECTRODE SYSTEM

Corrosion is defined as loss of metal due to chemical or electro chemical attack on its surface by its surroundings.

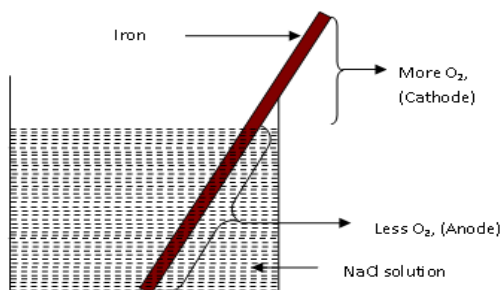
ELECTROCHEMICAL THEOR OF CORROSION TAKING IRON AS AN EXAMPLE

- According to electrochemical theory, the corrosion of metals under corrosive environment is due to formation of large number of anodic and cathodic regions on the same metal.
- Under corrosive environment if two dissimilar metals are in contact or when a metal is under stress or defects are present on the surface of the metal anodic & cathodic regions are formed.
- During the corrosion, oxidation of the metal and reduction of the species present in the solution takes place at anode and cathodic regions respectively.

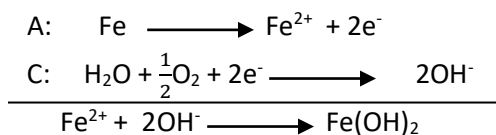


- The electrons are transferred through the metal from anode to cathode. Here the direct involvement of metal is only at anode hence the anodic part of the metal suffers from corrosion and cathode is unaffected.
- Corrosion reactions are:
 - At anode: $M \longrightarrow M^{n+} + ne^{-}$
 $Fe \longrightarrow Fe^{2+} + 2e^{-}$
 - At cathode: Cathodic reaction depends on the constituents present in the corrosive medium. Hence cathodic reaction proceeds via two mechanisms: i) Hydrogen liberation ii) Oxygen absorption
 - i) Hydrogen Liberation Mechanism: It takes place in absence of oxygen
 - a) In acidic medium and in absence of oxygen
 $2H^{+} + 2e^{-} \longrightarrow H_2 \uparrow$
 - b) In basic or neutral medium and in absence of oxygen
 $H_2O + 2e^{-} \longrightarrow H_2 \uparrow + 2OH^{-}$
 - ii) Oxygen absorption Mechanism: It takes place in presence of oxygen
 - a) In acidic medium and presence of oxygen
 $2H^{+} + \frac{1}{2}O_2 + 2e^{-} \longrightarrow H_2O$
 - b) In basic or neutral medium and in presence of oxygen
 $H_2O + \frac{1}{2}O_2 + 2e^{-} \longrightarrow 2OH^{-}$

Here the part of the metal which is less aerated acts as anode and the part of the metal which is more aerated acts as cathode as oxygen is having the natural tendency to accept the electrons readily.

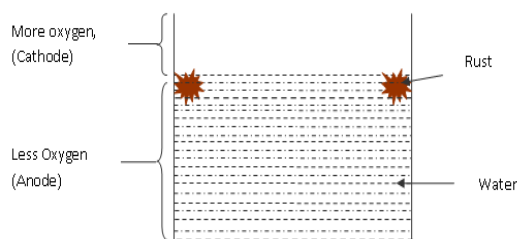


For example consider an iron rod which is partially immersed in water. Here the part of the metal which is immersed in water is exposed to only dissolved oxygen hence it acts as anode, whereas the part of the metal above the water level is exposed to atmospheric air hence acts as cathode. The reactions involved are as follows



Water line and pitting corrosion are two cases of differential corrosion.

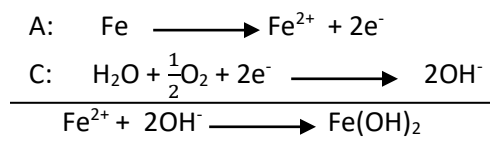
i) Water line corrosion: It is a case of differential aeration corrosion. The type of corrosion that takes place just below the water level is referred to as water line corrosion. Whenever a metal is partially covered by water differential aeration occurs. The part just below water acts as anode as it is less aerated relative to the part just above the water level. The part just above the water level acts as cathode. The corrosion product is formed just below the water line hence the name water line corrosion.



Ex:

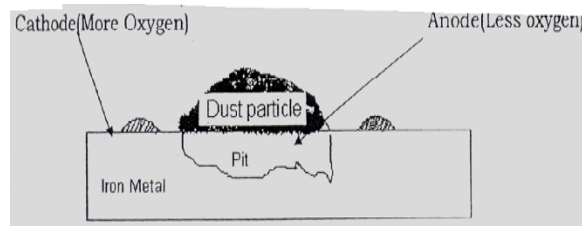
1. Corrosion of ocean going ships
2. Corrosion of water storage tanks
3. Corrosion of metal rod partially dipped in water.

The reactions involved are as follows



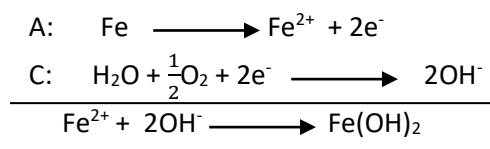
ii) Pitting corrosion: It is a case of differential aeration corrosion. “The type of corrosion that takes place due to small anodic and large cathodic areas on the surface of metal is called pitting corrosion”. It is a localized and intense type of corrosion.

Pitting corrosion is observed when small amount of dust is deposited over the metal surface.



The metal below the dust is exposed to lower oxygen concentration acts as anode and undergoes corrosion. The metal surrounding the deposit acts as cathode since it is exposed to higher concentration of oxygen. Because of the small anode and large cathode accelerated corrosion takes place below the deposit, leading to the formation of pit. Mechanical strength of the metal decreases due to pitting.

The reactions involved are as follows

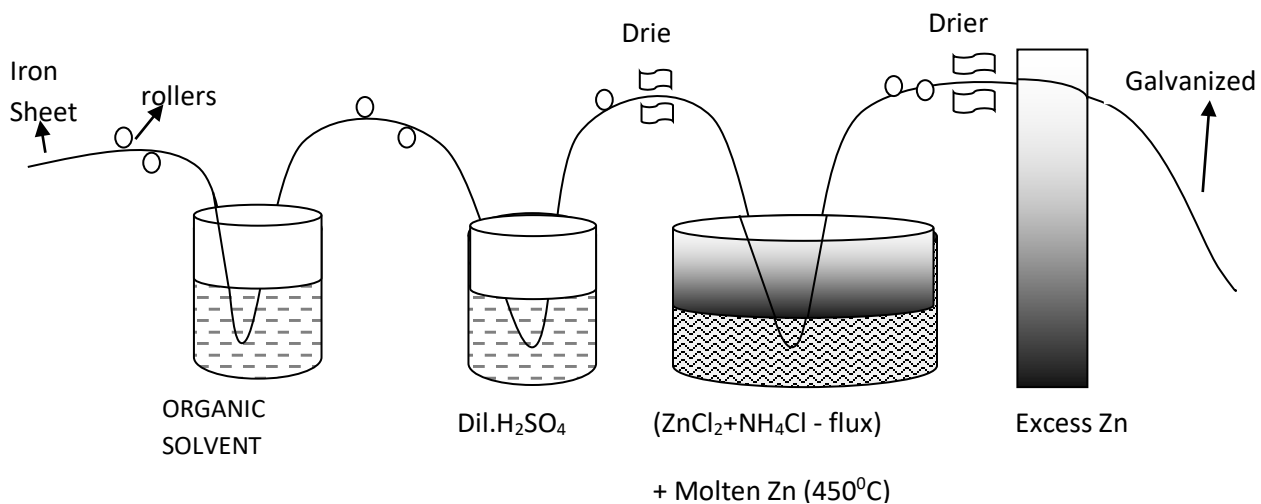


Corrosion Control:

Metallic coating: Coating the base metal with another metal in order to create a barrier between the base metal & corrosive environment is called metallic coating. Depending on the SRP of coated metal metallic coatings are classified into two types.

Anodic coating: Coating the base metal with another metal whose SRP is lower than the base metal is called anodic coating. Ex: Galvanization

Galvanisation: It is a process of coating a base metal (iron) with zinc(Zn) metal. This process usually carried out by hot dipping method.



Galvanising process:

Step1: The Fe article is cleaned with organic solvent to remove oil or grease present on the surface.

Step2: The article is washed with dil H_2SO_4 to remove scale formation, rust or oxide layer formation

Step3: Then the article is treated with aqueous mixture of $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$ which acts as flux.

Step4: Article should be dried

Step5: The dried article is dipped in molten Zn at 450°C

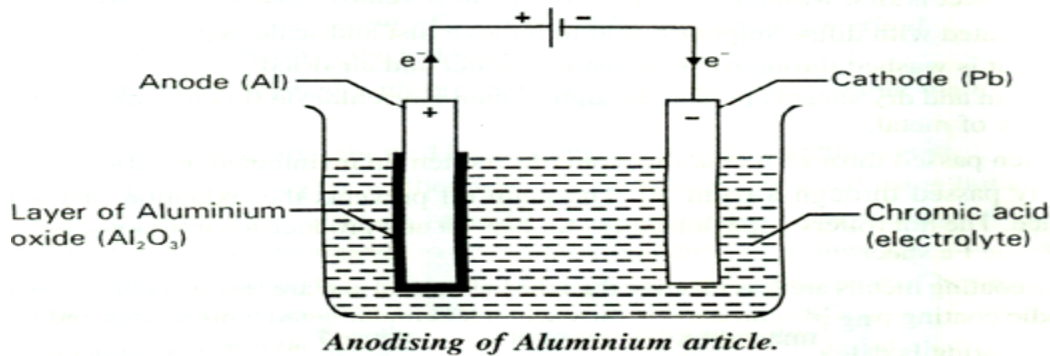
Step6: The excess Zn coated on iron article is removed by passing through rollers

Application: Galvanized articles are mainly used in roofing sheets, fencing wire, buckets, bolts nuts, pipes and tubes etc.

Cathodic coating: Coating the base metal with another metal whose SRP is higher than the base metal is called cathodic coating. Ex: Tinning

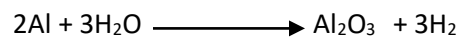
Anodizing of Al: Anodizing is the process of oxidation of outer layer of metal-to-metal oxide by electrolysis.

Anodizing is suitable for non-ferrous metals like Al, Mg, Cr, Ni, etc as their oxide layers are tightly adherent and insoluble.



Process: In anodizing of aluminium, the surface of the object is cleaned to remove oil/grease and rust. It is made connected to anodic terminal of the external battery. 10% chromic acid is used as electrolyte and steel or copper foil is used as a cathode. Temperature of the bath is maintained at 35°C. A voltage of 40V is applied from the external battery till the desired thickness of metal oxide layer develops.

The net reaction that occurs during anodizing of aluminium can be represented as



The oxide layer is slightly porous. The pores are covered by dipping the anodized aluminum object in boiling water. This process is called sealing. During sealing process Al_2O_3 gets hydrated to $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ which occupies more volume and reduces the porosity.

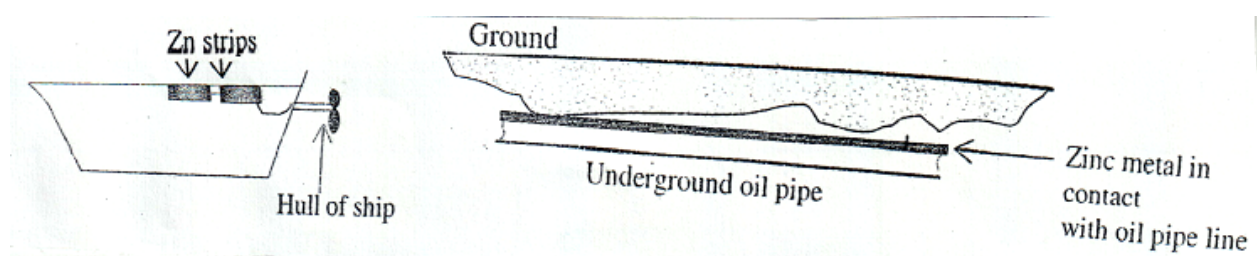
Cathodic Protection: The method of forcing a metal to be protected to act as cathode and thus protecting it from corrosion is called cathodic protection. There are two methods of cathodic protection

i) Sacrificial anode method:

The method involves the use of more active metals as sacrificial anode in contact with specimen (like iron, copper or brass). The active metals like Zn, Mg and their alloy acts as an auxiliary anode, and undergo preferential corrosion protecting the metal structure. Here the anode metals are sacrificed to protect the metal, the method is known as sacrificial anode method, exhausted anodes are replaced by new ones as and when required.

Egs: 1. Mg or Zn block connected to a buried oil tank

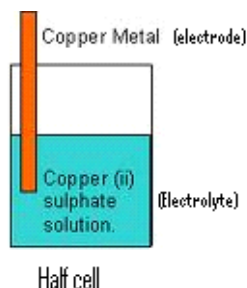
2. Mg bars are connected to ocean going ships



Sacrificial anode methods are simple with low installation cost and do not require power supply but involves recurring expenditure of replacement of consumed anodes.

ELECTRODE SYSTEM

INTRODCUTION: A cell is an energy conversion device consisting of two half cells (or single electrodes) namely anode and cathode. A half cell (or single electrode) is a combination of **electrode** and **electrolyte**. "A solid electric conductor through which an electric current enters or leaves is called an **electrode**". "A compound which conducts electricity in the molten or in aqueous solution is called an **electrolyte**".



In a cell, the half cell at which oxidation (loss of electrons) takes place is called **anode** and the half cell at which reduction (gain of electrons) takes place is called **cathode**.

ELECTROCHEMICAL CELLS: "These are the devices which convert chemical energy in to electrical and vice versa". Electrochemical cells are mainly divided into (i) Galvanic cells (ii) Electrolytic cells.

Galvanic cells: The devices that convert chemical energy into electric energy are called galvanic cells.

Electrolytic cells: The devices that bring chemical change by the expense of electrical energy are called electrolytic cells.

Irrespective whether the given cell is galvanic or electrolytic, oxidation it is important to note that **always oxidation takes place at anode and reduction takes place at cathode**. The major difference between these cells will be **anode will have negative charge in galvanic cells where as positive change**

in electrolytic cells. Similarly cathode will have positive change in galvanic cells and negative charge in electrolytic cells.

Single Electrode Potential: It is defined as the potential that exists between the metal and its ions in the solution when they are in equilibrium.

Standard Electrode Potential: It is defined as the potential that exists between the metal and its uni - molar solution at 298K.

ELECTROMOTIVE FORCE (EMF): The potential difference that causes the electrons to flow from one half cell to other half cell is called electro motive force.

Types of single electrodes

In electrochemical cells different types of electrodes are used depending upon the purpose for which they are used. Some important types are

METAL-METAL ION ELECTRODE: This type of electrode consists of a metal in contact with a solution of its own ions.

Egs: 1. Zinc in a solution of zinc sulphate.

2. Copper in a solution of copper sulphate.

The electrode potential depends on nature of the electrode, temperature and concentration of its own ions in solution.

Zn/ZnSO₄

Electrode reaction $\text{Zn}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$

According to Nernst equation reduction potential is given by the expression.

$$E_{\text{Zn}^{2+}/\text{Zn}} = E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} + \{0.0591/n\} \log [\text{Zn}^{2+}]$$

$$n=2$$

$$E = E^{\circ} + \{0.0591/2\} \log [\text{Zn}^{2+}]$$

METAL-METAL SALT ION ELECTRODE:

This type of electrode consists of a metal in contact with one of its sparingly soluble salts and a solution of a soluble salt having a common anion with the sparingly soluble salt.

Egs: 1. Calomel electrode $\text{Hg} / \text{Hg}_2\text{Cl}_2 / \text{Cl}^-$

2. Silver-Silver chloride electrode $\text{Ag} / \text{AgCl (s)} / \text{Cl}^-$

GAS ELECTRODE:

A gas electrode consists of a particular gas flushed around an inert electrode (Pt), which is dipped in a solution containing ions to which it is reversible.

Egs: SHE $\text{Pt} / \text{H}_2 (1\text{atm}) / \text{H}^+ (1\text{M})$

AMALGAM ELECTRODES

In amalgam electrodes, a metal dissolved in Hg is in contact with metal salt solution.

An advantage of liquid amalgam electrode is that it eliminates polarization at the electrode surface. It is useful when the pure metal itself reacts with the solution.

Ex. $\text{NaHg}(c_1)$, $\text{Na}^+(c_2)$; $\text{KHg}(c_1)$, $\text{K}^+(c_2)$

OXIDATION-REDUCTION ELECTRODE:

This type of electrode consists of an inert electrode (Pt Or Au) immersed in a mixed solution containing both the oxidized and reduced forms of a molecule or ion.

Egs: $\text{Pt} / \text{Fe}^{2+} : \text{Fe}^{3+}$

$\text{Pt} / \text{Sn}^{2+} : \text{Sn}^{4+}$

ION SELECTIVE ELECTRODES

Possesses the ability to respond only to certain specific ions, thereby developing potential w.r.t that species only in a mixture and ignoring the other ions totally. In other words, the potential developed by an ion-selective electrode depends only on the concentration of species or ions of interest. For ex. Glass membrane is only H^+ ions selective.

1.4 REFERENCE ELECTRODE:

Reference electrodes are those whose potentials are known.

PRIMARY REFERENCE ELECTRODE [SHE]: Hydrogen gas at a pressure of one atmosphere in equilibrium with one molar hydrochloric acid in the presence of platinum is called standard hydrogen electrode.

SECONDARY REFERENCE ELECTRODE:

1. Calomel electrode
2. Ag-AgCl electrode
3. Ion-selective electrode.

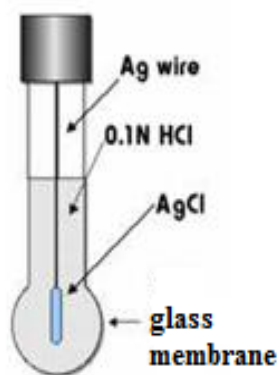
ION SELECTIVE ELECTRODES

“The electrodes which are specifically selective to a particular ion in presence of other ions and develop a potential which is proportional to the concentration of that ion”.

PRINCIPLE, CONSTRUCTION AND WORKING OF GLASS ELECTRODE

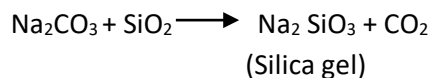
Principle: When Silica gel is placed between 0.1M HCl and an unknown sample having H^+ ions, boundary potential develops across the membrane due to difference in the concentration of H^+ ion. The measure of this boundary potential gives the concentration of H^+ ions in the unknown sample.

Construction: The glass electrode consist a very fragile glass bulb made up of corning glass. The composition of corning glass is 72% SiO_2 , 22% Na_2O , and 6% CaO . The glass bulb is filled with 0.1N HCl which acts as internal reference solution. A Silver wire fused with silver chloride is dipped in HCl solution. It acts as internal reference electrode and provides electrical contact. .

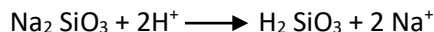


Representation: $\text{Ag} | \text{AgCl} | 0.1\text{N HCl} | \text{Membrane} | \text{Test solution}$

Working: Silica gel membrane used in glass electrode construction is made by fusing Na_2CO_3 with SiO_2 .



When the membrane comes in contact with 0.1N HCl (internal reference soln.) the Na^+ ions present in the inner layer of the membrane are replaced with H^+ ions.



Similar reaction will take place at the outer layer of the membrane when glass electrode is dipped in an unknown sample containing H^+ ions (x N). Therefore either sides the membrane will be hydrated. Due to the difference in the concentration of H^+ ions on both sides a potential called boundary potential is developed across the membrane. The developed boundary potential is measured using Ag-AgCl wire. The measure of this potential gives the concentration of H^+ ions in unknown sample.

Expression for glass electrode:

By using Nernst equation the boundary potential developed may be written as

$E_b = 0.0591/n \log [C_x]/[C_1]$ at standard conditions. Here $[C_x]$ = concentration of H^+ ions in unknown sample. $[C_1]$ = concentration of H^+ ions in reference solution.

When $[C_x] = [C_1]$ then $E_b = 0$. But in practicality there exist a small potential due to the following reasons

- i) Ag – AgCl dipped in HCl (for electrical contact) will act as internal reference solution, hence develops potential.
- ii) Due to unevenness on either sides of the surface of the membrane there exist small potential called asymmetric potential.

Therefore glass electrode potential may be written as

$$E_g = E_b + E_{\text{int.ref}} + E_{\text{Assymetry}}$$

$$E_g = 0.0591/n \log [C_x]/[C_1] + E_{\text{int.ref}} + E_{\text{Assymetry}}$$

$$E_g = 0.0591/n \log [C_x] + 0.0591/n \log 1/[C_1] + E_{\text{int.ref}} + E_{\text{Assymetry}}$$

Since the concentration of H^+ ions in reference solution, Potential of internal reference electrode and Potential due to asymmetry are constant, they will be replaced with another constant i.e., E_g^0 .

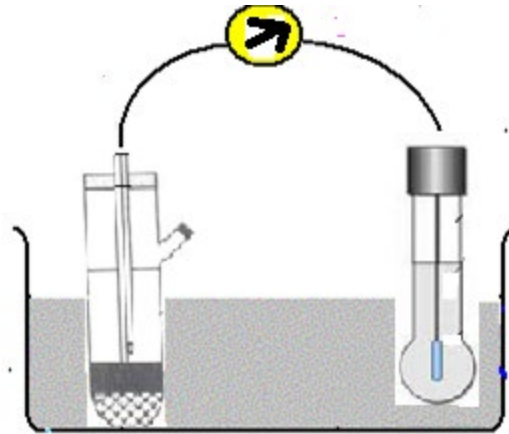
$$E_g = E_g^0 + 0.0591/n \log [C_x] = E_g^0 + 0.0591/1 \log [H^+] \quad \{n = 1\}$$

$$E_g = E_g^0 + 0.0591 \log [H^+]$$

$$E_g = E_g^0 - 0.0591 \text{ pH} \quad \{ \log [H^+] = -\text{pH} \}$$

DETERMINATION OF pH OF UNKNOWN SAMPLE USING GLASS ELECTRODE

As glass electrode is H^+ ion selective electrode, it is used for determination of pH of unknown sample. Since single electrode potential cannot be measured directly, it is coupled with a reference electrode such as Ag – AgCl. In this cell, depending up on the concentration of H^+ ions in the unknown sample, the glass electrode may act as anode or cathode. Consider that glass electrode is anode.



The formed cell is represented as: $\text{Ag}|\text{AgCl}|0.1\text{N HCl}|\text{Membrane}|\text{Test solution} || \text{KCl (XM)}|\text{AgCl}|\text{Ag}$

We know that $E_{\text{Cell}} = E_C - E_A$

$$E_{\text{Cell}} = E_{\text{Ag-AgCl}} - E_g$$

$$E_{\text{Cell}} = E_{\text{Ag-AgCl}} - [E_g^0 - 0.0591 \text{ pH}]$$

$$\text{pH} = E_{\text{Cell}} - E_{\text{Ag-AgCl}} + E_g^0/0.0591.$$

REFERENCE ELECTRODES

“Electrodes whose potential is exactly known under given set of conditions and with which we can measure the potential of other half cell is called reference electrode”.

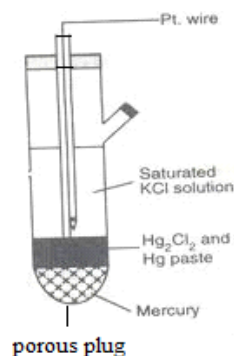
Primary reference Electrode: The first ever man made reference electrode is SHE. Its potential at 25°C is taken as zero. Since it is difficult to maintain always 1 atm H₂ pressure, 1M HCl concentration scientists have thought of portable and less complicated reference electrodes. These are called secondary reference electrodes.

Secondary reference electrodes: The reference electrodes whose potential is fixed with reference to Standard Hydrogen Electrode and with which we can find the potential of other half cell are called secondary reference electrodes. Ex: Calomel Electrode, Ag-AgCl electrode

CONSTRUCTION AND WORKING OF CALOMEL ELECTRODE

Construction:

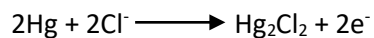
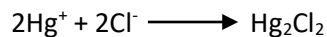
Calomel electrode is an example for metal and its sparingly soluble salt dipped in a solution having common ions. It consists a glass tube in which metallic mercury is placed at the bottom. On top of the mercury a paste of mercury and mercurous chloride is placed, remaining part is filled with KCl solution. A Pt wire is dipped for electrical contact purpose. The porous plug at the bottom acts as salt bridge.



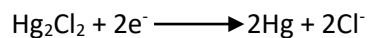
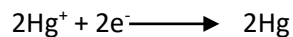
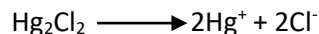
Cell representation: Pt, Hg | Hg₂Cl₂ | KCl (XM)

Working:

When it acts as anode the following reactions will take place.



When it acts as cathode the following reactions will take place



The net overall reaction may be represented as: $\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightleftharpoons 2\text{Hg} + 2\text{Cl}^-$

Expression

for calomel electrode:

Apply law of mass action for the above spontaneous reaction

$$K = \frac{[\text{Hg}]^2[\text{Cl}^-]^2}{[\text{Hg}_2\text{Cl}_2]} = [\text{Cl}^-]^2$$

According to the Nernst Equation $E = E^0 - 0.0591/n \log 1/[M^{n+}]$

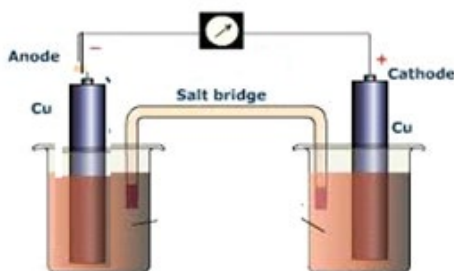
$$E_{\text{Cal}} = E^0 - 0.0591/2 \log [\text{Cl}^-]^2 = E^0 - 0.0591/2 \cdot 2 \log [\text{Cl}^-] = E^0 - 0.0591 \log [\text{Cl}^-]$$

From the above equation it is clear that the potential of calomel electrode depends on the concentration of chloride ions. As the concentration of chloride ions increases the potential decreases and vice versa.

CONCENTRATION CELLS

“Concentration cells are the galvanic cells in which both half cells will have same electrode and electrolyte material but emf will be generated due to difference in the concentration of electrolyte”.

In concentration cells the half cell in which concentration of electrolyte is less will act as anode and the half cell in which the concentration of electrolyte is more will act as cathode. Concentration cell generates emf as long as their exist concentration gradient between the two half cells.



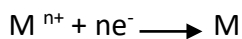
Cell representation: $M|M^{n+}(C1) || M^{n+}(C2) | M$

Cell reaction:

At Anode



At Cathode



Expression for concentration cell:

We know that $E_{\text{cell}} = E_c - E_A$

But $E_c = E_c^0 + 0.0591/nF \log [C_2]$

And $E_A = E_A^0 + 0.0591/n \log [C_1]$

$E_{\text{cell}} = E_c^0 + 0.0591/n \log [C_2] - E_A^0 - 0.0591/n \log [C_1]$

$E = E_c^0 = E_A^0$

$$E_{\text{cell}} = 0.0591/n \log [C_2]/[C_1]$$

Numerical Problems: Refer class notes and solve problems from textbooks.

ANALYTICAL TECHNIQUES

CONDUCTOMETRY

The ease of flow of electric current through a body is called its conductance. In metallic conductors it is caused by the movement of electrons, while in electrolytic solutions it is caused by ions of electrolyte. The electrolytic conductance of a medium is equal to the reciprocal of its electrical resistance R .

$$C = 1/R$$

Ohm's Law states that the current I (amperes) flowing in a conductor is directly proportional to the applied electromotive force E (volts) and inversely proportional to the resistance, R (ohms) of the conductor

$$I = E/R$$

But the resistance of a solution is directly proportional to the distance between the electrodes and inversely proportional to the electrode surface area.

$$R \propto l/A$$

Or

$$R = \rho l/A$$

Where ρ (rho) is proportionality constant is called resistivity and it is the resistance offered by a conductor of unit length and unit area of cross section.

$$\text{Since } C = 1/R = 1/\rho l/A = \kappa A/l \quad (\kappa = 1/\rho)$$

where κ is reciprocal of specific resistance called as specific conductance or conductivity. In SI system, the unit for conductance is 'Siemens' and, given the symbol 'S'. This quantity may be the conductance of a cubic material.

Types of conductance: There are three type's namely specific conductance, equivalence conductance, and molar conductance.

Specific conductance (K) is conductance of the solution which are placed between two electrodes of area 1cm^2 and at 1cm apart

$$K = 1/R (l/a) \quad K = \text{Siemen } \text{m}^{-1}$$

Equivalence conductance (λ) is the conductance of the solution when 1g equivalent weight of solution is placed between two electrodes of area 1cm^2 at 1cm apart.

Molar conductance (μ) is the conductance of the solution when 1g molecular weight of solute is placed between two electrodes of area 1cm^2 at 1cm apart

Conductometric Titrations

Principle: Conductance measurements are used to find the end points of acid base and precipitation titrations. The principle involved is that the electrical conductance depends upon the number of ions and their mobility. The conductance reading corresponding to various added amounts of titrants is plotted. The intersection of these lines gives the end point of the titration.

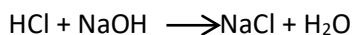
Instrumentation: The basic unit used in measuring the conductivity of a solution is called conductivity cell. It consists of two platinum foils coated with platinum black, separated by unit distance $l\text{cm}$ and an area of cross section equal to $A\text{sq cm}$. The foils are sealed to glass so that the distance between them remains constant. For a given cell, l and A are constant, and the quantity (l/A) is called the cell constant (k). $K_{\text{cell}} = l/A$

Acid – base titrations:

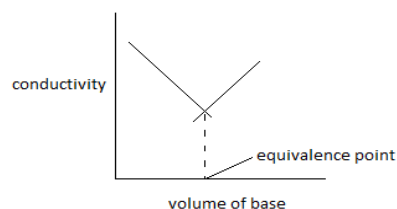
Strong acid v/s strong base

HCl v/s NaOH

If the strong acid like HCl is titrated against a strong base such as NaOH, the conductance first decreases due to replacement of fast-moving H^+ ions by slow moving Na^+ ions



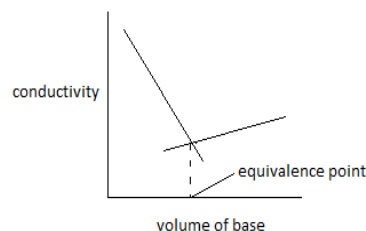
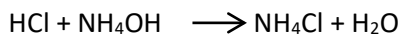
After the neutralization point, conductivity rapidly rises with further addition of NaOH because of continuous addition of fast moving OH^- ions. A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.



Strong acid v/s weak base

HCl v/s NH_4OH

Conductivity of the solution decreases due to the replacement of fast-moving H^+ ions by NH_4^+ ions but after equivalence point, conductivity almost remains constant, since NH_4OH is weak electrolyte and ionizes to small extent giving very small conductivity.

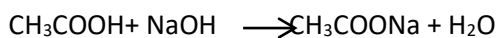


A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.

Weak acid v/s Strong base

Consider the titration of acetic acid against NaOH.

The conductance of the acid will be initially low since acetic acid is a weak electrolyte. When NaOH is added to the acid, the salt increases. On complete neutralization of the acid, further addition of base leads to an increase in the number of mobile OH^- ions. Hence the conductance

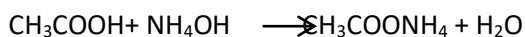


A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.

Weak acid v/s weak base

Consider the titration of acetic acid against NH_4OH . The conductance of acid will be initially low since acetic acid is a weak electrolyte.

When NH_4OH is added to acid salt is formed and the conductance of the solution increases. On complete neutralization of acid conductance does not change rapidly since NH_4OH is a weak base.

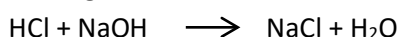


A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.

Mixture of strong acid and weak acid v/s strong base

HCl , CH_3COOH v/s NaOH

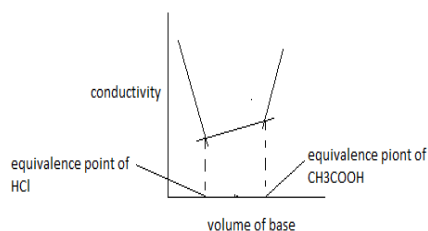
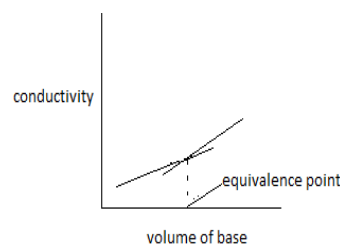
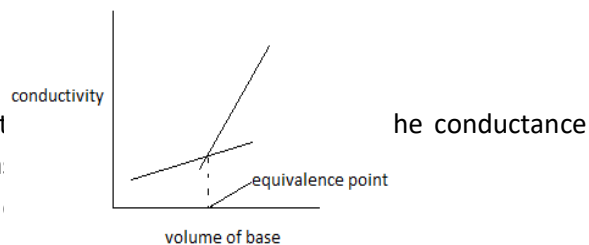
the strong acid like HCl is titrated against a strong base such as NaOH , the conductance first decreases due to replacement of fast-moving H^+ ions by slow moving Na^+ ions



The weak acid does not get neutralized initially because of the well-known common ion effect.

In the presence of excess of H^+ ions, the ionization of the

weak acid is suppressed and hence, weak acid like CH_3COOH ionizes gradually after the first end point and the available H^+ ions are neutralized giving the second end point. Because of common ion effect dissolution of acetic acid is suppressed. Hence it does not provide H^+ ions which required for neutralization. After the neutralization point of HCl , CH_3COOH , conductivity rapidly rises with further addition of NaOH because of continuous addition of fast moving OH^- ions. A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.



POTENTIOMETRY

Principle: Potentiometry involves the determination of concentration of an ionic species in solution by measuring the potential developed at the electrode. The relationship between the potential developed at an electrode and concentration of ions is given by Nernst's Equation

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

The electrode whose potential depends upon the concentration of the ions to be determined is called indicator electrode. Since single electrode potential cannot be measured so it is combined with a reference electrode whose potential remains constant. The emf of the cell changes gradually in the beginning by the addition of titrant and reaches maximum at the equivalence point. The results are interpreted by graphical method.

The titration of Mohr's Salt solution with $K_2Cr_2O_7$ in the presence of H_2SO_4 is a redox titration.

Before the titration is started, the solution contains only ferrous ions in the solution. When a small volume of the dichromate solution is added, equivalent small quantity of Fe^{2+} ions are converted into Fe^{3+} ions. In the process, the Cr^{6+} ion in dichromate is reduced to Cr^{3+} ion.



In the presence of both Fe^{2+} and Fe^{3+} ions in the solution developing an electrode potential which is picked up by a Pt wire $[Fe^{3+}/Fe^{2+}]$, whose electrode potential is given by

$$E = E^0 + \frac{0.0591}{n} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

The electrode potential of the indicator electrode depends upon the ratio of the concentrations of oxidized and reduced species in the solution. As the titration proceeds, the concentration of Fe^{3+} goes on increasing and that of Fe^{2+} goes on decreasing. As a result, the ratio in the above expression for electrode potential goes on increasing and the increase in the value of the ratio becomes very large near the end point. This results in the large increases in the electrode potential and in turn, in the measured emf of the cell.

At the equivalence point, all the Fe^{2+} ions are converted into Fe^{3+} ions, the $Pt/Fe^{3+}, Fe^{2+}$ electrode ceases to exist. But addition of a slight excess of dichromate solution introduces Cr^{6+} ions into the solution, which along with the Cr^{3+} ions in the solution (formed during the oxidation of Fe^{2+}) form a new oxidation reduction electrode, $Pt/Cr^{6+}, Cr^{3+}$.

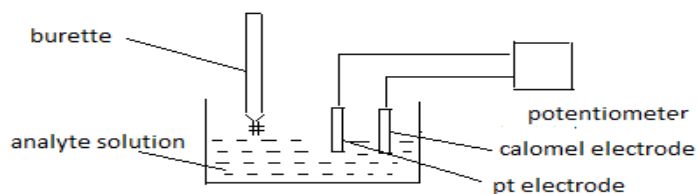
After the equivalence point potential of the redox reaction is determined by the equation

$$E = E^0 + \frac{0.0591}{n} \log \frac{[Cr_2O_7^{2-}]}{[Cr^{3+}]}$$

Instrumentation: A potentiometer consists of

- 1) An indicator electrode. Ex: Pt electrode in red-ox reactions, glass electrodes in acid – base reactions.
- 2) A standard reference electrode. Ex: Calomel or Ag-AgCl electrode
- 3) A meter to measure the variation in potential

INSTRUMENTATION



A potentiometer consists of an indicator electrode (e.g.: Platinum), A standard reference electrode (E.g.: Calomel electrode), & potentiometer to read the values directly as change in potential.

PROCEDURE: Pipette out 25cm³ of FAS solution into a 25cm³ beaker. Add one test tube full of dil H₂SO₄. Immerse Pt. & calomel electrodes into the solution & connect the electrodes to a Potentiometer.

Fill the burette with K₂Cr₂O₇ solution. Add K₂Cr₂O₇ solution from the burette with increment of 0.5cm³, stir well and measure the potential after each addition. Continue the titration till the potential indicates a rapid jump with a drop of titrant.

Plot the graph of $\Delta E / \Delta V$ v/s vol. of K₂Cr₂O₇

The following changes take place during the course of the reaction

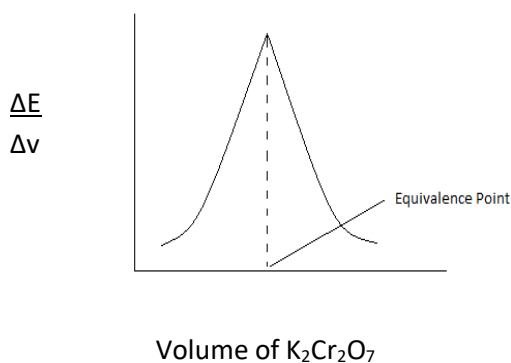


Applying Nernst's eq for the above reaction

$$E = E^0 + 0.0591/n \log [\text{Fe}^{3+}] / [\text{Fe}^{2+}]$$

The potential of the indicator electrode increases gradually as the concentration of Fe³⁺ increases after each addition of K₂Cr₂O₇. There will be a rapid jump at the equivalence point as the platinum electrode changes from Pt_{Fe³⁺/Fe²⁺} to Pt_{Cr⁶⁺/Cr³⁺}.

To identify the exact equivalence point, plot a graph of $\Delta E / \Delta V$ against the volume of K₂Cr₂O₇



Anodic coating: Coating the base metal with another metal whose SRP is lower than the base metal is called anodic coating. Ex: Galvanization

Galvanisation: It is a process of coating a base metal (iron) with zinc(Zn) metal. This process usually carried out by hot dipping method.

Process: First the base metal surface is washed properly with organic solvents to remove any organic matter (like oil, grease etc) on the surface afterwards it washed with dil. H_2SO_4 to remove any inorganic matter (like rust). Finally the base metal is well washed with water and air dried. The base metal then dipped in a bath of molten zinc maintained at $425-430^\circ\text{C}$ and covered with a flux of NH_4Cl to prevent the oxidation of molten zinc. Then excess zinc on the surface is removed by passing through a pair of hot rollers. So that a proper thin coating is obtained.

Application: Galvanized articles are mainly used in roofing sheets, fencing wire, buckets, bolts nuts, pipes and tubes etc.