Electrochemistry

Section (A) : Basic Terminology and Construction of Electrochemical Cell and Its Repsentation, Salt Bridge

Introduction

Batteries are everywhere in modern societies. They provide the electric current to start our autombiles and to power a host of products such as pocket caculators, digital watches, heart pacemaker, radio, and tape recorders.

Electrochemistry is the area of chemistry concerned with the interconversion of chemical and electrical. A battery is a an electrochemical cell, a device for interconverting chemical and electrical energy. A battery takes the energy relased by a spontaneous chemical reaction and uses it to produce electricity.

Electrochemical cell :

It is device for converting chemical energy in to electrical energy.

Electrochemical cell are of two types

Galvanic cells or Voltaic cell	Electrolytic cell.
● A spontaneous chemical reaction generates an electric current.	● An electric current drives a nonspontaneous reaction.

❍ ***The two types of cells are therefore reverse of each other***

Construction/ Working principle

When ever an metal strip is put in an electrolyte the process of oxidation and reduction takes place simultaneously within the system. Due to this there is a potential difference between the metal phase and the liquid phase.

On joining the metal strips through a wire (of negligible resistence) the current flows as long as the potential difference exists between the metal phase and the liquid phase.

l **Anode :**

Some metals (which are reactive) are found to have tendency to go into the solution phase when these are placed in contact with their ions or their salt solutions.

For example : Zn rod is placed in $ZnSO_4$solution.

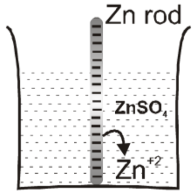


Figure : 1

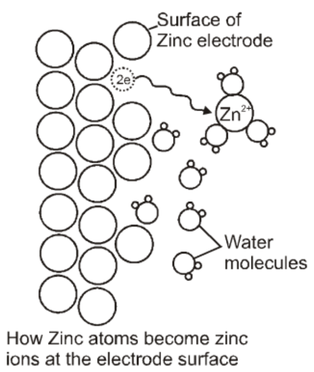


Figure : 2

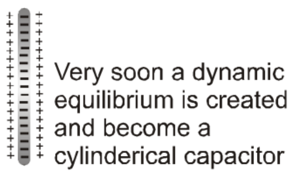


Figure : 3

The Zn atom or metal atoms will move in the solution to form Zn^{+2}. After some time following equilibrium will be established. $Zn(s) \rightleftharpoons Zn^{2+} + 2e^{-}$

There will be accumulation of sufficient negative charge on the rod which will not allow extra zinc ions to move in the solution. i.e. solution will be saturated with Zn^{+2} ions.

The positive charge will be more concentrated nearly the rod.

The extra positive charge of the solution will be more concentrated around the negatively charged rod. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution which is known as electrode potential

This particular electrode is known as anode :

- On anode oxidation will take place. (release of electron).
- To act as source of electrons.
- It is of negative polarity.
- The electrode potential is represented by $E_{Zn(s) / Zn2+ (aq)}$

II Cathode :

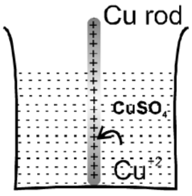


Figure : 1

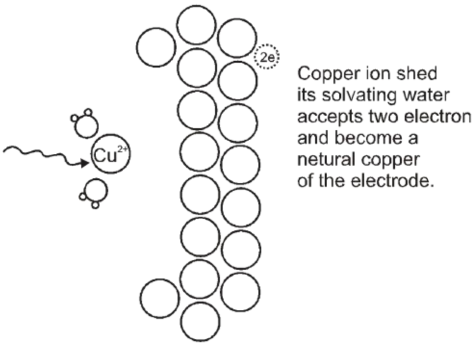


Figure : 2

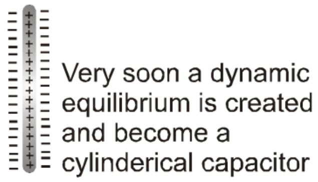


Figure : 3

Some metals(Cu, Ag, Au etc.,) are found to have the opposite tendency i.e. when placed in contact with their aqueous ions, the ions from the solution will get deposited on the metal rod.

The following equilibrium will be established : $Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$.

So rod will have deficiency of electron (positive charge).Extra negative charge will surround this positively charged rod and form double layer. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution which is known as electrode potential. This will be known as cathode.

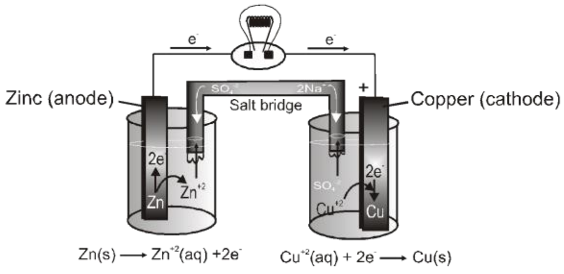
- At cathode reduction will take place.(gain of e^- will take place)
- To act as sink of electron.
- Positive polarity will be developed.
- Their electrode potential can be represented by : $E_{Cu2+(aq)/Cu(s)}$

Anode :
Is where oxidation occurs
Is where electrons are produced
Has a negative sign

Cathode :
Is where reduction occurs
Is where electrons are consumed
Has a positive sign

Construction of Cell :

- It has two **half–cells**,each having a beaker containing a metal strip that dips in its aqueous solution.
- The metal strips are called **electrodes** and are connected by an conducting wire.
- Two solutions are connected by a **salt bridge.**
- The oxidation and reduction half reactions occur at a separate electrodes and electric current flows through the wire.



Selection of electrolyte for Salt Bridge :

- The electrolyte in salt bridge should be such that speed of it's cation equals speed of it's anion in electrical field.
- For that charge and sign of the ions should be almost equal.

  Transport number of cation = Transport number of anion

  or

  Mobility of cation = Mobility of anion

  KCl is generally preffered but KNO_3 or NH_4NO_3 can also be used.

○ If Ag^+, Hg_2^{2+}, Pb^{2+}, Tl^+ ions are present in a cell then in salt bridge KCl is not used because there can be formation of precipitate of AgCl, Hg_2Cl_2, $PbCl_2$ or TlCl at mouth of tube which will prevent the migration of ions and its functioning will stop.

Functions of Salt Bridge :

- A **salt bridge** is a U–shaped inverted tube that contains a gel permeated with an inert electrolyte.
- It connects the solution of two half cell to complete the circuit.
- It minimise the liquid junction potential. The potential difference between the junction of two liquids.
- It maintains the electhical neutrality of the solution in order to give continious flow or generation of current.

  " The simultaneous electrical neutrality of the anodic oxidation chamber and cathodic reduction chamber is due to same mobility or velocity of K^+ and NO_3^- ions taken into salt bridge.
- If the salt bridge is removed then voltage drops to zero.
- The ions of the inert electrolyte do not react with other ion in the solution and the ions are not oxidised or reduced at the electrodes.
- Generally tube is filled with a paste of agar-agar powder with a natural electrolyte/generally not common to anionic/cathodic compartment with porous plugs at each mouth of tube.
- It prevents mechanical mixing of two electrolytic solution.

Electrode Potential :

- The driving force that pushes the negative charge electrons away from the anode and pulls them towards the cathode is an electrical potential called **electromotive force** also known as **cell potential** or the **cell voltage.** Its unit is volt
- The potential difference devepoled between metal electrode and its ions in solution in known as electrode potential.
- Electrode potential depends upon :
  - ○ Concentration of the solution.
  - ○ Nature of the electrolyte.
  - ○ Nature of the metal.
  - ○ Pressure temperature conditions.
- The potential difference developed between metal electrodes and the solution of its ions at 1 M concentration at 1 bar pressure and 298 K is known as standard electrode potential.

Oxidation Potential (O.P.) :	Reduction Potential (R.P.)
• The electrode potential for oxidation half reaction	• The electrode potential for reduction half reaction
• Tendency to get oxidised.	• Tendency to get reduced.
• **Greater the O.P. then greater will be tendency to get oxidised.**	• **Greater the R.P. greater will be tendency to get reduced.**

Type of Electrode		Electrode reaction in standard condition	Representation
1.	Metal electrode	Reduction : $Zn^{2+} + 2e^- \rightarrow Zn(s)$	$E^0_{Zn^{2+}/Zn(s)}$ (SRP)
	(Zn electrode, Cu electrode etc.)	Oxidation : $Zn(s) \rightarrow Zn^{2+} + 2e^-$	$E^0_{Zn(s)/Zn^{2+}}$ (SOP)
2.	Hydrogen peroxide	Reduction : $2e^- + 2H^+ + H_2O_2 \rightarrow 2H_2O$	$E^0_{H_2O_2/H_2O}$
	electrode	Oxidation : $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	$E^0_{H_2O_2/O_2}$
3.	Redox electrode	Reduction : $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	$E^0_{MnO_4^-/Mn^{2+}}$
4.	Metal Metal	Reduction : $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$	$E^0_{AgCl(s)/Ag(s)/Cl^-}$
	salt insoluable electrode	Oxidation : $Ag(s) + Cl^- \rightarrow AgCl(s) + e^-$	$E^0_{Ag(s)/AgCl(s)/Cl^-}$

Reference electrode :

- The potential of a singal electode cannot be determined what were the potential difference between two electrodes can be accurately measured using a reference electrode.
- An electrode is chosen as a reference with respect to which all other electrodes are valued.
- Standard Hydrogen Electrode **(SHE)** is taken as standard reference electrode. Its electrode potential is arbitrarily assumed to be 0.00 volt.
- Standard Hydrogen Electrode **(SHE)** consists of a platinum electrode in contact with H_2 gas and aqueous H^+ ions at standard state conditions (1 atm H_2 gas, 1 M H^+ (aq), 25°C).

$$2H^+ (aq, 1M) + 2e^- \rightarrow H_2 (g, 1\ atm) \qquad E° = 0V$$

$$H_2(g, 1atm) \rightarrow 2H^+ (aq, 1M) + 2e^- \qquad E° = 0V$$

Cell potential :

- The difference in electrode potentials of the two half cell reactions (oxidation half cell and reduction half cell) is known as emf of the cell or cell potential.

  The emf of the cell or cell potential can be calculated from the values of electrode potential of the two half cell constituning the cell. The following three methode are in use :

  ○ When oxidation potential of anode and reduction potential of cathode are taken into account :

  $E°_{cell}$ = oxidation potential of anode + reduction potential of cathode = $E°_{ox}$ (anode) + $E°_{red}$ (cathode)

  ○ When reduction potential of both electrodes are taken into account :

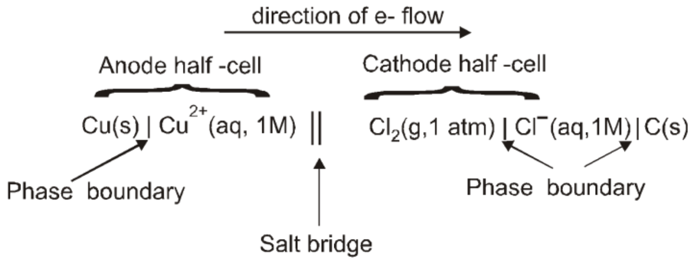
  $E°_{cell}$ = Reduction potential of cathode – Reduction potential of anode = $E°_{cathode} – E°_{anode}$ both are reduction potential.

  ○ When oxidation potential of both electrodes are taken into account :

  $E°_{cell}$ = oxidation potential of anode – Oxidation potential of cathode = $E°_{ox}$ (anode) – $E°_{ox}$ (cathode)
- The standard cell potential E° is the cell potential when both reactants and products are in their standard states – solutes at 1 M concentration, gases at a potential pressure of 1 atm, solids and liquids in pure from, with all at a specified temperature, usually 25° C.
- $E°_{cell}$ is intensive property so on multiplying/Dividing cell reaction reaction by any number, the $E°_{cell}$ value would not change.

Short Hand Notation for Galvanic Cells

- We require two half cells to produce an electrochemical cell, which can be represented by follwing few rules;
  - The anode half-cell is always written on the left followed on the right by cathode half cell.
  - The separation of two phases (state of matter) is shown by a vertical line.
  - The various materials present in the same phase are shown together using commas.
  - The salt bridge is represented by a double slash (||).
  - The significant features of the substance viz. pressure of a gas, concentration of ions etc. are indicated in brackets immediately after writing the substance.
  - For a gas electrode, the gas is indicated after the electrode for anode and before the electrode in case of cathode. (i.e Pt H_2 / H^+ or H^+ /H_2 Pt)



Solved Examples

Ex.1 Write short hand notation for the following reaction, Sn^{2+} (aq) + $2Ag^+$ (aq) → Sn^{4+} (aq) + 2Ag(s).

Sol. The cell consists of a platinum wire anode dipping into an Sn^{+2} solution and a silver cathode dipping into an Ag^+ solution therefore Pt(s) | Sn^{2+}(aq), Sn^{4+} (aq) || Ag^+ (aq) | Ag(s).

Ex.2 Write the electrode reaction and the net cell reaction for the following cells. Which electrode would be the positive terminal in each cell ?

(a) Zn | Zn^{2+} || Br^-, Br_2 | Pt
(b) Cr| Cr^{3+} || I^- , I_2 | Pt
(c) Pt | H_2, H^+ || Cu^{2+} | Cu
(d) Cd | Cd^{2+} || Cl^- , AgCl | Ag

Sol. **(a)** Oxidation half cell reaction, $Zn \longrightarrow Zn^{2+} + 2e^-$

reduction half cell reaction, $Br_2 + 2e^- \longrightarrow 2Br^-$

Net cell reaction $Zn + Br_2 \longrightarrow Zn^{2+} + 2Br^-$ (Positive terminal : cathode Pt)

(b) Oxidation half reaction, $[Cr \longrightarrow Cr^{3+} + 3e^-] \times 2$

reduction half reaction, $[I_2 + 2e^- \longrightarrow 2I^-] \times 3$

Net cell reaction $2Cr + 3I_2 \longrightarrow 2Cr^{3+} + 6I^-$ (Positive terminal : cathode Pt)

(c) Oxidation half reaction, $H_2 \longrightarrow 2H^+ + 2e^-$

reduction half reaction, $Cu^{2+} + 2e^- \longrightarrow Cu$

Net cell reaction $H_2 + Cu^{2+} \longrightarrow Cu + 2H^+$(Positive terminal : cathode Cu)

(d) Oxidation half reaction, $Cd \longrightarrow Cd^{2+} + 2e^-$

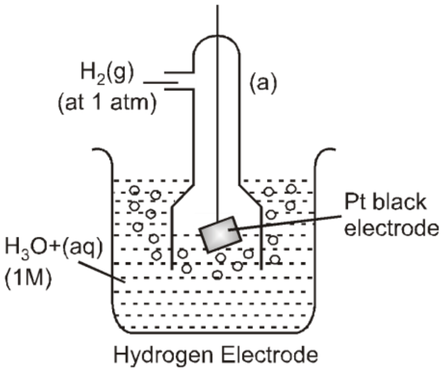
reduction half reaction, $[AgCl + e^- \longrightarrow Ag + Cl^-] \times 2$

Net cell reaction $Cd + 2AgCl \longrightarrow Cd^{2+} + 2Ag + 2Cl^-$ (Positive terminal : cathode Ag)

Section (B) : Application of Electrochemical Series

Calculation of electrode potential :

At Anode	**At Cathode**
$H_2(g) \rightleftharpoons 2H^+ + 2e^-$	$2H^+ + 2e^- \rightleftharpoons H_2(g)$
- Oxidation potential O.P. = $E_{H_2(g)/H^+(aq.)}$	- Reduction Potential (R.P.) $E_{H^+/H_2(g)}$ = RP
- under standard state	- under standard state.
- $E^0_{H_2(g)/H^+(aq.)}$ = SOP	- $E^0_{H^+/H_2(g)}$ = SRP



Hydrogen Electrode

- For SHE reference potential is taken to be zero at all temperature.

  SOP = – SRP = 0 for SHE.

- To calculate standard potential of any other electrode a cell is coupled with standard hydrogen electrode (SHE) and it's potential is measured that gives the value of electrode potential of that electrode.

Anode : Zinc electrode

Cathode : SHE

Cell : Zinc electrode || SHE

Cell potential :

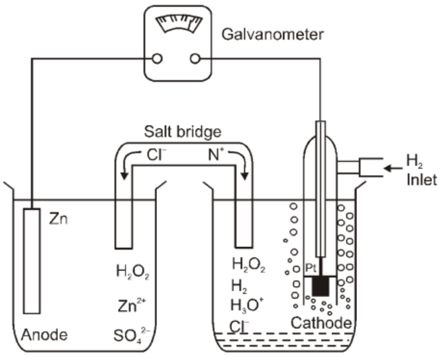
$E_{cell} = E_{H^+/H_2(g)} - E°_{Zn^{2+}/Zn}$

= 0.76 V (at 298 K experimentaly)

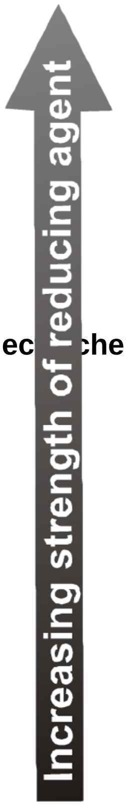
So, $E^0_{Zn^{2+}/Zn}$ = – 0.76 V (SRP)

$E^0_{Zn/Zn^{2+}(aq)}$ = 0.76 V(SOP)

- So, w.r.t. H_2 , Zn has greater tendency to get oxidised.In similar manner reduction potentials (SRP) at 298 K for many other electrodes are calculated and are arranged in a series increasing order known as electro chemical series.



A galvanic cell measuring the Zn^{2+} |Zn half-cell potential



Elec chemical Series :

Electrode	Reaction	SRP (at 298 K)
* Li	$Li^+ + e^- \rightarrow Li(s)$	– 3.05 V
K	$K^+ + e^- \rightarrow K(s)$	– 2.93 V
Ba		
Ca	$Ca^{+2} + 2e^- \rightarrow Ca(s)$	– 2.87 V
Na	$Na^+ + e^- \rightarrow Na(s)$	– 2.71 V
Mg	$Mg^{+2} + 2e^- \rightarrow Mg(s)$	– 2.37 V
Al	$Al^{+3} + 3e^- \rightarrow Al$	– 1.66 V
* Electrolytes (H_2O)	$H_2O(l) + e^- \ H_2 + \rightarrow \frac{1}{2} OH^-$	– 0.828 V
* Zn	$Zn^{+2} + 2e^- \rightarrow Zn(s)$	– 0.76 V
Cr	$Cr^{+3} + 3e^- \rightarrow Cr(s)$	– 0.74 V
* Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	– 0.44 V
Cd	$Cd^{+2} + 2e^- \rightarrow Cd(s)$	– 0.40 V
Co		
Ni	$Ni^{+2} + 2e^- \rightarrow Ni(s)$	– 0.24 V
Sn	$Sn^{+2} + 2e^- \rightarrow Sn(s)$	– 0.14 V
Pb	$Pb^{+2} + 2e^- \rightarrow Pb(s)$	– 0.13 V
* H_2	$2H^+ + 2e^- \rightarrow H_2(g)$	0.00 V
Cu	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.34 V
I_2		
Fe	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77 V
Hg	$Hg_2^{2+} + 2e^- \rightarrow Hg(l)$	0.79 V
Ag	$Ag^+ + e^- \rightarrow Ag$	0.80 V

Hg	$Hg^{2+} \rightarrow Hg(l)$	0.85 V
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	1.06 V

* Electrolytes $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O(\ell)$ 1.23 V
* $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$ 1.33 V
* $Cl_2 \rightarrow Cl_2 + 2e^- \rightarrow 2\,Cl^-$ 1.36 V
* $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ 1.51 V
* $F_2 + 2e^- \rightarrow 2F^-$ 2.87 V

Solved Examples

Ex.3 Calculate E^0_{cell} of (at 298 K),
$Zn(s) / ZnSO_4(aq) \,||\, CuSO_4(aq) / Cu(s)$
given that $E^0_{Zn/Zn^{2+}(aq)} = 0.76$ V ; $E^0_{Cu(s)/Cu^{2+}(aq)} = -0.34$ V

Sol. $E^0_{cell} = (S.R.P)_{cathode} - (S.R.P)_{anode}$
$= 0.34 - (-0.76) = 1.1$ V

Ex.4 Given the cell Ag AgCl(s) | NaCl (0.05 M) || Ag NO_3 (0.30) | Ag

(a) Write half reaction occurring at the anode. (b) Write half reaction occurring at the cathode.

(c) Write the net ionic equation of the reaction. (d) calculate $E°_{cell}$ at 25°C.

(e) Does the cell reaction go spontaneous as written ?

(Given $E°_{AgCl,Cl}$ = + 0.22 volt); $E^0_{Ag^+/Ag}$ = + 0.80 volt)

Sol. (a) LHS electrode is anode and half reaction is oxidation.

$$Ag_+ + Cl_- \longrightarrow AgCl(s) + e_- \qquad ...\ (i)$$

(b) RHS electrode is cathode and half reaction is reduction.

$$Ag + e \longrightarrow Ag(s) \qquad ...\ (ii)$$

(c) From equation (i) and (ii) cell reaction is : Cl^- (0.05 M) + Ag^+ (0.30 M) $\longrightarrow$ AgCl(s)

(d) $E°_{cell} = E°_{right} – E°_{left}$ = (0.80 – 0.22 volt = 0.58 volt

(e) Yes, the e.m.f. value is positive, the reaction will be spontaneous as written in the cell reaction.

Ex.5 An aqueous solution containing Na^+ , Sn^{2+}, Cl^- & SO_4^{2-} ions, all at unit concentration, is electrolysed between a silver anode and a platium cathode. What changes occcur at the electrodes when current is passed through the cell? Given : $E^0_{Ag^+|Ag}$ = 0.799 V,

$E^0_{Sn^{2+}|Sn}$ = – 0.14 V, $E^0_{Cl_2\,|Cr^-}$ = 1.36 V , $E^0_{S_2O_8^{2-}|SO_4^{2-}}$ = 2 V, $E^0_{S_2O_8^{2-}|SO_4^{2-}}$ = 0.13 V

(A) Sn^{2+} is reduced and Cl^- is oxidized (B) Ag is oxidized and Sn^{2+} is reduced

(C) Sn^{2+} is reduced and Sn^{2+} is oxidized (D) H^+ is reduced and Sn^{2+} is oxidised

Sol. At anode either Ag can oxidised to Ag^+ or Sn^{2+} to Sn^{4+} or Cl^- to Cl_2 or SO_4^{2-} to $S_2O_8^{2-}$ Their respective oxidation poential values are –0.799 V, 0.13 V, –1.36 V and –2 V. From these values, it is evident that Sn^{2+} would be oxidised first, followed by Ag at anode. At cathode, either Na^+ can get reduced to Na. or Sn^{2+} to Sn or H^+ to H_2. The reduction potential value for Na^+ is highly negative while for Sn^{2+} | Sn is –0.14 V and for $H^+ + e^- \longrightarrow 1/2\ H_2$ $\left(E_{H^+|H_2} = 0.059 \log \frac{1}{10^{-7}}\right)$ is –0.413 V. Thus Sn^{2+} will get reduced at cathode followed by H^+ ∴ (C)

- **Calculation of Electrode Potential of unknown electrode with the help of given (two) electrode.**

  - Obtain the reaction of the 3rd electrode with the help of some algebraic operations on reactions of the given electrodes.
  - Then calculate ΔG of the 3rd reaction with the help of some algebaic operations of $ΔG^0$ of 1st and 2nd reactions.
  - Use $ΔG^0 = –nF\ E^0_{elec.}$ to calculate unknown E.P.
  - E^0_{cell} is intensive property so if we multiply/Devide electrode reaction by any number the E^0_{cell} value would not changed

  i.e. $Zn^{2+} + 2e^- \rightarrow Zn(s)$ $E° = – 0.76$ V

  Multiply by 2

  $2Zn^{2+} + 4e^- \rightarrow 2Zn(s)$ $E° = – 0.76$ V (remain same)

Solved Examples

Ex.6 Given that $E^0_{Cu^{2+}/Cu} = 0.337$ V and $E^0_{Cu^{+}/Cu^{2+}} = -0.153$ V. Then calculate $E^0_{Cu^{+}/Cu}$.

Sol. (i) $Cu^{2+} + 2e^- \rightarrow Cu$ $\quad \Delta G_1$

(ii) $Cu^+ \rightarrow Cu^{2+} + e^-$ $\quad \Delta G_2$

after adding $Cu^+ + e^- \rightarrow Cu$

$\Delta G_1 + \Delta G_2 = \Delta G_3$

$-2F E_1^0 - F E_1^0 = -F E_1^0$

$E_3 = 2 E_1^0 + E_2^0$

$= 2 \times 0.337 - 0.153 = 0.674 - 0.153 = 0.521$ V

Ex.7 $E^0_{Mn^{2+}/MnO_4^-} = -1.51$ V ; $E^0_{MnO_2/Mn^{+2}} = +1.23$ V

$E^0_{MnO_4^-/MnO_2} = ?$ (All in acidic medium)

Sol. $4H_2O + Mn^{2+} \rightarrow MnO_4^- + 8H^+ + 5e^-$ $\quad \Delta G_1$

(i) $\leftarrow MnO_4^- + 8H^+ + 5e^- \rightarrow 4H_2O + Mn^{2+}$ $\quad -\Delta G_1$

$2e^- + MnO_2 + 4H^+ \rightarrow Mn^{2+} + 2H_2O$ $\quad \Delta G_2$

(ii) $\leftarrow 2H_2O + Mn^{2+} \rightarrow MnO_2 + 4H^+ + 2e^-$ $\quad -\Delta G_2$

(iii) $\leftarrow 4H^+ + Mn + 3e^- \rightarrow MnO_2 + 2H_2O$ $\quad \Delta G_3$

(i) + (ii) = (iii)

$\Delta G_3 = -\Delta G_1 - \Delta G_2$

$-3E_3F = 5F E_1^0 + 2 E_2^0 F$

$$E = \frac{-[5E_1 + 2E_2]}{3} = \frac{-[5(-1.51) + 2(1.23)]}{3} = \frac{-[-7.55 + 2.46]}{3} = \frac{+5.09}{3} = 1.69 \text{ V}$$

Section (C) : Concept of ΔG and Nernst Equation

Free energy changes ΔG for cell reaction :

- The free energy change ΔG (a thermochemical quantity) and the cell potential E(an electrochemical quantity) both measure the driving force of a chemical reaction.
- The values of ΔG and E are directly proportional and are related by the equation.

$\Delta G = -nFE$

where n = Number of moles of electron transfered in the reaction.

F = Faraday constant = 96485 C/mole e^- ≈ 96500 C/mole e^-

Nernst Equation :

- Cell potentials depend on temperature and on the composition of the reaction mixtures.
- It depends upon the concentration of the solute and the partial pressure of the gas, if any.
- The dependence upon the concentration can be derived from thermodynamics.

From thermodynamics

$\Delta G = \Delta G° + RT \ln Q$

$-nFE = -nFE° + 2.303\, RT \log Q$

$$E = E° - \frac{2.303RT}{nF} \log Q$$

Take T = 298 K , R = 8.314 J/mol K , F = 96500 C

Now we get, $E = E° - \frac{0.059}{n} \log Q$

Where n = number of transfered electron , Q = reaction quotient

- Nernst equation can be used to calculate cell potentials for non standard conditions also.
- Nernst equations can be applied to half cell reactions also.

Section (D) : Application Nernst Equation in Different type of Electrodes and Cells

Applications of Nerst equation

- **Nernst Equation for Electrode Potential**

$M^{n+}(aq) + ne^- \rightleftharpoons M(s)$

$$E_{Redn} = E^0_{red} - \frac{RT}{nF} \ell n \left[\frac{M(s)}{M^{n+}}\right]$$

$$E_{Redn} = E^0_{red} - \frac{2.303RT}{nF} \log \left[\frac{M(s)}{M^{n+}}\right]$$

at 298K,

$$E_{Redn} = E^0_{Red^n} - \frac{0.059}{n} \log \left[\frac{1}{M^{n+}}\right]$$

- **Hydrogen Electrode**

$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$

$$E = E^0 - \frac{0.0591}{2} \log \left[\frac{(H^+)^2}{P_{H_2}}\right]$$

- **Metal–metal soluble salt electrode.**

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

$$E_{Redn} = E^0_{Red^n} - \frac{2.303RT}{nF} \log \left(\frac{1}{Zn^{+2}}\right) \text{ at 298K}$$

$$E_{Redn} = E^0_{red} - \frac{0.059}{2} \log \left(\frac{1}{Zn^{+2}}\right)$$

- **Gas – electrode Hydrogen electrode.**

$2H^+ + 2e^- \rightarrow H_2(g)$

$$E_{Redn} = E^0_{Red^n} - \frac{0.059}{2} \log \left(\frac{P_{H_2}}{[H^+]^2}\right)$$

- **Redox electrode**

$4H_2O + Mn^{2+} \rightarrow MnO_4^- + 8H^+ + 5e^-$

$$E_{OX} = E^0_{ox} - \frac{0.059}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{+2}]}$$

Solved Examples

Ex.8 Calculate R.P. of hydrogen electrode at 298K which is prepared with the help of aq. solution of acetic acid with 0.1 M conc at 1 atm pressure Ka = 1.8 x 10^{-5}.

Sol. $[H^+] = \sqrt{Ka \times c} = \sqrt{1.8 \times 10^{-5} \times 10^{-1}} = \sqrt{1.8 \times 10^{-6}}$

$2H^+ + 2e^- \rightarrow H_2$

$E_{Redn} = E^0_{red} - \frac{0.059}{2} \log \frac{P_{H_2}}{[H^+]^2}$ $(E^0_{Redn} = 0)$

$E_{Redn} = -\frac{0.059}{2} \log \left(\frac{1}{1.8 \times 10^{-6}}\right)$ $= -\frac{0.059}{2}$ [6 – log (1.8)]

$E_{Redn} = -\frac{0.059}{2}$ x 5.74 = –0.169 V

Ex.9 Which is stronger oxidizing agent

(i) $K_2Cr_2O_7$ in solution in which $[Cr_2O_7^{2-}] = 0.1$ M, $[Cr^{3+}] = 10^{-2}$ M and $[H^+] = 10^{-1}$ M

(ii) $KMnO_4$ in a solution in which $[MnO_4^-] = 10^{-1}$M, $[Mn^{2+}] = 10^{-2}$M, $[H^+] = 10^{-2}$ M

$E^0_{Cr_2O_7^{2-}/Cr^{+3}} = 1.33$ V $E^0_{MnO_4^-/Mn^{+2}} = 1.51$ V

Sol. (i) $14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{+3} + 7H_2O + 6e^-$

$E_{Redn} = 1.33 - \frac{0.059}{6} \log\left[\frac{10^{-4} \times 10}{10^{-14}}\right] = 1.33 - \frac{0.059}{6} \times 11$

$E_{Redn} = 1.33 - \frac{0.649}{6} = 1.330 - 0.108 = 1.222$ V

(ii) $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

$E_{Redn} = 1.51 - \frac{0.059}{5} \log\left[\frac{10^{-2}}{10^{-16} \times 10^{-1}}\right] = 1.51 - 0.059 \times 3 = 1.51 - 0.18 = 1.33$ V

E_{Redn} is more so, good oxidising agent

- ### Nernst Equation for cell Potential :

$aA + bB \rightleftharpoons CC + dD$

$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln Q$

n – no. of electrons which gets cancelled out while making cell reaction.

Equilibrium in electrochemical cell

$\Delta G^0 = -nF E^o_{cell}$

$\boldsymbol{\Delta G = -nF}\ E_{cell}$

From thermo dynamics

$\Delta G = \Delta G^0 + RT\ell nQ$

at chemical equilibrium $\Delta G = 0$

$E_{cell} = 0 \rightarrow$ cell will be of no use

so, $\Delta G^0 = -RT\ell n K_{eq}$

at equilibrium $-nF E^o_{cell} = -2.303 RT \log (K_{eq})$

$\log K_{eq} = \frac{nF}{2.303RT} E^o_{cell}$

at 298 K and R = 8.314 J/mol K

$\log K_{eq} = \frac{n}{0.059} E^o_{cell}$

Solved Examples

Ex.10 Calculate E_{cell} of Pt(s) $\left|\begin{matrix} Cl_2(g) \\ 0.1\text{atm} \end{matrix}\right|\begin{matrix} Cl^-(aq) \\ 10^{-2}M \end{matrix}\left|\right|\begin{matrix} Cr_2O_7^{2-}, & Cr^{+3} (\text{in } H_2SO_4) = 0.05M \\ 0.01M & 0.1M \end{matrix}\left.\right|$

given that $E^0_{Cr_2O_7^{2-}/Cr^{+3}} = 1.33$ V

E^0 Cl^- | Cl_2 = –1.36 V

Sol. $6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{+3} + 7H_2O$

$[2Cl^- \rightarrow Cl_2 + 2e^-] \times 3$

$14H^+ + 6Cl^- + Cr_2O_7^{2-} \rightarrow 3Cl_2 + 2Cr^{+3} + 7H_2O \quad \Rightarrow \quad E^0_{cell} = 1.33 - (+1.36) = -0.03$

$$E_{cell} = -0.03 - \frac{0.059}{6} \log \frac{[Cr^{3+}]^2[P_{Cl_2}]^3}{[H^+]^{14}[Cl^-]^6[Cr_2O_7^{2-}]} = -0.03 - \frac{0.059 \times 23}{6}$$

$E_{cell} = -0.26$ V

Ex.11 The E°_{cell} for the reaction $Fe + Zn^{2+} \rightleftharpoons Zn + Fe^{2+}$, is – 0.32 volt at 25°C. What will be the equilibrium concentration of Fe^{2+}, when a piece of iron is placed in a 1 M Zn^{2+} solution ?

Sol. We have the Nernst equation at equilibrium at 25°C

$E^\circ = \frac{0.0591}{n} \log K$ ... (i)

Since E°_{Cell} for the given reaction is negative, therefore, the reverse reaction is feasible for which E°_{cell} will be + 0.32 V, Thus for $Zn + Fe^{2+} \rightleftharpoons Fe + Zn^{2+}$; E°_{Cell} + 0.32 V

Now , $E^\circ = \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Fe^{2+}]}$ or $0.32 = \frac{0.0591}{2} \log \frac{1}{[Fe^{2+}]}$

$\log [Fe^{2+}] = -10.829$ Taking antilog,

$[Fe^{2+}] = 1.483 \times 10^{-11}$ M

Work done by a cell :

(i) Let 'n' faraday charge be taken out of a cell of EMF 'E' ; then work done by the cell will be calculated as : work = Charge × Potential = nFE

(ii) Work done by cell = Decrease in free energy

so $-\Delta G = nFE$

or $W_{max} = +nFE^o$ where E^o is standard EMF of the cell

Solved Examples

Ex.12 Calculate the maximum work that can be obtained from the Daniell cell given below -

Zn(s) | Zn^{2+} (aq) || Cu^{2+} (aq) | Cu (s). Given that $E^o_{Zn^{2+}/Zn} = -0.76$ V and $E^o_{Cu^{2+}/Cu} = +0.34$ V.

Sol. Cell reaction is : $Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$ Here n = 2

$E^o_{cell} = E^o_{cathode} - E^o_{anode}$ (On the basis of reduction potenital)

$= +0.34 - (0.76) = 1.10$ V

We know that : $W_{max} = \Delta G^o = -nFE^o$

$= -(2\ mol) \times (96500\ C\ mol) \times (1.10\ V) = -212300\ C.V. = -212300\ J$

or $W_{max} = -212300\ J$

Concentration cells :

- A concentration cell consists of two electrodes of the same material, each electrode dipping in a solution of its own ions and the solution being at different concentrations.
- The two solutions are separated by a salt bridge.

e.g. $Ag(s)\ |\ Ag^+(a_1)\ ||\ Ag^+(a_2)\ |\ Ag(s)$ $(a_1 < a_2)$ a_1, a_2 are concentrations of each half cell

At LHS electrode Anode : $Ag(s) \longrightarrow Ag^+(a_1) + e^-$

At RHS electrode Cathode : $Ag^+(a_2) + e^- \longrightarrow Ag(s)$

The net cell reaction is : $Ag^+(a_2) \longrightarrow Ag^+(a_1)$

for concentration cells $E^o_{Cell} = 0$.

The nernst eq. is

$$E_{cell} = -\frac{0.059}{n} \log \frac{a_1}{a_2} \quad \text{(Here n = 1, Temp, 298 K)}$$

- Likewise, the e.m.f. of the cell consisting of two hydrogen electrodes operating at different pressure P_1 and P_2 $(P_1 > P_2)$ and dipping into a solution HCl is :

$$E_{cell} = \frac{0.059}{2} \log \frac{P_1}{P_2} \quad \text{(at 298 K)}$$

Section (E) : Electrolysis and Applications of Electrolysis (Faraday's law)

Electrolysis & Electrolytic cell :

Electrolysis :

- Electrolyte is a combination of cations and anions which in fused state can conduct electricity.
- This is possible due to the movement of ions from which it is made of and electrolyte.
- The process of using an electric current to bring about chemical change is called electrolysis.
- Electrolysis is a process of oxidation and readuction due to current in the electrolyte.
- The product obtained during electrolysis depends on following factors.
  - ○ The nature of the electrolyte
  - ○ The concentration of electrolyte
  - ○ The charge density flowing during electrolysis.
  - ○ The nature of the electrode

Active vs Inactive electrodes :

- The electrodes in the cell that are active because the metals themselves are components of the half reactions.
- As the cell operates, the mass of the zinc electrode gradually decreases, and the $[Zn^{2+}]$ in the anode half – cell increases. At the same time, the mass of the copper electrode increases and the $[Cu^{2+}]$ in the cathode half – cell decreases; we say that the Cu^{2+} "plates out" on the electrode.

- For many redox reactions, however, there are no reactants or products capable of serving as electrodes. Inactive electrodes are used, most commonly rods of graphite or platinum, materials that conduct electrons into or out of the cell but cannot take part in the half -reactions.

- In a voltaic cell based on the following half reactions, for instance, the species cannot act as electrodes :

$2I^-(aq) \longrightarrow I_2(s) + 2e^-$ [anode ; oxidation]

MnO_4^- (aq) + $8H^+$ (aq) + $5e^- \longrightarrow Mn^{2+}$ (aq) + $4H_2O(\ell)$ [cathode ; reduction]

Therefore, each half – cell consists of inactive electrodes immersed in an electrolyte solution that contains all the species involved in that half -reaction. In the anode half-cell, I^- ions are oxidized to solid I_2. The electrons released flow into the graphite anode, through the wire, and into the graphite cathode. From there, the electrons are consumed by MnO_4^- ions as they are reduced to Mn^{2+} ions.

Examples of Electrolysis

- Using inert (pt/graphite) electrodes.

Cathode (red) : $Pb^{2+} + 2e^- \rightarrow Pb(s)$ $E^0 = 0.126V$

Anode : $2Br^- \rightarrow Br_2 + 2e^-$ $E^0 = -1.08$ V

$E_{cell} = -0.126 - (0.108) \times 10 = -1.206$ V

$E_{ext} > 1.206$ V

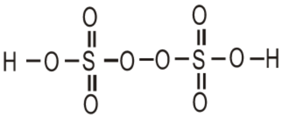
- Electrolysis of $CuSO_4$ molten

Cathode : $Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = +0.34$ V

Anode : $2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$ $E^0 = -2.05$ V

$H_2S_2O_8$ – marchall's acid (peroxy disulphuric acid).

$E_{cell} = 0.34 - (2.05) = -1.71$ V (negative ∴ not feasible)



$$H-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-O-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O-H$$

- Electrolysis of aq $CuSO_4$

Cathode : $Cu^{2+} + 2e^- \rightarrow Cu(s)$ $E^0 = 0.34$ V

$2e + 2H_2O(\ell) \rightarrow H_2(g) + 2OH^-(aq)$ $E^0 = -0.83V$

Anode : $2SO_4^{2-}\ S_2O_8^{2-} + 2e^-$ $E^0 = -2.05$ V

$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$ $E^0 = -1.23$ V

- Electrolysis of aq NaBr solution (initially PH = 7)

Cathode : $Na^+(aq) + e^- \rightarrow Na(s)$ $E^0 = -2$ V

$2e^- + 2H_2O(\ell) \rightarrow H_2 + 2OH^-$ $E^0 = -0.83$ V

Anode : $2Br^- \rightarrow Br_2 + 2e^-$ $E^0_{OX} = -1.08$ V

$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$ $E^0_{OX} = -1.23$ V

- Electrolysis of aq NaCl

Cathode : $Na^+ + e^- \rightarrow Na$ $E^0 = -2V$

$2e^- + 2H_2O(\ell) \rightarrow H_2(g) + 2OH^-$ $E^0 = -0.83$ V

Anode : $2Cl^- \rightarrow Cl_2 + 2e^-$ $E^0_{OX} = -1.30$ V

$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$ $E^0_{OX} = -1.23$ V

Rate of production of Cl_2 is more than rate of production of O_2 gas.

Note : According to thermodynamics, oxidation of H_2O to produce O_2 should take place on anode but experimentally (experiment from chemical kinetics) the rate of oxidation of water is found to be very slow. To increase it's rate, the greater potential difference is applied called over voltage or over potential but because of this oxidation of Cl^- ions also become feasible and this takes place on anode.

Electrolysis using attachable (reactive) electrodes.

- Electrolysis of aq. $CuSO_4$ using Cu electrode.

Cathode (reduction) : $Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = +0.34$ V

$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E^0 = -0.83$ V

Anode (oxidation) : $SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$ $E^0_{OX} = -2.05$ V

$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$ $E^0 = -1.23$ V

$Cu(s) \rightarrow Cu^{2+} + 2e-$ $E^0 = -0.34$ V

electrolytic refining

- $AgNO_3(aq)$ using Cu cathode & Ag anode.

Cathode : $Ag^+ + e^- \rightarrow Ag(s)$ $E^0 = 0.8$ V

$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E^0 = -0.083$ V

Anode : $NO_3^- \rightarrow X$ (No reaction)

$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$ $E^0 = -1.23$ V

$Ag(s) \rightarrow Ag^+(aq) + e^-$ $E^0 = -0.80$ V

Section (F) : Faraday laws (Electrolysis)

Faraday's Law of Electrolysis :

- **1st Law :** The mass deposited/released/produced of any substance during electrolysis is proportional to the amount of charge passed into the electrolyte.

$W \propto Q$

$W = ZQ$

Z – electrochemical equivalent of the substance.

Unit of Z = $\frac{\text{mass}}{\text{coulomb}}$ = Kg/C or g/C

Z = Mass deposited when 1 C of charge is passsed into the solution.

Equivalent mass (E) : mass of any substance produced when 1 mole of e^- are passed through the solution during electrolysis.

$$E = \frac{\text{Molar mass}}{\text{no.of } e^- \text{ involved in oxidation/reduction}}$$

e.g.

$Ag^+ + e^- \rightarrow Ag$ $E = \frac{M}{1}$ $Cu^{2+} + 2e^-$ Cu(s) $E = \frac{M}{2}$

$Al^{3+} + 3e^- \rightarrow Al(s)$ $E = \frac{M}{3}$

1 mole of e^- = 1 Faraday of charge.

∵ 96500 C – Charge deposite E gram metal charge

∴ $1C \rightarrow \left(\frac{E}{96500}\right)g$ $Z = \frac{E}{96500}$

$$W = \frac{EQ}{96500} = \frac{\text{Molar mass}}{(\text{no.of } e^- \text{involved})} \times \frac{Q}{96500}$$

$\int dQ = i\int dt$ $Q = it$ $W = \frac{i \times t}{96500} \times \frac{\text{Molar mass}}{(\text{no. of } e^- \text{ involved})}$

- **2nd Law :** When equal charge is passed through 2 electrolytic cells and these cells are connected in series then mass deposited at electrode will be in the ratio of their electrochemical equivalents or in the ratio of their equivalent masses.

$$W = ZQ = \frac{EQ}{96500} \qquad \frac{W_1}{W_2} = \frac{z_1}{z_2} = \frac{E_1}{E_2} \quad (Q = \text{same})$$

Current Efficiency :

$$\text{current efficiency} = \frac{\text{charge actually used in electricity}}{\text{charge passed}} \times 100$$

$$\text{current efficiency} = \frac{\text{mass actually produced}}{\text{mass that should have been produced}} \times 100$$

Solved Examples

Ex.13 Calculate volume of the gases liberated at STP if 1 L of 0.2 molar solution of $CuSO_4$ is electrolysed by 5.79 A current for 10000 seconds.

Sol. No. of moles of e^- = $\frac{5.79 \times 10000}{96500} = \frac{579}{965} = 0.6$

Cathode : $Cu^{2+} + 2e^- \rightarrow Cu(s)$

0.2 mole 0.4 mole

$2H_2O(\ell) + 2e^- \rightarrow H_2 + 2OH^-$

0.2 mole of e^- → 0.1 mole of H_2 at S.T.P.

Anode : $2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$

4 mole of e^- → 1 mole of O_2

0.6 mole of e^- → 0.15 mole of O_2

so, total moles = 0.25 mole

Total volume = 5.6 Ltr.

Ex.14 How many cc of chlorine will be deposited by 100 amp. current flowing for 5 hours through melted NaCl.

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

$W = ZQ = \frac{E}{96500} \times 18 \times 10^5 = \frac{18 \times 35.5}{965} \times 10^3 = 662.2$ gm

∴ Volume of 71 gm Cl_2 at NTP = $\frac{22.4}{71}$ 22.4 litre

∴ volume of 662.2 gm Cl_2 at NTP = ´ 662.2 = 208.9 litre

Ex.15 The time required to coat a metal surface of 80 cm^2 with 0.005 mm thick layer of silver (density = 10.5 gm cm^{-3}) with the passage of 3A current through silver nitrate solution is :

Sol. ∴ Volume of layer of silver = $0.005 \times 10^{-1} \times 80 = 0.04\ cm^3$

∴ mass = Density × volume = $10.5 \times 0.04 = 0.42$ gm

So $w = \frac{E}{96500} \times It \qquad 0.42 = \frac{108}{96500} \times 3 \times t$

$t = \frac{0.42 \times 96500}{108 \times 3} = 125.09$ seconds.

Section(G): Electrical Conductance (Basic Definitions and Calculation of Conductance of Different Mixtures)

Electrolytic Conductance :

Conductors

Metallic Conductors	Electrolytic Conductors
1. Charge carries are e^-	1. Charge carries ions (cations/ anions)
2. No chemical changes	2. Decomposition of electrolyte takes place.
3. No transfer of mass	3. Transfer of mass
4. Resistance is because of collision of e^- s with fixed metal atoms.	4. Resistance is because of collision of ions with solvent molecules & because of interionic force of attraction
5. Temp ↑R ↑	5. Temp ↑R ↓
6. Low resistance generally good conductor.	6. High resistance generally

Factors Affecting Conductance & Resistance :

1. Solute – Solute interactions (Inter – Ionic force of attraction) Greater the force of attraction, greater will be the resistance.
   Force $\propto$ Charge
2. Solute – Solvent Interaction (Hydration/Solvation of Ions)
   Greater the solvation
   Solvation $\propto$ Charge $\propto \frac{1}{\text{size}}$, greater will be resistance
   Li^+ (Hydrated largest) Cs^+ (Hydrated smallest)
   resistance of LiCl > resistance of CsCl
3. Solvent solvent interaction (Viscosity) : greater the viscosity greater will be resistance
4. Temperature
   T↑ R↓
5. Nature of electrolyte
   Weak electrolyte – high resistance, strong electrolyte – Low resistance

Resistance :

$R = \frac{V}{I}$ (Ohm's law (Ω))

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

ρ – resistivity/specific resistance

– resistance of unit length wire of unit area of cross section = constant = (Ω m)

$\rho = \frac{RA}{\ell}$

Resistivity of a solution is defined as the resistance of the solution between two electrodes of 1 cm^2 area of cross section and 1 cm apart.

or

Resistance of 1 cm^3 of solution will be it's resistivity.

Conductance :

$\rho = \frac{1}{R}$ = mho = Ω^{-1}

= S (Siemens)

Conductivity/specific conductance

$K = \frac{1}{\rho} = \frac{\ell}{RA} = \rho\frac{\ell}{A}$

unit Ω^{-1} cm^{-1}

= conductivity of 1 cm^3 of solution

α concentration of ions

$K = \frac{1}{\rho}$ $G = \frac{1}{R}$

K (no. of ions) no. of charge carries

- Since conductivity or resistivity of the solution is dependent on it's concentration, so two more type of conductivities are defined for the solution.

- **Molar conductivity/molar conductance (λ_m)** :

Conductance of a solution containing 1 mole of an electrolyte between 2 electrodes which are 1cm apart.

- Let the molarity of the solution 'C'

C moles of electrolyte are present in 1 Lt. of solution.

so molar conductance = K

$\lambda_m = KV$ $\lambda_m = \frac{K \times 1000}{C}$ $\Rightarrow$ $\lambda_m = \frac{K \times 1000}{\text{molarity}}$

- Its units are Ohm^{-1} cm^2 mol^{-1}

- **Equivalent conductance :** Conductivity of a solution containing 1 g equivalent of the electrolyte.

λ_{eq} – equivalent conductivity/conduction.

$\lambda_{eq} = \frac{K \times 1000}{\text{Normality}}$

- Its units are Ohm^{-1} cm^2 eq^{-1}

Solved Examples

Ex.16 If resistivity of 0.8 M KCl solution is $2.5 \times 10^{-3}\,\Omega$ cm calculate λ_m of the solution.

Sol. $\rho = 2.5 \times 10^{-3}\ \Omega$ cm

$K = \frac{10^3}{2.5} = 4 \times 10^2$

$\lambda_m = \frac{4 \times 10^2 \times 1000}{0.8} = 5 \times 10^5\ \Omega^{-1}\ cm^2\ mole^{-1}$

Ex.17 The resistance of a 1 N solution of salt is 50 Ω. Calculate the equivalent conductance of the solution, if the two platinum electrodes in solution are 2.1 cm apart and each having an narea of 4.2 cm^2.

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

and $\lambda_{eq.} = \frac{k \times 1000}{N} = \frac{1000}{100} = 10$

Ex.18 Which of the following have maximum molar conductivity.

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

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

Sol. (i) $\lambda_M = \frac{k \times 1000}{M} = 2 \times 10^{-2} \times \frac{1000}{0.08} = 250\ \Omega^{-1}\ cm^2\ mol^{-1}$

(ii) $\lambda_M = \frac{k \times 1000}{M}$

$\therefore k = \frac{1}{\rho}$

$\therefore l_M = \frac{1}{50} \times \frac{1000}{0.1} = 200\,\Omega^{-1}\,cm^2\,mol^{-1}$

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

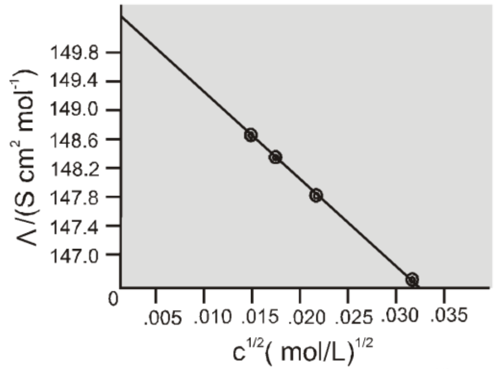
● Variation of conductivity and molar conductivity with concentration

- Conductivity always decreases with the decrease in concentration both for weak and strong electrolytes.
- The number of ions per unit volume that carry the current in a solution decreases on dilution.
- Molar conductivity increases with decreases in concentration. This is because the total volume, V of solution containing one mole of electrolyte also increases.
- Molar conductivity is the conductance of solution.
- When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol Λ°.

Strong Electrolytes :

- For strong electrolytes. Λ° increses slowly with dilution and can be represented by the equation $\Lambda = \Lambda^\circ - A\,C^{1/2}$
- The value of the constant 'A' for a given slovent and temperature depends on the type of electrolyte i.e. the charges on the cations and anions produced on the dissociation of the electrolyte in the solution.

  Example : Thus NaCl, $CaCl_2$, $MgSO_4$ are known as 1-1 , 2-1 and 2-2 electrolyte respectively.
- All electrolytes of a particular type have the same value for 'A'.



Variation of Λ against $c^{1/2}$

Section (H) : Kohlrausch Law and Its Applications

Kohlarausch's Law :

- "At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards equivalent conductance of the electrolyte irrespective of the nature of the ion with which it is associated and the value of equivalent conductance at infinite dilution for any electrolyte is the sum of contribution of its constituent ions."

  i.e., $\lambda_\infty = \lambda_+ + \lambda_-$

- At infinite dilution or near zero concentration when dissociation is 100%, each ion makes a definite contribution towards molar conductivity of electrolyte irrespective of the nature of the other ion. (because interionic forces of attraction are zero)

$$\lambda^0{}_{m\ \text{electrolyte}} = {}^0_m\nu_+\ \lambda^0_{m+} + \nu_-\ \lambda^0_{m-}$$

ν_+ = no. of cation in one formula unit of electrolyte, ν_- = no. of anions in one formula unit of electrolyte

For NaCl $\nu_+ = 1\ \nu_- = 1$

For $Al_2(SO_4)_3$ $\nu_+ = 2\ \nu_- = 3$

$$\lambda^0_{eq}{}_{\text{electrolyte}} = \lambda^{\infty}_{eq+} + \lambda^{\infty}_{eq-}$$

$$\lambda^0_{eq+} = \frac{\lambda^0_m}{\text{charge on the cation}} \qquad \lambda^0_{eq}.Al^{3+} = \frac{\lambda^0_m Al^{3+}}{3}$$

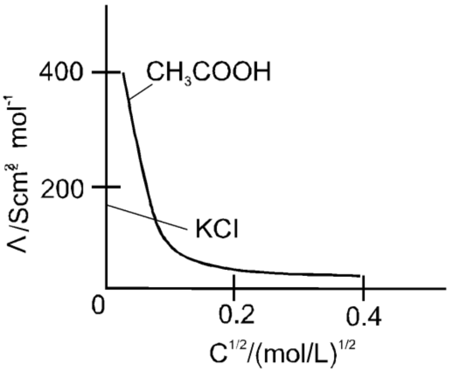
$$\lambda^0_{eq} = \frac{\lambda^0_m}{\text{charge on the anion}} \qquad \lambda^0_{eq},\text{electrolyte} = \frac{\lambda^0_m\ \text{electrolyte}}{\text{total} + \text{ve charge on cation}}\ \text{or}\ \text{total} - \text{ve charge on anion}$$

$$\lambda^0_{eq}Al_2(SO_4)_3 = \lambda^0_{eq}Al^{3+} + \lambda^0_{eq}SO_4^{2-} = \frac{\lambda^0_m Al^{3+}}{3} + \frac{\lambda^0_m SO_4^{2-}}{2}$$

$$\lambda^0_{eq}Al_2(SO_4)_3 = \frac{2\lambda^0_{mAl^{3+}} + 3SO_4^{2-}}{6}$$

Weak electrolytes

- Weak electrolytes like acetic acid have lower degree of dissociation at higher concentration and hence for such electrolytes, the change Λ in with dilution is due to increases in the number of ions in total volume of solution that contains 1 mol of electrolyte.
- At infinite dilution (i.e. concentration c → zero) electrolyte dissociates completely ($\alpha = 1$),but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately.
- Molar conductivity versus $c_{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.



Solved Examples

Ex.19 λ^0_m $Na^+ = 150\ \Omega^{-1}\ cm^2\ mole^{-1}$; $\lambda^0_{eq}Ba^{2+} = 100\ \Omega^{-1}\ cm^2\ eq^{-1}$

$\lambda^0_{eq}\ SO_4^{2-} = 125\ \Omega^{-1}\ cm^2\ eq^{-1}$; $\lambda^0_m\ Al^{3+} = 300^{-1}\Omega\ cm^2\ mole^{-1}$

$\lambda^0_m\ NH_4^+ = 200\ \Omega^{-1}\ cm^2\ mole^{-1}$; λ^0_m, $Cl^- = 150\ \Omega^{-1}\ cm^2\ mole^{-1}$

Then calculate

(a) λ^0_{eq}, Al^{3+} (b) λ^0_{eq} $Al_2(SO_4)_3$ (c) λ^0_m $(NH_4)_2SO_4$

(d) λ^0_m NaCl, $BaCl_2 . 6H_2O$(e) λ^0_m, $(NH_4)_2\ SO_4\ Al_2(SO_4)_3 . 24H_2O$ (f) λ^0_{eq} NaCl

Sol. (a) $\lambda^0_{eq} Al^{3+} = \frac{300}{3} = 100$ (b) $\lambda^0_{eq} Al_2(SO_4)_3 = 100 + 125 = 225$

(c) $\lambda^0_m (NH_4)_2SO_4 = 2 \times 200 + 2 \times 125 = 650$

(d) $\lambda^0_m NaCl.BaCl_2.6H_2O = 150 + 200 + 3 \times 150 = 800\ r^{-1}$

(e) λ^0_m, $(NH_4)_2\ SO_4\ Al_2(SO_4)_3 . 24H_2O\ \lambda^0_m (NH_4)_2 = 400 + 600 + 4 \times 250 = 2000$

(f) $\lambda^0_{eq} NaCl = 300^{-1}\ \Omega\ cm^2\ eq^{-1}$

Ex.20 To calculate λ^0_m or λ^0_{eq} of weak electrolyte

$$\lambda^0_{mCH_3COOH} = \lambda^0_{mCH_3COO^-} + \lambda^0_m H^+ = (\lambda^0_{mCH_3COO^-} + \lambda^0_{mNa^+}) - \lambda^0_{mNa^+} + \lambda^0_{mH^+} + \lambda^0_{mCl^+} - \lambda^0_{mCl^-}$$

$$\lambda^0_{CH_3COOH} = \lambda^0_{mCH_3COONa} + \lambda^0_{mHCl} - \lambda^0_{mNaCl}$$

Ex.21 Calculate λ^0_m of oxalic acid, given that

$\lambda^0_{eq} Na_2C_2O_4 = 400\ \Omega^{-1}\ cm^2\ eq^{-1}$

$\lambda^0_m H_2SO_4 = 700\ \Omega^{-1}\ cm^2\ mole^{-1}$

$\lambda^0_{eq} Na_2SO_4 = 450\ \Omega^{-1}\ cm^2\ eq^{-1}$

Sol. $\lambda^0_m H_2C_2O_4 = 700 + 800 - 900 = 600\ \Omega^{-1}\ cm^2\ mole$

$\lambda^0_{eq} = 400 + \frac{700}{2} - 450$

$\frac{\lambda_m}{2} = 350 - 50 = 300$

$\lambda_m = 600$

Applications of Kohlaraushch's law

- Calculate Λ° for any electrolyte from the Λ° of individual ions.
- Determine the value of its **dissociation constant** once we known the Λ° and Λ at a given concentration c.
- **Degree of dissociation :** At greater dilution the ionization become 100%, therefore called infinite dilution.

At lower dilution the ionization (dissociation into ions) is less than 100% and equivalent conductance become lower,

i.e., $\lambda_{eq} < \lambda^\circ_{eq}$

$\therefore$ degree of dissociation

$$\alpha = \frac{\lambda_{eq}}{\lambda^0_{eq}} = \frac{\text{equivalent conductance at a given concentration}}{\text{equivalent conductance at at infinite dilution}}$$

- **Dissociation constant** of weak electrolyte :

$K_C = \frac{C\alpha^2}{1-\alpha}$; α = degree of dissociation

C = concentration

- The degree of dissociation then it can be approximated to the ratio of molar conductivity Λ_c at the concentration c to limiting molar conductivity, Λ°, Thus we have :

$\alpha = \Lambda / \Lambda^\circ$

But we known that for a weak electrolyte like acetic acid.

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = \frac{c\Lambda^2}{\Lambda^\circ(1-\Lambda/\Lambda^\circ)} = \frac{c\Lambda^2}{\Lambda^\circ(\Lambda-\Lambda^\circ)}$$

- **Solubility(s) and K_{SP} of any sparingly soluble salt.**

Sparingly soluble salt = Very small solubility

Solubility = molarity = 0

so, solution can be considered to be of zero conc or infinite dilution.

$$\lambda_m\text{, saturated} = \lambda_M^\infty = \frac{K \times 1000}{\text{Solubility}} \Rightarrow S = \frac{K \times 1000}{\lambda_M^0}, \; K_{SP} = S^2$$

Solved Examples

Ex.22 If conductivity of water used to make saturated solution of AgCl is found to be 3.1 x $10^{-5}\,\Omega^{-1}\,cm^{-1}$ and conductivity of the solution of AgCl = 4.5 x $10^{-5}\,\Omega^{-1}\,cm^{-1}$

If λ_M^0 $AgNO_3$ = 200 Ω^{-1} cm^2 mole^{-1} , λ_M^0 $NaNO_3$ = 310 Ω^{-1} cm^2 mole^{-1}

calculate K_{SP} of AgCl.

Sol. $\kappa_{AgCl} = \kappa_{solution} - \kappa_{H2O}$; λ_M^0 AgCl = 140 = $4.5 \times 10^{-5} - 3.1 \times 10^{-5} = 1.4 \times 10^{-5}$.

Total conductance = 10^{-5}

$$S = \frac{1.4 \times 10^{-5} \times 10^3}{140} = 10^{-4}$$

$S^2 = 1 \times 10^{-8}$

Ex.23 To calculate K_W of water

Sol. $H_2O(\ell) + H_2O(\ell) \rightarrow H_2O^+(aq) + OH^-(aq)$

$\lambda_m = \lambda^0_{M,H_2O} = \lambda_M^0\, H^+ + \lambda_M^0\, OH^- = \frac{K \times 1000}{\text{molarity}}$ - Concentration of water molecules 100% dissociated Ask

$$\text{molarity} = [H^+] = [OH^-] = \frac{K \times 1000}{\lambda_M^\infty}$$

$$K_W = [H^+][OH^-] = \left[\frac{K \times 1000}{\lambda_M^0}\right]^2 \quad K_a \text{ or } K_b = \frac{[H^+][OH^-]}{H_2O}$$

Ex.24 At infinite dilution the equivalent conductance of Al^{+3} and SO_4^{-2} ion are 189 and 160 Ω^{-1} cm^{-2} eq^{-1} respectively. calculate the equivalent and molar conductivity at infinite dilute of $Al_2(SO_4)_3$.

Sol. $\lambda^\infty_{eq[Al_2(SO_4)_3]} = \frac{1}{3}\lambda^\infty_{Al^{+3}} + \frac{1}{2}\lambda^\infty_{SO_4^{-2}}$

$\frac{1}{3} \times 189 + \frac{1}{2} \times 160 = 143\,\Omega^{-1}$ cm^2 eq^{-1}

Molar conductivity = λ_{eq}^{∞} × V.F. = 143 × 6 = 858 Ω^{-1} cm^2 mol^{-1}

Variation of K, λ_m & λ_{eq} of solutions with Dilution

K $\propto$ conc. of ions in the solution. In case of both strong and weak electrolytes on dilution the concentration of ions will decrease hence K will decrease.

λ_m or λ_{eq} (K $\propto$ C) strong electrolyte

$\lambda_m = \frac{1000 \times K}{\text{normality}}$ (K $\propto \sqrt{K_a c}$) weak electrol.

$\lambda_{eq} = \frac{1000 \times K}{\text{normality}}$

For strong electrolyte : $\lambda_m \propto \frac{K}{C} \propto \frac{C}{C}$ = constant

For weak electrolyte : $\lambda_m \propto \frac{K}{C} \propto \frac{\sqrt{K_a c}}{C} \propto \frac{1}{\sqrt{C}}$

Section (I) : Comercial cells and corrosion :

Some Primary Cells

- **Primary cells :** These cells can not be recharge dry cell (lechlanche cells)

mercury cells (miniature cell used in ethes electronic devices)

E_{cell} = constant

as all substances used are either pure solids or pure liquids.

- **Secondary cells :** Lead storage batteries used is automobiles (Cars/bikes)

Anode : Pb(s)

Cathode : $PbO_2(s)$

H_2SO_4(conc.) about 38% sollution of H_2SO_4 is taken.

Anode : Pb(s) $\rightarrow$ Pb^{2+} (aq) + $2e^-$

$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$

$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4 + 2e^-$

most of the $PbSO_4(s)$ ppt sticks to the lead rod.

Cathode : $2e^- + 4H^+ + PbO_2(s) \rightarrow Pb^{2+}(aq) + 2H_2O(\ell)$

$Pb^{2+}(aq) + SO_4^{2-}(aq) + 4H^+ + 2e^- \rightarrow PbSO_4(s) + 2H_2O(\ell)$

$PbSO_4(s)$ sticks to cathode rod.

$Pb(s) + PbO_2 + 4H^+ + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(\ell)$

E_{cell} = 2.05 V

Note : During the working of the cell discharge H_2SO_4 will be consumed so it's concentration in the solution hence density of the solution will decrease during charging of the cell $PbSO_4$ will get converted into Pb(s) and, $PbO_2(s)$ and H_2SO_4 will be produced.

Nickel – cadmium battery.

E_{cell} = constant as cell reaction has pure solide/liquids only.

Anode : Cd(s)

Cathode : $NiO_2(s)$

electrolyte : KOH

$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$

$2e^- + NiO_2 + 2H_2O \rightarrow Ni(OH)_2(s) + 2OH^-$

$$Cd(s) + NiO_2(s) + 2H_2O(\ell) \rightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

Fuel cells (H$_2$ – O$_2$ cell) :

Anode : $H_2 \rightarrow 2H^+ + 2e^- \times 2$

Cathod : $4e^- + 4H^+ + O_2 \rightarrow 2H_2O$

$$2H_2 + O_2 \rightarrow 2H_2O(\ell)$$

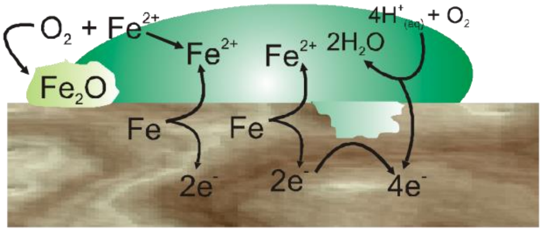
CH$_4$ – O$_2$ fuel cells :

Anode : $2H_2O + CH_4 \rightarrow CO_2 + 8H^+ + 8e^-$

Cathod : $4e^- + 4H^+ + O_2 \rightarrow 2H_2O$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O(\ell)$$

Mechanisum of corrosion



Oxidation : $Fe(s) \rightarrow Fe_{2+}(aq) + 2e_{-}$

Reduction : $2O_{2-}(g) + 4H_{+}(aq) \rightarrow 2H_2O(l)$

Atomospheric

oxidation : $2Fe_{2+}(aq) + 2H_2O(l) + 1/2O_2 \rightarrow Fe_2O_3(s) + 4H_{+}(aq)$

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. Calculate the EMF of the cell Mg (s)/Mg^{2+} (0.2M) || Ag^+ (1×10^{-3} M)/ Ag; $E^{\Theta}_{Mg^{2+}/Mg} = -2.37$ V, $E^{\Theta}_{Ag^+/Ag} = +0.80$V. What will be the effect on EMF if concentration of Mg^{2+} ion is decreased to 0.1 M ?

Sol. The net cell reaction is

$$Mg(s) + 2Ag^+(aq) \longrightarrow 2Ag(s) + Mg^{2+}(aq)$$

According to Nernst equation,

$$E_{cell} = E^{\Theta}_{cell} + \frac{0.059}{n} \log \frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$= 0.80 - (-2.37) + \frac{0.059}{2} \log \frac{(0.2)}{(1+10^{-3})^2}$$

$$= 3.17 + 0.0295 \times 5.3010 = 3.32 \text{ V}$$

When, conc of Mg^{2+} is decreased to 0.1, the new emf is

$$E_{cell} = 3.17 + 0.0295 \times \log \frac{0.1}{(1\times 10^{-3})^2} = 3.34$$

2. Explain the following.

(i) Rusting of iron becomes rapid in saline water than ordinaryy water.

(ii) Mobility of H^+ ions is high through the ice than the liquid water.

(iii) Why does a cell stops working after some time.

Sol. (i) The concenration of electrolyte in saline water is much higher than that in ordinary water. The ions present in saline water help in rapid flow of current in miniature electrochemical cells set up on the surface of iron which makes rusting process rapid.

(ii) In ice the water molecules are highely associated giving rise to rigid tetrahedral structure, whereas in liquid water the H_2O molecules are randomly associated and they donot adopt so rigid structure. Due to proper orientations of water molecules in ice, the movement of H^+ ions becomes faster as compared to that in randomly distributed aggregates of H_2O molecules in water.

(iii) We know that $E_{cell} = E_{cathode} – E_{anode}$ with the passage of time the concentration of metal ions around cathode decrease, thereby decreasing the value of $E_{cathode}$. Similarly, at a anode, the concentration of metal ions increases causing increases in the value of E_{anode}. As a result the difference $E_{cathode} – E_{anode}$ goes on decreasing and gradually becomes zero. At this stage the flow of current stops and cell becomes dead.

3. Zinc electrode is constituted at 298 K by placing zinc rod in 0.1 M aqueous solution of zinc sulphate which is 95% dissociated at this concentration. What will be the electrode potential ($E_{Zn^{2+}/Zn}$) of the electrode given that $E^{\ominus}_{Zn^{+2}/Zn} =– 0.76$ V

Sol. $[ZnSO_4] = 0.1$ M

% Dissociation = 95%

$\therefore \quad [Zn^{2+}] = \frac{0.1 \times 95}{100} = 0.095$ M

The electrode reaction is $Zn^{2+} + 2e^- \longrightarrow 2n$

According to Nernst equation,

$$E_{Zn^{+2}/Zn} = E^{\ominus}_{Zn^{+2}/Zn} + \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[Zn]} = – 0.76(V) + \frac{0.059}{2} \log (0.095) \quad \therefore [Zn] = 1 \quad = – 0.79 \text{ V.}$$

4. The emf of the cell,
Ag/AgCl (saturated sol.) || 0.01 M $AgNO_3$ |Ag at 298 K is 0.169 V.Calculate solubility and solubility product of AgCl at 298 K.

Sol. The given cell is a concentration cell and can be represented as
$Ag/Ag^+(C) \, || \, Ag^+ (0.01 \text{ M}) /Ag$.
The E_{cell} is given by

$$E_{cell} = \frac{0.059}{1} \log \frac{[Ag^+]_{cathode}}{[Ag^+]_{anode}}$$

$$0.169 = \frac{0.059}{1} \log \frac{0.01}{C}$$

$$\log \frac{0.01}{C} = \frac{0.169}{0.059} = 2.864$$

$$\frac{0.01}{C} = \text{antilog } 2.864 = 731.13$$

$C = 1.36 \times 10^{–5}$ M

or

Thus solubility of AgCl = $1.36 \times 10^{–5}$ mol $L^{–1}$

or $1.36 \times 10^{–5} \times 142.5 = 1.94 \times 10^{–3}$ $gL^{–1}$

K_{sp} of AgCl = $[Ag^+] [Cl^{–1}] = (\text{solubility})^2 = (1.36 \times 10^{–5}) = 1.84 \times 10^{–10}$ $mol^2 L^{–2}$

5. Consider the reaction given below

$Hg^{2+} + Ag \longrightarrow Ag^{+} + Hg$. Comment on the feasibility of reaction under different concentration of ions given below.

(i) $[Hg^{2+}] = 10^{-4}$ M ; $[Ag^{+}] = 10^{-1}$ M

(ii) $[Ag^{+}] = 10^{-4}$ M ; $[Hg^{2+}] = 10^{-1}$ M

Given $E^{\ominus}_{Ag^{+}/Ag} = 0.80$ V ;

$E^{\ominus}_{Hg^{2+}/Hg} = 0.79$ V

Sol. The cell reaction is :

$Hg^{2+} + 2\,Ag \longrightarrow 2Ag^{2+} + Hg$

$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode} = 0.79 \quad 0.80$

Case – I

$$E_{cell} = E^{\ominus}_{cell} + \frac{0.059}{2}\log\frac{[Hg^{2+}]}{[Ag^{+}]^{2}}$$

$\therefore$ [Ag] and [Hg] = 1

$$= -0.01 + 0.0295\log\frac{\left(10^{-4}\right)}{\left(10^{-1}\right)^{2}}$$

$= -0.01 - 0.059 = -0.069$ V

since E_{cell} is –ve, the reaction is no feasible

Case – II

$$E_{cell} = -0.01 + 0.0295\log\frac{\left(10^{-1}\right)}{\left(10^{-4}\right)^{2}} = -0.01 + 0.0295 \times 7 = 0.1965 \text{ V}$$

Since E_{cell} is +ve, the reaction is feasible.

6. Given that $E^{\ominus}_{Mn^{3+}/Mn^{2+}} = +1.51$ V; $E^{\ominus}_{Mn^{2+}/Mn} = -1.18$ V

$E^{\ominus}_{Cr^{3+}/Cr^{2+}} = -0.41$ V ; $E^{\ominus}_{Cr^{2+}/Cr} = -0.91$ V

Which oxidation state (+2 or +3) will be more stable for manganese and chromium as per the data.

Sol. (i) Conversion of Mn^{3+} to Mn^{2+} is represented by +ve value of $E^{\ominus}$ (1.51 V) but conversion of Mn^{2+} to Mn has – ve value of $E^{\ominus}$ (–1.18 V). This means that for manganese Mn^{2+} is more stable.

(ii) Conversion of Cr^{3+} to Cr^{2+} or Cr^{2+} to Cr both have negative values of $E^{\ominus}$. This means that for chromium Cr^{3+} state is more stable.

7. Na-amalgam is prepared by electrolysis of NaCl solution using liquid Hg as cathode. How long should the current of 10 amp. is passed to produce 10% Na – Hg on a cathode of 10 gm Hg. (atomic mass of Na = 23).

(A) 7.77 min (B) 9.44 min. (C) 5.24 min. (D) 11.39 min.

Sol. **(A)**

90 gm Hg has 10 gm Na

$$\therefore 10 \text{ gm Hg} = \frac{10}{90} \times 10 = \frac{10}{9} \text{ gm Na}$$

∴ weight of Na = $\frac{M}{n} \times \frac{i \times t}{96500}$

$\frac{10}{9} = \frac{23}{1} \times \frac{10 \times t}{96500}$ [∴ $Na^+ + e \rightarrow Na$]

∴ $t = \frac{10 \times 96500}{9 \times 10 \times 23}$ = 7.77 min

8 At what $\frac{[Br^-]}{\sqrt{[CO_3^{2-}]}}$ does the following cell have its reaction at equilibrium?

Ag(s) Ag_2CO_3(s) Na_2CO_3 (aq) KBr(aq) AgBr(s) Ag(s)

$K_{SP} = 8 \times 10^{-12}$ for Ag_2CO_3 and $K_{SP} = 4 \times 10^{-13}$ for AgBr

(A) $\sqrt{1} \times 10^{-7}$ (B) $\sqrt{2} \times 10^{-7}$ (C) $\sqrt{3} \times 10^{-7}$ (D) $\sqrt{4} \times 10^{-7}$

Sol. **(B)**

anode : $Ag(s) \longrightarrow Ag^+(aq) + 1e^-$

cathode : $Ag^+(aq) + 1e^- \longrightarrow Ag$

---

net : $Ag^+_{(AgBr)} \xrightarrow{1e^-} Ag^+_{(Ag_2CO_3)}$

$$0 = 0 + \frac{0.059}{1}\log\frac{\left(\frac{K_{SP}AgBr}{[Br^-]}\right)}{\sqrt{\frac{K_{SP}Ag_2CO_3}{[CO_3^{2-}]}}} \Rightarrow \frac{K_{SP}\,AgBr}{[Br^-]} = \sqrt{\frac{K_{SP}\,Ag_2CO_3}{[CO_3^{2-}]}}$$

$$\Rightarrow \frac{4 \times 10^{-13}}{\sqrt{8 \times 10^{-12}}} = \frac{[Br^-]}{\sqrt{[CO_3^{2-}]}} \Rightarrow \frac{[Br^-]}{\sqrt{[CO_3^{2-}]}} = \sqrt{2} \times 10^{-7}$$

9. Calculate the cell EMF in mV for

Pt H_2 (1atm) HCl (0.01 M) AgCl(s) Ag(s) at 298 K

if $\Delta G_f°$ values are at 25°C

$-109.56 \frac{kJ}{mol}$ for AgCl(s) and

$-130.79 \frac{kJ}{mol}$ for $(H^+ + Cl^-)$ (aq)

(A) 456 mV (B) 654 mV (C) 546 mV (D) None of these

Sol. **(A)**

$\Delta G^0_{\text{cell reaction}}$ = 2 (– 130.79) – 2 (– 109.56)
= – 42.46 kJ/mole

(for $H_2 + 2AgCl \longrightarrow 2Ag + 2H^+ + 2Cl^-$)

∴ $E^0_{cell} = \frac{-42460}{-2 \times 96500}$ = + 0.220 V

Now $E_{cell} = +0.220 + \frac{0.059}{2}\log\frac{1}{(0.01)^4}$ = 0.456 V = 456 mV.

10. Consider the cell Ag(s)|AgBr(s)|Br^-(aq)||AgCl(s) | Cl^-(aq)| Ag(s) at 25^o C . The solubility product constants of AgBr & AgCl are respectively 5×10^{-13} & 1×10^{-10} . For what ratio of the concentrations of Br^- & Cl^- ions would the emf of the cell be zero ?

(A) 1 : 200 (B) 1 : 100 (C) 1 : 500 (D) 200 : 1

Sol. **(A)**

$$E^0_{Br^-/AgBr/Ag} = E^0_{Ag^+/Ag} + \frac{0.059}{1} \log K_{SP}\,AgBr = E^0_{Ag^+/Ag} - 0.7257$$

and $$E^0_{Cl^-/AgCl/Ag} = E^0_{Ag^+/Ag} + \frac{0.059}{1} \log K_{SP}\,AgCl = E^0_{Ag^+/Ag} - 0.59$$

Now cell reaction is

$$\begin{array}{l} Ag + Br^- \longrightarrow AgBr + 1e^- \\ AgCl + 1e^- \longrightarrow Ag + Cl^- \\ \hline Br^- + AgCl \xrightarrow{1e^-} Cl^- + AgBr \end{array}$$

$$0 = (0.7257-0.59) + \frac{0.059}{1} \log \frac{[Br^-]}{[Cl^-]} \Rightarrow \frac{[Br^-]}{[Cl^-]} = 0.005$$