Electrochemistry

INTRODUCTION

* Electrochemistry deals with the study of electrical properties of solutions of electrolytes and with the inter-relation of chemical phenomenon and electrical energies. Electrical energy is carried through matter in the form of electric curent with the help of suitable source and charge carriers (ions or electrons)

Conductors and non conductors

Substances are devided into two classes (a) Non conductor or insulator (b) Conductor

(a) Non - conductor :-

Substances which do not allow electric current to pass through them are called non-conductors or insulators examples - pure water, ice, glass, rubber etc.

(b) Conductor :- Substances which allow electric current to flow through them are called conductors. Examples - Metals, Aqueous solution of acids, bases and salts, fused salts and impure water etc.

Conductors are of two types -

- (i) Metallic conductors
- (ii) Electrolytic conductors or electrolytes.

(i) Metallic conductors :-

The conductors which conduct electric current by movement of electrons without undergoing any chemical change are known as metallic conductors. Metals (Cu,Ag,Fe,Al etc), non metals (graphite) and various alloys and minerals are examples.

(ii) Electrolytic conductors :-

Those substances whose water solution conducts the electric current and which are decomposed by the passage of current are called electrolytes. In this case, conduction takes place by movement of ions. electrolytes also conduct ele ctricity in fused state and undergo decomposition by passage the electric current.

* Substances whose aqueous solution does not conduct electric current are called non-electrolytes.

They do not conduct electricity in the fused state. Solutions of cane suger, glycerine, glucose, urea etc. are the examples of non electrolytes.

Strong electrolyte :-

Electrolytes which are completely ionized in aqueous solution or in their molten state; are called strong electrolyte.

Example - all salts, strong acid and strong base

Weak electrolyte :-

Electrolytes which are not completely ionized in aqueous soluion or in their molten state; are called weak electrolytes.

Examples :- All carbonic acids (except sulphonic acid), CH₃COOH, HCN, NH₃, amine, etc.

	Metallic conduction	Electrolytic conduction
(i)	Electrons flow from negative end	Ions flow towards the oppositely charged electrodes
	to positve end	
(ii)	Flow of electricity takes place without	Flow of electricity takes place by chemical changes
	the decomposition of the substance	at electrodes.
(iii)	No transfer of matter takes place.	Transfer of matter takes place in the form of ions
(iv)	The resistance to the flow of current	The resistance to the flow of current decreases
	increases with the increase in	with the increase in temperature and hence
	temperature and hence the increase in	increase in temperature increases the conduction.
	temperature decreases the conduction.	
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Difference between metallic and electrolytic conduction

ELECTROLYSIS :-

The process of decomposition of an electrolyte by the passage of electricity is called electrolysis or electrolytic dissociation. It is carried out in electrolytic cell where electrical energy is converted into chemical energy. For electrolysis to take place two suitable electrodes are immersed in the liquid. The solution of an electrolyte contains ions. When an electric potential is applied between the electrodes, the positively charged ions move towards the cathode and negatively ions move towards the anode, when a cation reaches the cathode, its takes up electron(s) and thus gets its charge neutralised. Thus the gain of electrons (decrease in oxidation number) means reduction takes place at the cathode. Similarly an anion when it reaches the anode, gives up electron(s) and thus gets discharged. Loss of electrons(Increase in oxidation number) means oxidation takes place at anode.

- * The tendency of an electrode to loose electrons is known as the oxidation potential.
- * The tendency of an electrode to gain electrons is known as the reduction potential.

(a) Electrolysis of fused sodium chloride :-

When fused sodium chloride is electrolysed, Na^+ ions moves towards the cathode and Cl^- ions moves towards the anode. At cathode Na^+ ions accept electrons to form sodium metal. At anode each Cl^- ion loses an electron to form Cl_2 gas.

At anode

 $Cl^{-} \xrightarrow{-\bar{e}} Cl$ $Cl + Cl \longrightarrow Cl_{2}$

At cathode $Na^+ \xrightarrow{+\bar{e}} Na$ (b) Electrolysis of aqueous solution of NaCl

The solution of NaCl containts Na^+ , Cl^- and small amounts of H^+ , OH^- (due to small dissociation of water)

If more than one types of ions are present at a given electrode, then the one liberated is the ion which requires least energy. The energy required to liberate an ion is provided by the applied potential between electrodes. This potential is called discharge or deposition potential

At cathode $H^+ \xrightarrow{+\bar{e}} H$ $H + H \longrightarrow H_2$ At anode $Cl^- \xrightarrow{-\bar{e}} Cl$ $Cl + Cl \longrightarrow Cl_2$

 Na^+ ions move towards the cathode and combine with OH^- ions furnished by feebly ionised water to form NaOH.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

Na⁺ + OH⁻ \rightarrow NaOH

	INODU			
S.	Electrolyte	Electrode	Product obtained	Product obtained at
No.			at anode	cathode
(i)	Aqueous NaCl	Pt or Graphite	Cl ₂	H_2
(ii)	Fused NaCl	Pt or Graphite	Cl ₂	Na
(iii)	Aqueous NaOH	Pt or Graphite	0,	H_{2}
(iv)	Fused NaOH	Pt or Graphite	0,	Na
(v)	Aqueous CuSO ₄	Pt or Graphite	0,	Cu
(vi)	Aqueous CuSO ₄	Copper	Cu oxides to Cu ⁺² Ions	-
(vii)	Aqueous CuCl ₂	Pt or Graphite	Cu oxides to Cu ⁺² ions	Cu
(viii)	Dilute HCl	Pt or Graphite	Cl ₂	H_2
(ix)	Dilute H ₂ SO ₄	Pt or Graphite	0,	H ₂
(x)	Aqueous AgNO ₃	Pt of Graphite	0 ₂	Ag

PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

ELECTROLYTIC CONDUCTANCE :-

(a) Resistance (R) :- Metallic and electrolytic conductors obey ohm's law according to which the resistance of a conductor is the ratio of the applied potential difference (V) to the current following(I).

 $R = \frac{V}{I}$ * R is expressed in ohms.

(b) Conductance (C) :- The conductance of a conductor is equal to reciprocal of resistance

 $C = \frac{1}{R}$ * C is expressed in mho.

(c) Specific resistance (ρ) The resistance (R) of a conductor of uniform cross section is directly proportional to its length(L) and inversely proportional to its area of cross section (A)

$$R \propto \frac{L}{A}$$
 $R = \rho \frac{L}{A}$

whre ρ is a constant and called resistivity or specific resistance.

When L = 1, A = 1, then $\rho = R$ thus the specific resistance may be defined as the resistance of a conductor of unit length and unit area of cross section.

* Unit of ρ ohm - cm

(d) Specific conductance (κ) :- It is defined as the reciprocal of specific resistance

$$\kappa = \frac{1}{\rho}$$

The above definitions apply to metallic conductors and electrolytes.

- * In the case of solution of electrolytes, the resistance offered by the solution to the flow of current is.
- (a) Directly proportional to the distance between the electrodes

 $R \propto L$

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(b) Inversely proportional to the area of cross section of the electrodes

$$\mathbf{R} \propto \frac{1}{\mathbf{A}} \implies \mathbf{R} = \rho \frac{\mathbf{L}}{\mathbf{A}}$$

The conductance $C = \frac{A}{\rho L}$

$$\therefore \frac{1}{\rho} = \mathbf{\kappa} \text{ so } \mathbf{\kappa} = \frac{\text{CL}}{\text{A}}$$

If
$$L = 1 \text{ cm}$$
, $A = 1 \text{ cm}^2$ then $\kappa = C$

Hence specific conductivity of a solution is defined as the conductance of one centimeter cube of the solution of the electrolyte.

$$\mathbf{\kappa} = \frac{\mathrm{CL}}{\mathrm{A}}$$
 Where $\frac{\mathrm{L}}{\mathrm{A}} = \text{cell constant}$

* Cell constant (x) is a fixed quantity for a particular cell and is defined as the distance between two parallel electrodes of a cell devided by the area of cross section of the electrodes.

$$\kappa = C \times \text{cell constant}$$

cell constant = $\frac{\kappa}{C} = \kappa R$ = Specific conductivity x resistance

- * Unit of κ is ohm⁻¹ cm⁻¹
- (e) Equivalent Conductance (λ_{eq}) :- It is defined as the product of specific conductance (κ) and the volume (V in m ℓ) of the solution which contain one gram equivalent of the electrolyte.

$$\therefore \lambda_{eq} = \kappa \times V$$

If concentration of solution is C - gram equivalent per litre then $\lambda_{eq} = \frac{\kappa \times 1000}{C}$

* Unit \rightarrow ohm⁻¹ cm² per gram equivalent

Solved Examples

Ex.1 The resistance of a 1N solution of salt is 50 Ω . Calculate the equivalent conductance of the solution, if the two platinum electrodes in solution are 2.1cm apart and each having an area of 4.2cm².

Sol.
$$\kappa = \frac{1}{\rho} = \frac{1}{R} \left(\frac{L}{A} \right) = \frac{1}{50} \times \frac{2.1}{4.2} = \frac{1}{100}$$

and $\lambda_{eq.} = \frac{\kappa \times 1000}{N} = \frac{1}{100} \times \frac{1000}{1} = 10$ S

(f) Molar conductance :- $(\lambda_m \text{ or } \mu)$

It is defined as the product of specific conductance (κ) and the volume $(V \text{ in } m\ell)$) in which contains one mole of the electrolyte

$$\lambda_{\rm m} = \mu = \kappa \times v$$
 and $\lambda_{\rm m} = \frac{\kappa \times 1000}{M}$

Unit \rightarrow ohm⁻¹ cm² per mole

Solved Examples

Ex.2 Which of the following have maximum molar conductivity.

(i) 0.08M solution and its specific conductivity is 2 \times $10^{-2}~\Omega^{-1}.$

(ii) 0.1M solution and its resistivity is 50Ω cm.

Sol. (i)
$$\lambda_{M} = \frac{\kappa \times 1000}{M} = 2 \times 10^{-2} \times \frac{1000}{0.08}$$

= 250 Ω^{-1} cm² mol⁻¹
(ii) $\lambda_{M} = \frac{\kappa \times 1000}{M}$
 $\therefore \kappa = \frac{1}{\rho} \therefore \lambda_{M} = \frac{1}{50} \times \frac{1000}{0.1} = 200 \,\Omega^{-1} \,\text{cm}^{2} \,\text{mol}^{-1}$

So, the molar conductivity of 0.08M solution will be greater than 0.1M solution

Relation between $\lambda_{eq.}$ and λ_{M} :-

. . . .

$$\lambda_{_{M}} = \frac{\kappa \times 1000}{M} \qquad \text{and} \qquad \lambda_{_{eq.}} = \frac{\kappa \times 1000}{N}$$

We know that

Normality = Valency Factor \times Molarity

or
$$N = n \times M$$
 so $\lambda_{eq.} = \frac{\lambda_M}{V.F.}$

FACTORS INFLUENCING THE CONDUCTIVITY OF ELECTROLYTE

(a) Inter ionic attraction :-

If inter ionic attraction between solute is more, then the conductivity will be less.

(b) Polarity of solvent :-

If the solvant is greater polarized then the ionization and conductivity will be more

(c) Viscosity of medium :-

By increasing the viscosity of medium, the conductivity decreases.

(d) Temperature :-

As the temperature of electrolyte solution is increased, the conductivity increases because K.E. of ions increases and all type of attraction forces decreases and the viscosity of medium decreases.

(e) **Dilution :-**

(i) The degree of ionisation increases with the increase of dilution of the solution the conductivity is increases due to increasing the no. of ions.

(ii) Effect of dilution on specific conductance :-

Specific conductance decreases with the increase of dilution of the solution due to the presence of number of ions in 1cm³ solution decreases.

(iii) Effect of dilution on equivalent/ molar conductivity:-

The equivalent/molar conductivity increases with dilution. This is due to the fact that degree of ionisation increases with dilution.

- * when the whole of the electrolyte has ionised, further addition of the water bring a small change in the value of equivalent/molar conductance. This stage is called infinite dilution.
- * The ratio of equivalent conductivity at any dilution to equivalent dilution at infinite dilution is called conductivity ratio or degree of dissociation of solute-

$$\alpha = \frac{\lambda}{\lambda_{\infty}}$$

Solved Examples

Ex.3 The equivalent conductivity of H_2SO_4 at infinite dilution is $384 \ \Omega^{-1} \ cm^2 \ eq^{-1}$. If $49 \ g \ H_2SO_4$ per litre is present in solution and specific resistance is 184 Ω then calculate the degree of dissociation.

Sol. Equivalent of
$$H_2SO_4 = \frac{49}{49} = 1N$$

specific conductance =
$$\frac{1}{\text{specific resistance}} = \frac{1}{18.4}$$

$$\lambda_{eq.} = \frac{1000 \times \kappa}{N} = \frac{1000 \times 1}{18.4} = 55$$

Degree of dissociation (α) = $\frac{\lambda_{eq.}^{C}}{\lambda_{eq.}^{\infty}} = \frac{55}{384} = 0.14$ = 14%

(f) Effect temperature and pressure :-

Conductivity of all electrolytes increases with increase in temperature. Conductivity of solution is slightly changed with change in pressure due to change in viscosity of medium.

The viscosity of dilute solution decreases with increase in pressure. i.e., equivalent conductivity increases.

TRANSPORT NUMBER :-

The fraction of the current carried by an anion is termed as its transport number. If n_a and n_c are the transport numbers of anion and cation respectively then :-

$$n_{a} = \frac{Current carried by anion}{Total current carried}$$

$$n_{c} = \frac{Current carried by cation}{Total current carried} \qquad n_{a} + n_{c} = 1$$

* The transport number can be determined by Hittorf's method, moving boundry method, EMF method and from ionic mobility.

KOHLRAUSCH LAW :-

This law states that the equivalent conductivity of any electrolyte at infinite dilution $(\lambda_{eq.}^{\infty})$ is the sum of ionic conductances of the cation and anion given by the electrolytes at infinite dilution.

$$\lambda_{eq}^{\infty} = \lambda_{a}^{\infty} + \lambda_{C}^{\infty}$$

consider a salt NaCl, its equivalent conductivity at infinite dilution is the sum of two terms i.e.

$$\lambda_{eq}^{\infty} = \lambda_{Na^{+}}^{\infty} + \lambda_{Cl^{-}}^{\infty}$$

These terms are known as ionic mobilities of anion and cation . The ratio of ionic mobilities is equal to their transport numbers

$$\frac{\lambda_{a}}{\lambda_{c}}\,=\,\frac{n_{a}}{n_{c}}\,=\,\frac{n_{a}}{(1-n_{a})}$$

For $A_x B_y$ type solution :-

$$\lambda_{eq}^{\infty} = \frac{1}{Z^{\scriptscriptstyle +}} \lambda_{C}^{\infty} + \frac{1}{Z^{\scriptscriptstyle -}} \lambda_{a}^{\infty}$$

here $c = cation \& a = anion and Z^+, Z^-$ are the charges on the cation and anion respectively.

$$\lambda_{\rm eq}^{\scriptscriptstyle \infty} = \frac{1}{y} \lambda_{\rm C}^{\scriptscriptstyle \infty} + \frac{1}{x} \lambda_{\rm a}^{\scriptscriptstyle \infty}$$

Solved Examples

Ex.4 At infinite dilution the equivalent conductance of Al⁺³ and SO₄⁻² ion are 189 and 160 Ω^{-1} cm²eq⁻¹ respectively. Calculate the equivalent and molar conductivity at infinite dilute of Al₂(SO₄)₃.

Sol.
$$\lambda_{eq.[Al_2(SO_4)_3]}^{\infty} = \frac{1}{3} \lambda_{Al^{+3}}^{\infty} + \frac{1}{2} \lambda_{SO_4^{-2}}^{\infty} = \frac{1}{3} \times 189 + \frac{1}{2} \times 160$$

= 143 Ω^{-1} cm² eq⁻¹

 $\begin{array}{lll} Molar \ conductivity = \ \lambda_{eq} \times V. \ F. & = \ 143 \times 6 \\ = & 858 \ \Omega^{-1} \ cm^2 \ mol^{-1} \end{array}$

Application :- This law can be used to

- (a) Determine the equivalent conductivities of weak electrolytes at infinite dilution.
- (b) To determine the ionic mobilities and absolute velocity of ions.
- (c) Determination of degree of dissociation, since α , the degree of dissociation of an electrolyte at the

dilution V is given by
$$\alpha = \frac{\lambda}{\lambda_{\infty}}$$
 where $\lambda_{\infty} = \lambda_{a} + \lambda_{a}$

FARADAY'S LAWS OF ELECTROLYSIS

Michael Faraday deduced two important law:-

(a) **Faraday's first law of elecrolysis :** This law states that "The amount of a substance deposited or dissolved at an electrode is directly proportional to the charge passing through the electrolytes.

If a currect of I amperes is passed for t seconds, the quantity of charge Q in coulombs. If Wgram of substances is deposited by Q coulombs of electricity, then

$$W \propto Q \propto It$$
 or $W = z It = \frac{E}{96500} It$

Where z is constant of proportionality and is known as electrochemical equivalent.

* When Q = 1 coulomb, W = z

thus electro chemical equivalent may be defined as the weight in grams of an element liberated by the passage of 1 coulomb of electricity.

Solved Examples

Ex.5 How many cc of chlorine will be deposited by 100A current flowing for 5 hours through melted NaCl.

Sol.
$$Q = It = 100 \times 5 \times 60 \times 60 = 18 \times 10^{5}$$

W = ZQ =
$$\frac{E}{96500} \times 18 \times 10^5 = \frac{18E}{96500} \times 10^3 =$$

 $\frac{18 \times 35.5}{965} \times 10^3 = 662.2 \text{ g}$
 \therefore Volume of 71 g Cl₂ at NTP = 22.4 L

:. volume of 662.2 g Cl₂ at NTP = $\frac{22.4}{71} \times 662.2$ = 208.9 L

- **Ex.6** The time required to coat a metal surface of 80 cm^2 with 0.005mm thick layer of silver (density = 10.5 g cm^{-3}) with the passage of 3A current through silver nitrate solution is –
- **Sol.** : Volume of layer of silver = $0.005 \times 10^{-1} \times 80$ = 0.04 cm³

$$\therefore \text{ Mass} = \text{Density} \times \text{volume} = 10.5 \times 0.04$$
$$= 0.42 \text{ g}$$

So w =
$$\frac{E}{96500}$$
 × It or 0.42 = $\frac{108}{96500}$ × 3 × t
or t = $\frac{0.42 \times 96500}{108 \times 3}$ = 125.09 seconds.

(b) Faraday's second law : This law states that the amounts of different substances deposited at electrodes by passage of the same quantity of electricity are proportional to their chemical equivalent(E).

 $W \propto E$

If W_1 and W_2 be the amounts of two different substances deposited at electrodes and E_1 and E_2 be the equivalent weights then $-\frac{W_1}{W_2} = \frac{E_1}{E_2}$ combining the two laws $W \propto \text{It } E$ or $W = \frac{\text{It} E}{F}$

Where $\frac{1}{F}$ is proportionality constant and F is called faraday.

when It = F then W = E

Hence faraday (F) is the quantity of charge in coulombs required to deposit one gram equivalent of any substance.

* The Faraday (F) is also the quantity of charge carried by one mole of electrones

 $F = e \ge N = 1.6 \ge 10^{-19} \ge 6.023 \ge 10^{23} = 96500$ coulombs.

* To deposit one mole of any metal of valency Z, requires Z moles of electrons.

thus
$$M = zZF$$
 ($M \rightarrow mass of one mole$)

$$\therefore w = zQ$$
 $\therefore \frac{W}{M} = \frac{zQ}{zZF} = \frac{Q}{ZF} \Rightarrow \boxed{\frac{W}{M} = \frac{Q}{ZF}}$

- * The equivalent weight $E = \frac{M}{Z}$
- * When atoms of the element are deposited, M is called gm atomic weight and when molecules are deposited M is called gm molecular weight.

Solved Examples

- **Ex.7** The same current if passed through solution of silver nitrate and cupric salt connected in series. If the weight of silver diposited is 1.08 g. Calculate the weight of copper deposited
- Sol. According to faradays second law

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \implies \frac{1.08}{W_2} = \frac{108}{31.75} \implies W_2 = 0.3175 \text{ g}$$

ELECTRO CHEMICAL CELL/ GALVANAIC CELL/VOLTAIC CELL

Example-Daniel Cell

- * A cell in which the chemical energy is transformed into electrical energy.
- * The chemical reaction occuring in a galvanic cell is always a redox reaction.
- * During the chemical process, the reduction in free energy will obtain as a result in the form of electrical energy.



Salt bridge :-

- 1. It allows to flow of current by completing the circuit.
- 2. It maintains electrical neutrality of electrolytes in two half cells.

Characteristics of electrolyte used in salt bridge:

- 1. The electrolyte should be inert
- 2. The cations and anions of the electrolyte used should be of the same ionic mobality

Cell reaction –

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

Representation of Galvanic cell.

$$Zn/Zn^{+2} // Cu^{+2} / Cu$$

$$\begin{array}{c|c} (C_1) & (C_2) \\ Anode \bullet & Cathode \end{array}$$

salt bridge

Electrode potential : When a strip of metal is brought in contact with the solution containing its own ions then the strip of metal gets positively charged or negatively charged and results into a potential being developed between the metallic strip and its solution which is known as electrode potential.

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At anode M \rightarrow M^{+n} + ne^- (Oxidation Potential)
At cathode M^{+n} + ne^- \rightarrow M (Reduction Potential)
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- The value of electrode potential depends upon :
- (1) the nature of electrode
- (2) the concentration of solution
- (3) the temperature

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Standard electrode potnetial (E^0) : If the concentration of ions is unity, temperature is $25^{\circ}C$ and pressure is 1 atm (standard conditions), the potential of the electrode is called standard electrode potential.

The given value of electrode potential be regarded as reduction potential unless it is specifically mentioned that it is oxidation potential.

Electro motive force of cell or cell voltage : The difference in the electrode potentials of the two electrodes of the cell is termed as electro motive force [EMF] or cell voltage.

 $E_{cell} = E_{red} (cathode) - E_{red} (anode)$ or $E_{cell} = E_{oxi.}(anode) - E_{oxi.}(Cathode)$ or $E_{cell} = E_{oxi.}(anode) + E_{red}(cathode)$

ELECTRO CHEMICAL SERIES

The arrangement of various elements in order of increasing values of standard reduction potentials is called electrochemical series.

Standard electrode Potential	E° _{red} (Volt)
Ц	-3.05
Κ	-2.925
Ba	-2.90
Ca	-2.87
Na	-2.714
Mg	-2.37
Al	-1.66
Mn	-1.305
Zn	-0.7628
Cr	-0.74
Fe	-0.44
Cd	-0.403
Со	-0.28
Ni	-0.25
Sn	-0.14
Pb	-0.13
Н	0.00
Cu	+0.337
I_2	+0.535
Ag	+0.799
Hg	+0.885
Br ₂	+1.08
Cl_2	+1.36
Pt	+1.20
Au	+1.50
F_2	+2.87

Important points about series :-

- 1. Electrode whose standard reduction potential is less, act as anode, and other one which has high reduction potential acts as cathode.
- 2. Metals near the top of the series are strongly electropositive.

	Metals near the top of the series can displace more electronegative metal below them from their salt.
	for example :
	$2AgNO_{c} + Cu \rightarrow Cu(NO_{c}) + 2Ag$
	$CuSO + Ag \rightarrow Reaction is not observed$
4	Metal above hydrogen can displace H from dilute.
	acid
	For example :
	$Na + H_2SO_4 \rightarrow Na_2SO_4 + H_2\uparrow$
	$Cu + H_2SO_4 \rightarrow Reaction is not observed$
5.	Hydro oxides of metal in the upper part of series are strongly basic while hydro oxides of a metal in lower part are weakly basic.
6.	The activity of non metals increases from top to bottom.
7.	The metals which come below copper form unstable oxides, i.e., these are decomposed on heating.
NE	CRNST EQUATION
	With the help of Nernst equation, we can calculate the electrode potential of electrode or EMF of cell.
	$E_{cell} = E^0 - \frac{RT}{nf} \log_e \frac{[Product]}{[Reactant]}$
	Where - E^0 = standard electrode potential, R = gas constant, T = temperature (in K)
	Where - E^0 = standard electrode potential, R = gas constant, T = temperature (in K) F = Faraday (96500 coulomb mol ⁻¹), n = number of e ⁻ gained or loosed in balanced equation.
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	Where - E^0 = standard electrode potential, R = gas constant, T = temperature (in K) F = Faraday (96500 coulomb mol ⁻¹), n = number of e ⁻ gained or loosed in balanced equation. or $E_{cell} = E^0 - \frac{0.059}{n} \log_e \frac{[Product]}{[Reactant]}$ Let, in the cell : at Anode : $M_1 \rightarrow M_1^{+n} + ne^-$ for this reaction : $E_{oxi} = E_{oxi}^0 - \frac{0.059}{n} \log_{10} \frac{[M_1^{+n}]}{[M_1]}(1)$
	Where - E^0 = standard electrode potential, R = gas constant, T = temperature (in K) F = Faraday (96500 coulomb mol ⁻¹), n = number of e ⁻ gained or loosed in balanced equation. or $E_{cell} = E^0 - \frac{0.059}{n} \log_e \frac{[Product]}{[Reactant]}$ Let, in the cell : at Anode : $M_1 \rightarrow M_1^{+n} + ne^-$ for this reaction : $E_{oxi} = E_{oxi}^0 - \frac{0.059}{n} \log_{10} \frac{[M_1^{+n}]}{[M_1]} - \dots (1)$ at Cathode : $M_2^{+n} + ne^- \rightarrow M_2$
	Where - E^0 = standard electrode potential, R = gas constant, T = temperature (in K) F = Faraday (96500 coulomb mol ⁻¹), n = number of e ⁻ gained or loosed in balanced equation. or $E_{cell} = E^0 - \frac{0.059}{n} \log_e \frac{[Product]}{[Reactant]}$ Let, in the cell : at Anode : $M_1 \rightarrow M_1^{+n} + ne^-$ for this reaction : $E_{oxi} = E_{oxi}^0 - \frac{0.059}{n} \log_{10} \frac{[M_1^{+n}]}{[M_1]}(1)$ at Cathode : $M_2^{+n} + ne^- \rightarrow M_2$ for this reaction :

Note :

Concentration of solid taken as unity.

so
$$[M_1] = [M_2] = 1$$

We know that EMF of cell

$$EMF = E_{oxi} + E_{red.}$$
(Anode) (Cathode)

is

By adding equation (1) & (2) we get –

$$\begin{split} & \text{EMF} = \text{E}_{\text{oxi}}^{0} - \frac{0.059}{n} \log \left[\text{M}_{1}^{+n} \right] \\ & + \text{E}_{\text{red.}}^{0} - \frac{0.059}{n} \log \frac{1}{\left[\text{M}_{2}^{+n} \right]} \\ & = \left(\text{E}_{\text{oxi}}^{0} + \text{E}_{\text{red.}}^{0} \right) - \frac{0.059}{n} \left[\log \left[\text{M}_{1}^{+n} \right] - \log \left[\text{M}_{2}^{+n} \right] \right] \\ & \text{EMF} = \text{E}_{\text{cell}} = \text{E}_{\text{cell}}^{0} - \frac{0.059}{n} \log \frac{\left[\text{M}_{1}^{+n} \right]}{\left[\text{M}_{2}^{+n} \right]} \end{split}$$

Solved Examples

Ex.8 The 0.1M copper sulphae solution in which copper electrode is dipped at 25°C. Calculate the electrode potential of copper electrode [Given $E_{Cu+2/Cu}^0 = 0.34V$]

Sol.
$$Cu^{+2} + 2e^{-} \rightarrow Cu$$

$$E_{red} = E_{red}^{0} - \frac{0.059}{n} \log \frac{[Product]}{[Reactant]}$$

here n = 2

so
$$E = 0.34 - \frac{0.059}{2} \log 10$$

Calculate = $0.34 - 0.03 = 0.31$ Volts

Ex.9 The EMF of the cell

 $Cr / Cr^{+3} (0.1M) // Fe^{+2} (0.01M) / Fe$

(Given
$$E_{Cr^{+3}/Cr}^{\circ} = -0.75V$$
, $E_{Fe^{+2}/Fe}^{\circ} = -0.45V$)

Sol. Half cell reactions are -

- At Anode & $[Cr \rightarrow Cr^{+3} + 3e^{--}] \times 2$
- At Cathode & $[Fe^{+2} + 2e^{-} \rightarrow Fe] \times 3$

over all reaction $2Cr + 3Fe^{+2} \rightarrow 2Cr^{+3} + 3Fe$

 $E^{\circ}_{cell} = oxidation potantial + Reduction potantial$ = 0.70 + (-0.45) = 0.30

$$E_{cell} = E^{0} - \frac{0.059}{n} \log \frac{[Product]}{[Reactant]}$$
$$= 0.30 - \frac{0.059}{6} \log \frac{[Cr^{+3}]^{2}}{[Fe^{+2}]^{3}}$$
$$= 0.30 - \frac{0.059}{6} \log \frac{[0.1]^{2}}{[0.01]^{3}}$$
$$= 0.30 - \frac{0.24}{6} = 0.26 \text{ Volt.}$$

Note :

- 1. The value of electrode potential does not depend on sticheometry of half reactions.
- 2. In electrolytic cell, cathode is negative terminal whereas in Galvanic cell cathode is positive terminal.
- 3. Work obtained by electro chemical cell = free energy of cell

$$\Delta G = -nFE_{cells} \qquad \Delta G^{\circ} = -nFE^{\circ}_{cells}$$

4. Cell reaction is spontaneous, if AG = -ve or E = +ve

e.g. $\Delta G = 0$ or $-nFE_{cell} = 0$ or $E_{cell} = 0$

6. In nernst equation :

$$\begin{split} E_{cell} &= E_{cell}^{0} - \frac{0.059}{n} \log_{10} \frac{[Product]}{[Reactant]} \\ \text{If } E_{cell} &= 0, \text{ then } \qquad E_{cell}^{0} = \frac{0.059}{n} \log_{10} \frac{[Product]}{[Reactant]} \\ \text{or } E_{cell}^{0} &= \frac{0.059}{n} \log_{10} \text{ K} \qquad \text{or } \qquad E_{cell}^{0} = \frac{\text{RT}}{\text{nF}} \log_{\text{e}} \text{ K} \\ \text{put the value of } E_{cell}^{0} \text{ in } : \Delta \text{G}^{\circ} = -\text{nFE}_{cell}^{\circ}, \text{ we get} \\ \Delta \text{G}^{0} &= -\text{nF} \frac{\text{RT}}{\text{nF}} \log_{\text{e}} \text{ K} \qquad \text{or } \quad \Delta \text{G}^{\circ} = -\text{RT} \log_{\text{e}} \text{ K} \end{split}$$

Applications of Electrolysis :-

- (a) Electrometallurgy :- The metals (Na, K, Mg, Al etc.) are obtained by the electrolysis of fused electrolytes.
- (b) Electro refining of metals :- A large number of metals (Cu, Ag, Au, Al, Sn) are purified by electrolysis.
- (c) Electroplating :- Deposition of precious metals (Au, Ag, Pt) on less expensive metals (Cu) is carried out by electrolysis.

- (d) Manufacture of non metals :- Electrolysis has been employed in the manufacture of H_2 , Cl_2 , F_2 etc.
- (e) Manufacture of compounds :-

Electrolysis has been used in the large scale production of various compounds such as NaOH, KOH, KCl, Na₂CO₃, H_2O_2 etc.

Reversible cell :- A cell is said to work reversible

(a) If the external emf is equal to that of cell, no current flows and no chemical reaction occurs in the cell.

(b) If the external emf is slightly smaller than the emf of the cell, a small current flows out the cell and a small amount of chemical reaction takes place in the cell.

(c) If the external e.m.f. is slightly greater than the e.m.f. of the cell current flows into the cell and cell reaction gets reversed.

The Daniell cell is a example of reversible cell.

- * The e.m.f of the Daniell cell is 1.10 volt
- * If an external e.m.f. equal to 1.10 volt is applied to this cell no current flow through the cell and no reaction will occure.
- * If external emf is slightly less than 1.10 volts a small current flow out of the cell and the reactions are

 $Zn(s) \rightarrow Zn^{+2} + 2e^{-} \qquad Cu^{+2} + 2e^{-} \rightarrow Cu(s)$

* If the external emf is slightly more than 1.10 volts, the curent will flow in to cell and reverse reactions occur :-

 $\operatorname{Zn}^{+2} + 2e^{-} \rightarrow \operatorname{Zn}(s) \qquad \operatorname{Cu}(s) \rightarrow \operatorname{Cu}^{+2} + 2e^{-}$

SOME COMMERCIAL BATTERIES

Any battery or cell that we use as a source of electrical energy is basically an electrochemical cell where oxidising and reducing agents are made to react by using a suitable device. In principle, any redox reaction can be used as the basis of an electrochemical cell, but there are limitations to the use of most reactions as the basis of practical batteries. A battery should be reasonably right and compact and its voltage should not vary appreciably during the use. There are mainly two types of cells : (i) primary cells and (ii) secondary cells. In primary cells, the reaction occurs only once and the battery then becomes dead over a period of time and cannot be used again. (For example, dry cell, mercury cell.) Contrary to this, secondary cells can be recharged by passing a current through them so that they can be used again and again.(For example, lead storage battery, nickelcadmium storage cell.)

PRIMARY CELLS

The most familiar type of battery is the dry cell which



is acompact of Leclanche cell known after its discover Leclanche (fig.). In this cell, the anode consists of a zinc container and the cathode is a graphite rod surrounded by powdered MnO_2 and carbon. The space between the electrodes is filled with a moist paste of NH_4Cl and $ZnCl_2$. The electrode reactions are complex, but they can be written approximately as follows.

Anode : $Zn(s) \longrightarrow Zn^{+2} + 2e^{-1}$

Cathode : $MnO_2+NH_4^++e^- \longrightarrow MnO(OH) + NH_3$ In the cathode reaction, manganese is reduced from the 4+ oxidation state to the 3+ state. Ammonia is not liberated as a gas but combines with Zn^{2+} to form $Zn(NH_3)_4^{2+}$ ion. Dry cells do not have an indenfinite life as acidic NH_4Cl corrodes the zinc container even when not in use. **Dry cells have a potential of approximately 1.25 to 1.5V.** A new type of dry cell which has found use in small electrical circuits (such as hearing aids, watches and camera) is the mercury cell. Here zinc-mercury amalgam is the anode; a paste of HgO and carbon is the cathode. The electrolyte is a paste of KOH and ZnO. The reaction of the cell is as follows :

Anode Zn(amalgam) + 2OH⁻ \longrightarrow ZnO(s) + H₂O + 2e⁻ Cathode HgO(s) + H₂O + 2e⁻ \longrightarrow Hg(I) + 2OH⁻

Overall reaction : $Zn(amalgam) + HgO(s) \longrightarrow$ ZnO(s) + Hg(I)

Since the overall cell reaction does not involve any ion in solution whose concentration can change, the cell shows a constancy in potential throughout its life. **The cell potential is approximately 1.35V.**

SECONDARY CELLS

The most important secondary cell is the lead



storage battery. It consists of a **lead anode** and a grid of lead packed with **lead dioxide as cathode**. A solution of sulphuric acid (38 percent by mass or having density 1.30 gm cm⁻³) is used as an electrolyte.

When the cell discharges, it operates as

a voltaic cell. The lead is oxidised to Pb^{+2} ion and lead plates acquire a negative charge.

At Anode: $Pb \longrightarrow Pb^{+2} + 2e^{-} \dots(i)$

 Pb^{+2} ions combine with sulphate ions of solution to form insoluble lead sulphate $PbSO_4$, when begins to coat lead electrode

 $Pb^{+2} + SO_4^{2-} \longrightarrow PbSo_4(Precipitation) \dots(ii)$

The electrons given by Pb are used at cathode (PbO_2 electrode)

At Cathode: $PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O$ (iii)

 $Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4$ (Precipitation)(iv)

Over all cell reaction \rightarrow add equation (i), (ii), (iii) & (iv)

 $\begin{array}{l} Pb + PbO_2 + 4H^+ + 2SO_4^{\ 2-} \longrightarrow 2PbSO_4 + 2H_2O \\ E_{cell} \text{ is } 2.041 \text{ volt} \end{array}$

(A 12 V lead storage battary is generally used which consist of 6 cells each producing 2 volt)

When a potential slightly greater than the potential of battery is applied, the battery can be reacharged. During recharging the cell is operated like an electrolytic cell ie. now electrical energy is supplied to it from an external source. The electrodes reactions are reverse of those that occur during discharge :

 $2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 2H_2SO_4$ It is clear that H_2SO_4 is used up during the discharge & produced during reaching reaction of cell.

Another secondary cell is the nickel-cadmium storage cell which has a longer life than the lead storage cell but it is more expensive to manufacture. We shall not go into details of these cells here.

FUEL CELLS

It is possible to make batteries in which the reactants



are fed continuously to the electrodes. Electrical cells that are designated to convert the free energy from the combustion of fuels such as hydrogen, carbon monoxide or methane directly into electrical energy are called FUEL CELLS. One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water (fig.). This cell has been used for electric power in the Appollo space programme. The water vapour produced was condensed and added to the drinking water supply for the astronauts. In the cell (fig.) hydrogen and oxygen are bubbled through a porous carbon electrode into concentrated aqueous sodium hydroxide. Catalysts are incorporated in the electrode. The electrode reactions are :

Anode $2[H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(\ell) + 2e^-]$ Cathode $O_2(g) + 2H_2O(\ell) + 4e^- \longrightarrow 4OH^-(aq)$

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

This cells runs continuously as long as the reactants are supplied. Since fuel cells convert the energy of a fuel directly to electricity, they are potentially more efficient than the conventional method of generating electricity on a large scale by burning hydrogen, carbon fuels or by using nuclear reactor. Although **theoretically we expect 100 percent efficiency in fuel cells, so far an efficiency of only 60-70 per cent has been attained**. Since fuel cells are efficient and free from pollution, efforts are being made to produce better commercially practical fuel cells.

CORROSION

Corrosion is basically an electrochemical phenomenon. The rusting of iron, the tarnishing of silver, development of a green coating on copper and bronze are some of the examples of corrosion. Corrosion causes enormous damage to building, bridges, ships and to many other articles made of iron. We spend crores of rupees every year on this account.

In corrosion, a metal is oxidised by loss of electrons to oxygen and forms metal oxide. Corrosion of iron(which is commonly known as rusting) occurs in presence of water and oxygen (air). Although the chemistry of corrosion is complex but it is understood that at one spot of an iron object oxidation occurs and that spot behaves as an anode.

Anode
$$\operatorname{Fe}(s) \longrightarrow \operatorname{Fe}^{2+}(aq) + 2e^{-}$$

$$(E^{0}_{Fe^{2+}/Fe} = -0.44V)$$

Electrons released at anode move through the metal and go to another spot on the metal and reduce the oxygen in presence of H^+ ions (which is believed to be available from H_2CO_3 formed due to dissolution of CO_2 in water). This spot works as a cathode :

Cathode $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(\ell);$ ($E^0 = 1.23 \text{ V}$)

Here Fe^{2+} ions move through water on the surface of the iron object. (If water present is saline, it will help more in carrying the current in the miniature cell thus formed and will enhance corrosion). The overall reaction of the miniature cell is the sum of the cathode and anode reactions as follows :

 $\begin{array}{l} 2Fe(s) + O_2(g) + 4H^{\scriptscriptstyle +}(aq) \longrightarrow 2Fe^{2+}(aq) + \\ 2H_2O(\ell); \ E^0_{\ Cell} = 1.67 \ V) \end{array}$

The Fe²⁺ ions are further oxidised by atmospheric oxygen to Fe³⁺ (as Fe₂O₃) and comes out as rust in the form of a hydrated iron (III) oxide expressed as Fe₂O₃, xH_2O .

 $\begin{array}{rcl} 4Fe^{2+}(aq)\,+\,O_2(g)\,+\,4H_2O(\ell) \longrightarrow & 2Fe_2O_3(s)\,+\\ 8H^+ \end{array}$

 $\rm H^{\scriptscriptstyle +}$ ions produced in the above reaction help further in rusting.

Impurities present in iron also enhance rusting by setting a number of miniature cells. Very pure iron does not rust quickly.



PREVENTION FROM CORROSION

Corrosion of a metal is prevented by applying protective coating (such as greese, paint or metal coatings) on its (metals) surface. In case of iron this coating is done in two ways : (i) electrolysis (Cr, Ni and Cd coating) (ii) dipping iron objects in a molten metal (Zn and Sn coating). Use of zinc coating to protect iron is called Galvanisation. In galvanising iron, zinc being more reactive than irons serves as an anode and is oxidised

 $(E^{0}_{Zn^{2+}/Zn} = -0.76V \text{ and } E^{0}_{Fe^{2+}/Fe} = -0.44V).$



Fig. : Galvanised iron. Cathodic protection of iron in contact with zinc is provided by galvanization.



Here it is important to note that iron does not rust even after zinc coating is broken which is not true in case of tin coating over iron ($E^{0}sn^{2+}/sn = -0.14V$). Now if the coating is broken, iron is exposed and iron being more active than both copper and tin, is corroded. Here iron corrodes more rapidly than it does in the absance of tin. But tin protects copper in the same way as zinc protects iron ($E^{0}Cu^{2+}/Cu = 0.34V$).

Instead of coating more reactive metals on iron, the use of such metals is made as sacrificial anode. This method of preventing iron from corrosion is called CATHODIC PROTECTION.

In this method, a plate of reactive metal (Zn or Mg) is burried beside the iron pipe or tank and connected to it by wires.

Here iron becomes **cathode** and more reactive metal becomes **anode**. The reactive metal anode is sacrificed to protect the iron. Since these reactive metal plates are oxidised quickly, they are replaced from time to time which is easy to do.

IMPORTANT POINTS

- 1. Electrolytes also conduct electricity in fused state and undergo decomposition by the passage of electric current.
- 2. The theory of ionisation was proposed by Arrhenius.
- 3. Galvanic cells are used to convert chemical energy to electrical energy.
- 4. The amount of current which produce one gm equivalent of any substance is called faraday.
- 5. Mg can librate H₂ gas from HCl
- 6. When zinc piece is added to CuSO_4 solution, copper gets precipitated because standard reduction potential of zinc is less than that of copper.
- 7. The electrode at which oxidation occurs is called positive electrode and at which reduction occurs is known as negative electrode.
- 8. In a galvanic cell cathode acts as positive electrode and anode as negative electrode.
- 9. In electrolytic cell cathode acts as negative electrode and anode as positive electrode.
- 10. More negative the standard reduction potential of a metal, the greater is its ability to displace hydrogen from acids.
- 11. More the reduction potential less is the reducing power.
- 12. Cell voltage is independent of the size of cell or electrodes.
- 13. Standard potential is the potential measured at 25°C, 1 atm. pressure and one molar concentration of the ions.