Chapter
12
Electrochemistry

Electrochemistry is the branch of physical chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reactions

Electrolytes and Electrolysis

(1) **Definition :** "*The substances whose aqueous solution undergo decomposition into ions when electric current is passed through them are known as **electrolytes** and the whole process is known as **electrolysis** or **electrolytic decomposition**.*"

Solutions of acids, bases, salts in water and fused salts etc. are the examples of electrolytes. Electrolytes may be **weak** or **strong**. Solutions of cane sugar, glycerine, alcohol etc., are examples of ***non-electrolytes***.

(2) **Electrolytic cell or Voltameter :** The device in which the process of electrolysis or electrolytic decomposition is carried out is known as ***electrolytic cell*** or ***voltameter***.

(i) Voltameter convert ***electrical energy into chemical energy***.

(ii) The electrode on which oxidation takes place is called ***anode*** (or +ve pole) and the electrode on which reduction takes place is called ***cathode*** (or –ve pole)

(iii) During electrolysis in voltameter ***cations are discharged on cathode*** and ***anions on anode***.

(iv) In voltameter, outside the ***electrolyte*** electrons flow from ***anode to cathode*** and ***current*** flow from ***cathode to anode***.

For voltameter, E_{cell} = –ve and ΔG = +ve.

Anode $\xrightarrow{\text{Flow of electrons}}$ Cathode

$\xleftarrow{\text{Flow of current}}$

(v) The anions on reaching the anode give up their electrons and converted into the neutral atoms.

At anode : $A^- \longrightarrow A + e^-$ (Oxidation)

(vi) On the other hand cations on reaching the cathode take up electrons supplied by battery and converted to the neutral atoms.

At cathode : $B^+ + e^- \longrightarrow B$ (Reduction)

This overall change is known as ***primary change*** and products formed is known as ***primary products***.

The primary products may be collected as such or they undergo further change to form molecules or compounds. These are called ***secondary products*** and the change is known as ***secondary change***.

(3) **Preferential discharge theory :** According to this theory "*If more than one type of ion is attracted towards a particular electrode, then the ion is discharged one which requires least energy or ions with lower discharge potential or which occur low in the electrochemical series*".

The potential at which the ion is discharged or deposited on the appropriate electrode is termed *the **discharge or deposition potential**,* (D.P.). The values of discharge potential are different for different ions.

The decreasing order of discharge potential or the increasing order of deposition of some of the ions is given below,

For cations : $Li^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, Fe^{2+}, Ni^{2+}, H^+, Cu^{2+}, Hg^{2+}, Ag^+, Au^{3+}.$

For anions : $SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-.$

Table : 12.1 Products of electrolysis of some electrolytes

Electrolyte	Electrode	Product at cathode	Product at anode
Aqueous $NaOH$	Pt or Graphite	$2H^+ + 2e^- \rightarrow H_2$	$2OH^- \rightarrow \dfrac{1}{2}O_2 + H_2O + 2e^-$
Fused $NaOH$	Pt or Graphite	$Na^+ + e^- \rightarrow Na$	$2OH^- \rightarrow \dfrac{1}{2}O_2 + H_2O + 2e^-$
Aqueous $NaCl$	Pt or Graphite	$2H^+ + 2e^- \rightarrow H_2$	$2Cl^- \rightarrow Cl_2 + 2e^-$
Fused $NaCl$	Pt or Graphite	$Na^+ + e^- \rightarrow Na$	$2Cl^- \rightarrow Cl_2 + 2e^-$
Aqueous $CuSO_4$	Pt or Graphite	$Cu^{2+} + 2e^- \rightarrow Cu$	$2OH^- \rightarrow \dfrac{1}{2}O_2 + H_2O + 2e^-$
Aqueous $CuSO_4$	Cu electrode	$Cu^{2+} + 2e^- \rightarrow Cu$	Cu oxidised to Cu^{2+} ions
Dilute H_2SO_4	Pt electrode	$2H^+ + 2e^- \rightarrow H_2$	$2OH^- \rightarrow \dfrac{1}{2}O_2 + H_2O + 2e^-$
Conc. H_2SO_4	Pt electrode	$2H^+ + 2e^- \rightarrow H_2$	Peroxodisulphuric acid $(H_2S_2O_8)$
Aqueous $AgNO_3$	Pt electrode	$Ag^+ + e^- \rightarrow Ag$	$2OH^- \rightarrow \dfrac{1}{2}O_2 + H_2O + 2e^-$
Aqueous $AgNO_3$	Ag electrode	$Ag^+ + e^- \rightarrow Ag$	Ag oxidised to Ag^+ ions

(4) **Application of electrolysis :** Electrolysis has wide applications in industries. Some of the important applications are, as follows,

(i) Production of hydrogen by electrolysis of water.

(ii) Manufacture of heavy water (D_2O).

(iii) The metals like Na, K, Mg, Al, etc., are obtained by electrolysis of fused electrolytes.

(iv) Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.

(v) In this method pure metal is deposited at cathode from a solution containing the metal ions Ag, Cu etc.

(vi) Compounds like $NaOH$, KOH, Na_2CO_3, $KClO_3$, white lead, $KMnO_4$ etc. are synthesised by electrosynthesis method.

(vii) *Electroplating* : The process of coating an inferior metal with a superior metal by electrolysis is known as *electroplating*. The aim of electroplating is, to prevent the inferior metal from corrosion and to make it more attractive in appearance. The object to be plated is made the cathode of an electrolytic cell that contains a solution of ions of the metal to be deposited.

For electroplating	Anode	Cathode	Electrolyte
With copper	Cu	Object	$CuSO_4$ + dilute H_2SO_4
With silver	Ag	Object	$K[Ag(CN)_2]$
With nickel	Ni	Object	Nickel ammonium sulphate
With gold	Au	Object	$K[Au(CN)_2]$
With zinc	Zn	Iron objects	$ZnSO_4$
With tin	Sn	Iron objects	$SnSO_4$

Thickness of coated layer : Let the dimensions of metal sheet to be coated be $(a\, cm \times b\, cm)$.

Thickness of coated layer $= c\, cm$

Volume of coated layer $= (a \times b \times c)\, cm^3$

Mass of the deposited substance $=$ Volume $\times$ density

$= (a \times b \times c) \times d\, g$

$\therefore\ (a \times b \times c) \times d = \dfrac{I \times t \times E}{96500}$

Using above relation we may calculate the thickness of coated layer.

Faraday's laws of electrolysis

The laws, which govern the deposition of substances (In the form of ions) on electrodes during the process of electrolysis, is called *Faraday's laws of electrolysis.* These laws given by *Michael Faraday in 1833*.

(1) **Faraday's first law :** It states that,

"*The mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed.*"*i.e.,* $W \propto Q$

Where,

$W =$ Mass of ions liberated in *gm*,

$Q =$ Quantity of electricity passed in Coulombs

$=$ Current in Amperes $(I) \times$ Time in second (t)

$\therefore\ W \propto I \times t$ or $W = Z \times I \times t$

In case current efficiency (η) is given, then

$$W = Z \times I \times t \times \dfrac{\eta}{100}$$

where, $Z =$ constant, known as *electrochemical equivalent* (ECE) of the ion deposited.

When a current of 1 Ampere is passed for 1 second (*i.e.,* $Q = 1$), then, $W = Z$

Thus, *electrochemical equivalent* (ECE) may be defined as "*the mass of the ion deposited by passing a current of one Ampere for one second (i.e., by passing Coulomb of electricity)*". It's unit is gram per coulomb.

Coulomb is the unit of electrical charge.

$96500\ Coulombs = 6.023 \times 10^{23}\ electrons = 1\ mole\ electrons.$

$1\ Coulomb = \dfrac{6.023 \times 10^{23}}{96500} = 6.28 \times 10^{18}\ electrons,$

or $1\ electronic\ charge = 1.6 \times 10^{-19}\ Coulomb.$

(2) **Faraday's second law :** It states that,

"*When the same quantity of electricity is passed through different electrolytes, the masses of different ions liberated at the electrodes are directly proportional to their chemical equivalents (Equivalent weights).*" *i.e.,*

$\dfrac{W_1}{W_2} = \dfrac{E_1}{E_2}$ or $\dfrac{Z_1 It}{Z_2 It} = \dfrac{E_1}{E_2}$ or $\dfrac{Z_1}{Z_2} = \dfrac{E_1}{E_2}$ $(\because W = ZIt)$

Thus the electrochemical equivalent (Z) of an element is directly proportional to its equivalent weight (E), *i.e.,*

$E \propto Z$ or $E = FZ$ or $E = 96500 \times Z$

where, $F =$ Faraday constant $= 96500\ C\, mol^{-1}$

So, 1 Faraday $= 1F =$ Electrical charge carried out by one mole of electrons.

$1F =$ Charge on an electron $\times$ Avogadro's number.

$1F = e^- \times N = (1.602 \times 10^{-19}\ c) \times (6.023 \times 10^{23}\ mol^{-1})$.

Number of Faraday $= \dfrac{\text{Number of electrons passed}}{6.023 \times 10^{23}}$

(3) **Faraday's law for gaseous electrolytic product** For the gases, we use

$$V = \dfrac{It\, V_e}{96500}$$

where, $V =$ Volume of gas evolved at *S.T.P.* at an electrode

$V_e =$ Equivalent volume $=$ Volume of gas evolved at an electrode at *S.T.P.* by 1 Faraday charge

(4) **Quantitative aspects of electrolysis :** We know that, one Faraday $(1F)$ of electricity is equal to the charge carried by one mole (6.023×10^{23}) of electrons. So, in any reaction, if one mole of electrons are involved, then that reaction would consume or produce $1F$ of electricity. Since $1F$ is equal to 96,500 Coulombs, hence 96,500 Coulombs of electricity would cause a reaction involving one mole of electrons.

If in any reaction, n moles of electrons are involved, then the total electricity (Q) involved in the reaction is given by,

$Q = nF = n \times 96,500\ C$

Thus, the amount of electricity involved in any reaction is related to,

(i) The number of moles of electrons involved in the reaction,

(ii) The amount of any substance involved in the reaction.

Therefore, 1 Faraday or 96,500 C or 1 mole of electrons will reduce,

(a) 1 mole of monovalent cation,(b) 1/2mole of divalent cation,

(c) 1/3 mole of trivalent cation,   (d) 1/n mole of n valent cations.

Metallic and Electrolytic conductors

All substances do not conduct electrical current. The substances, which allow the passage of electric current, are called **conductors**. The best metal conductors are such as copper, silver, tin, etc. On the other hand, the substances, which do not allow the passage of electric current through them, are called **non-conductors or insulators**. Some common examples of insulators are rubber, wood, wax, etc.

The conductors are broadly classified into two types,
Metallic and electrolytic conductors.

Metallic conduction	Electrolytic conduction
(i) It is due to the flow of electrons.	(i) It is due to the flow of ions.
(ii) It is not accompanied by decomposition of the substance.(Only physical changes occurs)	(ii) It is accompanied by decomposition of the substance. (Physical as well as chemical change occur)
(iii) It does not involve transfer of matter.	(iii) It involves transfer of matter in the form of ions.
(iv) Conductivity decreases with increase in temperature.	(iv) Conductivity increases with increases in temperature and degree of hydration due to decreases in viscosity of medium.

The electrolyte may, therefore, be defined as the substance whose aqueous solution or fused state conduct electricity accompanied by chemical decomposition. The conduction of current through electrolyte is due to the movement of ions.

On the contrary, substances, which in the form of their solutions or in their molten state do not conduct electricity, are called non-electrolytes.

Electrolytic conduction

When a voltage is applied to the electrodes dipped into an electrolytic solution, ions of the electrolyte move and, therefore, electric current flows through the electrolytic solution. The power of the electrolytes to conduct electric current is termed *conductance* or *conductivity*.

(1) **Ohm's law :** This law states that the current flowing through a conductor is directly proportional to the potential difference across it, *i.e.,* $I \propto V$

where I is the current strength (In Amperes) and V is the potential difference applied across the conductor (In Volts)

or $I = \dfrac{V}{R}$ or $V = IR$

where R is the constant of proportionality and is known as resistance of the conductor. It is expressed in Ohm's and is represented as Ω. The above equation is known as Ohm's law. Ohm's law may also be stated as,

"*the strength of current flowing through a conductor is directly proportional to the potential difference applied across the conductor and inversely proportional to the resistance of the conductor.*"

(2) **Resistance** : *It measures the obstruction to the flow of current*. The resistance of any conductor is directly proportional to the length (l) and inversely proportional to the area of cross-section (a) so that

$$R \propto \dfrac{l}{a} \quad \text{or} \quad R = \rho \dfrac{l}{a}$$

where ρ (rho) is the constant of proportionality and is called specific resistance or resistivity. The resistance depends upon the nature of the material.

Units : The unit of resistance is ohm (Ω). In terms of SI, base unit is equal to $(kgm^2)/(s^3 A^2)$.

(3) **Resistivity or specific resistance :** We know that resistance R is

$$R = \rho \dfrac{l}{a}; \text{ Now, if } l = 1\,cm, a = 1\,cm^2 \text{ then } R = \rho$$

Thus, resistivity is defined as the resistance of a conductor of 1 cm length and having area of cross-section equal to $1\,cm^2$.

Units : The units of resistivity are $\rho = R\dfrac{a}{l} = Ohm\dfrac{cm^2}{cm}$

$= Ohm.\,cm$

Its *SI* units are Ohm metre $(\Omega\,m)$. But quite often Ohm centimetre $(\Omega\,cm)$ is also used.

(4) **Conductance :** It is a measure of the ease with which current flows through a conductor. It is an additive property. It is expressed as G. It is reciprocal of the resistance, *i.e.,*

$$G = \dfrac{1}{R}$$

Units : The units of conductance are reciprocal Ohm (ohm^{-1}) or mho. Ohm is also abbreviated as Ω so that Ohm^{-1} may be written as Ω^{-1}.

According to SI system, the units of electrical conductance is Siemens, S (*i.e.,* $1S = 1\Omega^{-1}$).

(5) **Conductivity :** The inverse of resistivity is called conductivity (or specific conductance). It is represented by the symbol, κ (Greek kappa). The *IUPAC* has recommended the use of term conductivity over specific conductance. It may be defined as, *the conductance of a solution of 1 cm length and having 1 sq. cm as the area of cross-section*. In other words, *conductivity is the conductance of one centimetre cube of a solution of an electrolyte*.

Thus, $\kappa = \dfrac{1}{\rho}$

Units : The units of conductivity are

$$\kappa = \dfrac{1}{Ohm.\,cm} = Ohm^{-1}\,cm^{-1} \text{ or } \Omega^{-1}\,cm^{-1}$$

In *SI* units, l is expressed in m area of cross-section in m^2 so that the units of conductivity are $S\,m^{-1}$.

(6) **Molar conductivity or molar conductance :** Molar conductivity is defined as *the conducting power of all the ions produced by dissolving one mole of an electrolyte in solution*.

It is denoted by Λ (lambda). Molar conductance is related to specific conductance (κ) as,

$$\Lambda = \frac{\kappa}{M}$$

where, M is the molar concentration.

If M is in the units of molarity *i.e.,* moles per litre ($mol\, L^{-1}$), the Λ may be expressed as,

$$\Lambda = \frac{\kappa \times 1000}{M}$$

For the solution containing 1 *gm* mole of electrolyte placed between two parallel electrodes of 1 *sq. cm* area of cross-section and one *cm* apart,

$$\text{Conductance}(G) = \text{Conductivity} = \text{Molar conductivity}(\Lambda)$$

But if solution contains 1 *gm* mole of the electrolyte therefore, the measured conductance will be the molar conductivity. Thus,

$$\text{Molar conductivity}(\Lambda) = 100 \times \text{Conductivity}$$

In other words, $(\Lambda) = \kappa \times V$

where V is the volume of the solution in cm^3 containing one gram mole of the electrolyte.

If M is the concentration of the solution in mole per litre, then

M mole of electrolyte is present in $1000\, cm^3$

1 mole of electrolyte is present in $= \frac{1000}{M}\, cm^3$ of solution

Thus, $\Lambda = \kappa \times \text{Volume in } cm^3$ containing 1 mole of electrolyte.

or $\Lambda = \frac{\kappa \times 1000}{M}$

Units of Molar Conductance : The units of molar conductance can be derived from the formula ,

$$\Lambda = \frac{\kappa \times 1000}{M}$$

The units of κ are $S\, cm^{-1}$ and units of Λ are,

$$\Lambda = S\, cm^{-1} \times \frac{cm^3}{mol} = S\, cm^2\, mol^{-1} = S\, cm^2\, mol^{-1}$$

According to *SI* system, molar conductance is expressed as $S\, m^2\, mol^{-1}$, if concentration is expressed as $mol\, m^{-3}$.

(7) **Equivalent conductivity** : It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution.

It is expressed as Λ_e and is related to specific conductance as

$$\Lambda_e = \frac{\kappa \times 1000}{C} = \kappa \times \frac{1000}{M} \quad (M \text{ is Molarity of the solution})$$

where C is the concentration in gram equivalent per litre (or Normality). This term has earlier been quite frequently used. Now it is replaced by molar conductance. The units of equivalent conductance are $Ohm^{-1}\, cm^2\, (gm\, equiv)^{-1}$.

(8) **Experimental measurement of conductance**

(i) The conductance of a solution is reciprocal of the resistance, therefore, the experimental determination of the conductance of a solution involves the measurement of its resistance.

(ii) ***Calculation of conductivity*** : We have seen that conductivity (κ) is reciprocal of resistivity (ρ) , *i.e.,*

$$\kappa = \frac{1}{\rho} \quad \text{and} \quad \rho = R\frac{a}{l}$$

$$\therefore \quad \kappa = \frac{1}{R}\left(\frac{l}{a}\right) \quad \text{or} \quad \kappa = G\left(\frac{l}{a}\right)$$

where G is the conductance of the cell, l is the distance of separation of two electrodes having cross section area $a\, cm^2$.

The quantity $\left(\frac{l}{a}\right)$ is called cell constant and is expressed in cm^{-1}. Knowing the value of cell constant and conductance of the solution, the specific conductance can be calculated as,

$$\kappa = G \times \text{Cell constant}$$

i.e., $\text{Conductivity} = \text{Conductance} \times \text{Cell constant}$

Factors affecting the electrolytic conductance

In general, conductance of an electrolyte depends upon the following factors,

(1) **Nature of electrolyte :** The conductance of an electrolyte depends upon the number of ions present in the solution. Therefore, the greater the number of ions in the solution the greater is the conductance. The number of ions produced by an electrolyte depends upon its nature. The strong electrolytes dissociate almost completely into ions in solutions and, therefore, their solutions have high conductance. On the other hand, weak electrolytes, dissociate to only small extents and give lesser number of ions. Therefore, the solutions of weak electrolytes have low conductance.

(2) **Concentration of the solution :** The molar conductance of electrolytic solution varies with the concentration of the electrolyte. In general, the molar conductance of an electrolyte increases with decrease in concentration or increase in dilution.

The molar conductance of strong electrolyte (HCl, KCl, KNO_3) as well as weak electrolytes (CH_3COOH, NH_4OH) increase with decrease in concentration or increase in dilution. The variation is however different for strong and weak electrolytes.

The variation of molar conductance with concentration can be explained on the basis of conducting ability of ions for weak and strong electrolytes.

For weak electrolytes the variation of Λ with dilution can be explained on the bases of number of ions in solution. The number of ions furnished by an electrolyte in solution depends upon the degree of dissociation with dilution. With the increase in dilution, the degree of dissociation increases and as a result molar conductance increases. The limiting value of molar conductance (Λ^0) corresponds to degree of dissociation equal to 1 *i.e.,* the whole of the electrolyte dissociates.

Thus, the degree of dissociation can be calculated at any concentration as,

$$\alpha = \frac{\Lambda^c}{\Lambda^0}$$

where α is the degree of dissociation,

Λ^c is the molar conductance at concentration C and

Λ^0 is the molar conductance at infinite dilution.

For strong electrolytes, there is no increase in the number of ions with dilution because strong electrolytes are completely ionised in solution at all concentrations (By definition). However, in concentrated solutions of strong electrolytes there are strong forces of attraction between the ions of opposite charges called inter-ionic forces. Due to these inter-ionic forces the conducting ability of the

ions is less in concentrated solutions. With dilution, the ions become far apart from one another and inter-ionic forces decrease. As a result, molar conductivity increases with dilution. When the concentration of the solution becomes very-very low, the inter-ionic attractions become negligible and the molar conductance approaches the limiting value called molar conductance at infinite dilution. This value is characteristic of each electrolyte.

(3) **Temperature** : The conductivity of an electrolyte depends upon the temperature. With increase in temperature, the conductivity of an electrolyte increases.

Migration of ions

Electricity is carried out through the solution of an electrolyte by *migration of ions*. Therefore,

(1) Ions move toward oppositely charged electrodes at different speeds.

(2) During electrolysis, ions are discharged or liberated in equivalent amounts at the two electrodes, *no matter what their relative speed is*.

(3) Concentration of the electrolyte changes around the electrode due to difference in the speed of the ions.

(4) Loss of concentration around any electrode is proportional to the speed of the ion that moves away from the electrode, so

$$\frac{\text{Loss around anode}}{\text{Loss around cathode}} = \frac{\text{Speed of cation}}{\text{Speed of anion}}$$

The relation is valid only when the discharged ions do not react with atoms of the electrodes. But when the ions combine with the material of the electrode, the concentration around the electrode shows an increase.

Transport number or Transference number

(1) **Definition :** "*The fraction of the total current carried by an ion is known as transport number, transference number or Hittorf number may be denoted by sets symbols like t_+ and t_- or t_c and t_a or n_c and n_a*".

From this definition,

$$t_a = \frac{\text{Current carried by an anion}}{\text{Total current passed through the solution}}$$

$$t_c = \frac{\text{Current carried by a cation}}{\text{Total current passed through the solution}}$$

evidently, $t_a + t_c = 1$.

(2) **Determination of transport number :** Transport number can be determined by *Hittorf's method, moving boundary method, emf method and from ionic mobility*.

(3) **Factors affecting transport number**

A rise in temperature tends to bring the transport number of cation and anion more closer to 0.5

(4) **Transport number and Ionic mobility :** Ionic mobility or Ionic conductanc*e* is the conductivity of a solution containing 1 *g* ion, at infinite dilution, when two sufficiently large electrodes are placed 1 *cm* apart.

$$\text{Ionic mobilities}\,(\lambda_a \text{ or } \lambda_c) \propto \text{speeds of ions}\,(u_a \text{or } u_c)$$

Unit of ionic mobility is Ohm^{-1} cm^2 or V^{-1}S^{-1}cm^2

Ionic mobility and transport number are related as,

$$\lambda_a \text{ or} \lambda_c = t_a \text{ or } t_c \times \lambda_\infty$$

Absolute ionic mobility is the mobility with which the ion moves under unit potential gradient. It's unit is $cm\,sec^{-1}$.

$$\text{Absolute ionic mobility} = \frac{\text{Ionic mobility}}{96,500}$$

Kohlrausch's law

(1) *Kohlrausch law* states that, "*At time infinite dilution, the molar conductivity of an electrolyte can be expressed as the sum of the contributions from its individual ions*" i.e., $\Lambda_m^\infty = v_+ \lambda_+^\infty + v_- \lambda_-^\infty$, where, v_+ and v_- are the number of cations and anions per formula unit of electrolyte respectively and, λ_+^∞ and λ_-^∞ are the molar conductivities of the cation and anion at infinite dilution respectively. The use of above equation in expressing the molar conductivity of an electrolyte is illustrated as,

The molar conductivity of *HCl* at infinite dilution can be expressed as,

$\Lambda_{HCl}^\infty = v_{H^+} \lambda_{H^+}^\infty + v_{Cl^-} \lambda_{Cl^-}^\infty$; For *HCl*, $v_{H^+} = 1$ and $v_{Cl^-} = 1$.

So, $\Lambda_{HCl}^\infty = (1 \times \lambda_{H^+}^\infty) + (1 \times \lambda_{Cl^-}^\infty)$; Hence, $\Lambda_{HCl}^\infty = \lambda_{H^+}^\infty + \lambda_{Cl^-}^\infty$

(2) **Applications of Kohlrausch's law :** Some typical applications of the Kohlrausch's law are described below,

(i) **Determination of Λ_m^∞ for weak electrolytes** : The molar conductivity of a weak electrolyte at infinite dilution (Λ_m^∞) cannot be determined by extrapolation method. However, Λ_m^∞ values for weak electrolytes can be determined by using the Kohlrausch's equation.

$$\Lambda_{CH_3COOH}^\infty = \Lambda_{CH_3COONa}^\infty + \Lambda_{HCl}^\infty - \Lambda_{NaCl}^\infty$$

(ii) **Determination of the degree of ionisation of a weak electrolyte** : The Kohlrausch's law can be used for determining the degree of ionisation of a weak electrolyte at any concentration. If λ_m^c is the molar conductivity of a weak electrolyte at any concentration *C* and, λ_m^∞ is the molar conductivity of a electrolyte at infinite dilution.

Then, the degree of ionisation is given by, $\alpha_c = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{\Lambda_m^c}{(v_+ \lambda_+^\infty + v_- \lambda_-^\infty)}$

Thus, knowing the value of Λ_m^c, and Λ_m^∞ (From the Kohlrausch's equation), the degree of ionisation at any concentration (α_c) can be determined.

(iii) **Determination of the ionisation constant of a weak electrolyte** : Weak electrolytes in aqueous solutions ionise to a very small extent. The extent of ionisation is described in terms of the degree of ionisation (α). In solution, the ions are in dynamic equilibrium with the unionised molecules. Such an equilibrium can be described by a constant called *ionisation constant*. For example, for a weak electrolyte *AB*, the ionisation equilibrium is, $AB \rightleftharpoons A^+ + B^-$; If *C* is the initial concentration of the electrolyte *AB* in solution, then the equilibrium concentrations of various species in the solution are, $[AB] = C(1 - \alpha)$, $[A^+] = C\alpha$ and $[B^-] = C\alpha$

Then, the ionisation constant of *AB* is given by,

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

We know, that at any concentration C, the degree of ionisation (α) is given by, $\alpha = \Lambda_m^c / \Lambda_m^\infty$

Then, $K = \dfrac{C(\Lambda_m^c / \Lambda_m^\infty)^2}{[1 - (\Lambda_m^c / \Lambda_m^\infty)]} = \dfrac{C(\Lambda_m^c)^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m^c)}$; Thus, knowing

Λ_m^∞ and Λ_m^c at any concentration, the ionisation constant (K) of the electrolyte can be determined.

(iv) *Determination of the solubility of a sparingly soluble salt* : The solubility of a sparingly soluble salt in a solvent is quite low. Even a saturated solution of such a salt is so dilute that it can be assumed to be at infinite dilution. Then, the molar conductivity of a sparingly soluble salt at infinite dilution (Λ_m^∞) can be obtained from the relationship,

$$\Lambda_m^\infty = v_+ \lambda_+^\infty + v_- \lambda_-^\infty \qquad ....(i)$$

The conductivity of the saturated solution of the sparingly soluble salt is measured. From this, the conductivity of the salt (κ_{salt}) can be obtained by using the relationship, $\kappa_{salt} = \kappa_{sol} - \kappa_{water}$, where, κ_{water} is the conductivity of the water used in the preparation of the saturated solution of the salt.

$$\Lambda_{salt}^\infty = \frac{1000 \, \kappa_{salt}}{C_m} \qquad ....(ii)$$

From equation (i) and (ii) ;

$$C_m = \frac{1000 \, \kappa_{salt}}{(v_+ \, \lambda_+^\infty + v_- \, \lambda_-^\infty)}, \quad C_m \text{ is the molar concentration of the}$$

sparingly soluble salt in its saturated solution. Thus, C_m is equal to the solubility of the sparingly soluble salt in the *mole per litre* units. The solubility of the salt in *gram per litre* units can be obtained by multiplying C_m with the molar mass of the salt.

Electrochemical or Galvanic cell

"*Electrochemical cell or Galvanic cell is a device in which a spontaneous redox reaction is used to convert chemical energy into electrical energy i.e. electricity can be obtained with the help of oxidation and reduction reaction*".

(1) **Characteristics of electrochemical cell :** Following are the important characteristics of electrochemical cell,
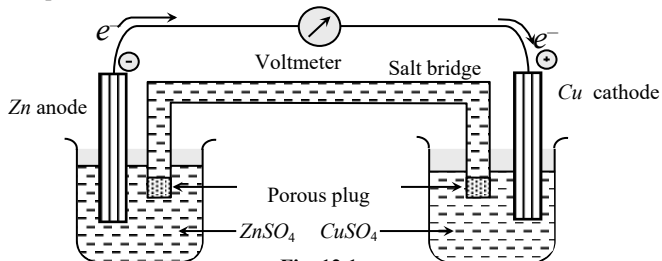

Fig. 12.1

(i) Electrochemical cell consists of two vessels, two electrodes, two electrolytic solutions and a salt bridge.

(ii) The two electrodes taken are made of different materials and usually set up in two separate vessels.

(iii) The electrolytes are taken in the two different vessels called as half - cells.

(iv) The two vessels are connected by a salt bridge/porous pot.

(v) The electrode on which oxidation takes place is called the **anode** (or – ve pole) and the electrode on which reduction takes place is called the **cathode** (or + ve pole).

(vi) In electrochemical cell, ions are discharged only on the cathode.

(vii) Like electrolytic cell, in electrochemical cell, from outside the electrolytes electrons flow from anode to cathode and current flow from cathode to anode.

(viii) For electrochemical cell, $E_{cell} = +ve$, $\Delta G = -ve$.

(ix) In a electrochemical cell, cell reaction is exothermic.

(2) **Salt bridge and its significance**

(i) Salt bridge is U – shaped glass tube filled with a gelly like substance, agar – agar (plant gel) mixed with an electrolyte like KCl, KNO_3, NH_4NO_3 etc.

(ii) The electrolytes of the two half-cells should be inert and should not react chemically with each other.

(iii) The cation as well as anion of the electrolyte should have same ionic mobility and almost same transport number, viz. $KCl, KNO_3, NH_4 NO_3$ etc.

(iv) The following are the functions of the salt bridge,

(a) It connects the solutions of two half - cells and completes the cell circuit.

(b) It prevent transference or diffusion of the solutions from one half cell to the other.

(c) It keeps the solution of two half - cells electrically neutral.

(d) It prevents liquid – liquid junction potential *i.e.* the potential difference which arises between two solutions when they contact with each other.

(3) **Representation of an electrochemical cell**

The cell may be written by arranging each of the pair left – right, anode – cathode, oxidation – reduction, negative and positive in the alphabetical order as,
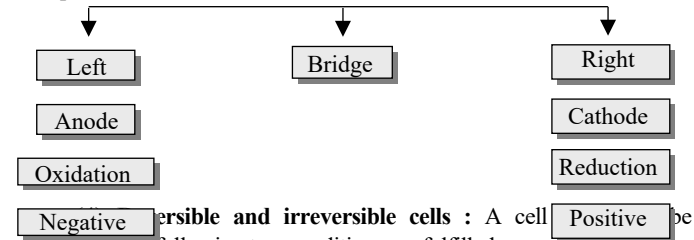
(4) **Reversible and irreversible cells :** A cell be reversible if the following two conditions are fulfilled

(i) The chemical reaction of the cell stops when an exactly equal external *emf* is applied.

(ii) The chemical reaction of the cell is reversed and the current flows in opposite direction when the external *emf* is slightly higher than that of the cell. Any other cell, which does not obey the above two conditions, is termed as irreversible. Daniell cell is reversible but $Zn \mid H_2SO_4 \mid Ag$ cell is irreversible in nature

(5) **Types of electrochemical cells :** Two main types of electrochemical cells have been reported, these are,

(i) *Chemical cells* : The cells in which electrical energy is produced from the energy change accompanying a chemical reaction or a physical process are known as chemical cells. Chemical cells are of two types,
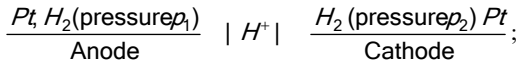
(a) *Chemical cells without transference :* In this type of chemical cells, the liquid junction potential is neglected or the transference number is not taken into consideration. In these cells, one electrode is reversible to cations while the other is reversible to the anions of the electrolyte.

(b) *Chemical cells with transference :* In this type of chemical cells, the liquid-liquid junction potential or diffusion potential is developed across the boundary between the two solutions. This

potential develops due to the difference in mobilities of $+ve$ and $-ve$ ions of the electrolytes.

(6) **Concentration cells :** *"A cell in which electrical energy is produced by the transference of a substance from a system of high concentration to one at low concentration is known as **concentration cells"**.* Concentration cells are of two types.

(i) **Electrode concentration cells** : In these cells, the potential difference is developed between two electrodes at different concentrations dipped in the same solution of the electrolyte. For example, two hydrogen electrodes at different gaseous pressures in the same solution of hydrogen ions constitute a cell of this type.

$$\underset{\text{Anode}}{\underline{Pt, H_2(\text{pressure}\, p_1)}} \mid H^+ \mid \underset{\text{Cathode}}{\underline{H_2\,(\text{pressure}\, p_2)\, Pt}} ;$$

$E_{cell} = \dfrac{0.0591}{2} \log \dfrac{(p_1)}{(p_2)}$ at $25^o C$ If $p_1 > p_2$, oxidation occurs at L. H. S. electrode and reduction occurs at R. H. S. electrode.

In the amalgam cells, two amalgams of the same metal at two different concentrations are immersed in the same electrolytic solution.

$$M(Hg\, C_1) \mid M^{n+} \mid Zn(Hg\, C_2)$$

The *emf* of the cell is given by the expression,

$$E_{cell} = \dfrac{0.0591}{n} \log \dfrac{C_1}{C_2} \text{ at } 25^o C$$

(ii) **Electrolyte concentration cells** : In these cells, electrodes are identical but these are immersed in solutions of the same electrolyte of different concentrations. The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration. With the expiry of time, the two concentrations tend to become equal. Thus, at the start the *emf* of the cell is maximum and it gradually falls to zero. Such a cell is represented in the following manner (C_2 is greater then C_1).

$$M \mid M^{+n}(C_1) \mid\mid M^{n+}(C_2) \mid M$$

or $\underset{\text{Anode}}{\underline{Zn \mid Zn^{2+}(C_1)}} \mid\mid \underset{\text{Cathode}}{\underline{Zn^{2+}(C_2) \mid Zn}}$
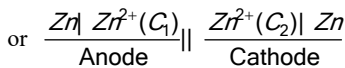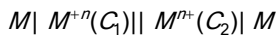
The *emf* of the cell is given by the following expression,

$$E_{cell} = \dfrac{0.0591}{n} \log \dfrac{C_{2(R.H.S)}}{C_{1(L.H.S)}} e \text{ at } 25^o C$$

The concentration cells are used to determine the solubility of sparingly soluble salts, valency of the cation of the electrolyte and transition point of the two allotropic forms of metal used as electrodes, etc.

(7) **Heat of reaction in an electrochemical cell** : Let n Faraday charge flows out of a cell of *emf* E, then

$$-\Delta G = nFE \qquad\qquad \text{.......(i)}$$

Gibbs – Helmholtz equation from thermodynamics may be given as

$$\Delta G = \Delta H + T\left(\dfrac{\partial \Delta G}{\partial T}\right)_P \qquad \text{.......(ii)}$$

From equation (i) and (ii) we get,

$$-nFE = \Delta H + T\left[\dfrac{\partial(-nFE)}{\partial T}\right]_P = \Delta H - nFT\left(\dfrac{\partial E}{\partial T}\right)_P$$

$$\Delta H = -nFE + nFT\left(\dfrac{\partial E}{\partial T}\right)_P$$

where $\left(\dfrac{\partial E}{\partial T}\right)_P$ = Temperature coefficient of cell

Case I: When $\left(\dfrac{\partial E}{\partial T}\right)_P = 0$, then $\Delta H = -nFE$

Case II: When $\left(\dfrac{\partial E}{\partial T}\right) > 0$, then $nFE > \Delta H$, *i.e.* process inside the cell is endothermic.

Case III: When $\left(\dfrac{\partial E}{\partial T}\right) < 0$, then $nFE < \Delta H$, *i.e.*, process inside the cell is exothermic.

Some Commercial cell (Batteries)

One of the main use of galvanic cells is the generation of portable electrical energy. These cells are also popularly known as **batteries.** The term battery is generally used for two or more Galvanic cells connected in series. Thus, a **battery** *is an arrangement of electrochemical cells used as an energy source*. The basis of an electrochemical cell is an oxidation – reduction reaction.

Types of commercial cells : There are mainly two types of commercial cells,

(1) **Primary cells :** In these cells, the electrode reactions cannot be reversed by an external electric energy source. In these cells, reactions occur only once and after use they become dead. Therefore, they are **not chargeable.** Some common example are, dry cell, mercury cell, Daniell cell and alkaline dry cell
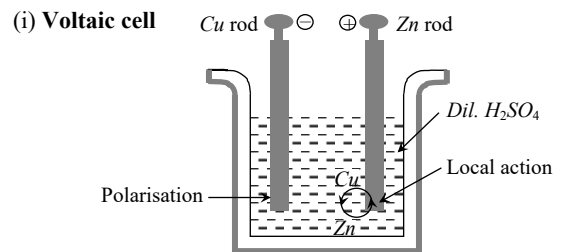
(i) **Voltaic cell**

Fig. 12.2

Cathode : Cu rod   **Anode** : Zn rod
Electrolyte : dil. H_2SO_4 **Emf** : $1.08\ V$

At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

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

Over all reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

(ii) **Daniel cell**
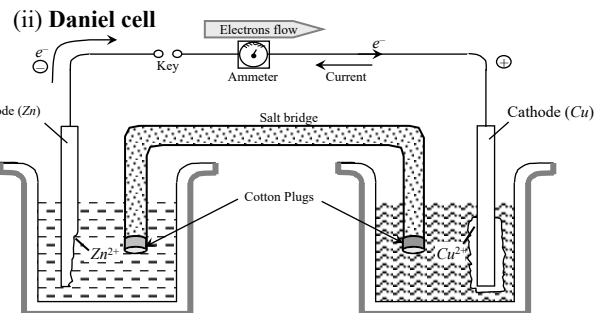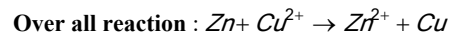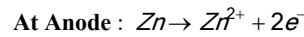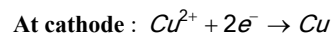
Fig. 12.3

Cathode : Cu rod   **Anode** : Zn rod
Electrolyte : dil. H_2SO_4 **Emf** : $1.1\ V$

At cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

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

Over all reaction : $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$
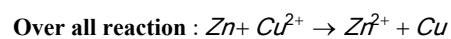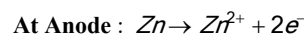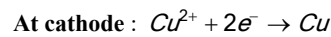
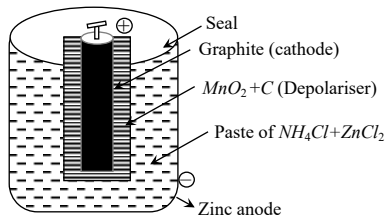(iii) **Lechlanche cell (Dry cell)**

Fig. 12.4

Cathode : Graphite rod   **Anode** : Zn pot

Electrolyte : Paste of $NH_4Cl + ZnCl_2$ in starch

Emf : 1.2 V to 1.5 V

At cathode : $NH_4^+ + MnO_2 + 2e^- \rightarrow MnO(OH)^- + NH_3$

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

Over all reaction :

$Zn + NH_4^+ + MnO_2 \rightarrow Zn^{2+} + MnO(OH)^- + NH_3$

(iv) **Mercury cell**

$\longrightarrow$

Cathode : Mercury (II) oxide   **Anode** : Zn rod
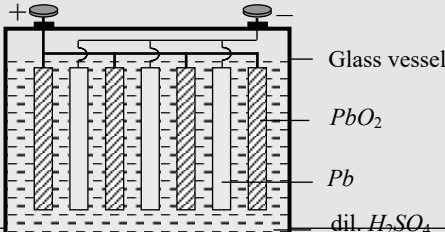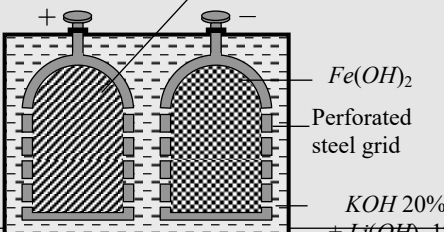
Electrolyte : Paste of $KOH + ZnO$ **Emf** : 1.35 V

At cathode : $HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2OH^-_{(aq)}$

At Anode : $Zn_{(s)} + 2OH^-_{(aq)} \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$
(amalgam)

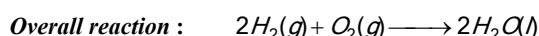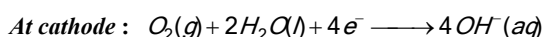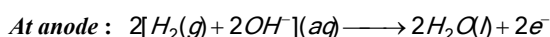**Over all reaction** : $Zn_{(s)} + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$

(2) **Secondary cells :** In the secondary cells, the reactions can be reversed by an external electrical energy source. Therefore, these cells can be *recharged* by passing electric current and used again and again. These are also celled *storage cells.* Examples of secondary cells are, lead storage battery and nickel – cadmium storage cell.

| In charged	Lead storage cell	Alkali cell
	Glass vessel — PbO_2 — Pb — dil. H_2SO_4	$Ni(OH)_2$ — $Fe(OH)_2$ — Perforated steel grid — KOH 20% + $LiOH$, 1%
Positive electrode	Perforated lead plates coated with PbO_2	Perforated steel plate coated with $Ni(OH)_4$
Negative electrode	Perforated lead plates coated with pure lead	Perforated steel plate coated with Fe
Electrolyte	dil. H_2SO_4	20% solution of KOH + 1% $LiOH$
During charging	**Chemical reaction** **At anode** : $PbSO_4 + 2H^+ + 2e^- \rightarrow Pb + H_2SO_4$ **At cathode** : $PbSO_4 + SO_4^{--} + 2H_2O - 2e^- \rightarrow PbO_2$ $+ 2H_2SO_4$ Specific gravity of H_2SO_4 increases and when specific gravity becomes 1.25 the cell is fully charged. **Emf of cell**: When cell is fully charged then $E = 2.2$ *volt*	**Chemical reaction** **At anode** : $Ni\,(OH)_2 + 2OH^+ - 2e^- \rightarrow Ni(OH)_4$ **At cathode** : $Fe(OH)_2 + 2K^+ + 2e^- \rightarrow Fe + 2KOH$ **Emf of cell :** When cell is fully charged then $E = 1.36$ *volt*
During discharging	**Chemical reaction** **At anode** : $Pb + SO_4^{--} - 2e^- \rightarrow PbSO_4$ **At cathode** : $PbO_2 + 2H^+ + 2e^- + H_2SO_4 \rightarrow PbSO_4 +$ $2H_2O$ Specific gravity of H_2SO_4 decreases and when specific gravity falls below 1.18 the cell requires recharging. **Emf of cell** : When emf of cell falls below 1.9 *volt* the cell requires recharging.	**Chemical reaction** **At anode** : $Fe + 2OH^- - 2e^- \rightarrow Fe(OH)_2$ **At cathode** : $Ni(OH)_4 + 2K^+ + 2e^- \rightarrow Ni(OH)_2 +$ $2KOH$ **Emf of cell** : When emf of cell falls below 1.1 V it requires charging.
Efficiency	80%	60%

Fuel cells

These are Voltaic cells in which the reactants are continuously supplied to the electrodes. These are designed to convert the energy from the combustion of fuels such as H_2, CO, CH_4, etc. directly into electrical energy. The common example is *hydrogen-oxygen fuel cell* as described below,

In this cell, hydrogen and oxygen are bubbled through a porous carbon electrode into concentrated aqueous sodium hydroxide or potassium hydroxide. Hydrogen (the fuel) is fed into the anode compartment where it is oxidised. The oxygen is fed into cathode compartment where it is reduced. The diffusion rates of the gases into the cell are carefully regulated to get maximum efficiency. The net reaction is the same as burning of hydrogen and oxygen to form water. The reactions are

At anode : $2[H_2(g) + 2OH^-](aq) \longrightarrow 2H_2O(l) + 2e^-$

At cathode : $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Overall reaction : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

Each electrode is made of porous compressed carbon containing a small amount of catalyst (Pt, Ag or CoO). This cell runs continuously as long as the reactants are fed. Fuel cells convert the energy of the fuel directly into electricity EMF of fuel cell is 1.23 V. This cell has been used for electric power in the *Apollo space programme.* The important advantages of fuel cells are

Anode ⊖ ↑ H_2O ⊕ Cathode

Porous carbon electrode

OH^-

$H_2 \rightarrow$ ← O_2

Electrolyte

Fig. 12.6
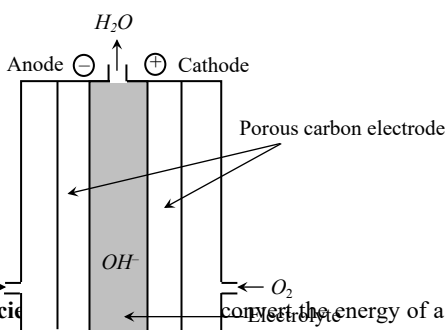
(1) **High efficiency :** Fuel cells convert the energy of a fuel directly into electricity and therefore, they are more efficient than the conventional methods of generating electricity on a large scale by burning hydrogen, carbon fuels. Though we expect 100 % efficiency in fuel cells, so far *60 – 70% efficiency* has been attained. The conventional methods of production of electrical energy involve combustion of a fuel to liberate heat which is then used to produce electricity. The efficiency of these methods is only about 40%.

(2) **Continuous source of energy :** There is no electrode material to be replaced as in ordinary battery. The fuel can be fed continuously to produce power. For this reason, $H_2 - O_2$ fuel cells have been used in space crafts.

(3) **Pollution free working :** There are no objectionable byproducts and, therefore, they do not cause pollution problems. Since fuel cells are efficient and free from pollution, attempts are being made to get better commercially practical fuel cells.

Electrode Potential

(1) When a metal (*M*) is placed in a solution of its ions (M^{++}), either of the following three possibilities can occurs, according to the *electrode potential solution pressure theory of Nernst.*

(i) A metal ion M^{n+} collides with the electrode, and undergoes no change.

(ii) A metal ion M^{n+} collides with the electrode, gains *n* electrons and gets converted into a metal atom *M,* (*i.e.* the metal ion is reduced).
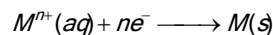
$$M^{n+}(aq) + ne^- \longrightarrow M(s)$$

(iii) A metal atom on the electrode *M* may lose an electrons to the electrode, and enter to the solution as M^{n+}, (*i.e.* the metal atom is oxidised). $M(s) \longrightarrow M^{n+}(aq) + ne^-$.

Thus, "*the electrode potential is the tendency of an electrode to lose or gain electrons when it is in contact with solution of its own ions.*"

(2) The magnitude of electrode potential depends on the following factors,

(i) Nature of the electrode, (ii) Concentration of the ions in solution, (iii) Temperature.

(3) **Types of electrode potential :** Depending on the nature of the metal electrode to lose or gain electrons, the electrode potential may be of two types,

(i) *Oxidation potential* : When electrode is negatively charged with respect to solution, *i.e.,* it acts as anode. Oxidation occurs.

$M \longrightarrow M^{n+} + ne^-$
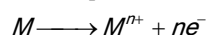
(ii) *Reduction potential* : When electrode is positively charged with respect to solution, *i.e.* it acts as cathode. Reduction occurs.

$M^{n+} + ne^- \longrightarrow M$
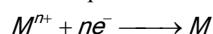
(4) **Standard electrode potential :** "*If in the half cell, the metal rod (M) is suspended in a solution of one molar concentration, and the temperature is kept at 298 K, the electrode potential is called **standard electrode potential,** represented usually by E^o*". **'or'**

The standard electrode potential of a metal may be defined as "*the potential difference in volts developed in a cell consisting of two electrodes, the pure metal in contact with a molar solution of one of its ions and the normal hydrogen electrode (NHE)*".

Standard oxidation potential for any half - cell = – (Standard reduction potential)
Standard reduction potential for any half - cell = – (Standard reduction potential)

(5) **Reference electrode or reference half - cells**

It is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally. It is, therefore, necessary to couple the electrode with another electrode whose potential is known. This electrode is termed as *reference electrode or reference half - cells.* Various types of half – cells have been used to make complete cell with spontaneous reaction in forward direction. These half – cells have been summarised in following table,

Table : 12.2 Various Types of Half – cells

Type	Example	Half – cell reaction	$Q =$	Reversible to	Electrode Potential (oxidn), $E =$
Gas ion half - cell	$Pt(H_2)\mid H^+(aq)$ $Pt(Cl_2)\mid Cl^-(aq)$	$\frac{1}{2}H_2(g) \rightarrow H^+(aq) + e^-$ $Cl^-(aq) \rightarrow \frac{1}{2}Cl_2(g) + e^-$	$[H^+]$ $\dfrac{1}{[Cl^-]}$	H^+ Cl^-	$E^0 - 0.0591\log[H^+]$ $E^0 + 0.0591\log[Cl^-]$
Metal – metal ion half – cell	$Ag\mid Ag^+(aq)$	$Ag(s) \rightarrow Ag^+(aq) + e^-$	$[Ag^+]$	Ag^+	$E^0 - 0.0591\log[Ag^+]$
Metal insoluble salt anion half – cell	$Ag, AgCl\mid Cl^-(aq)$	$Ag(s) + Cl^-(aq) \rightarrow AgCl(s) + e^-$	$\dfrac{1}{[Cl^-]}$	Cl^-	$E^0 + 0.0591\log[Cl^-]$
Calomel electrode	$Hg, Hg_2Cl_2\mid Cl^-(aq)$	$2Hg(l) + 2Cl^-(aq) \rightarrow$ $Hg_2Cl_2(s) + 2e^-$	$\dfrac{1}{[Cl^-]^2}$	Cl^-	$E^0 + 0.0591\log[Cl^-]$
Metal – metal oxide hydroxide half - cell	$Hg, HgO\mid OH^-(aq)$	$Hg(l) + 2OH^-(aq) \rightarrow$ $HgO(s) + H_2O(l) + 2e^-$	$\dfrac{1}{[OH^-]^2}$	OH^-	$E^0 + 0.0591\log[OH^-]$
Oxidation – reduction half – dell	$Pt\mid Fe^{2+}_{(aq)}, Fe^{3+}_{(aq)}$	$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$	$\dfrac{[Fe^{3+}]}{[Fe^{2+}]}$	Fe^{2+}, Fe^{3+}	$E^0 - 0.0591\log\dfrac{[Fe^{3+}]}{[Fe^{2+}]}$

Cell potential or EMF of the cell

(1) "*The difference in potentials of the two half – cells of a cell known as **electromotive force** (emf) of the cell or cell potential.*"

The difference in potentials of the two half – cells of a cell arises due to the flow of electrons from anode to cathode and flow of current from cathode to anode.

$$\text{Anode} \underset{\text{Flow of current}}{\overset{\text{Flow of electrons}}{\rightleftharpoons}} \text{Cathode}$$
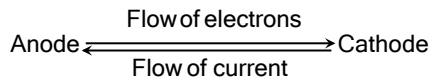
(2) The *emf* of the cell or cell potential can be calculated from the values of electrode potentials of two half – cells constituting the cell. The following three methods are in use :

(i) When oxidation potential of anode and reduction potential of cathode are taken into account

E^0_{cell} = Oxidation potential of anode + Reduction potential of cathode = E^0_{ox} (anode) + E^0_{red} (cathode)

(ii) When reduction potentials of both electrodes are taken into account

E^0_{cell} = Reduction potential of cathode − Reduction potential of anode

$= E^0_{Cathode} - E^0_{Anode} = E^0_{right} - E^o_{left}$

(iii) When oxidation potentials of both electrodes are taken into account

E^o_{cell} = Oxidation potential of anode – Oxidation potential of cathode = E^0_{ox}(anode) − E^0_{ox}(cathode)

(3) **Difference between *emf* and potential difference**

| Emf	Potential difference
It is the potential difference between two electrodes when no current is flowing in the circuit.	It is the difference of the electrode potentials of the two electrodes when the cell is under operation.
It is the maximum voltage that the cell can deliver.	It is always less then the maximum value of voltage which the cell can deliver.
It is responsible for the steady flow of current in the cell.	It is not responsible for the steady flow of current in the cell.

(4) **Cell EMF and the spontaneity of the reaction :**

We know, $\Delta G = -nFE_{cell}$

Nature of reaction	ΔG(or ΔG°)	E_{cell}(or E°_{cell})
Spontaneous	−	+
Equilibrium	0	0
Non – spontaneous	+	−

Nernst's equation

(1) **Nernst's equation for electrode potential**

The potential of the electrode at which the reaction,

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$
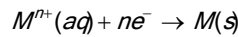
takes place is described by the equation,

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF}\ln\frac{[M(s)]}{[M^{n+}(aq)]}$$

or $E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{2.303\,RT}{nF}\log\frac{[M(s)]}{[M^{n+}(aq)]}$

above *eq.* is called the **Nernst equation**.

Where,

$E_{M^{n+}/M}$ = the potential of the electrode at a given concentration,

$E^0_{M^{n+}/M}$ = the standard electrode potential

R = the universal gas constant, $8.31\ J\,K^{-1}\,mol^{-1}$

T = the temperature on the absolute scale,

n = the number of electrons involved in the electrode reaction,

F = the Faraday constant : (96500 *C*),

$[M(s)]$ = the concentration of the deposited metal,

$[M^{n+}(aq)]$ = the molar concentration of the metal ion in the solution,

The concentration of pure metal $M(s)$ is taken as unity. So, the Nernst equation for the M^{n+}/M electrode is written as,

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{2.303\,RT}{nF}\log\frac{1}{[M^{n+}(aq)]}$$

At 298 *K,* the Nernst equation for the M^{n+}/M electrode can be written as,

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}(aq)]}$$

For an electrode (half - cell) corresponding to the electrode reaction,

Oxidised form $+ ne^- \rightarrow$ Reduced form
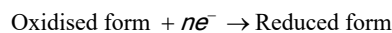
The Nernst equation for the electrode is written as,

$$E_{half-cell} = E^0_{half-cell} - \frac{2.303\,RT}{nF}\log\frac{[Reduced form]}{[Oxidised form]}$$

At 298 *K,* the Nernst equation can be written as,

$$E_{half-cell} = E^0_{half-cell} - \frac{0.0591}{n}\log\frac{[Reduced form]}{[Oxidised form]}$$

(2) **Nernst's equation for cell EMF**

For a cell in which the net cell reaction involving *n* electrons is,

$aA + bB \rightarrow cC + dD$

The Nernst equation is written as,

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Where, $E^0_{cell} = E^0_{cathode} - E^0_{anode}$.

The E^o_{cell} is called the standard cell potential.
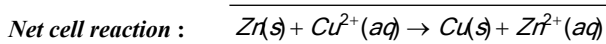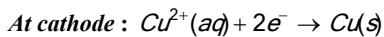
or $E_{cell} = E^o_{cell} - \dfrac{2.303\,RT}{nF}\log\dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

At 298 K, above eq. can be written as,

or $E_{cell} = E^o_{cell} - \dfrac{0.0592}{n}\log\dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

It may be noted here, that the concentrations of A, B, C and D referred in the eqs. are the concentrations at the time the cell *emf* is measured.

(3) **Nernst's equation for Daniells cell :** Daniell's cell consists of zinc and copper electrodes. The electrode reactions in Daniell's cell are,

At anode : $\qquad Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

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

Net cell reaction : $\quad \overline{Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)}$

Therefore, the Nernst equation for the Daniell's cell is,

$E_{cell} = E^0_{cell} - \dfrac{2.303\,RT}{2F}\log\dfrac{[Cu(s)][Zn^{2+}(aq)]}{[Zn(s)][Cu^{2+}(aq)]}$

Since, the activities of pure copper and zinc metals are taken as unity, hence the Nernst equation for the Daniell's cell is,

$E_{cell} = E^0_{cell} - \dfrac{2.303\,RT}{2F}\log\dfrac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$

The above *eq.* at 298 K is,

$E_{cell} = E^o_{cell} - \dfrac{0.0591}{2}\log\dfrac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}\ V$

For Daniells cell, $E^0_{cell} = 1.1\ V$

(4) **Nernst's equation and equilibrium constant**

For a cell, in which the net cell reaction involving *n* electrons is, $aA + bB \rightarrow cC + dD$

The Nernst equation is

$E_{Cell} = E^0_{cell} - \dfrac{RT}{nF}\ln\dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ \qquad .....(i)

At equilibrium, the cell cannot perform any useful work. So at equilibrium, E_{Cell} is zero. Also at equilibrium, the ratio

$\dfrac{[C]^c[D]^d}{[A]^a[B]^b} = \left[\dfrac{[C]^c[D]^d}{[A]^a[B]^b}\right]_{equilibrium} = K_c$

Relationship between potential, Gibbs energy and equilibrium constant

The electrical work (electrical energy) is equal to the product of the *EMF* of the cell and electrical charge that flows through the external circuit *i.e.*,

$W_{max} = nFE_{cell}$ \qquad ......(i)

According to thermodynamics the free energy change (ΔG) is equal to the maximum work. In the cell work is done on the surroundings by which electrical energy flows through the external circuit, So

$-W_{max,} = \Delta G$ \qquad ......(ii)

from eq. (i) and (ii) $\Delta G = -nFE_{cell}$

In standard conditions $\Delta G^0 = -nFE^0_{cell}$

Where $\Delta G^0 =$ standard free energy change

But $E^0_{cell} = \dfrac{2.303}{nF}RT\log K_c$

$\therefore \Delta G^0 = -nF \times \dfrac{2.303}{nF}RT\log K_c$

$\Delta G^0 = -2.303\,RT\log K_c$ or $\Delta G = \Delta G^\circ + 2.303\,RT\log Q$

$\Delta G^0 = -RT\ln K_c$ \qquad $(2.303\log X = \ln X)$

Electrochemical series

(1) The standard reduction potentials of a large number of electrodes have been measured using standard hydrogen electrode as the reference electrode. These various electrodes can be arranged in increasing or decreasing order of their reduction potentials. The arrangement of elements in order of increasing reduction potential values is called *electrochemical series*.It is also called *activity series*, of some typical electrodes.

(2) **Characteristics of Electrochemical series**

(i) The negative sign of standard reduction potential indicates that an electrode when joined with *SHE* acts as anode and oxidation occurs on this electrode. For example, standard reduction potential of zinc is –0.76 *volt*, When zinc electrode is joined with SHE, it acts as anode (*–ve* electrode) *i.e.*, oxidation occurs on this electrode. Similarly, the *+ve* sign of standard reduction potential indicates that the electrode when joined with *SHE* acts as cathode and reduction occurs on this electrode.

(ii) The substances, which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials. All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

(iii) The substances, which are stronger oxidising agents than H^+ ion are placed below hydrogen in the series.

(iv) The metals on the top (having high negative value of standard reduction potentials) have the tendency to lose electrons readily. These are active metals. The activity of metals decreases from top to bottom. The non-metals on the bottom (having high positive values of standard reduction potentials) have the tendency to accept electrons readily. These are active non-metals. The activity of non-metals increases from top to bottom.

Table : 12.3 Standard reduction electrode potentials at 298K

Element	Electrode Reaction (Reduction)	Standard Electrode Reduction potential E^0, volt
Li	$Li^+ + e^- = Li$	–3.05
K	$K^+ + e^- = K$	–2.925
Ba	$Ba^{++} + 2e = Ba$	–2.90
Sr	$Sr^{++} + 2e = Sr$	–2.89
Ca	$Ca^{2+} + 2e^- = Ca$	–2.87
Na	$Na^+ + e^- = Na$	–2.714
Mg	$Mg^{2+} + 2e^- = Mg$	–2.37
Al	$Al^{3+} + 3e^- = Al$	–1.66
Mn	$Mn^{++} + 2e = Mn$	–1.18

tendency to accept electrons Increasing strength as oxidising agent

ength as reducing agent Increasing tendency to lose electrons

Zn	$Zn^{2+}+2e^-=Zn$	–0.7628
Cr	$Cr^{3+}+3\,e^-=Cr$	–0.74
Fe	$Fe^{2+}+2e^-=Fe$	–0.44
Cd	$Cd^{2+}+2e^-=Cd$	–0.403
Co	$Co^{++}+2e=Co$	–0.27
Ni	$Ni^{2+}+2e^-=Ni$	–0.25
Sn	$Sn^{2+}+2e^-=Sn$	–0.14
Pb	$Pb^{++}+2e=Pb$	–0.12
H_2	**$2H^++2e^-=H_2$**	**0.00**
Cu	$Cu^{2+}+2e^-=Cu$	+0.337
I_2	$I_2+2e^-=2I^-$	+0.535
Hg	$Hg^{2+}+2e^-=Hg$	+0.885
Ag	$Ag^++e^-=Ag$	+0.799
Br_2	$Br_2+2e^-=2Br^-$	+1.08
Pt	$Pt^{++}+2e=Pt$	+1.20
Cl_2	$Cl_2+2e^-=2Cl^-$	+1.36
Au	$Au^{3+}+3e=Au$	+1.50
F_2	$F_2+2e^-=2F^-$	+2.87

(3) Application of Electrochemical series

(i) *Reactivity of metals*: The activity of the metal depends on its tendency to lose electron or electrons, *i.e.*, tendency to form cation (M^{n+}). This tendency depends on the magnitude of standard reduction potential. The metal which has high negative value (or smaller positive value) of standard reduction potential readily loses the electron or electrons and is converted into cation. Such a metal is said to be chemically active. The *chemical reactivity of metals decreases from top to bottom in the series*. The metal higher in the series is more active than the metal lower in the series. For example,

(a) Alkali metals and alkaline earth metals having high negative values of standard reduction potentials are chemically active. These react with cold water and evolve hydrogen. These readily dissolve in acids forming corresponding salts and combine with those substances which accept electrons.

(b) Metals like *Fe*, *Pb*, *Sn*, *Ni*, Co, etc., which lie a little down in the series do not react with cold water but react with steam to evolve hydrogen.

(c) Metals like *Cu*, *Ag* and *Au* which lie below hydrogen are less reactive and do not evolve hydrogen from water.

(ii) *Electropositive character of metals* : The electropositive character also depends on the tendency to lose electron or electrons. Like reactivity, the electropositive character of metals decreases from top to bottom in the electrochemical series. On the basis of standard reduction potential values, metals are divided into three groups

(a) *Strongly electropositive metals* : Metals having standard reduction potential near about – 2.0 *volt* or more negative like alkali metals, alkaline earth metals are strongly electropositive in nature.

(b) *Moderately electropositive metals* : Metals having values of reduction potentials between 0.0 and about – 2.0 *volt* are moderately electropositive *Al*, *Zn*, *Fe*, *Ni*, *Co*, etc., belong to this group.
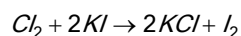
(c) *Weakly electropositive* : The metals which are below hydrogen and possess positive values of reduction potentials are weakly electropositive metals. *Cu*, *Hg*, *Ag*, etc., belong to this group.

(iii) *Displacement reactions*

(a) *To predict whether a given metal will displace another, from its salt solution*: A metal higher in the series will displace the metal from its solution which is lower in the series, i.e., The metal having low standard reduction potential will displace the metal from its salt's solution which has higher value of standard reduction potential. A metal higher in the series has greater tendency to provide electrons to the cations of the metal to be precipitated.

(b) *Displacement of one nonmetal from its salt solution by another nonmetal*: A non-metal higher in the series (towards bottom side), *i.e.*, having high value of reduction potential will displace another non-metal with lower reduction potential, *i.e.*, occupying position above in the series. The non-metal's which possess high positive reduction potentials have the tendency to accept electrons readily. These electrons are provided by the ions of the nonmetal having low value of reduction potential,. Thus, Cl_2 can displace bromine and iodine from bromides and iodides.

$$Cl_2 + 2KI \rightarrow 2KCl + I_2$$

$$2I^- \rightarrow I_2 + 2e^- \qquad\qquad .....(Oxidation)$$

$$Cl_2 + 2e^- \rightarrow 2Cl^- \qquad\qquad .....(Reduction)$$

[*The activity or electronegative character or oxidising nature of the nonmetal increases as the value of reduction potential increases.*]

(c) *Displacement of hydrogen from dilute acids by metals* : The metal which can provide electrons to H^+ ions present in dilute acids for reduction, evolve hydrogen from dilute acids.

$$Mn \rightarrow Mn^{n+} + ne^- \qquad\qquad .....(Oxidation)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad\qquad .....(Reduction)$$

The metal having negative values of reduction potential possess the property of losing electron or electrons.

Thus, the metals occupying top positions in the electrochemical series readily liberate hydrogen from dilute acids and on descending in the series tendency to liberate hydrogen gas from dilute acids decreases.

The metals which are below hydrogen in electrochemical series like *Cu, Hg, Au, Pt,* etc., do not evolve hydrogen from dilute acids.

(d) *Displacement of hydrogen from water* : Iron and the metals above iron are capable of liberating hydrogen from water. The tendency decreases from top to bottom in electrochemical series. Alkali and alkaline earth metals liberate hydrogen from cold water but *Mg, Zn* and *Fe* liberate hydrogen from hot water or steam.
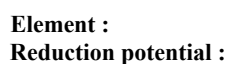
(iv) *Reducing power of metals*: Reducing nature depends on the tendency of losing electron or electrons. More the negative reduction potential, more is the tendency to lose electron or electrons. Thus reducing nature decreases from top to bottom in the electrochemical series. The power of the reducing agent increases, as the standard reduction potential becomes more and more negative. Sodium is a stronger reducing agent than zinc and zinc is a stronger reducing agent than iron. (decreasing order of reducing nature)
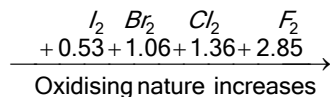
Element :	Na >	Zn >	Fe
Reduction potential :	– 2.71	– 0.76	– 0.44
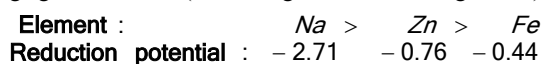
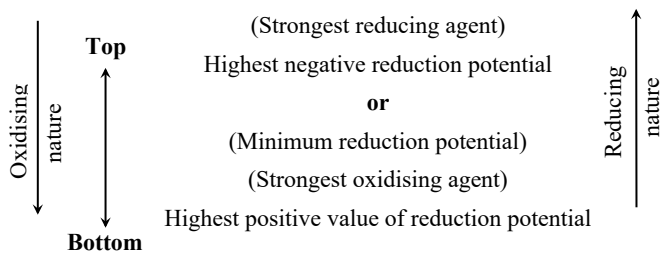*Alkali and alkaline earth metals are strong reducing agents.*

(v) *Oxidising nature of non-metals* : Oxidising nature depends on the tendency to accept electron or electrons. More the value of reduction potential, higher is the tendency to accept electron or electrons. Thus, oxidising nature increases from top to bottom in the electrochemical series. The strength of an oxidising agent increases as the value of reduction potential becomes more and more positive.

F_2 (Fluorine) is a stronger oxidant than Cl_2, Br_2 and I_2, Cl_2 (Chlorine) is a stronger oxidant than Br_2 and I_2
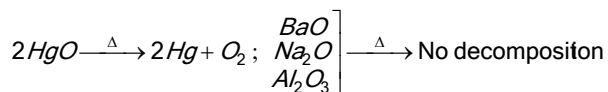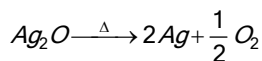
Element :
Reduction potential :

$$\begin{array}{cccc} I_2 & Br_2 & Cl_2 & F_2 \\ +0.53 & +1.06 & +1.36 & +2.85 \end{array}$$
→
Oxidising nature increases

Thus, in *electrochemical series*

Top
(Strongest reducing agent)
Highest negative reduction potential
or
(Minimum reduction potential)
(Strongest oxidising agent)
Highest positive value of reduction potential
Bottom

Oxidising nature ↓ (left) Reducing nature ↑ (right)

(vi) *Thermal stability of metallic oxides* : The thermal stability of the metal oxide depends on its electropositive nature. As the electropositivity decreases from top to bottom, the thermal stability of the oxide also decreases from top to bottom. The oxides of metals having high positive reduction potentials are not stable towards heat. The metals which come below copper form unstable oxides, i.e., these are decomposed on heating.

$$Ag_2O \xrightarrow{\Delta} 2Ag + \frac{1}{2}O_2$$

$$2HgO \xrightarrow{\Delta} 2Hg + O_2 \;;\; \left.\begin{array}{l} BaO \\ Na_2O \\ Al_2O_3 \end{array}\right] \xrightarrow{\Delta} \text{No decompositon}$$

(vii) *Extraction of metals* : A more electropositive metal can displace a less electropositive metal from its salt's solution. This principle is applied for the extraction of *Ag* and *Au* by cyanide process. silver from the solution containing sodium argento cyanide, $NaAg(CN)_2$, can be obtained by the addition of zinc as it is more electro-positive than *Ag.*

$$2NaAg(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2Ag$$
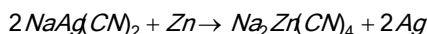
Corrosion

(1) When metals are exposed to atmospheric conditions, they react with air or water in the environment to form undesirable compounds (usually oxides). This process is called *corrosion*. Almost all metals except the least active metals such as gold, platinum and palladium are attacked by environment *i.e.*, undergo corrosion. For example, silver tarnishes, copper develops a green coating, lead or stainless steel lose their lusture due to corrosion. Corrosion causes enormous damage to building, bridges, ships and many other articles made of iron.

Thus *corrosion* is a process of deterioration of a metal as a result of its reaction with air or water (environment) surrounding it.

In case of iron, corrosion is called rusting. Chemically, rust is hydrated form of ferric oxide, $Fe_2O_3 . xH_2O$. Rusting of iron is generally caused by moisture, carbon dioxide and oxygen present in air. It has been observed that rusting takes place only when iron is in contact with moist air. Iron does not rust in dry air and in vacuum.

(2) **Factors which affect corrosion** : The main factors which affect corrosion are

More the reactivity of metal, the more will be the possibility of the metal getting corroded.

The impurities help in setting up voltaic cells, which increase the speed of corrosion

Presence of electrolytes in water also increases the rate of corrosion

Presence of CO_2 in natural water increase rusting of iron.

(v) When the iron surface is coated with layers of metals more active than iron, then the rate of corrosion is retarded.

A rise in temperature (with in a reasonable limit) increases the rate of corrosion.

(3) **Classification of corrosion process** : Depending upon the nature of corrosion, and the factors affecting it, the corrosion may be classified as follows.

(i) *Chemical corrosion* : Such corrosion, generally takes place when

(a) Reactive gases come in contact with metals at high temperatures *e.g.*, corrosion in chemical industry.

(b) Slow dissolution of metal takes place when kept in contact with non conducting media containing organic acids.

(ii) *Bio-chemical corrosion or Bio-corrosion*: This is caused by the action of microorganisms. Soils of definite composition, stagnant water and certain organic products greatly favour the bio-corrosion.

(iii) *Electrochemical corrosion* : It occurs in a gaseous atmosphere in the presence of moisture, in soils and in solutions.

(4) **Mechanism of rusting of iron** : *Electrochemical theory of rusting*.

The overall rusting involves the following steps,

(i) Oxidation occurs at the anodes of each electrochemical cell. Therefore, at each anode neutral iron atoms are oxidised to ferrous ions.

At anode : $Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$.

Thus, the metal atoms in the lattice pass into the solution as ions, leaving electrons on the metal itself. These electrons move towards the cathode region through the metal.


Schematic representation of mechanism of rusting of iron
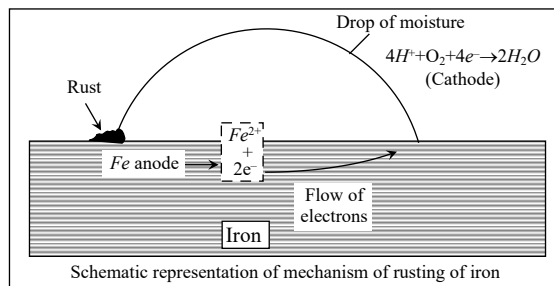
(ii) At the cathodes of each cell, the electrons are taken up by hydrogen ions (reduction takes place). The H^+ ions are obtained either from water or from acidic substances (e.g. CO_2) in water

$$H_2O \longrightarrow H^+ + OH^- \text{ or } CO_2 + H_2O \longrightarrow H^+ + HCO_3^-$$
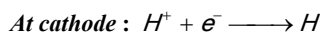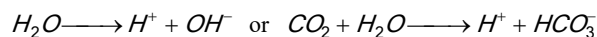
At cathode : $H^+ + e^- \longrightarrow H$

The hydrogen atoms on the iron surface reduce dissolved oxygen. $4H + O_2 \longrightarrow 2H_2O$

Therefore, the overall reaction at cathode of different electrochemical cells may be written as,
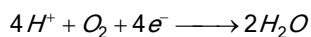
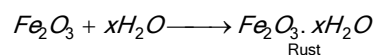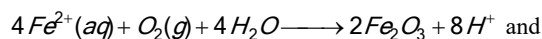$$4H^+ + O_2 + 4e^- \longrightarrow 2H_2O$$

(iii) The overall redox reaction may be written by multiplying reaction at anode by 2 and adding reaction at cathode to equalise number of electrons lost and gained i.e.

Oxi. half reaction : $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-] \times 2$ $(E = -0.44\,V)$

Red. half reaction : $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$ $(E = 1.23\,V)$

Overall cell reaction : $2Fe(s) + 4H^+ + O_2 \rightarrow 2Fe^{2+}(aq) + 2H_2O$

$$(E_{Cell} = 1.67\,V)$$

The ferrous ions are oxidised further by atmospheric oxygen to form rust.

$4Fe^{2+}(aq) + O_2(g) + 4H_2O \longrightarrow 2Fe_2O_3 + 8H^+$ and

$Fe_2O_3 + xH_2O \longrightarrow \underset{Rust}{Fe_2O_3 \cdot xH_2O}$

It may be noted that salt water accelerates corrosion. This is mainly due to the fact that salt water increases the electrical conduction of electrolyte solution formed on the metal surface. Therefore, rusting becomes more serious problem where salt water is present.

(5) **Corrosion protection** : Corrosion of metals can be prevented in many ways. Some commonly used methods are

(i) *By surface coating*

(a) By applying, oil, grease, paint or varnish on the surface.

(b) By coating/depositing a thin layer of any other metal which does not corrode. For example, iron surface can be protected from corrosion by depositing a thin layer of zinc, nickel or chromium on it. Copper/brass can be protected by coating it with a thin layer of tin. Tinning of brass utensils is a very common practice in our country.

(c) *By Galvanization* : Prevention of corrosion of iron by *Zn* coating.

(ii) *By connecting metal to a more electropositive metal* : As long as the more electropositive metal is there, the given metal does not get corroded. For example, iron can be protected from corrosion by connecting it to a block/plate of zinc or magnesium. This method of corrosion protection is called *cathodic protection*.

(iii) *By forming insoluble phosphate or chromate coating* : Metal surfaces are treated with phosphoric acid to form an insoluble phosphate. Formation of a thin chromate layer also prevents the corrosion of metals.

(iv) *Using anti – rust solutions* : Solutions of alkaline phosphates and alkaline chromates are generally used as anti – rust solutions. For example, iron articles are dipped in boiling alkaline sodium phosphate solutions, when a protective insoluble sticking film of iron phosphate is formed.

⊤ Tips & Tricks

- ✍ When two or more ions compete at the electrodes then the ion with higher reduction potential gets liberated at the cathode while the one with lower reduction potential at the anode.
- ✍ Cell constant is determined with the help of conductivity bridge, where a standard solution of *KCl* is used.
- ✍ If the external *EMF* is slightly more than the actual *EMF,* the current will flow into the cell and reverse reaction takes place.
- ✍ Identification of cathode and anode is done by the use of galvanometer.

- ✍ *KCl / NaCl / NH₄Cl etc.,* can not be used in the salt bridge of a cell containing silver salt as one of the electrodes as *Cl⁻* ions form a ppt. of *AgCl* with silver ion.
- ✍ Weston cell is a common example of standard cell. The *emf* of a standard cell does not change with temperature.
- ✍ In Appolo moon flights, $H_2 - O_2$ fuel cell was the source of energy and drinking water.
- ✍ Conductivity water is the highly purified water whose on conductance is very small. It is prepared by the demineralisation of ordinary water by passing through cation and anion exchange resins.