MODULE 3: CORROSION CHEMISTRY AND ELECTRODE SYSTEM

Corrosion Chemistry: Introduction, electrochemical theory of corrosion, types of corrosion-differential metal and differential aeration. Corrosion control - galvanization, anodization and sacrificial anode method. Corrosion Penetration Rate (CPR) - Introduction and numerical problem.

Electrode System: Introduction, types of electrodes. Ion selective electrode – definition, construction, working and applications of glass electrode. Determination of pH using glass electrode. Reference electrode - Introduction, calomel electrode – construction, working and applications of calomel electrode. Concentration cell– Definition, construction and Numerical problems.

Analytical Techniques: Introduction, principle and instrumentation of Conductometry; its application in the estimation of weak acid. Potentiometry; its application in the estimation of iron.

CORROSION CHEMISTRY

The term corrosion is used to denote a change. A metal changes from its elementary state to the combined state when it comes in contact with liquid medium. This is actually due to the chemical interaction between the metal and the environment.

Definition: *"The spontaneous deterioration and consequent loss of a metal/alloy due to chemical/electrochemical attack by the environment".*

Example: When iron metal is exposed to the moist environment, the metal forms a hydrated ferric oxide called rust which is relatively non-protective.

Most of the corrosion cases are electrochemical in nature taking place by an electrochemical attack on the metal in the presence of air and moisture (H_2O) called *wet corrosion.* The mechanism of the wet corrosion is explained on the basis of electrochemical theory of corrosion.

Electrochemical theory of corrosion:

According to this theory,

1. When a metal is in contact with moist air or when dissimilar metals are contact with each other in a solution, large numbers of galvanic cells are formed with the existence of anodic and cathodic area on the metal.
2. In this corrosion, oxidation of the metal and reduction of species present in solution takes place.
3. The anodic part of the metal undergo oxidation and suffers from corrosion, cathodic part undergo reduction and protected fromcorrosion.
4. The electrons are transferred through the metal from anode to cathode.
5. During corrosion the following reactions takesplace.

At anode (oxidation reaction) $\qquad\qquad : M \rightarrow M^{n+} + ne^-$
The reaction at cathode (reduction reaction) depends on the nature of the environment: If the medium is acidic,
In the presence ofdissolved oxygen: $\quad 2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O$
In the absence ofdissolvedoxygen: $\quad 2H^+ + 2e^- \rightarrow H_2$

If the medium is alkaline/neutral,

In the presence of dissolved oxygen: $H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2OH^-$

In the absence of dissolved oxygen: $2H_2O + 2e^- \rightarrow 2OH^- + H_2 \uparrow$

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 presence of oxygen: $2Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow Fe_2O_3.2H_2O$

<div align="center">(Rust)</div>

Types of corrosion:

Corrosion can be classified into 2 types as follows

1) Differential metal corrosion (Galvanic corrosion)
2) Differential aeration corrosion

Differential metal corrosion (Galvanic corrosion)

1) When two dissimilar metals are in direct contact with one another and exposed to a corrosive medium, the metal with lower electrode potential becomes anode and suffers from corrosion, whereas the metal with higher electrode potential becomes cathode and protected from corrosion. This type of corrosion is known as differential metal corrosion or galvanic corrosion.
2) The rate of corrosion depends mainly on the difference in the position of the two metals in galvanic series.
3) Higher the difference, faster is the rate of corrosion.

Example: Electrode potential of iron (-0.44 V) is less than that of copper (0.34 V). Therefore when iron is in contact with copper, iron becomes anodic and undergoes corrosion, whereas copper becomes cathodic and protected from the corrosion.

$At\ Anode$: $Fe \rightarrow Fe^{2+} + 2e^-$

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

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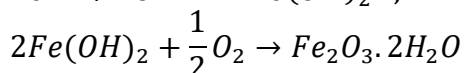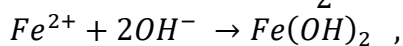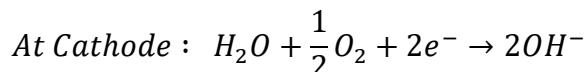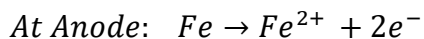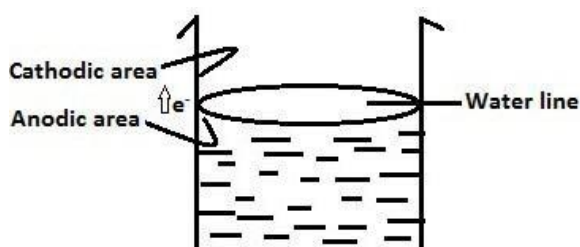
$2Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow Fe_2O_3.2H_2O$

Differential aeration corrosion

1. When a metal is exposed to different concentration of air (O_2), part of the metal exposed to lower concentration of O_2 becomes anodic and undergoes corrosion.
2. Other part of the metal exposed to higher concentration of O_2 becomes cathodic and protected from thecorrosion.
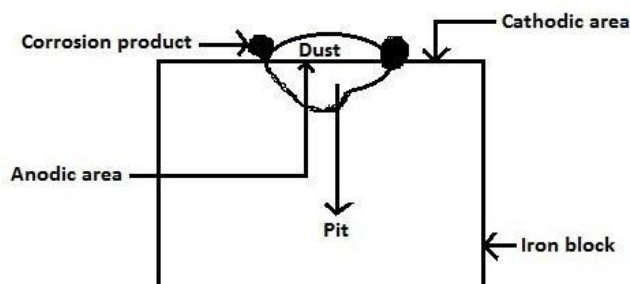3. The difference in O_2 concentration produces a potential difference and causes corrosion. This type of corrosion is called differential aeration corrosion.
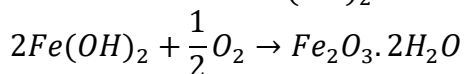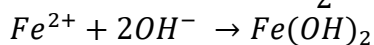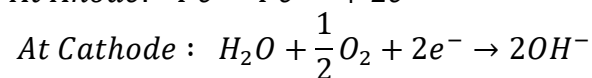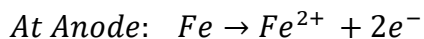
Example: 1 Water line corrosion

1) It is observed in steel or iron water tank partially filled with water. Part of the tank just below water level is exposed to lower concentration of O_2 becomes anodic and undergoescorrosion.
2) Part of the tank above the water line which is exposed to higher concentration of O_2 becomes cathodic and protected from the corrosion.
3) More corrosion is observed just below the water line; hence this type is called water line corrosion.

Reactions:

$$At\ Anode:\ \ Fe \rightarrow Fe^{2+} + 2e^-$$
$$At\ Cathode:\ \ H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2OH^-$$
$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2\ ,$$
$$2Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow Fe_2O_3.2H_2O$$

Example: 2 pitting corrosion

1) Pitting corrosion is observed when dust particles get deposited over the metalsurface.
2) The portion of the metal covered by dust which is less aerated becomes anodic and suffers fromcorrosion.
3) Thus, metal is lost below the surface of dust particle forming a deep and narrowpit.
4) The adjacent area of the metal which is exposed to higher concentration of O_2becomes cathodic and protected fromcorrosion.

Reactions:

$$At\ Anode:\ \ Fe \rightarrow Fe^{2+} + 2e^-$$

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

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

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

Corrosion Control:

Galvanization

Coating of zinc on iron or steel by hot dipping process is called galvanizing. (M.P of Zn=419 $^{\circ}$C)
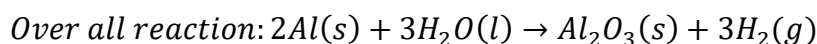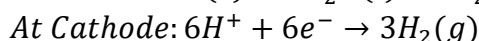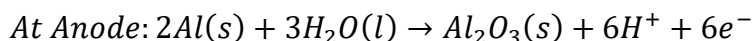
It is carried out as follows,
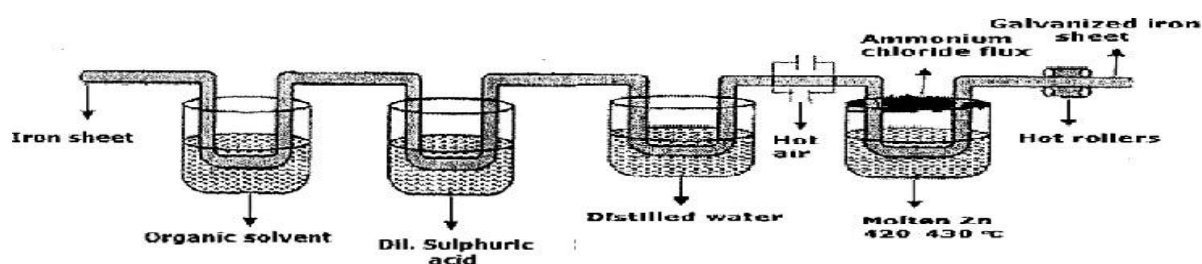
1) The iron sheet is subjected to pretreatment by degreasing with organicsolvent.
2) The sheet is passed through dilute H_2SO_4 to remove anyrust.
3) Washed with distilled water and dried by supplying hotair.
4) Then iron sheet is dipped in molten bath of Zn at 419°C and surface is covered with NH_4Cl flux which prevents the oxidation of Zn metal.
5) The excess of coated metal is removed by passing through a pair of hot rollers and cooled gradually.

Anodizing

Anodizing is the process of oxidation of outer layer of metal to its metal oxide by electrolysis. Oxide layer formed over the metal itself acts as protective layer.

Anode   : Aluminium
Cathode   : Steel orCopper
Electrolyte   : 5-10% chromicacid
Temperature   : 30-40 $^{\circ}$C
Appliedpotential   : 0-40V

Aluminum is made as anode and copper or steel is used as cathode. The electrodes are immersed in an electrolyte consisting of 5-10% chromic acid. The temperature is maintained at 30-40 $^{\circ}$C. Potential of 0-40 V is applied which oxidizes outer layer of Al to Al_2O_3 and that get deposited over the metal. The reactions involved are as follows

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

$$At\ Cathode: 6H^+ + 6e^- \rightarrow 3H_2(g)$$

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

The anodized coatings are thicker than the natural oxide film and possess improved corrosion resistance as well as resistance to mechanical injury.

Sacrificial anodic protection:

1) The metal to be protected is connected to a more anodic metal using a metallicwire.
2) The more active metal gets corroded while the parent structure is protected fromcorrosion.
3) The more active metal so employed is called sacrificialanode.
4) The sacrificial anodes to be replaced by fresh ones as and when it isrequired.
5) Commonly used sacrificial anodes are: Mg, Zn, Aletc.

Example: steel pipe is protected by connecting it to a block of Zn. In such cases steel acts as a cathode and is unaffected or protected from corrosion and Zn act as anode and undergoes sacrificial corrosion.
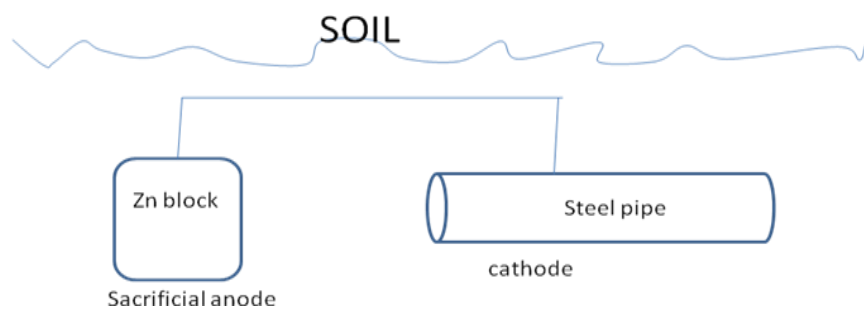
Corrosion Penetration Rate (CPR)

The corrosion penetration rate (CPR) is defined as "the speed at which any metal in a specific environment deteriorates due to chemical reactions when it is exposed to a corrosive environment" or the amount of corrosion loss per unit time in thickness or the speed at which corrosion spreads to the inner portions of a material. Corrosion rate depends on the metal and the environmental condition.

The CPR is given by

$$CPR = \frac{k \times W}{D \times A \times T}$$

Where k = a constant
W = total weight lost
T = time taken for the loss of metal
A = the surface area of the exposed metal
D = the metal density in g/cm³

The corrosion penetration rate is expressed in terms of thickness or weight loss when the surface of the metal corrodes uniformly across an area.

This method involves the exposure of a weighed piece of test metal or alloy to a specific environment for a specific time. This is followed by a thorough cleaning to remove the corrosion products and then determining the weight of the metal after corrosion.

The rate may vary if the rate expressed by the formula above is used to compare corrosion rates for a period longer than one year with rates calculated over short periods. This is because the short time periods are prone to fluctuating environmental changes from season to season and from day to day.

Note:-
Unit of CPR is mils per year if W is in mg, A in Inch2, D in g/cm3, t in hrs and k value will be 534. (1mil = 0.001 inch)
Unit of CPR is mm per year if W is in mg, A in cm2, D in g/cm3, t in hrs and k value will be 87.6. (1inch = 2.54 cm)
If CRP is less than 20m/year or 0.5 mm/year, it is acceptable for most of the application.

ELECTRODE SYSTEM

Types of electrodes:

1) *Metal-metal ion exchange:* In this electrode, a metal is immersed in the ionic solution of its own salts. Example: Cu/Cu^{2+}
2) *Redox electrode:* In this electrode, ions of a chemical species in two different oxidation states are in contact with each other. Example: Pt
3) *Gas Electrode:* In this electrode, an inert metal like platinum is in contact with gas molecules Examples: Standard Hydrogen electrode
4) *Metal-Insoluble salt electrode:* In this electrode, metal is in contact with its insoluble salt. Example: Calomel Electrode
5) *Amalgum electrode:* In this electrode, a known concentration of metal dissolved in liquid mercury is in contact with ionic solution of the metal. Example: Pb(Hg)
6) *Ion selective electrode:* This electrode is more selective towards a particular type of ion in the mixture. Example: Glass electrode

Ion-selective electrode

The electrode, which are responds to a specific ion in a mixture by ignoring other ions are called as ion selective electrodes. They consist of a thin membrane in contact with ion solution. Example, glasselectrode

Glass Electrode:

This electrode works on the principle that when a thin, low resistivity glass membrane is in contact with a solution containing H^+ions, a potential develops across the membrane and the solution. Potential developed depends on the concentration of hydrogen ions in thesolution.

Construction:

➤ It consists of a long glass tube with a thin-walled glass bulb containing 0.1 M HCl [C_1]. Ag/AgCl electrode placed inside the solution to provide electrical contact.
➤ The glass electrode is dipped in unknown solution of concentration C_2.
➤ Thepotential developed across the membraneby the exchange of ions with the composition of glass is known as the boundary potential E_b (E_2– E_1).
➤ Even when $C_1 = C_2$, E$\neq$ 0 a small potential is developed across the membrane, it is calledas *asymmetric potential (E_{asy}).*
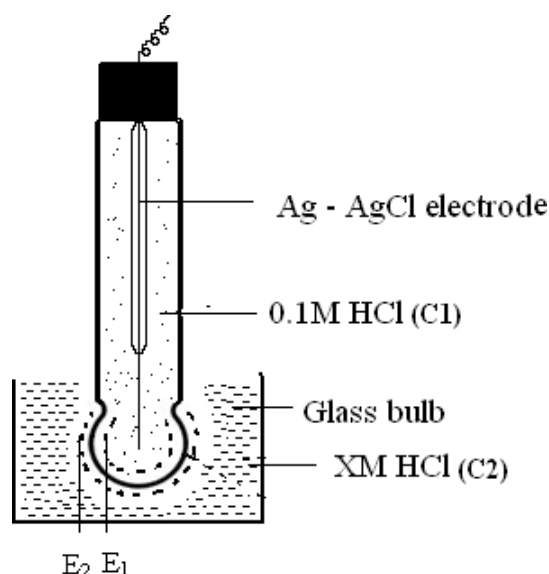
Cell representation: Ag / AgCl / HCl (0.1M) / unknown solution/ Glass

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

Therefore

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

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

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

$E_b = L - 0.0591p^H \qquad$ (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

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

$$\text{Consider} L_1 = L + E_{Ag/AgCl} + E_{Asy}, \text{ Therefore}$$
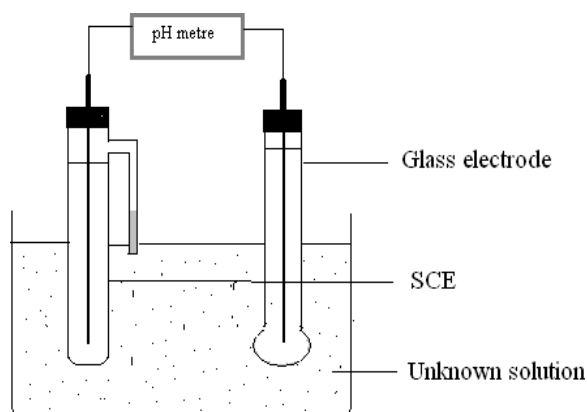
$$E_G = L_1 - 0.0591p^H$$

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/Hg₂Cl₂/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 $E_{SCE.}$

$$E_{Cell} = E_{Cathode} - E_{Anode}$$
$$E_{Cell} = E_G - E_{SCE}$$

$$E_{Cell} = L_1 - 0.0591p^H - E_{SCE}$$

$$p^H = \frac{K - E_{Cell}}{0.0591} \qquad [K = L_1 - E_{SCE}]$$

Where K= Electrode assembly constant.

Reference electrodes

Reference electrodes are the electrodes whose potential is known and used for determination of potential of unknown electrodes
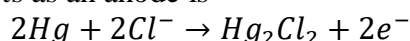
Calomel Electrode:

Construction:

1) Calomel electrode consists of long glass tube with two side tubes.
2) One at the top to fill saturated KCl solution and the other side tube is connected to the salt bridge. Mercury is placed at the bottom which is covered with a layer of Hg and Hg_2Cl_2 (calomel) paste.
3) The remaining portion is filled with saturated KCl solution.
4) A platinum wire is dipped into the mercury and is used to provide external electrical contact.
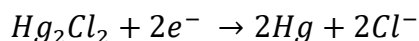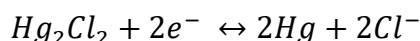➢ The calomel electrode is representedas,$Cl^-/Hg_2Cl_2/Hg$
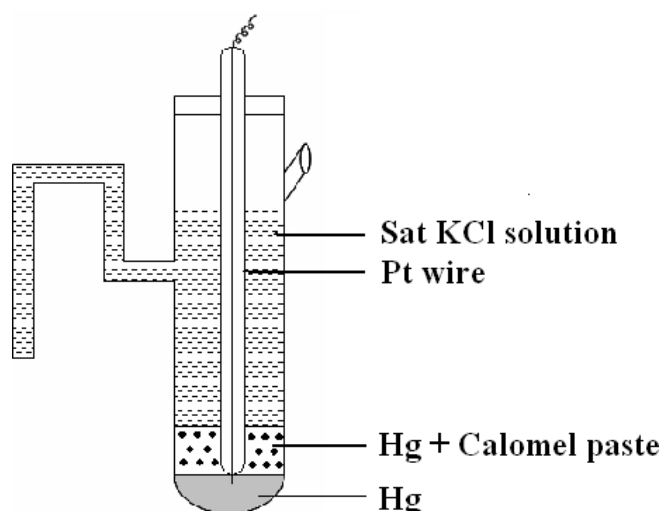
Working:

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

Applications:
1) Used to determine the potential of the otherelectrodes.
2) It is commonly used as reference electrode in all potentiometricdeterminations.

Electrolytic Concentration Cell:

It is galvanic cell, which consists of two identical electrodes, which are in contact with the same solution of electrolyte in different concentrations.

Example:

Consider two silver electrodes that in contact with the AgNO$_3$ solution of different concentrations (M$_1$ and M$_2$) connected through voltmeter. The electrolytes are connected through salt bridge.

The cell representation Ag/ AgNO$_3$ (M$_1$)// AgNO$_3$ (M$_2$)/Ag

Where M$_1$ and M$_2$ are the molar concentration of the Ag$^+$ ions in the two half-cells.
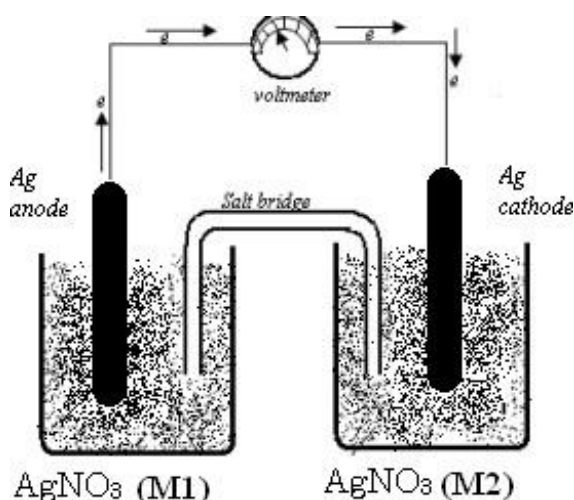
$At\ Anode: Ag \rightarrow Ag^+(M1) + e^-$

$At\ Cathode: Ag^+(M2) + e^- \rightarrow Ag$

$Net\ Cell\ Reaction: Ag^+(M2) \leftrightarrow Ag^+(M1)$

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, $E^0 = 0$

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

ANALYTICAL TECHNIQUES

Potentiometric Titration

Aim: Determination of the weight of ferrous ammonium sulphate and ferrous iron in the given solution by potentiometric titration method.

Theory: In this titration the amount of substance in the solution is determined by measuring the emf between two electrodes that are dipped into the solution. When the metal M is immersed in the solution containing its own ions M^{n+} ions, the electrode potential is given by Nernst equation,
$E = E^0 + \frac{0.0591}{n} log[M^{n+}]$
From this equation the potential of the electrode is directly proportional to the concentration of the ionic species present in the solution.

Instrumentation:

A potentiometer consists of a indicator electrode (e.g.: Platinum) and an saturated reference electrode (E.g.: Calomel electrode), stirrer & potentiometer to measure the potential values.
Emf of the solution can be measured by combining reference electrode with indicator electrode. The electrode which responds to the change in the concentration of the ion in the solution is called indicator electrode & reference electrode is one whose potential is constant. A known volume of the analyte is taken in beaker and its potential is measured. The titrant is added in increments of 0.5ml and potential is measured each time. Near the equivalence point there is a sharp increase in the potential. The end point is determined by plotting change in potential against volume of the titrant.
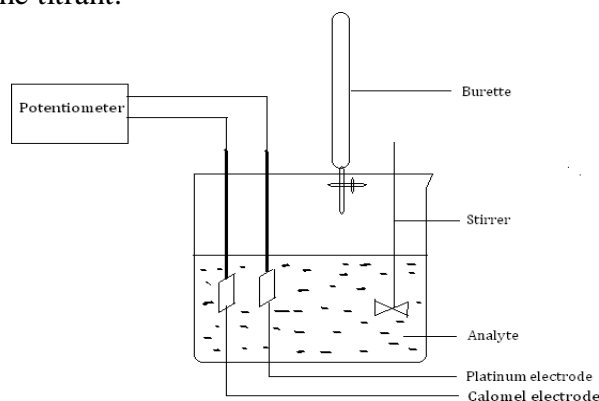
Applications
1. Estimation of concentration of the ionic species present in the givensolution.
2. Coloured solution can also betitrated
3. Acid-base titration can also be done in thismethod.
4. In this method Oxidation-reduction titrations can also be carriedout.
5. Precipitation reactions can also be carried outpotentiometrically.

For example:
Procedure: Pipette out 25cm^3 of FAS solution into a 50 cm^3 beaker. Add one test tube full of dil H$_2$SO$_4$. Immerse Pt. & calomel electrodes into the solution, & connect the electrodes to $\frac{\triangle E}{\triangle V}$ a potentiometer. Fill the burette with K$_2$Cr$_2$O$_7$ solution. Add K$_2$Cr$_2$O$_7$ solution from the burette with increment of 0.5cm^3, stir well and measure the potential after each addition. Continue the titration till the potential indicates a rapid jump with a drop oftitrant.Plot the graph of ΔE/ ΔV v/s vol. of K$_2$Cr$_2$O$_7$.
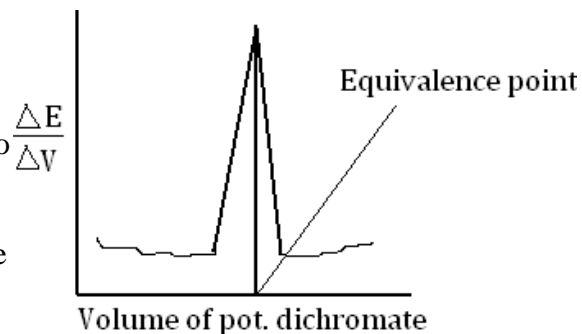
Conductometric Titration

Conductance is ease with which current flows through the solution. It is reciprocal of resistance.
C=1/R = Ω^{-1} or mho or siemen

Theory:

The Conductance of the solution is explained by considering ohm's law.
According to ohm's law the current flowing through the conductor is directly proportional to voltageand inversely proportional to the resistance.
$$I=\frac{E}{R} \text{or} \qquad E = I R$$
The resistance of the any conductor is directly proportional to the length, inverselyproportional
 to the area of cross section of the conductor Therefore R = S (l/a) where S is specific resistance
Therefore C = 1/R =1/S(a/l),   K(a/l),   K = specificconductance
It is defined as the conductance of the solution present between two parallel electrodes of 1cm^2 area of cross section and 1cm apart.
The conductance of the solution is depending on mobility of the ion and number of the ion.

Instrumentation:
It consists of two platinum electrodes each of unit area of cross section placed at unit distance apart. The electrodes are dipped in the electrolytic solution taken in a beaker. It is connected to a conductometer to measure the conductance. The conductance is measured after the addition of the titrant at interval of 0.5 ml.
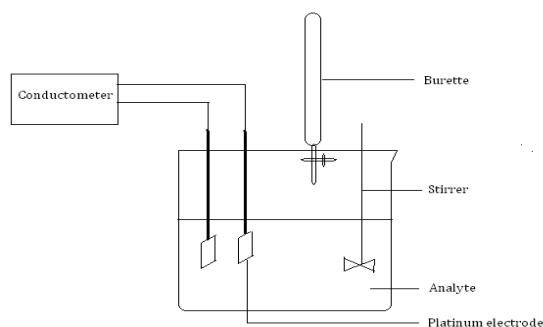
Types of conductance: There are three type's namely specific conductance, equivalence conductance, and molar conductance.

Specific conductance (K) is the conductance of the solution present between two parallel electrodes of 1cm^2 area of cross section and 1cm apart.

K = 1/R (l/a) K = Siemen 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

Application of Conductometric titration

It is used in the estimation of acids and bases present in the sample solutions. The possible combinations and conductance responses are explained below,
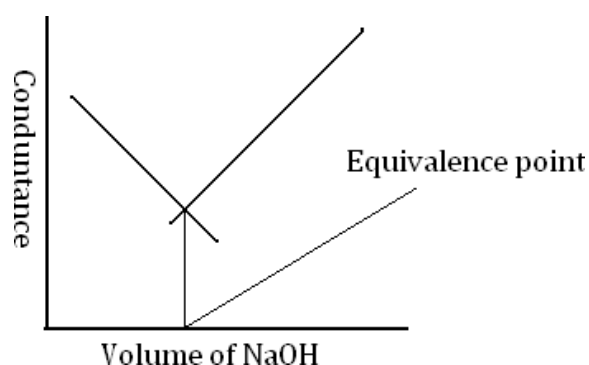
Strong acid v/s strong base (HCl v/s NaOH)

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

$$HCl + NaOH \rightarrow NaCl + H_2O$$
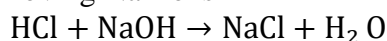
After the neutralization point, conductivity rapidly rises with further addition of NaOH because of continuous addition of fast moving OH$^-$ ions. A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.
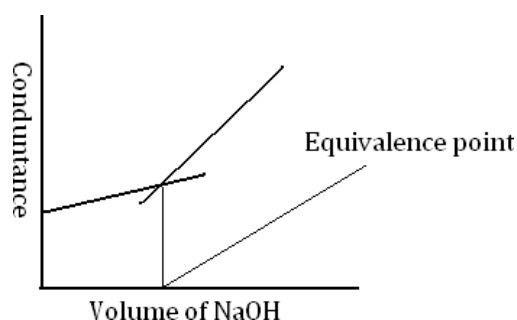

Weak acid v/s Strong base (CH$_3$COOH v/s NaOH)

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 formed is highly ionized and the conductance 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 increases sharply.
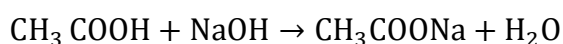
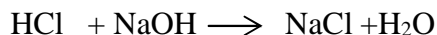$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

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.
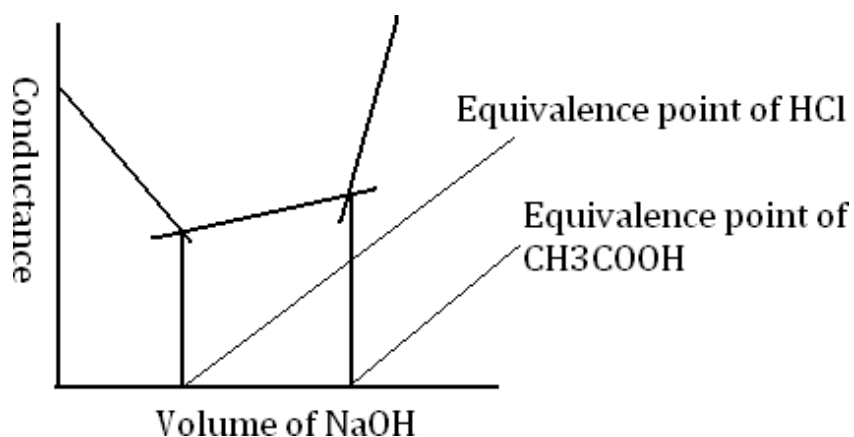
Mixture of strong acid and weak acid v/s strong base (HCl & CH₃COOH v/s NaOH)
The strong acid like HCl is titrated against a strong base such as NaOH, the conductance firs decreases due to replacement of fast-moving H⁺ ions by slow moving Na⁺ ions

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

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 CH₃COOH 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, CH₃COOH, 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.

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