# Electrochemistry

## Section (A) : Galvanic cell, its Representation & salt bridge

### Introduction :

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

*Electrochemistry is the area of chemistry concerned with the interconversion of chemical energy and electrical energy. A battery is an electrochemical cell, a device for interconverting chemical and electrical energy. A battery takes the energy released 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
- A spontaneous chemical reaction generates an electric current.

Electrolytic cell
- An electric current drives a nonspontaneous reaction.

***Thus the two types of cells are reverse of each other.***

### Construction/ Working principle

Whenever a 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 resistance) the current flows as long as the potential difference exists between the metal phase and the liquid phase.

I **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 solution.

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

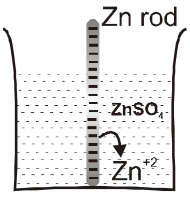
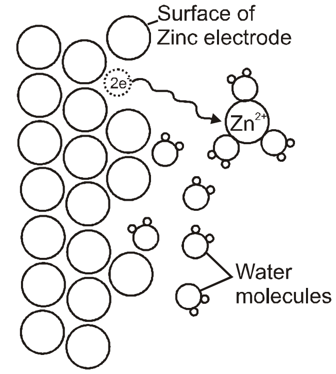


**Figure : 1**



How Zinc atoms become zinc ions at the electrode surface

**Figure : 2**

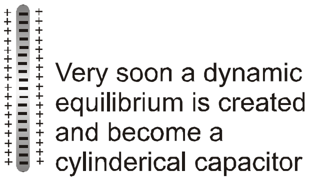


**Figure : 3**

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 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 $E_{Zn(s)/Zn^{2+}(aq)}$

**II** **Cathode :**

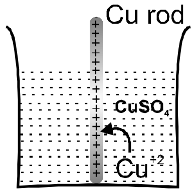
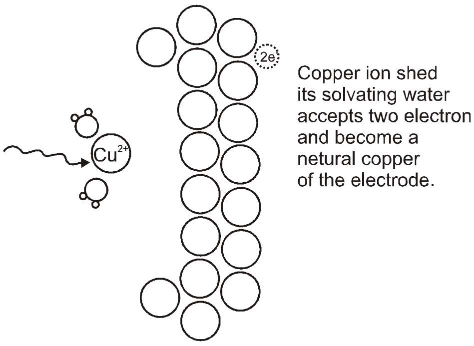
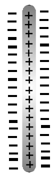


**Figure : 1**



Copper ion shed its solvating water accepts two electron and become a netural copper of the electrode.

**Figure : 2**



Very soon a dynamic equilibrium is created and it become a cylinderical capacitor

**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 : $Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$.

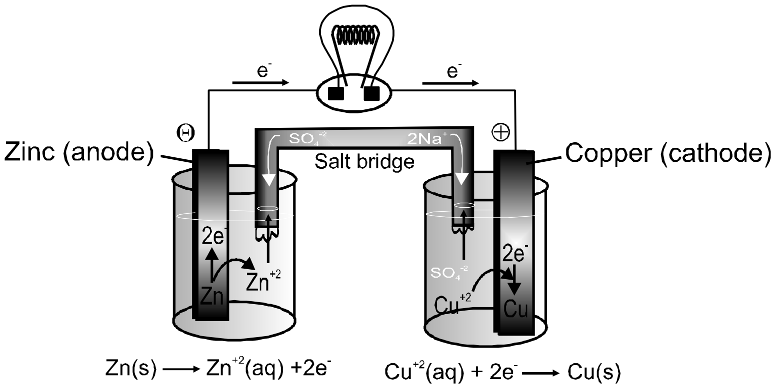
So rod will have deficiency of electron (positive charge). Extra negative charge will surround this positively charged rod and form double layer. An electrical double layer is developed in the system and hence a potential difference is created between the rod and the solution which is known as electrode 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 : $E_{Cu^{2+}(aq)/Cu(s)}$

**Anode :** $\begin{cases} \text{Is where oxidation occurs} \\ \text{Is where electrons are produced} \\ \text{Has a negative sign} \end{cases}$ **Cathode :** $\begin{cases} \text{Is where reduction occurs} \\ \text{Is where electrons are consumed} \\ \text{Has a positive sign} \end{cases}$

### 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 its cation equals speed of its 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 preferred 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 minimize the liquid junction potential. The potential difference between the junction of two liquids.
- It maintains the electrical neutrality of the solution in order to give continuous 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 anodic/cathodic compartment with porous plugs at each mouth of tube.
- It prevents mechanical mixing of two electrolytic solution.

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**Liquid-Liquid Junction Potential :**

The potential difference which arises between two solutions (during the progress of reaction) when in contact with each other.

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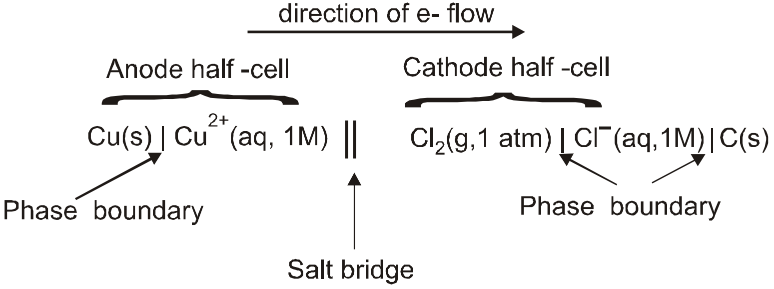
### Shorthand Notation for Galvanic Cells

- We require two half cells to produce an electrochemical cell, which can be represented by following 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, $Sn^{2+}(aq) + 2Ag^+(aq) \longrightarrow Sn^{4+}(aq) + 2Ag(s)$.

**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) : Electrochemical series & its Applications

### 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 developed between metal electrode and its ions in solution in known as electrode potential.
- Electrode potential depends upon :
  - ❍ Concentration of the solution.
  - ❍ Nature of the metal.
  - ❍ Nature of the electrolyte.
  - ❍ 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 at a particular temperature 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 (Zn electrode, Cu electrode etc.) | Reduction : $Zn^{2+} + 2e^- \rightarrow Zn(s)$ | $E^0_{Zn^{2+}/Zn(s)}$ ( SRP) |
| | | Oxidation : $Zn(s) \rightarrow Zn^{2+} + 2e^-$ | $E^0_{Zn(s)/Zn^{2+}}$ (SOP) |
| 2 | Hydrogen peroxide electrode | Reduction : $2e^- + 2H^+ + H_2O_2 \rightarrow 2H_2O$ | $E^0_{H_2O_2/H_2O}$ |
| | | 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 insoluable salt electrode | Reduction : $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$ | $E^0_{AgCl(s)/Ag(s)/Cl^-}$ |
| | | Oxidation : $Ag(s) + Cl^- \rightarrow AgCl(s) + e^-$ | $E^0_{Ag(s)/AgCl(s)/Cl^-}$ |

## Reference electrode :

- The potential of a single electrode 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),).

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

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

## 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 constituting the cell. The following three method 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 partial 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 by any number, the $E°_{cell}$ value would not change.

### Calculation of electrode potential :

**At Anode**

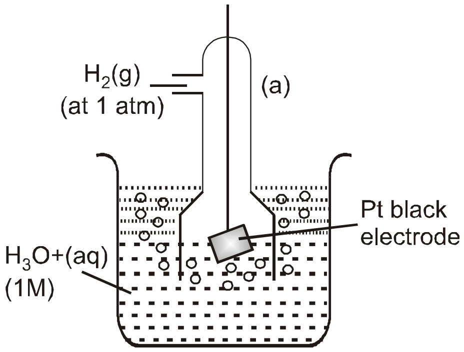
$H_2(g) \rightleftharpoons 2H^+ + 2e^-$

- Oxidation potential O.P. $= E_{H_2(g)/H^+(aq.)}$
- Under standard state
- $E^0_{H_2(g)/H^+(aq.)}$ = SOP

**At Cathode**

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

- Reduction Potential (R.P.) $E_{H^+/H_2(g)}$ = RP
- Under standard state.
- $E^0_{H^+/H_2(g)}$ = SRP



Hydrogen Electrode

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

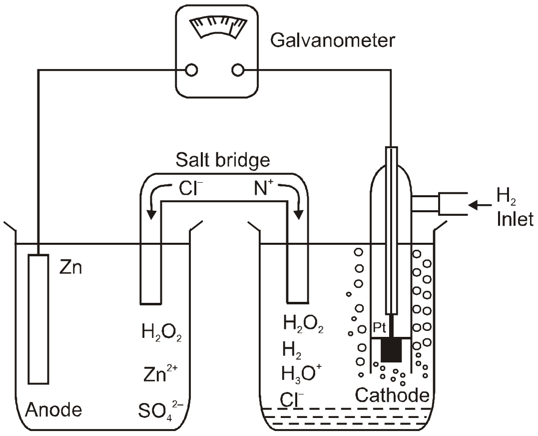
  SOP = – SRP = 0 for SHE.

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

**Anode** : Zinc electrode

**Cathode** : SHE

**Cell** : Zinc electrode || SHE



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

**Cell potential :**

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

= 0.76 V (at 298 K experimentaly)

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

$E^o_{Zn/Zn^{2+}(aq)}$ = 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 electrochemical series.

**Electrochemical Series :**

| | Electrode | Reaction | SRP (at 298 K) | |
|---|---|---|---|---|
| Increasing strength of reducing agent | *Li | $Li^+ + e^- \rightarrow Li(s)$ | – 3.05 V | Increasing strength of oxidising agent |
| | 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 | | | |
| | * Electrolytes ($H_2O$) | $H_2O(l) + e^- \rightarrow \frac{1}{2} H_2 + OH^-$ | – 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 | |
| | *$H_2$ | $2H^+ + 2e^-\ H_2(g)$ | 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 | $Ag^+ + e^- \rightarrow Ag$ | | |
| | Hg | $Hg^{2+} \rightarrow Hg(l)$ | | |
| | $Br_2$ | $Br_2 + 2e^- \rightarrow 2Br^-$ | 1.06 V | |
| | * Electrolytes | $\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O(□)$ | 1.23 V | |
| | * | $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$ | 1.33 V | |
| | * | $Cl_2 + 2e^- \rightarrow 2\,Cl^-$ | 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 $E^o_{cell}$ of (at 298 K), Zn(s) / $ZnSO_4$(aq) || $CuSO_4$(aq) / Cu(s)
Given that $E^o_{Zn/Zn^{2+}(aq)} = 0.76$ V, $E^o_{Cu(s)\,/\,Cu^{2+}(aq)} = -0.34$ V

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

**Ex-4** Given the cell Ag AgCl(s) | NaCl (0.05 M) || Ag $NO_3$ (0.30 M) | 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 $E^o_{cell}$ at 25°C.
(e) Does the cell reaction go spontaneous as written ?
(Given $E°_{AgCl,Cl} = +0.22$ volt) ; $E^o_{Ag^+/Ag} = +0.80$ volt)

**Sol.** (a) LHS electrode is anode and half reaction is oxidation.
$Ag^+ + Cl^- \longrightarrow AgCl(s) + e^-$ ... (i)
(b) RHS electrode is cathode and half reaction is reduction.
$Ag + e \longrightarrow Ag(s)$ ... (ii)
(c) From equation (i) and (ii) cell reaction is : $Cl^-$ (0.05 M) + $Ag^+$ (0.30 M) 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.

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## Section (C) : Concept of ΔG

### Free energy changes 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 transferred in the reaction.
F = Faraday constant = 96485 C/mole $e^-$ 96500 C/mole $e^-$

- **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 $\Delta G^o$ of the 3rd reaction with the help of some algebaric operations of $\Delta G^o$ of 1st and 2nd reactions.
  - Use $\Delta G^o = -nF\,E^o_{elec.}$ to calculate unknown E.P.
  - $E^0_{cell}$ is intensive property so if we multiply/Divide electrode reaction by any number the $E^0_{cell}$ value would not changed

i.e. $Zn^{2+} + 2e^- \rightarrow Zn(s)$ $E^o = -0.76$ V
Multiply by 2 $2Zn^{2+} + 4e^- \rightarrow 2Zn(s)$ $E^o = -0.76$ V (remain same)

## Solved Examples

**Ex-5** Given that $E^o_{Cu^{2+}/Cu} = 0.337$ V and $E^o_{Cu^+/Cu^{2+}} = -0.153$ V. Then calculate $E^o_{Cu^+/Cu}$.

**Sol.** (i) $Cu^{2+} + 2e^- \rightarrow Cu$ $\Delta G_1$
(ii) $Cu^+ \rightarrow Cu^{2+} + e^-$ $\Delta G_2$
After adding $Cu^+ + e^- \rightarrow Cu$
$\Delta G_1 + \Delta G_2 = \Delta G_3$
$-2F\,E_1^0 - F\,E_2^0 = -F\,E_3^0$
$E_3 = 2\,E_1^0 + E_2^0 = 2 \times 0.337 - 0.153 = 0.674 - 0.153 = 0.521$ V

**Ex-6** $E^0_{Mn^{2+}/MnO_4^-} = -1.51$ V ; $E^0_{MnO_2/Mn^{+2}} = +1.23$ V
$E^0_{MnO_4^-/MnO_2} = ?$ (All in acidic medium)

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

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

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

(iii) $4H^+ + MnO_4^- + 3e^- \rightarrow MnO_2 + 2H_2O$ $\Delta G_3$

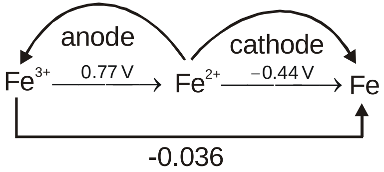
(i) + (ii) = (iii)

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

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

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

**Ex-7** Will $Fe^{2+}$ disproportionate or not



**Sol..** This is known as **latimer diagram.**

S.R.P to right of the species greater than SRP of it's left species will undergo disproportionation.

## Section (D) : Nernst equation & its Applications (including concentration cells)

### 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, $E = E° - \dfrac{0.059}{n} \log Q$

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.

### Applications of Nernst equation

- **Nernst Equation for Electrode Potential**

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

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

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

At 298K, $E_{Redn} = E^0_{Red^n} - \dfrac{0.059}{n} \log \left[\dfrac{1}{M^{n+}}\right]$

- **Hydrogen Electrode**

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

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

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

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

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

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

- **Gas – electrode Hydrogen electrode.**

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

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

- **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 concentration at 1 atm pressure Ka = 1.8 × $10^{-5}$.

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

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

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

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

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

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

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

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

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

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

**$E_{Redn}$ 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**

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

$\mathbf{\Delta G = -\,nF}\ E_{cell}$

From thermodynamics

$\Delta G = \Delta G^0 + RT\ln Q$

at chemical equilibrium $\Delta G = 0$

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

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

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

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

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

Given that $E^0_{Cr_2O_7^{2-}/Cr^{+3}}$ = 1.33 V ; $E^0_{Cl^-/Cl_2}$ = –1.36 V

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

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

$14H^+ + 6Cl^- + Cr_2O_7^{2-} \rightarrow 3Cl_2 + 2Cr^{+3} + 7H_2O$

$E^0_{cell}$ = 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

$$E° = \frac{0.0591}{n}\ \log K \qquad \text{... (i)}$$

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

$$\begin{matrix}Zn & + & Fe^{2+} & \rightleftharpoons & Fe & + & Zn^{2+} & ; & E°_{Cell} + 0.32\ V\\ - & & x & & - & & (1-x) & & \end{matrix}$$

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

$\log = \dfrac{[Zn^{2+}]}{[Fe^{2+}]} - 10.829$ 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 Daniel 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 potential)

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

We know that :

$W_{max} = \Delta G^o = - nFE^o$

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

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. $Ag(s) \mid Ag^+(a_1) \parallel Ag^+(a_2) \mid Ag(s) \longrightarrow$ ($a_1 < a_2$) $a_1$, $a_2$ 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 : $Ag^+(a_2) \longrightarrow Ag^+(a_1)$

**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

### Electrolysis & Electrolytic cell :

### Electrolysis :

- Electrolyte is a combination of cations and anions which in fused state or in aqueous solution can conduct electricity.
- This is possible due to the movement of ions from which it is made of.
- The process of using an electric current to bring about chemical change is called electrolysis.
- Electrolysis is a process of oxidation and reduction due to current in the electrolytic solution.
- 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 metal electrodes in the cell that are active, because the metals themselves are components of the half reactions.
- As the Daniel 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]

$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(□)$ [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):** $Pb^{2+} + 2e^- \rightarrow Pb(s)$ $E^o = 0.126V$

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

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

$E_{ext} > 1.206$ V

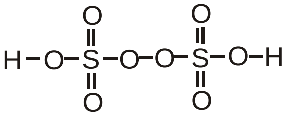
- Electrolysis of $CuSO_4$ molten

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

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

$H_2S_2O_8$ – Marchall's acid peroxy disulphuric acid.

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



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

- Electrolysis of aq $CuSO_4$

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

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

**Anode :** $2SO_4^{2-} \rightarrow S_2\ O_8^{2-} + 2e^-$ $E^o = -2.05$ V

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

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

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

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

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

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

- Electrolysis of aq NaCl

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

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

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

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

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

- Electrolysis of $CH_3COONa$

**Cathode :** $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$

**Anode :** $2CH_3COO^- \rightarrow 2CO_2 + C_2H_6 + 2e^-$

**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 its 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.

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**Electrolysis using attackable (reactive) electrodes.**

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

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

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

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

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

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

Electrolytic refining

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

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

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

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

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

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

## Section (F) : Faraday laws & its Applictions

- **Faraday's Law of Electrolysis :**
  - **$1^{st}$ 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 = $\dfrac{mass}{coulomb}$ = Kg/C or g/C

Z = Mass deposited when 1 C of charge is passed 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. $Ag^+ + e^- \rightarrow Ag$ $\qquad E = \dfrac{M}{1}$

$Cu^{2+} + 2e^- \rightarrow Cu(s)$ $\qquad E = \dfrac{M}{2}$

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

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

□ 96500 C – Charge deposit E gram metal charge

$\therefore$ $\quad 1C \rightarrow \left(\dfrac{E}{96500}\right)$ g $\qquad Z = \dfrac{E}{96500}$

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

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

- **$2^{nd}$ Law :** When equal charge is passed through 2 electrolytic cells and this 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.

$$W = ZQ = \frac{EQ}{96500}$$

$$\frac{W_1}{W_2} = \frac{z_1}{z_2} = \frac{E_1}{E_2} \text{ (Q = same)}$$

**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 $e^-$ = $\dfrac{5.79 \times 10000}{96500} = \dfrac{579}{965} = 0.6$

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

0.2 mole 0.4 mole

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

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 $e^- \rightarrow 1$ mole of $O_2$

$0.6$ mole of $e^- \rightarrow 0.15$ mole of $O_2$

so, total moles = 0.25 mole

Total volume = 5.6 Ltr.

**Ex-14** The electrochemical equivalent of copper is 0.0003296 g coulomb$^{-1}$. Calculate the amount of copper deposited by a current of 0.5 ampere flowing through copper sulphate solution for 50 minutes.

**Sol.** According to Faraday's first law, W = Zit

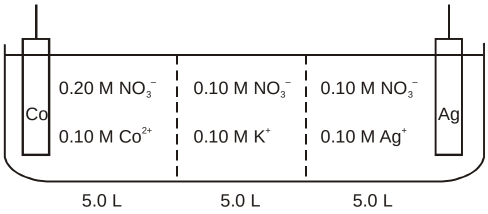
$W = 0.5 \times 50 \times 60 \times 0.003296 = 0.4944$ g

**Ex-15** An electric current is passed through three cells connected in series containing $ZnSO_4$, acidulated water and $CuSO_4$ respectively. What amount of Zn and $H_2$ are liberated when 6.25 g of Cu is deposited? Eq. wt. of Cu and Zn are 31.70 and 32.6 respectively.

**Sol.** ∵ Eq. of Cu = Eq. of Zn = Eq. of $H_2$

$$\frac{6.25}{31.70} = \frac{W_{Zn}}{32.6} = \frac{W_{H_2}}{1}$$

**Ex-16** The cell consists of three compartments separated by porous barriers. The first contains a cobalt electrode in 5.00 L of 0.100 M cobalt (II) nitrate; the second contains 5.00 L of 0.100 M $KNO_3$ and third contains 0.1 M $AgNO_3$. Assuming that the current within the cell is carried equally by the positive and negative ions, tabulate the concentrations of ions of each type in each compartment of the cell after the passage of 0.100 mole electrons.



Given : $Co^{2+} + 2e^- \rightarrow Co$ $\quad E^o = -.28$ V

$Ag^+ + e^- \rightarrow Ag$ $\quad E^o = 0.80$ V

**Sol.** Spontaneous reaction is : $2Ag^+ + Co \rightarrow Co^{2+} + 2Ag$ $\quad E^o = 1.08$

In the left compartment. Cobalt will be oxidized to cobalt (II) ion. In the right compartment, silver ion will be reduced to silver. The passage of 0.100 mol electrons will cause the following quantities of change.

| | **Compartment 1** | **Compartment 2** | **Compartment 3** |
|---|---|---|---|
| Effect of electrode | $+ 0.0500$ mol $Co^{3+}$ | | $- 0.100$ mol $Ag^+$ |
| Positive ion movement | $-0.0250$ mol $Co^{2+}$ | $+ 0.0250$ mol $Co^{2+}$ | $+ 0.0500$ mol $K^+$ |
| | | | $- 0.0500$ mol $K^+$ |
| Negative ion movement | $+0.0500$ mol $NO_3^-$ | | $- 0.0500$ mol $NO_3^-$ |

Changing the numbers of mol to concentrators in 5.0 L compartments and adding or subtracting yields the following results :

| | | | | | | |
|---|---|---|---|---|---|---|
| Final concentrations (M) | $Co^{2+}$ | 0.015 | $Co^{2+}$ | 0.00500 | $Ag^+$ | 0.0800 |
| | $NO_3^-$ | 0.210 | $K^+$ | 0.090 | $NO_3^-$ | 0.0900 |
| | $NO_3^-$ | 0.100 | $K^+$ | 0.0100 | | |

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## Section (G) : Commercial Cells & Corrosion

### Some Primary Cells

- **Primary cells :** These cells cannot be recharge i.e., dry cell (lechlanche cells) mercury cells (miniature cell used in the electronic devices)

  $E_{cell}$ = constant

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

**DRY CELLS and alkaline batteries :**

- Cell potential = 1.5 V
- Anode : $Zn(s) \longrightarrow Zn^{+2}(aq) + 2e^-$
- Cathode : $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

  $Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$
- Alkaline batteries contain basic material inside it.
- NaOH / KOH is used instead of the acidic salt $NH_4Cl$
- **Cathode :** $2MnO_2(s) + H_2O(\ell) + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq)$

  **Anode :** $Zn(s) + 2OH^-(aq) \longrightarrow ZnO(s) + H_2O(\ell) + 2e^-$
- Voltage produced by these cells = 1.54 V
- The cell potential does not decline under high current loads because no gases are formed.

**Hg cell :**

- Suitable for law current devices - Hearingaeds, watches
- **Anode :** $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

**Cathode :** $HgO + H_2O + 2e^- \longrightarrow Hg(□) + 2OH^-$

**Cell reaction :** $Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(□)$

- Cell potential = 1.35 V and remains constant.
- **Secondary cells :** Lead storage batteries used is automobiles (Cars/bikes)

**Anode :** Pb(s)

**Cathode :** $PbO_2(s)$

$H_2SO_4$(conc.) about 38% solution of $H_2SO_4$ is taken.

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

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

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

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

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

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

$PbSO_4(s)$ sticks to cathode rod.

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

$E_{cell} = 2.05$ V

---

**Note :** During the working of the cell or 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 solid/liquids only.

**Anode :** Cd(s)

**Cathode :** $NiO_2(s)$

**Electrolyte :** KOH

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

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

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

**Fuel cells ($H_2$–$O_2$ cell) :**

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

**Cathode :** $\underline{4e^- + 4H^+ + O_2 \rightarrow 2H_2O}$

$\underline{2H_2 + O_2 \rightarrow 2H_2O(□)}$

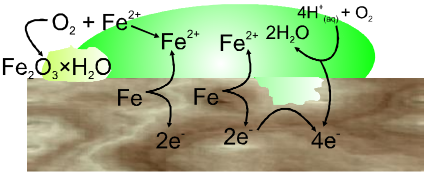
**$CH_4$–$O_2$ fuel cells :**

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

**Cathod :** $\underline{4e^- + 4H^+ + O_2 \rightarrow 2H_2O}$

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

## Mechanism of corrosion



**Oxidation :** $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

**Reduction :** $2O^{2-}(g) + 4H^+(aq) \rightarrow 2H_2O(l)$

Atmospheric

**Oxidation :** $2Fe^{2+}(aq) + 2H_2O(l) + 1/2O_2 \rightarrow Fe_2O_3(s) + 4H^+(aq)$

## Solved Examples

**Ex-17** During the discharge of a lead storage battery the density of $H_2SO_4$ falls from $\rho_1$ g/cc to $\rho_2$ g/C, $H_2SO_4$ of density of $\rho_1$ g/C. C is X% by weight and that of density of $\rho_2$ g/c.c is Y% by weight. The battery holds V litre of acid before discharging. Calculate the total charge released at anode of the battery. The reactions occurring during discharging are.

At anode : $Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

At cathode : $PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$

**Sol.** Mass of acid solution before discharge of lead storage battery (LSB) = $(V \times 10^3 \times \rho_1)$ g

$= (1000 \times V\rho_1)$g

Mass of $H_2SO_4$ before discharge of LSB = $\left(1000 \times V\rho_1 \times \dfrac{X}{100}\right)$ g = $(10 \times V\rho_1\ X)$g

Net reaction during discharging : $Pb + PbO_2 + 2H_2SO_4 \longrightarrow PbSO_4 + 2H_2O$

From the reaction, it is evident that the moles of electron exchanged (lost at anode and gain at cathode) is equal to the moles of $H_2SO_4$ consumed or moles of $H_2O$ produced. Let the moles of $H_2SO_4$ produced be x, then

Mass of $H_2O$ produced during discharge of LSB = (18x) g

Mass of $H_2SO_4$ consumed during discharge of LSB = (98x) g

Mass of $H_2SO_4$ after discharge of LSB = $[(10V\rho_1\ X)] - 98x]$ g

Mass of acid solution after discharge of LSB = $[(1000\ V\rho_1) - 98x + 18x] = [(1000\ V\rho_1) - 80x]$g

% of $H_2SO_4$ after discharge of LSB = $\dfrac{\text{Mass of } H_2SO_4 \text{ after discharge}}{\text{Mass of acid solution after discharge}} \times 100$

$Y = \dfrac{[(1000 \times V\rho_1) - 98x]}{[(1000 \times V\rho_1) - 80x]} \times 100$ x can be calculated as all other quantities are known.

Total charge released at cathode, Q = nF = xF.

**Ex-18** A lead storage cell is discharged which causes the $H_2SO_4$ electrolyte to change from a concentration of 34.6% by weight (density 1.261 g $ml^{-1}$ at 25°C) to one of 27% by weight. The original volume of electrolyte is one litre. Calculate the total charge released at anode of the battery. Note that the water is produced by the cell reaction as $H_2SO_4$ is used up. Over all reaction is.

$$Pb(s) + PbO_2(s) + 2H_2SO_4(\ell) \longrightarrow 2PbSO_4(s) + 2H_2O(\ell)$$

**Sol.** Before the discharge of lead storage battery,

Mass of solution = 1000 × 1.261 = 1261 g

Mass of $H_2SO_4$ = $\dfrac{1261 \times 34.6}{100}$ = 436.3 g.

Mass of water = 1261 – 436.3 = 824.7 g

After the discharge of lead storage battery,

Let the mass of $H_2O$ produce as a result of net reaction during discharge

$(Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O)$ is x g

Moles of $H_2O$ produced = $\dfrac{x}{18}$ = moles of $H_2SO_4$ consumed

Mass of $H_2SO_4$ consumed = $\dfrac{x}{18} \times 98$

Now, mass of solution after discharge = $1261 - \dfrac{98x}{18} + x$

% by the mass of $H_2SO_4$ after discharge = $\dfrac{\text{Mass of } H_2SO_4 \text{ left}}{\text{Mass of solution after discharge}} \times 100 = 27$

$= \dfrac{436.3 - \dfrac{98x}{18}}{1261 - \dfrac{98x}{18} + x} \times 100 = 27$ x = 22.59 g

## Section (H) : Electrical Conductance

### 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 $\propto \frac{1}{size}$ 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 :

$C = \frac{1}{R}$ = mho = $\Omega^{-1}$

= S (Siemens)

Conductivity/specific conductance

$\kappa = \frac{1}{\rho} = \frac{\ell}{RA} = \rho\frac{\ell}{A}$ unit $^{-1}\Omega$ $cm^{-1}$

= conductivity of 1 $cm^3$ of solution

α concentration of ions

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

$\kappa \propto$ (no. of ions) no. of charge carriers

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

- **Molar conductivity/molar conductance ($\Lambda_m$)** :
  Conductance of a solution containing 1 mole of an electrolyte between 2 electrodes which are unit length apart.
- Let the molarity of the solution 'C'
  C moles of electrolyte are present in 1 Lt. of solution.
  so molar conductance = $\Lambda_m$

$$\Lambda_m = \kappa V \qquad \Lambda_m = \frac{\kappa \times 1000}{C} \qquad \Rightarrow \qquad \Lambda_m = \frac{\kappa \times 1000}{\text{molarity}}$$

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

- **Equivalent conductance :** Conductivity of a solution containing 1 g equivalent of the electrolyte.
  $\Lambda_{eq}$ – equivalent conductivity/conductance.

$$\Lambda_{eq} = \frac{\kappa \times 1000}{\text{Normality}}$$

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

- **Ionic Mobility**
- Ionic Mobility = speed of the ion per unit electrical field

$$\mu = \frac{speed}{electrical\ \ field} = \frac{speed}{potential\ \ gradient}$$

- Its units are $\text{V}^{-1}\ \text{cm}^2\ \text{sec}^{-1}$

  Ionic mobility = u = $\dfrac{\Lambda_M^0}{96500} = \dfrac{\Lambda_M^0}{F}$

- **Transport Number**
  Transport Number of any ion is fraction of total current carried by that ion.

  Transport Number of cation = $\dfrac{\Lambda_M^0}{\Lambda_M^0\text{electrolyte}}$

## *Solved Examples*

**Ex-19** If resistivity of 0.8 M KCl solution is $2.5 \times 10^3$ cm calculate $\Lambda_m$ of the solution.

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

$$K = \frac{10^3}{2.5} = 4 \times 10^2 \qquad \Rightarrow \qquad \Lambda_m = \frac{4 \times 10^2 \times 1000 \times 10}{0.8} = 5 \times 10^5\ \Omega^{-1}\ \text{cm}^2\ \text{mole}^{-1}$$

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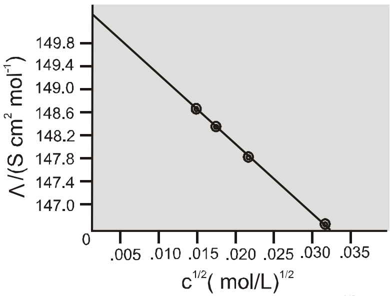
- **Variation of conductivity and molar conductivity with concentration**
  - Conductivity always decreases with the decrease in concentration both for weak and strong electrolytes.
  - The number of ions per unit volume that carry the current in a solution decreases on dilution.
  - Molar conductivity 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 $\Lambda^o$.

**Strong Electrolytes :**

- For strong electrolytes. $\Lambda$ increases slowly with dilution and can be represented by the equation

$$\Lambda = \Lambda^o - A\ C^{1/2}$$

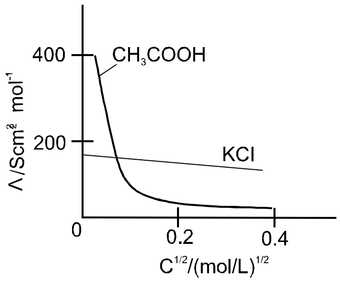
- The value of the constant 'A' for a given solvent and temperature depends on the type of electrolyte i.e. the charges on the cations and anion produced on the dissociation of the electrolyte in the solution.
  **Example :** Thus NaCl, $CaCl_2$, $MgSO_4$ are known as 1-1 , 2-1 and 2-2 electrolyte respectively.
- All electrolytes of a particular type have the same value for 'A'.



Variation of $\Lambda$ against $c^{1/2}$

### Weak electrolytes

- Weak electrolytes like acetic acid have lower degree of dissociation at higher concentration and hence for such electrolytes, the change in $\Lambda$ 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 $\rightarrow$ 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.



## Section (I) : 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)

$$\Lambda^{o}_{m\ \text{electrolyte}} = {}^{0}_{m}\nu_{+}\ \Lambda^{0}_{m} + \nu_{-}\ \Lambda^{0}_{m-}$$

$\nu_{+}$ = no. of cation in one formula unit of electrolyte

$\nu_{-}$ = no. of anions in one formula unit of electrolyte

For NaCl, $\nu_{+} = 1$ $\nu_{-} = 1$

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

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

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

$$\Lambda^{0}_{eq} = \frac{\Lambda^{0}_{m}}{\text{charge on the anion}} \qquad \Lambda^{0}_{eq}\text{, electrolyte} = \frac{\Lambda^{0}_{m}\ \text{electrolyte}}{\text{total} + \text{ve charge on cation}}$$

or

total $-$ ve charge on anion

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

$$\Lambda^{0}_{eq}Al_2(SO_4)_3 = \frac{2\Lambda^{0}_{mAl^{3+}} + 3\Lambda^{0}_{mSO_4^{2-}}}{6}$$

## Solved Examples

**Ex-20** $\Lambda^0_m$ $Na^+ = 150\,\Omega^{-1}\,cm^2\,mole^{-1}$ ; $\Lambda^0_{eq}$ $Ba^{2+} = 100\,\Omega^{-1}\,cm^2\,eq^{-1}$ ; $\Lambda^0_{eq}$ $SO_4^{2-} = 125\,\Omega^{-1}\,cm^2\,eq^{-1}$ ;

$\Lambda^0_m$ $Al^{3+} = 300\,\Omega^{-1}\,cm^2\,mole^{-1}$ ; $\Lambda^0_m$ $NH_4^+ = 200\,\Omega^{-1}\,cm^2\,mole^{-1}$ ; $\Lambda^0_m$ , $Cl^- = 150\,\Omega^{-1}\,cm^2\,mole^{-1}$

Then calculate :

(a) $\Lambda^0_{eq}$ , $Al^{3+}$
(b) $\Lambda^0_{eq}$ , $Al_2(SO_4)_3$
(c) $\Lambda^0_m$ , $(NH_4)_2SO_4$
(d) $\Lambda^0_m$ , NaCl, $BaCl_2.\ 6H_2O$
(e) $\Lambda^0_m$ , $(NH_4)_2\ SO_4\ Al_2(SO_4)_3\ .\ 24H_2O$
(f) $\Lambda^0_{eq}$ , NaCl

**Sol.** (a) $\Lambda^0_{eq}\,Al^{3+} = \dfrac{300}{3} = 100$
(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) $\Lambda^0_m$ $(NH_4)_2\ SO_4\ Al_2(SO_4)_3.24H_2O = 400 + 600 + 4 \times 250 = 2000$
(f) $\Lambda^0_{eq}$ $NaCl = 300\,\Omega^{-1}\,cm^2\,eq^{-1}$

**Ex-21** To calculate $\Lambda^0_m$ or $\Lambda^0_{eq}$ of weak electrolyte

**Sol.**

$$\Lambda^0_{mCH_3COOH} = \Lambda^0_{mCH_3COO^-} + \Lambda^0_m H^+$$

$$= (\Lambda^0_{mCH_3COO^-} + \Lambda^0_{mNa^+}) - \Lambda^0_{mNa^+} + \Lambda^0_{mH^+} + \Lambda^0_{mCl^+} - \Lambda^0_{mCl^-}$$

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

**Ex-22** Calculate $\Lambda^0_m$ 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

$\Lambda^0_{eq} = 400 + \dfrac{700}{2} - 450$ ; $\dfrac{\Lambda_m}{2} = 350 - 50 = 300$

$\Lambda_m = 600$

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### Applications of Kohlaraushch's law

- Calculate $\Lambda°$ for any electrolyte from the $\Lambda°$ of individual ions.
- Determine the value of its **dissociation constant** once we known the $\Lambda°$ and $\Lambda$ 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., $\Lambda_{eq} < \Lambda°_{eq}$

degree of dissociation

$$\alpha = \frac{\Lambda_{eq}}{\Lambda^0_{eq}} = \frac{equivalent\ \ conduc\tan ce\ \ at\ \ a\ \ given\ \ concentration}{equivalent\ \ conduc\tan ce\ \ at\ \ at\ \ \inf inite\ \ dilution}$$

- **Dissociation constant** of weak electrolyte:

$$K_C = \frac{C\alpha^2}{1-\alpha}\ ; \qquad \alpha = \text{degree of dissociation, C = concentration}$$

- The degree of dissociation then it can be approximated to the ratio of molar conductivity $\Lambda_c$ at the concentration c to limiting molar conductivity, $\Lambda^o$. Thus we have :

$$\alpha = \Lambda/\Lambda^o$$

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

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

- **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.

  $$\Lambda_m\text{, saturated} = \Lambda_M^{\infty} = \frac{K \times 1000}{Solubility} \quad S = \frac{K \times 1000}{\Lambda_M^0} \quad K_{SP} = S^2 \text{ (for AB type salt)}$$

## Solved Examples

**Ex-23** If conductivity of water used to make saturated solution of AgCl is found to be $3.1 \times 10^{-5-1}$ cm$^{-1}$ and conductance of the solution of AgCl = $4.5 \times 10^{-5-1}$ cm$^{-1}$

If $\Lambda_M^0$ $AgNO_3$ = 200 $\Omega^{-1}$ cm$^2$ mole$^{-1}$, $\Lambda_M^0$ $NaNO_3$ = 310 $\Omega^{-1}$ cm$^2$ mole$^{-1}$

Calculate $K_{SP}$ of AgCl

**Sol.** $\Lambda_M^0$ AgCl = 140 Total conductance = $10^{-5}$

$$S = \frac{140 \times 4 \times 10^{-5} \times 1000}{140} = \frac{1.4 \times 10^{-4}}{14} \; ; \quad S = 5.4 \times 10^{-4} ; \quad S^2 = 1 \times 10^{-8}$$

**Ex-24** To calculate $K_W$ of water

$H_2O(\square) + H_2O(\square) \rightarrow H_2O^+(aq) + OH^-(aq)$

$$\Lambda_m = \Lambda^0_{M,H_2O} = \Lambda_M^0 H^+ + \Lambda_M^0 OH^-$$

$$= \frac{K \times 1000}{molarity}$$ - Concentration of water molecules 100% dissociated Ask

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

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

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### Variation of κ, $\Lambda_m$ & $\Lambda_{eq}$ of solutions with Dilution

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

$\Lambda_m$ or $\Lambda_{eq}$ ($\kappa \propto C$) strong electrolyte

$\Lambda_m = \dfrac{1000 \times \kappa}{\text{molarity}}$ ($\kappa \propto \sqrt{K_aC}$ ) weak electrolyte.

$\Lambda_{eq} = \dfrac{1000 \times \kappa}{\text{normality}}$

For strong electrolyte $\Lambda_m \propto \dfrac{\kappa}{C} \propto \dfrac{C}{C}$ = constant

For weak electrolyte $\Lambda_m \propto \dfrac{\kappa}{C} \propto \dfrac{\sqrt{K_aC}}{C} \propto \dfrac{1}{\sqrt{C}}$

# Summary

**Electrochemistry** is the area of chemistry concerned with the interconversion of chemical and electrical energy. Chemical energy is converted to electrical energy in a galvanic cell, a device in which a spontaneous redox reaction is used to produce an electric current. Electrical energy is converted to chemical energy in an electrolytic cell, a cell in which an electric current drives a nonspontaneous reaction. It's convenient and reduction occur at separate electrodes.

The electrode at which oxidation occurs is called the anode, and the electrode at which reduction occurs is called the cathode. The cell potential E (also called the cell voltage or electromotive force is an electrical measure of the driving force of the cell reaction. Cell potentials depend on temperature, ion concentrations, and gas pressure. The standard cell are in their standard states. Cell potentials are related to free-energy changes by the equations $\Delta G = -nFE$ and $\Delta G^o = -nFE^o$, where F = 96,500 C/mol $e^-$ is the **faraday,** the charge on 1 mol of electrons.

The standard reduction potential for the a half-reaction is defined relative to an arbitrary value of 0 V for the standard hydrogen electrode (S.H.E.) : $2H^+(aq, 1\ M) + 2\ e^- \rightarrow H_2(g, 1\ atm)$ $E^o = 0\ V$

Tables of standard reduction potentials--- are used to arrange oxidizing and reducing agents in order of increasing strength, to calculate E° values for cell reactions, and to decide whether a particular redox reaction is spontaneous.

Cell potential under nonstandard-state conditions can be calculated using the Nernst equation,

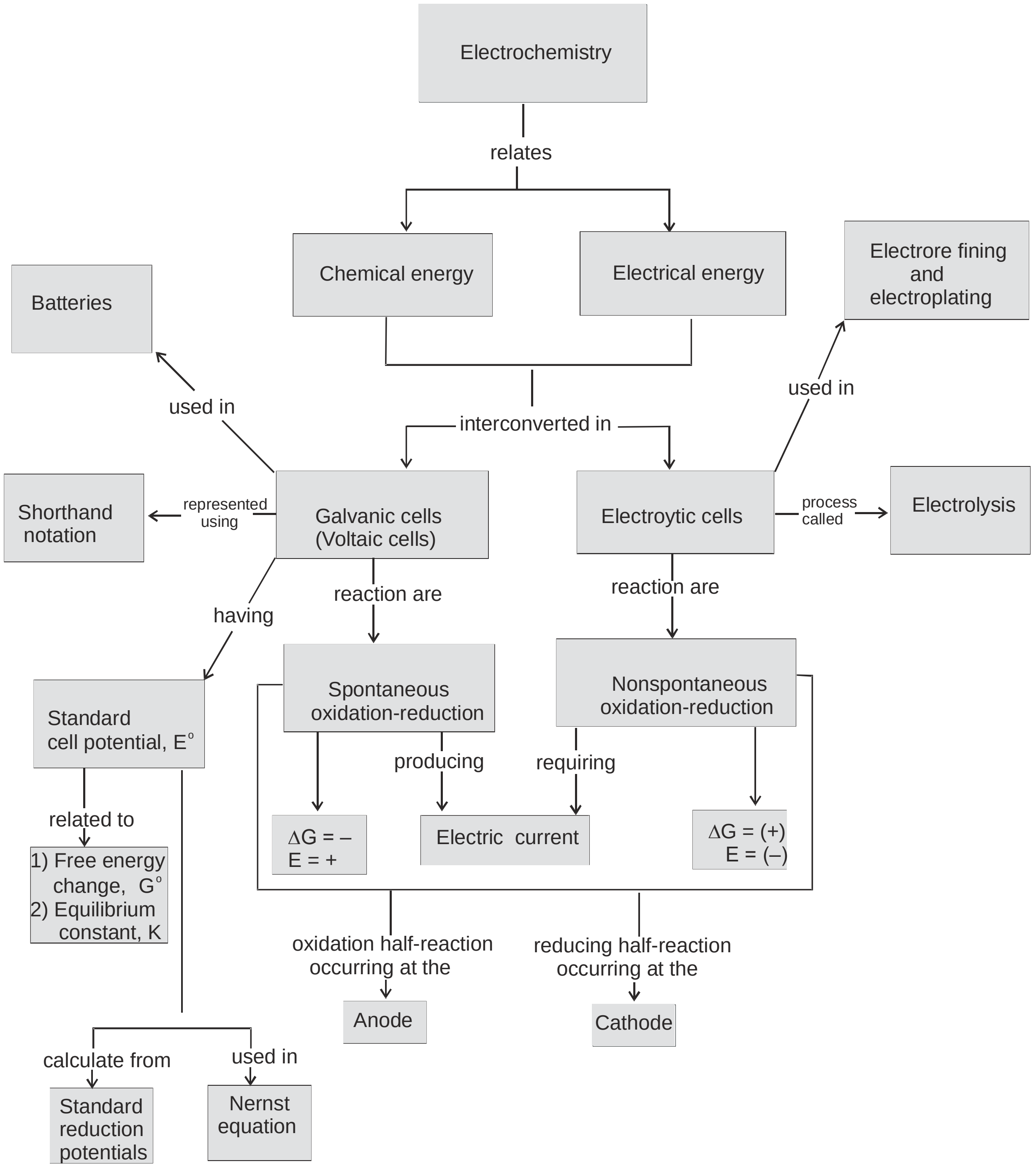
$$E = E^o - \frac{0.0592}{n} \log Q \text{ in volts, at } 25^oC$$

where Q is the reaction quotient. The equilibrium constant K and the standard cell potential E° are related by the equation $E^o = \frac{0.0592}{n} \log K$ in volts, at 25°C

A battery consists of one or more galvanic cells. A fuel cell differs from a battery in that the reactants are continuously supplied to the cell. **Corrosion** of iron (rusting) is an electrochemical process surface and oxygen is reduced in a cathode region. Corrosion can be prevented by covering iron with another metal, such as zinc, in the process called **galvanizing,** or simply by putting the iron in electrical contact with a second metal that is more easily oxidized, a process called **cathodic protection.**

**Electrolysis**, the process of using an electric current to bring about chemical change, is employed to produce sodium, chlorine, sodium hydroxide, and aluminum (Hall-Heroult process) and is used in electrorefining and electroplating. The product obtained at an electrode depends on the reduction potentials and overvoltage. The amount of product obtained is related to the number of moles of electrons passed through the cell, which depends on the current and the time that the current flows.

# *Electrochemistry*



$$E = E^\circ - \frac{.0592}{n}\log\frac{(\text{Products})}{(\text{Reactants})} \Rightarrow E = E^\circ - \frac{.0592}{n}\log\frac{(\text{Anodic ion concentration})}{(\text{Cathodic ion concentration})}$$

# MISCELLANEOUS SOLVED PROBLEMS (MSPs)

**1.** 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 g 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 g Hg has 10 g Na

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

$\therefore$ Weight of Na = $\frac{M}{n} \times \frac{i \times t}{96500}$

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

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

**2.** We have taken a saturated solution of AgBr. $K_{sp}$ of AgBr is $12 \times 10^{-14}$. If $10^{-7}$ mole of $AgNO_3$ are added to 1 litre of this solution then the conductivity of this solution in terms of $10^{-7}$ $Sm^{-1}$ units will be
[Given $\Lambda^o_{(Ag^+)} = 4 \times 10^{-3}$ $Sm^2$ $mol^{-1}$, $\Lambda^o_{(Br^-)} = 6 \times 10^{-3}$ S $m^2$ $mol^{-1}$, $\Lambda^o_{(NO_3^-)} = 5 \times 10^{-3}$ $Sm^2$ $mol^{-1}$]

(A) 39 (B) 55 (C) 15 (D) 41

**Sol.** **(A)**
The solubility of AgBr in presence of $10^{-7}$ molar $AgNO_3$ is $3 \times 10^{-7}$ M.
Therefore $[Br^-] = 3 \times 10^{-4}$ $m^3$, $[Ag^+] = 4 \times 10^{-4}$ $m^3$ and $[NO_3^-] = 10^{-4}$ $m^3$
Therefore $\kappa_{total} = \kappa_{Br^-} + \kappa_{Ag^+} + \kappa_{NO_3^-} = 39$ $Sm^{-1}$

**3.** A hydrogen electrode X was placed in a buffer solution of sodium acetate and acetic acid in the ratio a : b and another hydrogen electrode Y was placed in a buffer solution of sodium acetate and acetic acid in the ratio b : a. If reduction potential values for two cells are found to be $E_1$ and $E_2$ respectively w.r.t. standard hydrogen electrode, the $pK_a$ value of the acid can be given as

(A) $\frac{E_1 - E_2}{0.118}$ (B) $-\frac{E_1 + E_2}{0.118}$ (C) $\frac{E_1}{E_2} \times 0.118$ (D) $\frac{E_2 - E_1}{0.118}$

**Sol.** **(B)**

$H^+ + e^- \Rightarrow \frac{1}{2}H_2(g)$

$E_1 = 0 - 0.0591 \log \frac{1}{(H^+)_1}$

$E_1 = 0 + 0.0591 \log [H^+]_1 = -0.0591\ pH_1$

$E_2 = -0.0591\ pH_2$

$pH_1 = pk_a + \log \frac{Salt}{Acid}$

$pH_1 = pk_a + \log \frac{a}{b}$ .............. (1)

$pH_2 = pk_a + \log \frac{b}{a}$

$pH_2 = pk_a - \log \frac{a}{b}$ .............. (2)

Add (1) & (2)

$pH_1 + pH_2 = 2\ pk_a$

$2pk_a = -\frac{E_1}{0.0591} - \frac{E_2}{0.0591}$ $\Rightarrow$ $pk_a = -\left[\frac{E_1 + E_2}{0.118}\right]$

**4.** 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 : $Ag(s) \longrightarrow Ag^+(aq) + 1e^-$

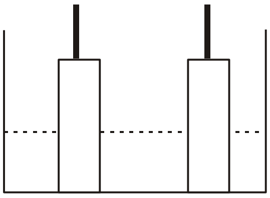
Cathode : $Ag^+(aq) + 1e^- \longrightarrow Ag$

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

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

$$\Rightarrow \quad \frac{4\times10^{-13}}{\sqrt{8\times10^{-12}}} = \frac{[Br^-]}{\sqrt{[CO_3^{2-}]}} \quad \Rightarrow \quad \frac{[Br^-]}{\sqrt{[CO_3^{2-}]}} = \sqrt{2} \times 10^{-7}$$

**5.** A resistance of 50Ω is registered when two electrodes are suspended into a beaker containing a dilute solution of a strong electrolyte such that exactly half of the them are submerged into solution. If the solution is diluted by adding pure water (negligible conductivity) so as to just completely submerge the electrodes, the new resistance offered by the solution would be



(A) 50 Ω (B) 100 Ω
(C) 25 Ω (D) 200 Ω

**Sol.** **(A)**

$R = \frac{1}{k} \frac{\ell}{A}$

The k is halved while the A is doubled. Hence R remains 50 Ω.

**6.** 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)**

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

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

$\therefore \quad E^0_{cell} = \frac{-42460}{-2\times96500} = +0.220$ V

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

**7.** Consider the cell Ag(s) | AgBr(s)|$Br^-$(aq) || AgCl(s) | $Cl^-$(aq)| Ag(s) at 25ºC. The solubility product constants of AgBr & AgCl are respectively $5 \times 10^{-13}$ & $1 \times 10^{-10}$. 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

$Ag + Br^- \longrightarrow AgBr + 1e^-$

$\underline{AgCl + 1e^- \longrightarrow Ag + Cl^-\qquad\qquad}$

$Br^- + AgCl \longrightarrow Cl^- + AgBr$

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

**8.** The conductivity of a solution may be taken to be directly proportional to the total concentration of the charge carries (ions) present in it in many cases. Using the above find the percent decrease in conductivity (k) of a solution of a weak monoacidic base BOH when its 0.1 M solution is diluted to double its original volume. ($K_b = 10^{-5}$ for BOH) (Take $\sqrt{50} = 7.07$) (Mark the answer to nearest integer),

**Sol.** Initially $[OH^-] = \sqrt{10^{-5} \times 0.1} = 10^{-3}$

$[\text{ions}]_{\text{total}} = 2 \times 10^{-3}$ M

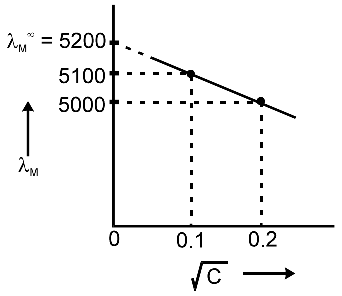
later $[OH^-] = \sqrt{10^{-5} \times \frac{1}{20}} = \sqrt{50} \times 10^{-4}$ M

$\therefore$ $[\text{ions}]_{\text{total}} = 2\sqrt{50} \times 10^{-4}$ M

$\therefore$ % change on $[\text{ions}]_{\text{total}} = \frac{2\sqrt{50} - 20}{20} \times 100 = -29.29\%$ **Ans. 29**

**9.** At 0.04 M concentration the molar conductivity of a solution of a electrolyte is 5000 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ while at 0.01 M concentration the value is 5100 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Making necessary assumption (Taking it as strong electrolyte) find the molar conductivity at infinite dilution and also determine the degree of dissociation of strong electrolyte at 0.04 M.

**Sol.** From the graph we can see the $\lambda_M^\infty$ value of 5200 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. Hence



$\alpha = \frac{5000}{5200} = 0.9615 \approx 0.96$ **Ans. 96**