ELECTROCHEMESTRY

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B.Sc:- II (Sub). Lecture-I

Introduction:-

Electrochemistry deals with the study of electrical properties of solutions of el ectrolytes and with the interrelation of chemical phenomenon and electrical en ergies. Electrical energy is carried through matter in the
form of electric current with the help of suitable source and charge carriers (i ons or electrons). 1 .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 calle d 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 w ater 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 witho ut undergoing any chemical change are known as metallic conductors.
Metals (Cu,Ag,Fe,Al etc), non metals (graphite) and various alloys and mineral s are examples. (i i) Electrolytic conductors :
Those substances whose water solution conducts the electric current and whic h are decomposed by the passage
of current are called electrolytes. In this case, conduction takes place by mov ement of ions.
electrolytes also conduct electricity in fused state and undergo decomposition by passage the electric current. u
Substances whose aqueous solution does not conduct electric current are call ed non-electrolytes.
They do not conduct electricity in the fused state also. 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 st ate, are called strong electrolytes. Example –
 all salts, strong acid and strong base Weak electrolyte :
Electrolytes which are not completely ionized in aqueous solution or in their molten state, are called weak electrolytes. Examples :-
 All carbonic acids (except sulphonic acid), $CH_3 COOH$, HCN, NH_3
, amine, etc.
DIFFERENCE BETWEEN METALLIC AND ELECTROLYTIC CONDUCTION :
Metallic conduction Electrolytic conduction (i)
Flow of electricity takes place without
Flow of electricity takes place by chemical changes
the decomposition of the substance at electrodes. (ii)

No transfer of matter takes place.

Transfer of matter takes place in the form of ions (iii)

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. ELECTROCHEMISTRY 2 .

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.
υ

The tendency of an electrode to loose electrons is known as the oxidation potential. υ

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 $Cl^- \longrightarrow e$

$\rightarrow Cl$ $Cl + Cl \longrightarrow Cl_2$ At cathode $Na^+ \longrightarrow + e \rightarrow Na$ (b)

Electrolysis of aqueous solution of NaCl The solution of NaCl contain Na^+

, Cl^- and small amounts of H^+ , OH^- (due to small dissociation of water) υ

If more than one types of ions are present at a given electrode, then the one ion is the liberated 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. θ

ORDER OF DISCHARGE POTENTIAL :

Higher be the discharge potential, lower will be the tendency of ion to get discharged at the respective electrode.

The decreasing order of discharge potential or increasing order of deposition of some of ions are given below : For cations : K^+ , Na^+

, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, H^+ , Cu^+ , Ag^{2+}, Ag^+ For anions : $SO_4 -$, $NO_3 -$

, OH^- , Cl^- , Br^- , I^- At cathode $H^+ e^- \longrightarrow + H$ $H + H \longrightarrow H_2$ At anode $Cl^- e^- \longrightarrow - Cl$ $Cl + Cl \longrightarrow Cl_2$

Na^+ ions move towards the cathode and combine with OH^- ions furnished by feebly ionised water to form NaOH. $2H_2 O + 2e^- \rightarrow H_2 + 2OH^-$

$Na + + OH^- \rightarrow NaOH$

PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

S. No.	Electrolyte	Electrode	Product obtained at anode	Product obtained at 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	O_2	H_2
(iv)	Fused NaOH	Pt or Graphite	O_2	Na
(v)	Aqueous $CuSO_4$	Pt or Graphite	O_2	Cu
(vi)	Dilute HCl	Pt or Graphite	Cl_2	H_2
(vii)	Dilute H_2SO_4	Pt or Graphite	O_2	H_2
(viii)	Aqueous $AgNO_3$	Pt of Graphite	O_2	Ag

3. 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(λ) and inversely proportional to its area of cross section (A)

$$R \propto \frac{\lambda}{A} \qquad R = \rho \frac{\lambda}{A}$$

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

When $\lambda = 1$, 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 $\rho \rightarrow$ 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 $R \propto \lambda$

(b) Inversely proportional to the area of cross section of the electrodes $R \propto \frac{1}{A}$

$$R = \rho \frac{\lambda}{A}$$

The conductance $C = \frac{A}{\rho\lambda}$ Θ $\frac{1}{\rho} = \kappa$ so $\kappa = \frac{C\lambda}{A}$

If $\lambda = 1$ cm and $A = 1$ cm2 then $\kappa = C$

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

$$\kappa = \frac{C\lambda}{A}$$

Where $\frac{A}{\lambda}$ = 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.

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

$\kappa = \kappa R =$ Specific conductivity × resistance

Unit of $\kappa \rightarrow$ ohm–1 cm–1

(e) Equivalent Conductance (λeq) : It is defined as the product of specific conductance (κ) and the volume (V in mL) 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 λeq $= \frac{1000}{C} \kappa \times$

Unit $\rightarrow$ ohm–