ELECTROCHEMISTRY

Electrochemical cells- reversible and irreversible cell- EMF measurement - single electrode potential- Nernst equation. Reference electrode – SHE - Calomel electrode - Glass electrode - measurement of p^H. Electrochemical series - significance- potentiometric titration – Redox titration – Conductometric titration. Primary and secondary batteries. Lead acid, Lithium batteries (Lithium ion), fuel cells (Hydrogen-oxygen). Corrosion –Inroduction and classification.

INTRODUCTION

Electro chemistry is a branch of chemistry which deals with the transformation of electrical energy into chemical energy or chemical into electrical energy.

IMPORTANT TERMS INVOLVED IN ELECTROCHEMISTRY CELL

Cell is an assembly of two electrodes and an electrolyte. Generally, it consists of two half cells. Each half cell contains an electrode material in touch with electrolyte.

Current: Current is a flow of electricity through a conductor. It is measured in ampere.

Electrode: Electrode is a material rod/bar/strip which conduct electrons.

Anode: Anode is an electrode at which oxidation occurs

Cathode: Cathode is an electrode at which reduction occur

Electrolyte: Electrolyte is a liquid or solution that conducts electric current.

There are three types of electrolytes.

      (a) Strong electrolytes: these are the substances which ionize completely at any concentration.

            Example: HCl, aqueous solutions of NaOH, NaCl and KCl

      (b)Weak electrolytes: Weak electrolytes are the substances which ionize partially in solution.

            Example: CH_3COOH, NH_4OH and aqueous solution of Na_2CO_3

      (c) Non electrolyte: Non electrolytes are the substances which do not ionize at any dilutions.

            Example: Glucose, Sugar, alcohol, petrol etc.

ELECTROCHEMICAL CELL

INTRODUCTION

A system in which two electrodes are in contact with an electrolyte is called as cell. There are two types of cells,

i) Electrolytic Cell

Electrolytic cell is a device which produces chemical change when an electrical energy from outside source is supplied. Here, electrical energy is converted into chemical energy.

ii) Electrochemical Cell

Electrochemical cell is a device in which chemical energy from a redox reaction is utilized to get electrical energy. Here, chemical energy is converted into electrical energy. Example: Daniel cell.

Galvanic Cell

Galvanic cells are electrochemical cells in which the electrons transferred due to redox reaction, are converted into electrical energy. A galvanic cell consists of two half cells with each half-cell contains an electrode. The electrode at which oxidation takes place is called anode and the electrode at which reduction occurs is called cathode. The electrons liberated to the electrolyte from the anode leaves the metal ions at anode. The electrons from the solution are accepted by metal ions at the cathode to become metal.

**Representation of cell:** Galvanic cell is generally represented as follows.

$$M1 / M1^+ \parallel M2^+ / M2 \qquad \text{----------------------- (or)}$$

$$M1 / (\text{Salt of } M1 \parallel (\text{Salt of } M)2) / M2$$
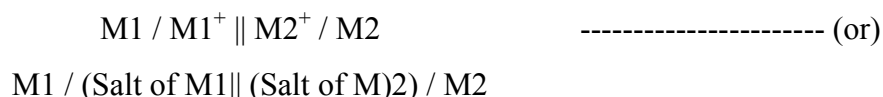
Where, M1 & M2 are Anode and Cathode respectively, and $M1^+$ & $M2^+$ are the metal ions in respective electrolyte. The symbol $\parallel$ denotes salt bridge. The above representation of galvanic cell is known as galvanic cell diagram.

$$\text{Example:} \qquad Zn / Zn^{2+} \parallel Cu^{2+} / Cu \quad \text{----------------------- (or)}$$

$$Zn / ZnSO_4 \parallel CuSO_4 / Cu$$
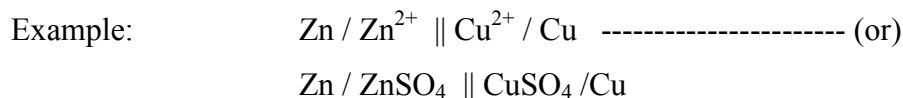
REVERSIBLE and IRREVERSIBLE Cells:

Reversible electrochemical cells are the cells whose cell reactions can be get reversed when an external emf greater than its capacity is applied. (A cell which obeys thermodynamic conditions of reversibility is known as reversible cells). For example: Daniel cell with Capacity 1.1 V, when an external emf of 1.1 V is applied, the cell reaction stops.

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$
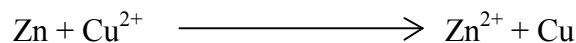
But when an increased amount of emf greater than 1.1 V is applied, the cell reaction is get reversed.

$$Zn^{2+} + Cu \longrightarrow Zn + Cu^{+2}$$

Irreversible electrochemical cells are the cells whose cell reactions can not be get reversed when an external emf greater than its capacity is applied. **(A cell which does not obey thermodynamic conditions of reversibility is known as irreversible cells).** For example, a cell which has Zn as an anode and Ag as a cathode with sulphuric acid as an electrolyte.

The cell reaction at the anode is (Zn/H+/Ag)

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$
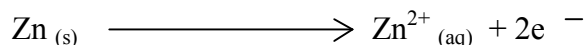
In the presence of electrolyte (H_2SO_4) : $Zn + 2 H^+ \longrightarrow Zn^{2+} + H_2$.

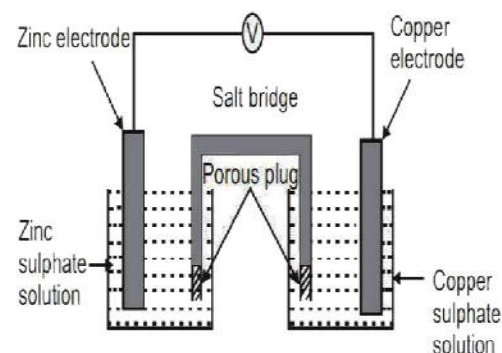The cell reaction at the cathode is

$$2 Ag^+ + 2e^- \longrightarrow 2 Ag$$
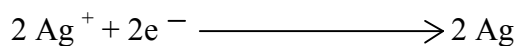
When an external emf applied to the cell, the chemical reactions are not reversed because one of the products of the reaction H_2 gas is escaped from the reaction system. Dry cells are another example for this type of cells.
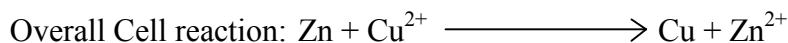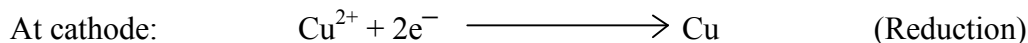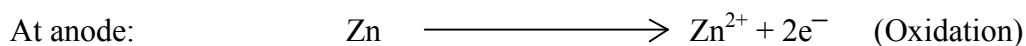
SINGLE ELECTRODE POTENTIAL

The measure of tendency of a metallic electrode to lose or gain electrons when in contact with a solution of its own salt in a half cell of an electrochemical cell is called as single electrode potential. The tendency of an electrode to lose electrons is called oxidation potential while the tendency of an electrode to gain electrons is called reduction potential.

Daniel Cell

This cell consists of a zinc rod as anode dipped in zinc sulphate solution (electrolyte) in a glass tank and copper rod as cathode dipped in copper sulphate (electrolyte) in another glass tank. Each electrode is known as half cell. The two half cells are interconnected by a salt bridge and zinc and copper electrodes are connected by a wire through voltameter. The salt bridge contains saturated solution of KCl in agar-agar gel. The cell diagram of Daniel cell is in figure


Redox reaction occurs at the electrodes of the Daniel cell:

At anode:	$Zn \longrightarrow Zn^{2+} + 2e^-$	(Oxidation)
At cathode:	$Cu^{2+} + 2e^- \longrightarrow Cu$	(Reduction)

Overall Cell reaction: $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$

EMF OF AN ELECTROCHEMICAL CELL

The flow of electric current in Galvanic cell is due to potential difference between two electrodes which is known as electrode potential.   Electrode potential is a measure of tendency of an electrode to gain or lose electrons. Each electrode has a different tendency to lose or gain electrons.
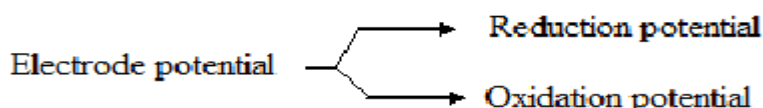
Reduction potential (conventionally used) is the measure of tendency of an electrode to lose electrons and oxidation potential is the measure of tendency of an electrode to lose electrons.

Electrodes with high reduction potential readily gains electrons and gets reduced.

Electrodes with low reduction potential (oxidation potential) readily looses electrons and gets oxidized.

The difference between the electrode potentials of the two electrodes constituting a galvanic cell is known as EMF or cell potential (expressed in volts).

$$\text{EMF} = E_{cell} = E^o_{cathode} - E^o_{anode} = E^o_{right} - E^o_{left}$$

The reduction potential of an electrode measured at 25oC, 1atm and 1M concentration of electrolyte is called standard reduction potential. The positive value of Ecell indicates that cell reaction is feasible.
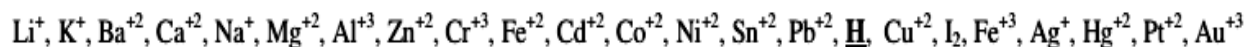
Factors affecting the EMF of a cell

- Nature of the electrolytes and electrodes.

- Concentration and composition of the electrolytes.

- pH and temperature of the solution.

Applications of EMF Measurements

o The valency of an ion can be determined.

o Solubility of a sparingly soluble salt can be determined.

o Potentiometric titrations can be carried out.

o Hydrolysis constant can be determined.

o Determination of standard free energy change and equilibrium constant

o Determination of **pH by using a standard hydrogen electrode.**

ELECTROCHEMICAL SERIES

- The arrangement of elements in increasing order of their standard electrode reduction potentials as compared to that of Standard Hydrogen Electrode (S.H.E) is called galvanic series.

- It is an arrangement of metals in the order of decreasing tendency of their atoms to lose electrons (Electro positive character) is known as galvanic series.

$Li^+, K^+, Ba^{+2}, Ca^{+2}, Na^+, Mg^{+2}, Al^{+3}, Zn^{+2}, Cr^{+3}, Fe^{+2}, Cd^{+2}, Co^{+2}, Ni^{+2}, Sn^{+2}, Pb^{+2}, \underline{H}, Cu^{+2}, I_2, Fe^{+3}, Ag^+, Hg^{+2}, Pt^{+2}, Au^{+3}$

* Increasing order of reduction potential
* Increasing power of oxidizing agent
* Decreasing order of oxidation potential
* Decreasing power of reducing agent

- Higher end of galvanic series acts as reducing agents (gets oxidized) and lower end of the series acts as oxidizing agents (gets reduced).

- Higher end of galvanic series can displace hydrogen gas from dilute acids.

$$Zn + HCl \longrightarrow ZnCl_2 + H_2$$

- Metals with lower reduction potentials can displace the metal with higher reduction potential.

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$

Applications of electrochemical series:

The galvanic series give more information on the following

1. The relative corrosion tendencies of the metals.
2. Relative ease of oxidation or reduction of metals.
3. Replacement of tendency of metals.
4. Calculating the equilibrium constant.

NERNST EQUATION

We know experimentally that the potential of a single electrode or half-cell varies with the concentration of ions in the cell. In 1889 Walter Nernst derived a mathematical relationship which enable us to calculate the half-cell potential, E, from the standard electrode potential, E°, and the temperature of the cell. This relation known as the **Nernst equation.**

Standard electrode potentials are measured at standard states i.e at1M concentration of electrolyte, temperature at 298 K and 1atm pressure.

However the electrode potentials depend upon concentration of electrolyte solutions and temperature. **Nernst equation gives the relationship between electrode potentials and concentration of electrolytic solutions.** For the general reduction reaction occurring at an electrode,

$$M^{n+}_{(aq)} + ne^- \longrightarrow M_{(s)}$$

$$E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{[M_{(s)}]}{[M^{n+}_{(aq)}]}$$

Where

E° = Standard EMF of the cell for 1 M solution at 298 K;
R = Gas constant; T = Kelvin temperature;
n = number of electrons involved in the cell reaction;
F = Faraday of electricity; E = electrode potential of the metal;
[M] = activity of metal in the metal phase and is taken as unity;
[M^{n+}] = activity of metal ions in the solution is taken equal to their molarities;

But at STP conditions, $R = 8.314 JK^{-1}mol^{-1}$; $T = 298K$; $F = 96500$ coulomb charge.

Then the Nernst equation becomes

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

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

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

Applications:

Nernst equation enables us to calculate the following:

1. Half cell potential or single electrode potential.

2. Cell potential or EMF of the cell.

3. Equilibrium constant for the cell reaction.

REFERENCE ELECTRODES

The electrode of standard potential with which we can compare the potentials of an other electrodes is called a reference electrode. The best reference electrode used is standard hydrogen electrode whose electrode potential at all temperature is taken as zero.

STANDARD HYDROGEN ELECTRODE (S.H.E)

S.H.E is a primary reference electrode. S.H.E consists of a platinum electrode coated with Pt-black immersed in 1 Molar solution of H^{+} ions maintained at $25^{o}C$. Hydrogen gas at 1atm pressure is constantly bubbled into the glass hood over the Pt-electrode. Hydrogen gets oxidized at the Pt-electrode and passes into the solution forming H^{+} ions and electrons. The standard electrode potential of Hydrogen electrode at these conditions is considered as zero. Depending upon the half cell to which it is combined, hydrogen electrode can act as either anode or cathode.
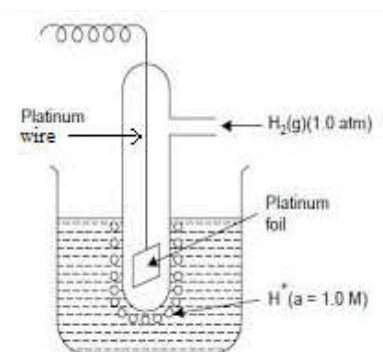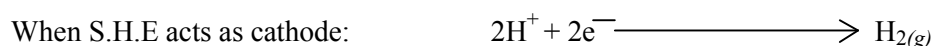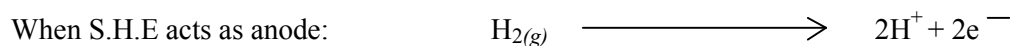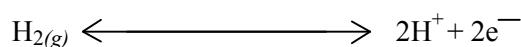

Figure: Standard Hydrogen Electrode.

When S.H.E acts as anode: $H_{2(g)} \longrightarrow 2H^{+} + 2e^{-}$

When S.H.E acts as cathode: $2H^{+} + 2e^{-} \longrightarrow H_{2(g)}$

Therefore S.H.E is regarded as reversible electrode. $H_{2(g)} \longleftrightarrow 2H^{+} + 2e^{-}$

Application:

Determination of pH for the unknown solution:
For a Hydrogen electrode at 298K, the Nernst equation is given as follows:

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2} H_{2(g)}$$

$$E_{Cell} = E° - \frac{2.303RT}{nF} \log \frac{[H_2]^{1/2}}{[H^+]}$$
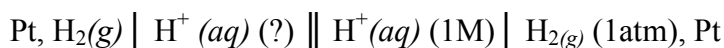
$$E_{Cell} = - \frac{0.0592}{nF} \log \frac{1}{[H^+]}$$

$(\because [H_2]^{1/2} = 1$ and $E° = 0)$

$$E_{Cell} = - 0.0592 (-\log[H^+])$$

$$E_{Cell} = - 0.0592 \, pH$$

In order to determine the pH of an unknown solution, a Pt-electrode is immersed into the solution and connected to S.H.E.

Cell representation:

Pt, $H_{2(g)}$ | H^+ (aq) (?) || H^+(aq) (1M) | $H_{2(g)}$ (1atm), Pt

$$E_{Cell} = E_{cathode} - E_{anode}$$
$$E_{Cell} = E_{S.H.E} - E_{H_2/H^+}$$
$$E_{Cell} = 0 - (-0.0592pH)$$
$$E_{Cell} = 0.0592pH$$
$$pH = \frac{E_{Cell}}{0.0592}$$

STANDARD CALOMEL ELECTRODE

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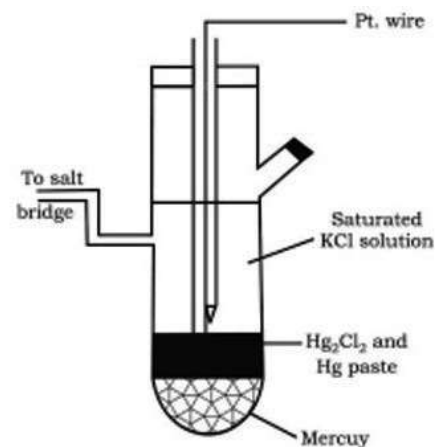

Figure: Std Calomel Electrode

The electrode is connected with the help of side tube on the left through salt bridge with the other electrode whose potential has to be determined. The potential of the calomel electrode depends upon the concentration of KCl.

Concentration of KCl	0.1N	1.0N	Saturated
Electrode potential (V)	0.3335	0.2810	0.2422

Representation of calomel electrode: Hg, $Hg_2Cl_{2(s)}$ | KCl (saturated solution)

Application:

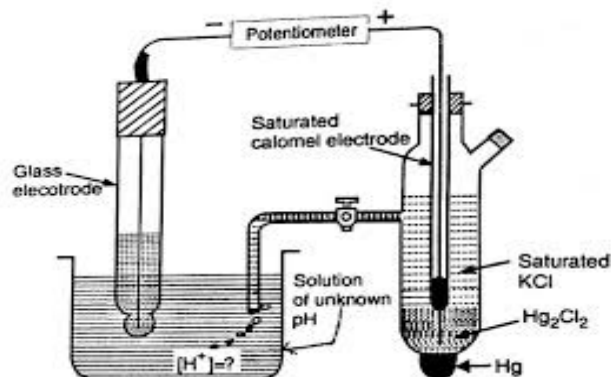Determination of pH of unknown solution by Saturated Calomel electrode:

Cell representation: Pt, H_2 (1atm) │ H^+ (?) ‖ KCl (*saturated*) Hg_2Cl_2 │ Hg

$$E_{Cell} = E_{Calomel} - E_{H_2/H^+}$$
$$E_{Cell} = 0.2422 - (-0.0592pH)$$
$$E_{Cell} = 0.2422 + 0.0592pH$$
$$pH = \frac{E_{Cell} - 0.2422}{0.0592}$$

ION SELECTIVE ELECTRODES

They possess an ability to respond to only certain specific ions thereby developing a potential with respect to that species only in a given mixture and ignore all the other ions totally. The potential developed by ion selective electrode depends on the concentration of specific ion of interest.

Eg.　Glass electrode specific for H^+ ions

Pressed pallet of Ag_2S + AgCl specific for Cl^- ions.

GLASS ELECTRODE

When two solutions of different pH values are separated by a thin glass membrane, a potential difference develops between the two surfaces of the membrane. This potential difference developed is proportional to the difference in pH value. The glass membrane functions as ion-exchange resin. An equilibrium is established between Na^+ ions of the glass and H^+ ions in the solution. The potential of the glass electrode is given by,

$$EG = E_oG + 0.0592 \text{ pH}$$

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

Cell representation of glass electrode is given by

Ag │ AgCl(s) H+ (0.1M) │ Glass or Pt, HCl (0.1M)│ Glass

HCl in the bulb furnishes constant H+ ion concentration.

Thus it is Ag-AgCl electrode reversible with respect to Cl- ions.
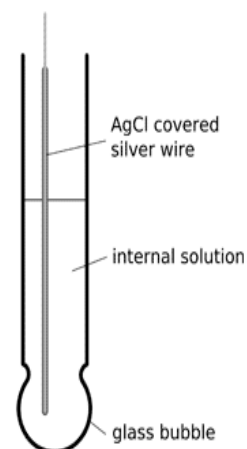
It is used as internal reference electrode for determining the pH of the solution especially the colored solution containing oxidizing or reducing agents.

Determination of pH of unknown solution by Quinhydrone electrode:

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

Cell representation: Pt, H_2Q | Q, H+ ‖ KCl (sat) Hg_2Cl_2(s) | Hg

$$E_{Cell} = E°_{Calomel} - E°_{Glass}$$
$$E_{Cell} = 0.2422 - [E°_{Glass} + 0.0592pH]$$
$$E_{Cell} = \frac{0.2422 - E_{Cell} - E°_{Glass}}{0.0592}$$

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

POTENTIOMETRIC TITRATIONS

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

1. Acid-Base Titrations:

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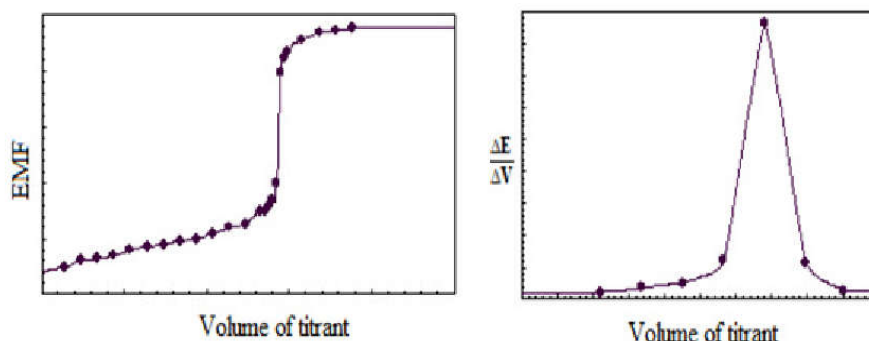
2. Redox titrations:

The EMF of the electrode is determined by the activity of ratio of the substance being oxidized or reduced. For example Fe^{2+} titrated against $K_2Cr_2O_7$. Ferrous iron solution is taken in the beaker and treated with dil. H_2SO_4. Platinum electrode and calomel electrode are dipped into the solution and they are connected to the potentiometer. The EMF of the solution after the addition of $K_2Cr_2O_7$ from burette is recorded. A graph is plotted with EMF and volume of $K_2Cr_2O_7$. The steep rise is the end point of the titration.

3. Precipitation reactions:

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

$$AgNO_3 + Cl^- \qquad\qquad AgCl (ppt) + NO_3^-$$

4. Determination of pH:

The EMF of a solution depends on the concentration of H+ ions or pH of the solution. A hydrogen electrode containing solution of unknown pH is paired with a standard calomel electrode.

Pt, H_2 (1 atm) / H^+ (unknown) // KCl (saturated) / Hg_2Cl_2, Hg
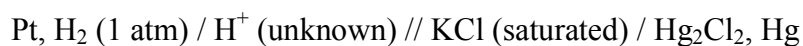
The EMF of this cell is measured by potentiometer and the pH of the unknown solution can be determined.

$$E_{cell} = E_{right} - E_{left} \qquad or$$
$$E_{cell} = 0.2415 - (-0.0591 \times pH)$$
$$E_{cell} = 0.2415 + 0.0591 \times pH$$

Advantages:

1. Colored solutions where the use of indicator is impossible are estimated by potentiometric titrations.

2. Solutions more than one halide can be analyzed in a single titration against silver nitrate.

CONDUTOMETRIC TITRATIONS:

Titrations involving conductivity measurements of electrolytes to get endpoint are called conductometric titrations. The end point is generally found out by plotting the conductance values on y-axis against the volume of electrolyte on x-axis.
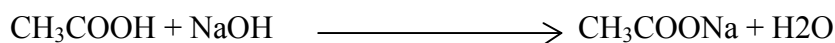
1. Strong acid Vs Strong base titrations:

In an acid–base titration, acid is taken in the conical flask and base is added through the burette. Consider the titration of strong acid (HCl) with strong base (NaOH). Before the addition of NaOH, the conductivity is mainly due to the H+ ions; hence the conductivity is high. On the gradual addition of NaOH from the burette, the fast moving H+ ions of acid are replaced by OH- ions. The conductivity of the solution decreases progressively by the addition of NaOH till the equivalence point is reached. The conductance again increases after the equivalence point.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$
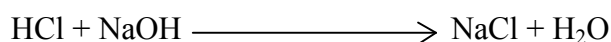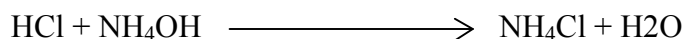
2. Weak acid Vs Strong base titration:

When weak acid is titrated with strong base, the conductance of the solution is low in the beginning, since the dissociation of weak acid is very low. On addition of base, highly dissociated sodium acetate is

formed. Due to the common ion effect, the acetate ion tends to suppress the ionization of acetic acid. Later the conductivity begins to increase due to the conductivity power of the highly ionized salt exceeds that of weak acid. After end point, the addition of NaOH contributes sharp increase in the conductivity of the solution. The point of intersection of the two cures gives the end point of the titration.

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H2O$$

3. Strong acid Vs weak base titrations:

When strong acid is titrated against a weak base, the conductance of the solution first decrease due to the replacement of fast moving H^+ ions with slow moving NH4+ ions. After the end point, the addition of excess of NH4OH will not result in any appreciable change in the conductivity.

$$HCl + NH_4OH \longrightarrow NH_4Cl + H2O$$

4. Weak acid Vs weak base Titration:

Consider the titration of acetic acid against ammonium hydroxide. The titration of weak acid with weak base does not give sharp end point by volumetric titrations. The initial conductance of the solution is low due to the poor dissociation of weak acid, but starts raising as CH_3COONH_4 is formed. After the equivalent point, the conductivity remains almost constant because the free base NH4OH is weak electrolyte. The end point is quite sharp by conductometric titrations

$$CH_3COOH + NH_4OH \longrightarrow CH_3COONH_4 + H_2O$$
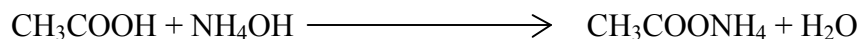
5. Precipitation titrations:
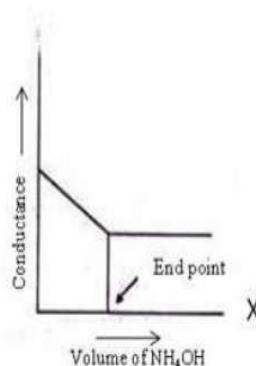
In precipitation titrations, sharp endpoint is obtained, e.g. The titration of KCl against AgNO3. There is no sharp increase in conductance after the addition of AgNO3, because the mobility of K+ and Ag + is one and the same. After the end point, there is a sharp increase in conductance due to an increase in the number of free ions in the solution.
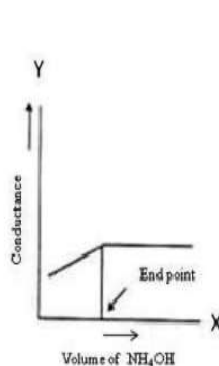
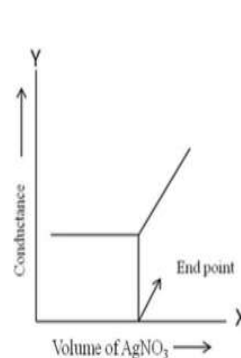$$KCl + AgNO_3 \longrightarrow KNO_3 + AgCl \text{ (ppt)}$$
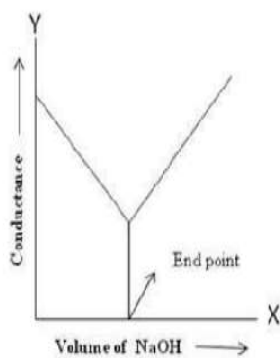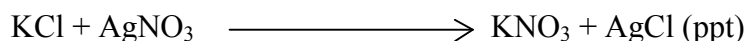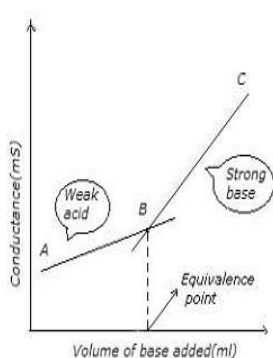
Fig 1   Fig 2   Fig 3   Fig 4   Fig 5

Advantages of conductometric titrations:

- The results obtained by conductometric titrations are more accurate because the end point is obtained graphically.

- The titrations of a weak acid with a weak base do not give a sharp end point with indicator in volumetric titrations. Accurate results are obtained in conductometric titrations.

- Colored solutions where no indicator is found to work satisfactorily can be successfully titrated.

- Conductometric titrations can be used even in case of polybasic acids.

Precautions:

- The temperature must be kept constant throughout the experiment.

- In acid–base titration, the titrant should be about 10 times stronger than the solution to be titrated so that the volume change is as little as possible.

BATTERIES

A battery is an electrochemical cell (or enclosed and protected material) that can be charged electrically to provide a static potential for power or released electrical charge when needed. A battery generally consists of an *anode*, a *cathode,* and an *electrolyte.* Common types of commercial batteries and some of their characteristics and advantages are summarized in the following table. Battery types not shown include the Zinc-Air, Flooded Lead Acid, and Alkaline batteries.

Battery types

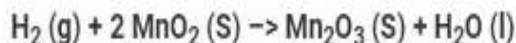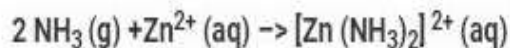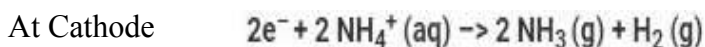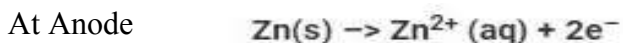Batteries can be broadly divided into two major types.

- Primary Cell (or) Primary battery
- Secondary Cell (or) Secondary battery

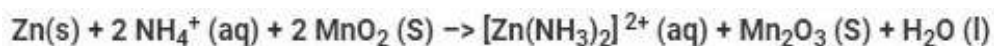**Primary Cell (or) Primary battery**

These are batteries where the redox reactions proceed in only one direction. The reactants in these batteries are consumed after a certain period of time, rendering them dead. A primary battery cannot be used once the chemicals inside it are exhausted.

An example of a primary battery is the dry cell – the household battery that commonly used to power TV remotes, clocks, and other devices. In such cells, a zinc container acts as the anode and a carbon rod acts as the cathode. A powdered mixture of manganese dioxide and carbon is placed around the cathode. The space left in between the container and the rod is filled with a moist paste of ammonium chloride and zinc chloride.

The redox reaction that takes place in these cells is:

At Anode $\quad\quad Zn(s) \rightarrow Zn^{2+} (aq) + 2e^-$

At Cathode $\quad 2e^- + 2\,NH_4^+\,(aq) \rightarrow 2\,NH_3\,(g) + H_2\,(g)$

$\quad\quad\quad\quad\quad 2\,NH_3\,(g) + Zn^{2+}\,(aq) \rightarrow [Zn\,(NH_3)_2]^{2+}\,(aq)$

$\quad\quad\quad\quad\quad H_2\,(g) + 2\,MnO_2\,(S) \rightarrow Mn_2O_3\,(S) + H_2O\,(l)$

Thus, the overall cell equation is:

$$Zn(s) + 2\,NH_4^+\,(aq) + 2\,MnO_2\,(S) \rightarrow [Zn(NH_3)_2]^{2+}\,(aq) + Mn_2O_3\,(S) + H_2O\,(l)$$
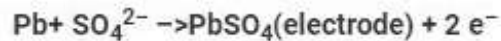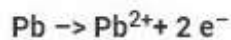
Another example of the primary cell is the mercury cell, where a zinc-mercury amalgam is used as an anode and carbon is used as a cathode. A paste of HgO is used as an electrolyte. These cells are used only in devices that require a relatively low supply of electric current (such as hearing aids and watches).

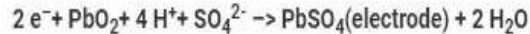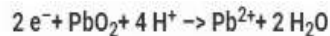**Secondary Cell (or) Secondary battery**

These are batteries that can be recharged after use by passing current through the electrodes in the opposite direction, i.e. from the negative terminal to the positive terminal.

For example, a lead storage battery that is used in automobiles and inverters can be recharged a limited number of times. The lead storage battery consists of a lead anode and the cathode is a lead grid packed with lead dioxide. Sulphuric acid with a concentration of 38% is used as an electrolyte. The oxidation and reduction reactions involved in this process are listed below.

At Anode

$$Pb \rightarrow Pb^{2+} + 2\,e^-$$

$$Pb + SO_4^{2-} \rightarrow PbSO_4(electrode) + 2\,e^-$$

At Cathode

$$2\,e^- + PbO_2 + 4\,H^+ \rightarrow Pb^{2+} + 2\,H_2O$$

$$2\,e^- + PbO_2 + 4\,H^+ + SO_4^{2-} \rightarrow PbSO_4(electrode) + 2\,H_2O$$

In order to recharge these batteries, the charge is transferred in the opposite direction and the reaction is reversed, thus converting $PbSO_4$ back to Pb and PbO_2.

Another example of the secondary cell is the nickel-cadmium cell. These cells have high storage capacities and their lifespan is relatively long (compared to other secondary cells). However, they are difficult to manufacture and maintain.

Lead acid storage cell

- A lead acid storage cell is a secondary battery, which can operate both as a voltaic cell and as an electrolytic cell. When it act as a voltaic cell, it supplies electrical energy and becomes run down. When it is recharged the cell operates as an electrolytic cell.
- A lead acid storage connected in battery consists of a number (3-6) voltaic cell to get 12V Battery. Here lead act as anode and PbO_2 act as cathode. A number of Pb and PbO_2 plates connected in parallel separated by rubber and glass immersed in dil.H2SO4 (38% by mass having a density of 1.30 gm/ml.

The cell may be represented as;

$$Pb \mid PbSO_4 \mid\mid H_2SO_4 \, _{(aq)} \mid PbO_2 \mid Pb$$

At anode: Lead is oxidized to Pb^{2+} ions, which further combines with SO_4^{2-} forms insoluble $PbSO_4$.

$$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \xrightleftharpoons[\text{charging}]{\text{discharging}} PbSO_{4\ (s)} + 2e^-$$
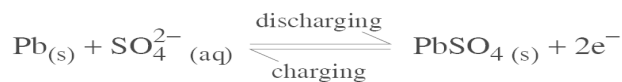
At cathode: PbO_2 is reduced to Pb^{2+} ions, which further combines with SO_4^{2-} forms insoluble $PbSO_4$.

$$PbO_{2\ (s)} + 4H^+ + SO_4^{2-} + 2e^- \xrightleftharpoons[\text{charging}]{\text{discharging}} PbSO_{4\ (s)} + 2H_2O$$
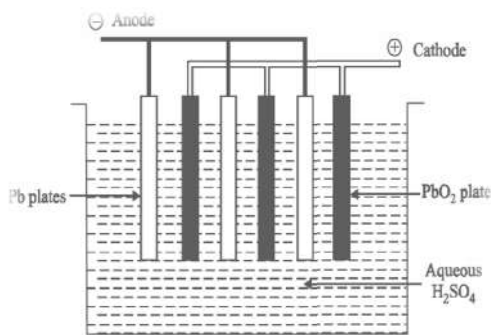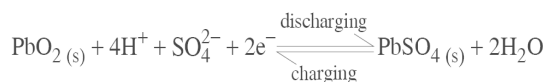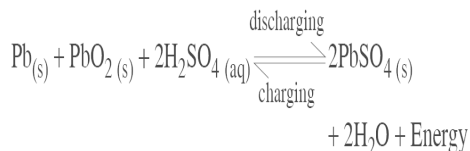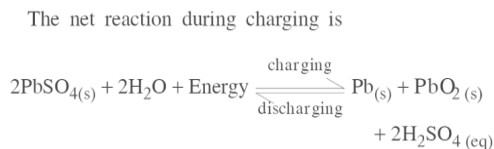

Fig. 6.2. Lead storage cell

As a result, the concentration of H_2SO_4 decreases and hence the density of H_2SO_4 falls below 1.2 gm/ml needs recharging.

Net reaction during discharging

$$Pb_{(s)} + PbO_{2\ (s)} + 2H_2SO_{4\ (aq)} \xrightleftharpoons[\text{charging}]{\text{discharging}} 2PbSO_{4\ (s)} + 2H_2O + Energy$$

Net reaction during charging

The net reaction during charging is

$$2PbSO_{4(s)} + 2H_2O + Energy \xrightleftharpoons[\text{discharging}]{\text{charging}} Pb_{(s)} + PbO_{2\ (s)} + 2H_2SO_{4\ (eq)}$$

Advantage

(i)   It is made easily.
(ii) It produces very high current.
(iii) The self-discharging rate is low when compared to other rechargeable batteries.
(iv) It also acts effectively at low temperature.

Uses

1. Lead storage cell is used to supply current mainly in automobiles such as cars, buses, trucks, etc.,

2. It is also used in gas engine ignition, telephone exchanges, hospitals, power stations, etc.,

Lithium battery

Lithium battery is a solid state battery because instead of liquid or a paste electrolyte, solid electrolyte is used.

When the electrolyte is connected to cathode, lithium ions moving from the anode to cathode are separated by polymers permits flow of ions and not electrons. The anode is elemental lithium and TiS_2 and elemental lithium which is the source of the lithium ions and electrons.

At anode: $Li(s) \rightarrow Li^+ + e^-$

At cathode: $TiS_{2(s)} + e^- \rightarrow TiS_2^-$

Overall reaction:

$$Li(s) + TiS_{2(s)} \rightarrow Li^+ + TiS_2^-$$

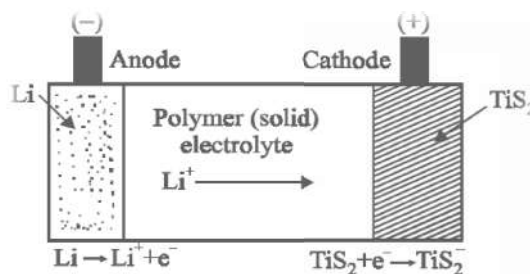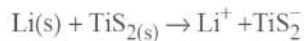$$Li^+ + TiS_2^- \rightarrow LiTiS_2$$

Fig. 6.3 Solid state lithium battery

Recharging Battery

The lithium battery can be recharged by supplying an external current, which drives the lithium ions back to the anode. The overall reaction is

$$LiTiS_2 \longrightarrow Li^+ + TiS_2^-$$

➡ **This cell is rechargeable and produces a cell voltage of 3.0 V.**

Advantage:

(i) Its cell voltage is high, 3.0 V.

(ii) Since Li is a light-weight metal, only 7g (1 mole) material is required to produce 1 mole of electrons.

(iii) Since Li has the most negative $E°$ value, it generates a higher voltage than the other types of cells.

Fuel Cells

Fuel cell is a voltaic cell, which converts the chemical energy of the fuels directly into electricity without combustion. It converts the energy of the fuel directly into electricity. In these cells, the reactants, products and electrolytes pass through the cell.

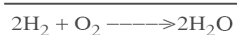Fuel + Oxygen $\longrightarrow$ Oxidation products + Electricity .

Hydrogen-oxygen fuel cell:

Hydrogen-oxygen fuel cell is the simplest and most successful fuel cell, in which the fuel-hydrogen and the oxidiser-oxygen and the liquid electrolyte are continuously passed through the cell.
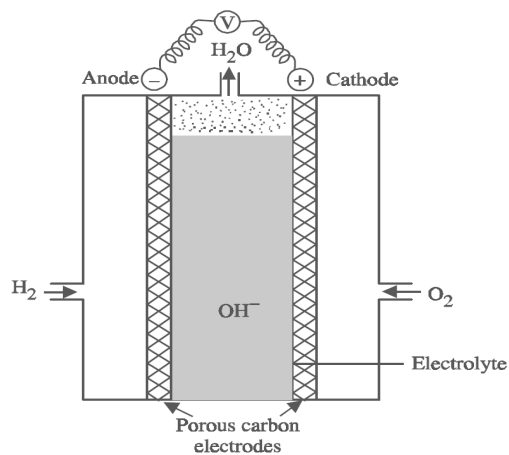

1. Description

It consists of two porous electrodes anode and cathode. These porous electrodes are made of compressed carbon containing a small amount of catalyst (Pt, Pd, Ag). In between the two electrodes an electrolytic solution such as 25% KOH or NaOH is filled. The two electrodes are connected through the volt meter.

2. Working

Hydrogen (the fuel) is bubbled through the anode compartment, where it is oxidised. The oxygen (oxidiser) is bubbled through the cathode compartment, where it is reduced.

4. Advantage

1. H_2-O_2 fuel cells are used as auxiliary energy source in space vehicles, submarines or other military-vehicles.

2. In case of H_2-O_2 fuel cells, the product of water is proved to be a valuable source of fresh water by the astronauts.

3. Overall reactions:

At anode: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

At cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

➡ **The emf of the cell = 0.8 to 1.0 V**

CORROSION

INTRODUCTION

Corrosion is a 'billion' dollar thief'. Even though it is a natural phenomenon in which the gases, moisture and other chemicals present in the atmosphere react chemically with metals to convert them into their salts, it results in loss of material and money. We know very well that metals have a strong crystalline structure and when they are converted into their salts they lose the metallic strength resulting in the damage to machineries in which they are used. Thus corrosion causes damage to metals and thereby to the society. The estimate of loss due to corrosion is approximately 2.5 billion dollars per annum all over the world. Hence it is necessary to understand the mechanism of corrosion.

In this lesson we are going to study about the causes and the mechanism of corrosion so that we can find ways to prevent this social enemy.

Corrosion is defined as the slow and continuous destruction of metal or alloy by the environment.

Due to corrosion the useful properties of a metal like malleability, ductility, electrical conductivity and also the surface appearance are lost.

The most familiar example of corrosion is rusting of iron when exposed to atmospheric conditions.

Another example is the formation of green film or basic Carbonate $[CuCO_3+Cu(OH)_2]$ on the surface of copper when exposed to moist air containing CO_2 and oxygen.

Definition

Corrosion is defined as the slow and continuous destruction of metal or alloy due to the chemical or electrochemical reaction with its environment.
It may be due to chemical or electrochemical reaction of the metals with the environment.
Example: Rusting of iron.

Causes of corrosion:

Metal occur in nature in two different forms. They are

1. Native state

2. Combined state.

1.Native state:

The metals occur in native, free, uncombined states or **pure metal are highly stable and non-reactive with the environment.** They do not combine with other elements. They are noble metals exist as such in the earth crust. They have very good corrosion resistance.

Ex. Au, Pt, Ag, Pd, Cu etc,

2.Combined state

Except noble metal, all other metals are reactive and form stable compounds as their oxides, sulphides, chloride and carbonates. They exist in the form of stable compounds called ores or mineral.
Ex.FeO_2.ZnO, PbS,$CaCO_3$ etc.,

Except noble metal, the other metals in the pure state are thermodynamically **unstable** as they are considered in excited state ie., higher energy state. Therefore, as soon as the metals are extracted from their ores, the reverse process begins and form stable **metallic compounds**, which are thermodynamically stable, i.e., lower energy state.

$$\text{Corrosion(oxidation)}$$
$$\text{Metal (unstable)} \underset{\longleftarrow}{\overset{\longrightarrow}{}} \text{Metallic Compound (stable)}$$
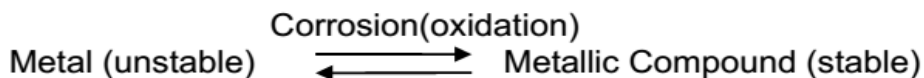
Higher energy Metallurgy(Reduction)   lower energy state
The properties such as electrical conductivity, ductility, malleability etc., are lost due to corrosion.

Types of Corrosion:

Corrosion is of two types.
1. Chemical Corrosion or Dry Corrosion
2. Electrochemical Corrosion or Wet Corrosion

1. Chemical Corrosion or Dry Corrosion

The direct chemical action of atmospheric gases like oxygen, halogens, H_2S etc., in a dry environment on metals is known as chemical Corrosion. Due to this, a dry layer of the Corrosion product is formed on the surface of the metal.

Example:

When magnesium is exposed to atmosphere, magnesium oxide is formed over the surface.

$$2Mg+O_2 \longrightarrow 2MgO$$

A solid film of the corrosion product is formed on the surface of the metal which protects the metal from further corrosion. If a soluble or volatile corrosion product is formed, then the metal is exposed to further attack.

For example, chlorine attack silver generating a protective film of silver halide on the surface which prevents the further corrosion.

$$2Ag + Cl_2 \longrightarrow 2AgCl$$

On the other hand, stannic chloride formed on tin is volatile and so corrosion is not prevented.

2. Electro Chemical Corrosion or wet corrosion

Wet corrosion

Wet corrosion occurs due to the electrochemical action of moisture and oxygen on metals. Corrosion of iron takes place due to electrochemical attack.

There are two theories to explain the rusting of iron.

1. Galvanic cell formation theory

2. Differential aeration theory.

1. Galvanic cell formation theory

Definition

"When a metal with impurities (or two dissimilar metals (Fe and Cu) are in contact with each other) is exposed to atmosphere in presence of an electrolyte or moisture, a mini galvanic cell is formed. The more anodic metal undergoes corrosion. This type of corrosion is known as galvanic corrosion".

Example: Rusting of iron

Corrosion is an oxidation process. Oxidation is a process which involves loss of electron. Oxidation takes place at **anode**.
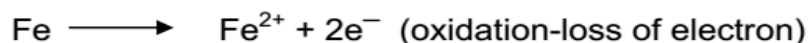
When iron metal with small amount impurities (Cu) is placed in the environment is exposed to the environment (moisture), it undergoes corrosion. Hence it acts as anode and under goes Oxidation. Iron metal loses its two electrons and becomes Fe^{+2}ion. Hence the iron metal undergoes oxidation when it is corroded.
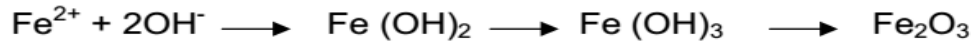
The impurities present in the metal act as **cathode** and undergo reduction. The electron released at anode is absorbed at cathode to form either Hydrogen or water or hydroxide ion depending on the environment. The moisture in the environment behaves like **electrolyte**. **Hence a galvanic cell is formed.**

Rusting of iron is explained as below.

Anodic reaction (oxidation)

The metal at the anode is oxidised into ferrous ions.

$$Fe \longrightarrow Fe^{2+} + 2e^- \text{ (oxidation-loss of electron)}$$

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \longrightarrow Fe(OH)_3 \longrightarrow Fe_2O_3$$

Fe^{2+} ions combine with OH^- in the environment forming ferrous hydroxide Fe $(OH)_2$, which under goes further oxidation to give ferric hydroxide Fe $(OH)_3$ the ferric hydroxide undergoes decomposition to give ferric oxide Fe_2O_3(Rust).

Thus rust formed is explained based on the theory of Galvanic cell formation.

Electrolyte

The moisture (H_2O) in the environment act as electrolyte. It dissociates to give H+ and OH^- ions.

$$H_2O \longrightarrow H^+ + OH^-$$
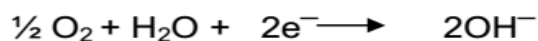
Cathodic reaction (Reduction)

The electrons released at anode are taken up by the H+ ion in the environment.

      (i) In acidic medium(reduction-gain of electron)

$$2H^+ + 2e^- \longrightarrow H_2 \text{ (gas)} \uparrow$$

      (ii) In neutral solution with oxygen

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

The ferric oxide formed (Fe_2O_3) over iron is called as Rusting of iron.

Examples:

1.   Corrosion of soldered metal around copper wire.
2.   Corrosion of steel shaft in bronze bearing.
3.   Corrosion of steel pipe connected to copper plumbing.

Differential aeration theory or concentration cell formation theory

According to this theory, when a metal is exposed to varying concentrations of air (oxygen) or an electrolyte, concentration cell is formed. The metallic area which is exposed to less amount of oxygen act as anode undergoes corrosion.

The metallic area which is exposed to greater amount of oxygen act as cathode. Corrosion of metal occurs due to difference in concentration of air or electrolyte. **Hence this theory is called as Differential aeration theory or concentration cell formation theory.**

Example:

1. Corrosion on wire fence

In an iron fence the point where wires cross is less exposed to oxygen and becomes anode. Therefore corrosion takes place at the point of contact where the wire crosses.
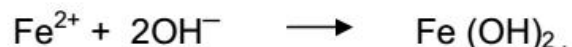
2. Metal partially immersed in water, the immersed portion is less exposed to oxygen and becomes anode. Therefore corrosion takes place.

3. Metal area covered by drop of water, sand or dust.

The less oxygenated area acts as Anode (gets corroded)
The more oxygenated area acts as the Cathode (Protected from Corrosion).
Reaction At anode- (less oxygenated area)-oxidation-loss of electron-corrosion takes place.

$$Fe \longrightarrow Fe^{2+} + 2e^- \text{ (oxidation or corrosion)}$$
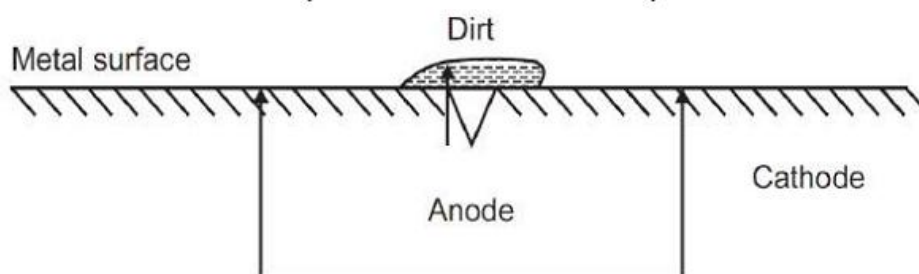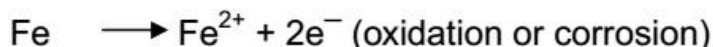
At cathode (more oxygenated area)

$$\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^- \text{ (Reduction)}$$

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

Which is further oxidized to $Fe(OH)_3$ .Since the anodic area is small and the cathodic area is large, corrosion is more concentrated at the anode. Thus, a small hole is formed on the surface of the metal. This type of intense localized corrosion is called pitting.