

EDUCATALYSTS

Class(12th)

Introduction to Electrochemistry

INTRODUCTION

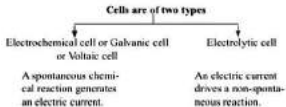
It deals with

- ② The use of electrical energy for the dissociation of chemical compounds (electrolysis)
- ② The use of chemical reactions for the production of electrical energy (Electro-chemical cells)
- ② The use of electrical energy in the study and preparation of chemical substances.
- ② The commercial power generating cells, namely secondary cells (batteries & fuel cells)

The basis of electrochemistry is thus a process in which electrons are transferred from one system to another.

CELL

Cell is a system or arrangement in which two electrodes are fitted in the same electrolyte or in two different electrolytes which are joined by a salt bridge.



— KEY NOTE —

The two types of cells are therefore reverse of each other.

Galvanic Or Voltaic Cell**Working Principle**

The cell in which **chemical energy** is converted into **electrical energy** is called **Galvanic cell**.

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.

Construction of Cell

- ② It has two half-cells, each having a beaker containing a metal strip dipped in its aqueous solution.
- ② The metal strips are called electrodes and are connected by a conducting wire.
- ② Two solutions are connected by a salt bridge.
- ② The oxidation and reduction half reactions occur at separate electrodes and electric current flows through the wire.

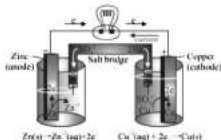


Fig.2 Galvanic Cell

(I) Anode

Zn rod is placed in ZnSO_4 solution.



The Zn atom will move in the solution to form Zn^{2+} . After some time following equilibrium will be established.



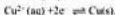
This particular electrode is known as anode :

- ② On anode, oxidation will take place (release of electron).
- ② Act as source of electrons.
- ② It is of negative polarity.
- ② The electrode potential is represented by $E_{\text{Zn}(s) : \text{Zn}^{2+}(aq)}$

(II) Cathode

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.

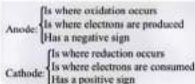
The following equilibrium will be established :



This will be known as cathode.

- ② At cathode reduction will take place (gain of e^- will take place).
- ② Act as sink of electron.
- ② Positive polarity will be developed.
- ② Their electrode potential can be represented by $E_{\text{Cu}^{2+}(aq) : \text{Cu}(s)}$

— KEY NOTE —



Selection of electrolyte for Salt Bridge

- ⊗ The electrolyte should be inert.
- ⊗ The electrolyte in salt bridge should be such that speed of its cation equals speed of its anion in electrical field.

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 maintains the electrical neutrality of the solution in order to give continuous flow or generation of current.

Daniel Cell

- ⊗ In Daniel cell instead of salt bridge, porous pot (or) porous diaphragm is used.

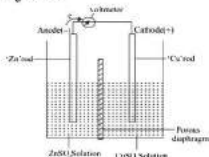


Fig.: Daniel cell having electrodes of Zinc and Copper dipping in the solution of their respective salts

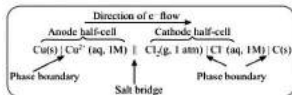
— KEY NOTE —

Daniel cell is also an electrochemical cell.

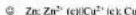
Shorthand Notation for Galvanic Cells

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. $\text{Pt}, \text{H}_2 / \text{H}^+ \text{ or } \text{H}^+ / \text{H}_2, \text{Pt}$)

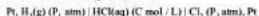


- ⊗ If it is Daniel Cell



- ⊗ In case of a Galvanic cell with a non-metal electrode, inert metal like Pt rod (wire) is introduced in solution which acts as electrode.

A Galvanic cell containing H_2 and Cl_2 gases as electrodes in an HCl solution is represented as,



Difference Between Electrochemical Cell And Electrolytic Cell

S. No	Electrochemical Cell	Electrolytic Cell
1.	It is a combination of two half cells, containing the same or different electrodes in the same or different electrolytes.	It is a single cell containing the same electrodes present in the same electrolyte.
2.	Anode is negative, Cathode is positive.	Anode is positive, Cathode is negative.
3.	It converts chemical energy into electrical energy, produced as a result of redox reaction.	It converts electrical energy into chemical energy. Energy is supplied to the electrolytic solution to bring about the redox reaction.
4.	Cell reaction is spontaneous.	Cell reaction is non-spontaneous.
5.	Salt bridge is required.	No salt-bridge is required.
6.	It is source of EMF.	It require EMF.
7.	It is reversible and spontaneous.	It is irreversible and non-spontaneous.

ELECTRODE POTENTIAL

- ⊗ The potential difference developed between metal electrode and its ions in solution is known as electrode potential.

- ⊗ Electrode potential depends upon :

- Concentration of the solution.
- Nature of the metal.
- Nature of the electrolyte.
- Pressure, temperature conditions

Electrode Potential

Oxidation Potential (O.P.)

- The electrode potential for oxidation half reaction
- Tendency to get oxidised
- Greater the O.P. then greater will be tendency to get oxidised.

Reduction Potential (R.P.)

- The electrode potential for reduction half reaction
- Tendency to get reduced.
- Greater the R.P., greater will be tendency to get reduced.

Standard Electrode Potential (E°)

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** or **standard reduction potential** (old name).

Table: Different types of electrode and their reaction in standard condition

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

— KEY NOTE —

- According to IUPAC, the given value of electrode potential is regarded as reduction potential unless it is specifically mentioned.
- The reduction potential of an electrode is exactly equal in magnitude but opposite in sign to its oxidation potential.

Electromotive Force (Or Emf) Of The Cell/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.

- $E_{cell}^0 = E_{oxd}^0$ (anode) + E_{red}^0 (cathode) [where, E_{oxd}^0 (anode) = oxidation potential of anode & E_{red}^0 (cathode) = reduction potential of cathode]
- $E_{red}^0 = E_{oxd}^0 - E_{anode}^0$ (both are either reduction potential or oxidation potential).
- $E_{cell}^0 = E_{oxd}^0$ (anode) - E_{red}^0 (cathode)

Free Energy Change 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 = $96485 \text{ C/mole } e^- \approx 96500 \text{ C/mole } e^-$

— KEY NOTE —

E_{cell}^0 is intensive property so on multiplying/Dividing cell reaction by any number, the E_{cell}^0 value would not change.

Train Your Brain

- Write shorthand notation for the following reaction, $Sn^{2+}(aq) + 2Ag^+(aq) \rightarrow Sn^{4+}(aq) + 2Ag(s)$.

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

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

- $Zn | Zn^{2+} | Br^-, Br_2 | Pt$
- $Cr | Cr^{3+} || I^-, I_2 | Pt$
- $Pt | H_2, H^+ || Cu^{2+} | Cu$
- $Cd | Cd^{2+} || Cl^-, AgCl | Ag$

- Oxidation half cell reaction, $Zn \rightarrow Zn^{2+} + 2e^-$

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

Net cell reaction $Zn + Br_2 \rightarrow Zn^{2+} + 2Br^-$ +ve terminal: cathode Pt
- Oxidation half reaction $[Cr \rightarrow Cr^{3+} + 3e^-] \times 2$

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

Net cell reaction $2Cr + 3I_2 \rightarrow 2Cr^{3+} + 6I^-$ +ve terminal: cathode Pt
- Oxidation half reaction, $H_2 \rightarrow 2H^+ + 2e^-$

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

Net cell reaction $H_2 + Cu^{2+} \rightarrow Cu + 2H^+$ +ve terminal: cathode Cu
- Oxidation half reaction, $Cd \rightarrow Cd^{2+} + 2e^-$

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

Net cell reaction $Cd + 2AgCl \rightarrow Cd^{2+} + 2Ag + 2Cl^-$ +ve terminal: cathode Ag

ELECTROCHEMICAL SERIES

- In the electrochemical series, the metals are arranged in the increasing order of reduction potentials.
- High reduction potential, metal ions undergo reduction first on cathode or it acts as cathode in the electrochemical cell.
- Low reduction potential metal (high negative value) undergo oxidation (or) it acts as anode. It is more reactive (or) more electropositive.
- In the electrochemical series metal placed above can displace the below metal ions from their solution.

Table: Electrochemical Series

Electrode	Reaction	SRP (at 298 K)
*Li	$\text{Li}^+ + e^- \rightarrow \text{Li(s)}$	-3.05 V
K	$\text{K}^+ + e^- \rightarrow \text{K}$	-2.93 V
Cu	$\text{Cu}^{+2} + 2e^- \rightarrow \text{Cu(s)}$	-2.87 V
Na	$\text{Na}^+ + e^- \rightarrow \text{Na(s)}$	-2.71 V
Mg	$\text{Mg}^{+2} + 2e^- \rightarrow \text{Mg(s)}$	-2.37 V
Al	$\text{Al}^{3+} + 3e^- \rightarrow \text{Al(s)}$	-1.66 V
* Electrolytes (H_2O)	$\text{H}_2\text{O(l)} + e^- \rightarrow \frac{1}{2}\text{H}_2 + \text{OH}^-$	-0.83 V
*Zn	$\text{Zn}^{+2} + 2e^- \rightarrow \text{Zn(s)}$	-0.76 V
Cr	$\text{Cr}^{+3} + 3e^- \rightarrow \text{Cr(s)}$	-0.74 V
* Fe	$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe(s)}$	-0.44 V
Cd	$\text{Cd}^{+2} + 2e^- \rightarrow \text{Cd(s)}$	-0.40 V
Co	$\text{Co} + 2e^- \rightarrow \text{Co(s)}$	-0.277 V
Ni	$\text{Ni}^{+2} + 2e^- \rightarrow \text{Ni(s)}$	-0.24 V
Sn	$\text{Sn}^{+2} + 2e^- \rightarrow \text{Sn(s)}$	-0.14 V
Pb	$\text{Pb}^{+2} + 2e^- \rightarrow \text{Pb(s)}$	-0.13 V
* H_2	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2(\text{g})$	0.00 V
Cu	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu(s)}$	0.34 V
I_2	$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	0.54 V
Fe	$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	0.77 V
Hg	$\text{Hg}_2^{2+} + 2e^- \rightarrow 2\text{Hg(l)}$	0.79 V
Ag	$\text{Ag}^+ + e^- \rightarrow \text{Ag(l)}$	0.80 V
Hg	$\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg(l)}$	0.85 V
Br_2	$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$	1.06 V
* Electrolytes $\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O(l)}$		1.23 V
* $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$		1.33 V
* $\text{Cl}_2 \rightarrow \text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$		1.36 V
* $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$		1.51 V
* $\text{F}_2(\text{g}) + 2e^- \rightarrow 2\text{F}^-$		2.87 V

Increasing strength of reducing agent

Increasing strength of oxidising agent

Train Your BrainQ. Calculate E_{cell}° of (at 298 K).

given that $E_{\text{Zn}^{2+}/\text{Zn}}^\circ = 0.76 \text{ V}$; $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = -0.34 \text{ V}$

$$\text{Ans. } E_{\text{cell}}^\circ = (\text{S.R.P.})_{\text{cathode}} - (\text{S.R.P.})_{\text{anode}}$$

$$= 0.34 - (-0.76) = 1.1 \text{ V}$$

Q. Given the cell $\text{Ag} \mid \text{AgCl(s)} \mid \text{NaCl (0.05 M)} \parallel \text{AgNO}_3 (0.30 \text{ M}) \mid \text{Ag}$

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?

$$(\text{Given } E_{\text{Ag}^+/\text{Ag}}^\circ = +0.22 \text{ volt}; E_{\text{AgCl}^-/\text{Ag}}^\circ = +0.80 \text{ volt})$$

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



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



(c) From equation (i) and (ii) cell reaction is:

(d) $E_{\text{cell}}^\circ = E_{\text{AgCl}^-/\text{Ag}}^\circ - E_{\text{Ag}^+/\text{Ag}}^\circ = (0.80 - 0.22) \text{ volt} = 0.58 \text{ volt}$

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

Important points about this series

- ① Metals near the top of the series are strongly electropositive (or weakly electronegative). They lose electrons readily to give cations.

- Weakly electronegative metals displaces metal below them from their salts. For example, iron displaces copper from CuSO_4 solution. Cu displaces silver from silver salt solution. silver displaces gold from gold salt solution as in photography during gold toning process.
- Hydroxides of metals in the upper part of the series are strongly basic and their salts do not undergo hydrolysis. On the other hand, hydroxides of the metals in the lower part of the series are weakly basic and their salts undergo hydrolysis.
- Metals lying above hydrogen are easily rusted. Those situated below are not rusted.
- Metals above hydrogen displace hydrogen from dilute acids.
- More strongly electropositive metals like K, Na, Ca, etc. displace hydrogen from water.
- Iron and other metals above it decompose steam and liberate hydrogen.
- Oxides of iron and other metals below it can be reduced easily.
- Oxides of manganese and other metals above it are reduced when heated in a current of hydrogen.
- Oxides of mercury and other metals below it are decomposed on heating.

Train Your Brain

Q. Given that $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.337\text{V}$ and $E_{\text{Cu}^+/\text{Cu}}^\circ = -0.153\text{V}$ then calculate $E_{\text{Cu}^+/ \text{Cu}^{2+}}^\circ$



$= 2 \times 0.337 - 0.153 = 0.674 - 0.153 = 0.521\text{V}$

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

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

$-n\text{FE}_{\text{cell}} = -n\text{FE}_{\text{cell}}^\circ + 2.303 RT \log Q$

$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303 RT}{nF} \log Q$

Taking $T = 298\text{K}$, $R = 8.314\text{J/mol K}$, $F = 96500\text{C}$

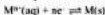
Now we get, $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log Q$

Where $n = \text{number of transferred electron}$, $Q = \text{reaction quotient}$

- 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



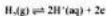
$E_{\text{Red}} = E_{\text{red}}^\circ - \frac{RT}{nF} \ln \left[\frac{\text{M}(\text{s})}{\text{M}^{n+}} \right]$

$E_{\text{Red}} = E_{\text{red}}^\circ - \frac{2.303 RT}{nF} \log \left[\frac{\text{M}(\text{s})}{\text{M}^{n+}} \right]$

$E_{\text{Red}} = E_{\text{Red}}^\circ - \frac{0.059}{n} \log \left[\frac{1}{\text{M}^{n+}} \right]$

$\Rightarrow E_{\text{Red}} = E_{\text{Red}}^\circ + \frac{0.059}{n} \log [\text{M}^{n+}]$

Hydrogen Electrode



$E = E^\circ - \frac{0.0591}{2} \log \left[\frac{(\text{H}^+)^2}{P_{\text{H}_2}} \right]$

Metal-metal soluble salt electrode



$E_{\text{Red}} = E_{\text{red}}^\circ - \frac{2.303 RT}{nF} \log \left(\frac{1}{\text{Zn}^{2+}} \right)$ at 298K

$E_{\text{Red}} = E_{\text{red}}^\circ - \frac{0.059}{2} \log \left(\frac{1}{\text{Zn}^{2+}} \right)$

Gas electrode - Hydrogen electrode



$E_{\text{Red}} = E_{\text{red}}^\circ - \frac{0.059}{2} \log \left[\frac{P_{\text{H}_2}}{[\text{H}^+]^2} \right]$

Redox electrode



$E_{\text{ox}} = E_{\text{ox}}^\circ - \frac{0.059}{5} \log \left[\frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]} \right]$

Nernst Equation for cell Potential



$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q$

$n = \text{no. of electrons exchanged during the reaction.}$

$E_{\text{cell}} = E_{\text{red}}^\circ (\text{cathode}) - E_{\text{red}}^\circ (\text{anode})$

$= \frac{0.059}{n} \log \left[\frac{\text{conc. of anode}}{\text{conc. of cathode}} \right]$

For example: in the cell $\text{Cu}|\text{Cu}^{2+}||\text{Ag}^{+}|\text{Ag}$ the cell reaction is
 $\text{Cu(s)} + 2\text{Ag}^{+} \rightarrow \text{Cu}^{2+} + 2\text{Ag}$

$$E_{\text{cell}} = (E_{\text{red}}^{\circ}(\text{Ag}^{+}) - E_{\text{red}}^{\circ}(\text{Cu}^{2+})) - \frac{0.059 \log \left[\frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^2} \right]}{2}$$

Calculation of equilibrium constant (K_{eq}) from Nernst Equation

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

$$\Delta G = -nFE_{\text{cell}}$$

From thermodynamics,

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

at chemical equilibrium, $\Delta G = 0$

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

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

$$\text{at equilibrium, } -nFE_{\text{cell}}^{\circ} = -2.303 RT \log (K_{\text{eq}})$$

$$\log K_{\text{eq}} = \frac{nF}{2.303 RT} E_{\text{cell}}^{\circ}$$

at 298 K and $R = 8.314 \text{ J/mol K}$

$$\log K_{\text{eq}} = \frac{n}{0.059} E_{\text{cell}}^{\circ}$$

$$K_{\text{eq}} = 10^{n E_{\text{cell}}^{\circ} / 0.059}$$

ELECTROLYSIS

- ① Electrolyte is a combination of cations and anions which in fused state can conduct electricity.
- ② This is possible due to the movement of ions from which it is made of.
- ③ The process of using an electric current to bring about chemical change is called electrolysis.
- ④ Electrolysis is a process of oxidation and reduction due to current flow.
- ⑤ The product obtained during electrolysis depends on following factors:
 - (a) The nature of the electrolyte
 - (b) The concentration of electrolyte
 - (c) The charge density flowing during electrolysis.
 - (d) The nature of the electrode

Faraday's Law of Electrolysis

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

$$W \propto Q$$

$$W = ZQ$$

Where, Z = electrochemical equivalent of the substance.

Q = charge

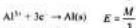
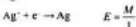
$$\text{Unit of } Z = \frac{\text{mass}}{\text{coulomb}} = \text{Kg/C or g/C}$$

- ② Z is defined as 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.



We know that,

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

i.e. 96500 C of charge deposits E gram metal

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

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

$$W = \frac{j \times t}{96500} \times E$$

- (ii) **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.

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

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

Train Your Brain

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

$$\text{Ans. } \because \text{Volume of layer of silver} = 0.005 \times 10^{-3} \times 80 = 0.04 \text{ cm}^3$$

$$\therefore \text{mass} = \text{Density} \times \text{volume} = 10.5 \times 0.04 = 0.42 \text{ gm}$$

$$\text{So } w = \frac{E}{96500} \times i \times t \quad 0.42 = \frac{108}{96500} \times 3 \times t$$

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

ELECTROLYTIC CONDUCTANCE

Conductors

Metallic Conductors

1. Charge carriers are e^{-}
2. No chemical changes
3. No transfer of mass
4. Resistance is because of collision of e^{-} s with fixed metal atoms.
5. Temp \uparrow R \uparrow
6. Low resistance generally (good conductor).

Electrolytic Conductors

1. Charge carriers are ions (cations/anion)
2. Decomposition of electrolyte takes place.
3. Transfer of mass
4. Resistance is because of collision of ions with solvent molecules & because of intermolecular force of attraction
5. Temp \uparrow R \downarrow
6. High resistance generally

Factors Affecting Conductance & Resistance

- ② Solute – Solute interactions (later – ionic force of attraction): Greater the force of attraction, greater will be the resistance.

$$\text{Force} \propto \text{Charge}$$

- ② Solute – Solvent interaction (Hydration/Solvation of ions): Greater the solvation, greater will be resistance.

$$\text{Solvation} \propto \text{Charge} \propto \frac{1}{\text{size}}$$

Example

Li^+ (Hydrated largest); Cs^+ (Hydrated smallest)

Resistance of $\text{LiCl} >$ resistance of CsCl

3. Solvent-solvent interaction (Viscosity): Greater the viscosity, greater will be resistance.
4. Temperature: $T \propto \frac{1}{R}$
5. Nature of electrolyte:
Weak electrolyte – high resistance
Strong electrolyte – Low resistance.

Resistance

$$R = \frac{V}{I} \text{ (ohm's law } (\Omega))$$

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

ρ – resistivity/specific resistance (constant).

SI unit is $\Omega \text{ m}$

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

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 its resistivity.

Conductance

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

= S (Siemens)

Conductivity/specific conductance:

$$\kappa = \frac{1}{\rho} = \frac{l}{RA} = \rho \frac{l}{A} \text{ where } \frac{l}{A} = x \text{ is cell constant}$$

unit: $\Omega^{-1} \text{ cm}^{-1}$

= conductivity of 1 cm^3 of solution

\propto concentration of ions

$$\kappa = \frac{1}{\rho} \quad G = \frac{1}{R}$$

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

- ② 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 (Λ_m):

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

Let the molarity of the solution be ' C '

$\therefore C$ moles of electrolyte are present in 1 L of solution.

so molar conductance = K

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

- ② Its unit is $\text{Ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$.

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

λ_{eq} – equivalent conductivity/conduction.

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

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

Train Your Brain

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

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

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

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

Variation of conductivity and molar conductivity with concentration

- ② Conductivity always decreases with the decrease in concentration both for weak and strong electrolytes.
- ② The number of ions per unit volume that carry the current in a solution decreases on dilution.
- ② Molar conductivity increases with decrease in concentration. This is because the total volume, V of solution containing one mole of electrolyte also increases.
- ② Molar conductivity is the conductance of solution.
- ② When concentration approaches zero, the molar conductivity is known as limiting molar conductivity and is represented by the symbol Λ° .

Strong Electrolytes

- ② For strong electrolytes, Λ increases slowly with dilution and can be represented by the equation $\Lambda = \Lambda^\circ - A C^{1/2}$
- 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 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 electrolytes respectively.

- ⊙ All electrolytes of a particular type have the same value for Λ°

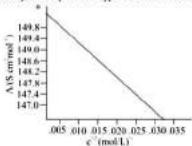
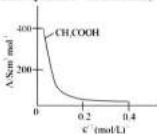


Fig.: Variation of Λ against $c^{1/2}$

Weak electrolytes

- ⊙ Weak electrolytes like acetic acid have lower degree of dissociation at higher concentration and hence for such electrolytes, the change in Λ with dilution is due to increase 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)



Effect of Dilution

- ⊙ With dilution " Λ " as well as " Λ_m° " of both weak/strong electrolytes increases.
- ⊙ Specific conductivity (κ) decreases with dilution because of decrease in no. of ions per cm^3 of electrolyte.
- ⊙ The molar (or) equivalent conductance of an electrolyte at infinite dilution (or) zero concentration is known as limiting molar conductance (or) limiting equivalent conductance.
- ⊙ Λ_0 value for any strong electrolyte is calculated graphically but for weak electrolyte it is determined by **Kohlrausch's law**.
- ⊙ The magnitude of increase in molar conductance for weak electrolyte is much larger than that for a strong electrolyte because strong electrolytes are almost completely ionised in all concentration and increase in Λ_{eq} (or) Λ_m with dilution is only due to decrease in interionic attractions.

Effect of Temperature

- ⊙ The conductivity of all electrolytes increases with increase in temperature.

CONDUCTANCE RATIO (α)

The ratio of the equivalent conductance at any concentration (Λ_c) to that at infinite dilution (Λ_0) is called conductance ratio (α).

$$\alpha = \frac{\Lambda_c}{\Lambda_0}$$

For weak electrolytes, α = degree of ionisation.

— KEY NOTE —

α is high for 0.01 M CH_3COOH solution when compared to that of 0.1 M CH_3COOH , because Λ_c is high in case of 0.01 M CH_3COOH

DEBYE - HUCKEL ONSAGER EQUATION

- ⊙ In the case of weak electrolytes like CH_3COOH , α is known as degree of dissociation (or) degree of ionisation of electrolyte.
- ⊙ The equivalent conductance at large dilution (or) at very low concentration is known as equivalent conductance at infinite dilution (Λ_0) or zero concentration (Λ_0)
- ⊙ The equivalent conductance of an electrolyte solution at any concentration (C) is related to Λ_0 for solutions is given by the following Debye-Huckel - Onsager equation.

$$\Lambda_c = \Lambda_0 - \left[\frac{82.4}{(DT)^{1/2}} + \frac{8.2 \times 10^5}{(DT)^{3/2}} \Lambda_0 \right] \sqrt{C}$$

Where

D = Dielectric constant of water

T = Temperature in kelvin scale

Λ_c = Equivalent conductance at conc. ' c '

Λ_0 = equivalent conductance at almost zero concentration or infinite dilution.

η = viscosity co-efficient of solvent.

In short form this equation is represented as

$$\Lambda_c = \Lambda_0 - b\sqrt{C}$$

Where b is constant and depends on the nature of the solvent and temperature.

KOHLRAUCH'S LAW

- ⊙ Based on κ (specific conductance) value, electrolytes are of two types.
 - (i) weak electrolytes: These have low ' κ ' value
Eg: weak acids, weak bases.
 - (ii) Strong electrolytes: These have high ' κ ' value
Eg: strong acids, strong bases, Salt solutions.
- ⊙ The conductance of an electrolyte is due to its ionisation.
- ⊙ The ionisation extent reaches maximum for weak electrolytes as dilution reaches maximum.

— KEY NOTE —

ClCH_2COOH has higher ' κ ' value than CH_3COOH since ClCH_2COOH is stronger acid than CH_3COOH .

Statement of Kohlrausch's Law

"The equivalent conductance at infinite dilution (Λ_0) of an electrolyte is equal to the algebraic sum of equivalent conductances (or) mobilities of anion (λ_0^-) and cation (λ_0^+) of the electrolyte at infinite dilution"

$$\Lambda_0(\text{electrolyte}) = \lambda_0^+ + \lambda_0^- (\text{ions})$$

$$\Lambda_{eq}^+ = \frac{1}{n^+} \lambda_0^+ + \frac{1}{n^-} \lambda_0^-$$

e.g. (i) $\Lambda_{KCl}^+ = \lambda_{K^+}^+ + \lambda_{Cl^-}^-$

(ii) $\Lambda_{CaCl_2}^+ = \frac{1}{2} \lambda_{Ca^{2+}}^+ + \lambda_{Cl^-}^-$

(iii) $\Lambda_{AlCl_3}^+ = \frac{1}{3} \lambda_{Al^{3+}}^+ + \lambda_{Cl^-}^-$

(iv) $\Lambda_{Fe_2(SO_4)_3}^+ = \frac{1}{3} \lambda_{Fe^{3+}}^+ + \frac{1}{2} \lambda_{SO_4^{2-}}^-$

Where n^+ and n^- are charge on each ion furnished by electrolyte. This law is valid at any dilution but is applied only at infinite dilution. Whereas "molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the cations and the anions each multiplied by the number of ions present in one formula unit of electrolyte" e.g. $A_x B_y$

$$\Lambda_{eq}^+ = x \times \lambda_0^+ + y \times \lambda_0^-$$

e.g. (i) $\Lambda_{BaCl_2}^+ = \lambda_{Ba^{2+}}^+ + 2\lambda_{Cl^-}^-$

(ii) $\Lambda_{Fe_2(SO_4)_3}^+ = 2\lambda_{Fe^{3+}}^+ + 3\lambda_{SO_4^{2-}}^-$

— KEY NOTE —

Ionic conductance is more for hydrated Cs^+ than hydrated Li^+

Applications

- ① Determination of Λ_0 for weak electrolytes

Eg: NH_4OH is a weak electrolyte its Λ_0 is calculated as

$$\Lambda_0(NH_4OH) = \Lambda_0(NH_4Cl) + \Lambda_0(NaOH) - \Lambda_0(NaCl)$$

- ② Degree of ionisation of weak electrolyte

$$(\alpha) = \frac{\Lambda_x}{\Lambda_0}$$

where, Λ_x = equivalent conductivity at given concentration

Λ_0 = limiting equivalent conductivity

- ③ Dissociation constant of weak electrolyte

$$K = \alpha^2$$

$$\alpha = \Lambda_x^0 / \Lambda_{eq}^0 \times \frac{\text{molecular weight}}{\text{equivalent weight}}$$

Expression for K

$$\Lambda_m^0 = n \times \Lambda_{eq}^0$$

- ③ Calculation of dissociation constant of weak electrolytes.

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow K_a = \frac{c \left(\frac{\Lambda_x}{\Lambda_0} \right)^2}{1 - \frac{\Lambda_x}{\Lambda_0}} = \frac{c\Lambda_x^2}{\Lambda_0(\Lambda_0 - \Lambda_x)}$$

Train Your Brain

Q. At infinite dilution the equivalent conductance of Al^{3+} and SO_4^{2-} ions are 189 and $160 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ respectively. Calculate the equivalent and molar conductivity at infinite dilution of $Al_2(SO_4)_3$.

$$\text{Ans. } \Lambda_{eq}^+(Al_2(SO_4)_3) = \frac{1}{3} \lambda_{Al^{3+}}^+ + \frac{1}{2} \lambda_{SO_4^{2-}}^-$$

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

$$\text{Molar conductivity} = \lambda_{eq}^+ \times V.F. = 143 \times 6 = 858 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

VARIAION OF K , λ_{eq} & 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.

($K \propto C$) strong electrolyte

$$\lambda_m = \frac{1000 \times K}{\text{molarity}} \Rightarrow \left(K \propto \sqrt{K_m \times c} \right) \text{ weak electrolyte}$$

$$\lambda_{eq} = \frac{1000 \times K}{\text{normality}} \quad [\text{Note: } \kappa = \text{Kappa}]$$

κ_a = equilibrium constant

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

$$\text{For weak electrolyte: } \lambda_m \propto \frac{\kappa}{C} \propto \frac{\sqrt{K_m \times c}}{C} \propto \frac{1}{\sqrt{C}}$$

CELL & BATTERIES

Primary cells:

- ② (i) It is an electrochemical cell which acts as a source of electrical energy without being previously charged up by an electric current from an external source of current.
- (ii) In which electrode reactions cannot be reversed by external source.

Example: Dry cell (Leclanche cells), mercury cells

$$E_{\text{cell}} = \text{constant}$$

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

Secondary cells:

- ② (i) Electrical energy from an external source is first converted into chemical energy (Electrolysis) and when the source is removed then the cell is made to operate in the reverse direction.
- (ii) Secondary cells are those which are rechargeable and can be used again and again.

Example: Lead storage batteries used in automobiles (Cars/bikes), Li-ion battery, hydrogen oxygen fuel cell etc.

Nickel – cadmium battery

E_{cell} = constant as cell reaction has pure solid/liquid only.

Anode : Cd(s)

Cathode : NiO₂(s)

Electrolyte : KOH

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

$2\text{e}^- + \text{NiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ni(OH)}_2(\text{s}) + 2\text{OH}^-$

$\text{Cd(s)} + \text{NiO}_2(\text{s}) + 2\text{H}_2\text{O(l)} \rightarrow \text{Cd(OH)}_2(\text{s}) + \text{Ni(OH)}_2(\text{s})$

Lead storage battery

The most important secondary cell is the lead storage battery commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO₂) as cathode. A 38% solution of sulphuric acid is used as an electrolyte.

The cell reactions when the battery is in use are given below:

Anode: $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$

Cathode: $\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$

i.e., overall cell reaction consisting of cathode and anode reactions is:

$\text{Pb(s)} + \text{PbO}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$

On charging the battery the reaction is reversed and PbSO₄(s) on anode and cathode is converted into Pb and PbO₂, respectively.

Fuel cells (H₂ – O₂ cell)

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. In such plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run a turbine to produce electricity. We know that a galvanic cell directly converts chemical energy into electricity and is highly efficient. It is now possible to make such cells in which reactants are fed continuously to the electrodes and products are removed continuously from the electrolyte compartment. Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called fuel cells.

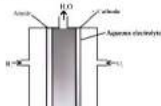


Fig.: Fuel cell using H₂ and O₂ produces electricity

One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water. The cell was used for providing electrical power in the Apollo space programme. The water vapours produced during the reaction were condensed and added to the drinking water supply for the astronauts. In the cell, hydrogen

and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions. The electrode reactions are given below:

Cathode: $\text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$

Anode: $2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \rightarrow 4\text{H}_2\text{O(l)} + 4\text{e}^-$

Overall reaction being:

$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O(l)}$

The cell runs continuously as long as the reactants are supplied. Fuel cells produce electricity with an efficiency of about 70 % compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes for increasing the efficiency of fuel cells. These have been used in automobiles on an experimental basis. Fuel cells are pollution free and in view of their future importance, a variety of fuel cells have been fabricated and tried.

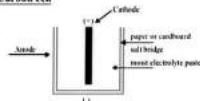
Dry Cell

A dry cell is one type of electric battery, which is generally used for the home and portable electronic devices. A battery is a device that consists of one or more electrochemical cells, which converts chemical energy into electrical energy.

A dry cell is an electrochemical cell consisting of low moisture immobilized electrolytes in the form of a paste, which restricts it from flowing. Due to this, it is easily transportable.

Primary cell

1. Zinc-Carbon cell



A dry cell consists of a metal container in which a low moisture electrolyte paste covers the graphite rod or a metal electrode. Generally, the metal container will be zinc whose base acts as a negative electrode (anode) and a carbon rod acts as a positive electrode (cathode). It is surrounded by manganese dioxide and low moisture electrolyte like ammonium chloride paste, which will produce a maximum of 1.5V of voltage, and they are not reversible.

The half cell reaction process has the following steps

Step 1: During the process, a reduction reaction occurs within the moistured electrolyte, which comprises manganese dioxide (MnO₂) and ammonium chloride (NH₄Cl) and graphite serves as solid support for the reduction reaction

$2\text{NH}_4^+ + 2\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 + 2\text{NH}_3 + \text{H}_2\text{O}$

Step 2: Zinc container serves as an anode and undergoes an oxidation reaction

$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

Zinc-carbon cell is the most common dry cell and is also called Leclanche cell. The alkaline battery has almost same half-cell reaction, where KOH or NaOH replaces the ammonium chloride and half-cell reactions are



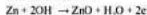
The overall reaction is,



2. Mercury cell

In the mercury cell, HgO serves as a cathode and zinc metal serves as an anode and the reaction involves the following steps

Step 1: At the anode



Step 2: At the cathode



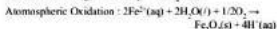
The overall reaction is of the cell



CORROSION

- ⑦ The natural tendency of conversion of a metal into its mineral compound form on interaction with the environment (Polluted air, water, associated other metals etc) is known as corrosion. E.g.: Iron converts itself into its oxide (Fe_2O_3 - haematite). Copper converts itself into its carbonate ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ - Malachite). Silver converts itself into its sulphide (Ag_2S - Argentite).
- ⑦ Corrosion of iron by conversion into iron oxide is known as rusting.
- ⑦ Corrosion of silver by conversion into its sulphide is known as tarnishing.

Mechanism of corrosion



Electrochemical corrosion

- ⑦ The process of corrosion may be chemical (or) electrochemical in nature.

The anodic dissolution of a metal under the conditions of corrosion is known as electrochemical corrosion



- ⑦ Corrosion occurs if the environmental conditions of the metal favour the formation of a voltaic cell with the metal acting as anode.
- ⑦ Electrochemical corrosion is basically of two types as:
 - (a) Hydrogen evolution type
 - (b) Differential oxygenation type

(i) Hydrogen Evolution type

- ⑦ This type of corrosion is exhibited by metals which can displace H_2 gas from aqueous solution.
- ⑦ This happens if the electrode potential of the metal under the conditions of corrosion is more negative than that of the hydrogen electrode under the given conditions.
- ⑦ This type of corrosion depends upon
 - (a) pH of the medium
 - (b) Chemical nature of the metal undergoing corrosion
- ⑦ Pure zinc does not corrode in salt solutions but in the presence of Cu as impurity, Zn corrodes.
- ⑦ Zn corrodes in 2M acid but not in neutral salt solution

(ii) Differential Oxygenation type

- ⑦ This type of corrosion occurs if O_2 concentration is not uniformly distributed on the surface of the metal
- ⑦ Corrosion of the metal generally occurs at the point where O_2 concentration is less
- ⑦ The portion of the metal with access to high concentration of O_2 functions as cathode and with access to low concentration of O_2 functions as anode. Hence, the metal with differential oxygenation acts as a galvanic cell.

Eg.: When an iron rod is immersed in NaCl solution the immersed part is corroded due to less oxygenation of the surface of the metal.

Prevention of Corrosion

The main principle underlying the methods of prevention of corrosion is to separate the metal (or) isolate the metal from the environment which is achieved by different ways. They are:

- ⑦ Painting
- ⑦ Alloying (galvanisation)
- ⑦ To prevent as far as possible the contact of the metal surface with good electrical conducting media.
- ⑦ Covering by some chemicals like bisphenol.
- ⑦ Cover the surface by other metals (Sn, Zn etc) that are inert (or) react to save the object.
- ⑦ Sacrificial electrode of another metal (like Mg, Zn, etc) which corrodes itself but saves the object.