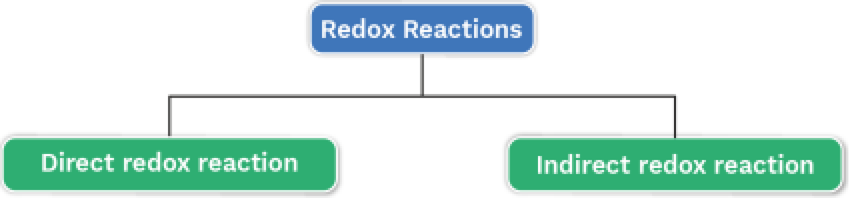
Electrochemistry

General Introduction

Redox reactions



Oxidation and reduction both carried out in same container

Oxidation and reduction occurs in two separate half cells

Oxidation and reduction

	Property	Oxidation	Reduction
1	Hydrogen	Loss	Gain
2	Oxygen	Gain	Loss
3	Electron	Loss	Gain
4	Oxidation No.	Increase	Decrease

	Oxidising agent or oxidant	Reducing agent or reductant
1	Under goes reduction	Undergoes oxidation
2	Gain electrons	Donates electrons
3	Oxidation no. of its atoms increases	Oxidation no. of its atoms decreases

For example, consider the reaction

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$

Or $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ **......(i)**

Zn is oxidized on Zn^{2+} ions while Cu^{2+} has been reduced to Cu.

Similarly in the reaction

$$Cu(s) + 2\,AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\,Ag(s)$$

Or $Cu(s) + 2\,Ag^{+} \rightarrow Cu^{2+}(aq) + 2\,Ag(s)$ **......(ii)**

Cu has been oxidized to Cu^{2+} ions while Ag+ has been reduced to Ag.

Concept Ladder

Displacement reactions can and can't be redox reactions. Single displacement reactions are redox reactions where as double displacement reactions are not redox reactions.

Again in the reaction

$$Zn(s) + H_2SO_4(aq) \rightarrow ZnSO_4(aq) + H_2(g)$$

Or $$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \quad \text{......(iii)}$$

Zn has been oxidized to Zn^{2+} whereas H^+ ions have been reduced to H_2 gas.

The substance which gets reduced oxidizes the other substance and is called **oxidizing agent** or **oxidant** while the substance which gets oxidized reduces the other substance and is called **reducing agent** or **reductant**. Thus, oxidizing agent is a substance which gains electrons while reducing agent is a substance which loses electrons.

Redox reaction is defined as the reaction which is considered to be made up of two half reactions, one involving oxidation, i.e. loss of electrons and the other involving reduction, i.e., gain of electrons. These are known as **oxidation half-reaction** and **reduction half-reaction**. For example, the reaction (i) may be split into two half reactions as under:

$$\begin{array}{l} Zn \longrightarrow Zn^{2+} + 2e^- \text{(oxidation half-reaction)} \\ Cu^{2+} + 2e^- \longrightarrow Cu \text{ (Reduction half-reaction)} \\ \hline Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu \end{array}$$

Electrochemistry

Electrochemistry is defined as the branch of physical chemistry, which deals with the study of conversion of electrical energy from chemical energy which is produced in a redox reaction or how to get redox reaction by using electrical energy, which is otherwise non-spontaneous.

Previous Year's Question

In acidic medium H_2O_2 changes $Cr_2O_7^{2-}$ to CrO_5 which has two (—O—O—) bonds. Oxidation state of Cr in CrO_5 is **[NEET-2014]**

(1) +5 (2) +3 (3) +6 (4) -10

Concept Ladder

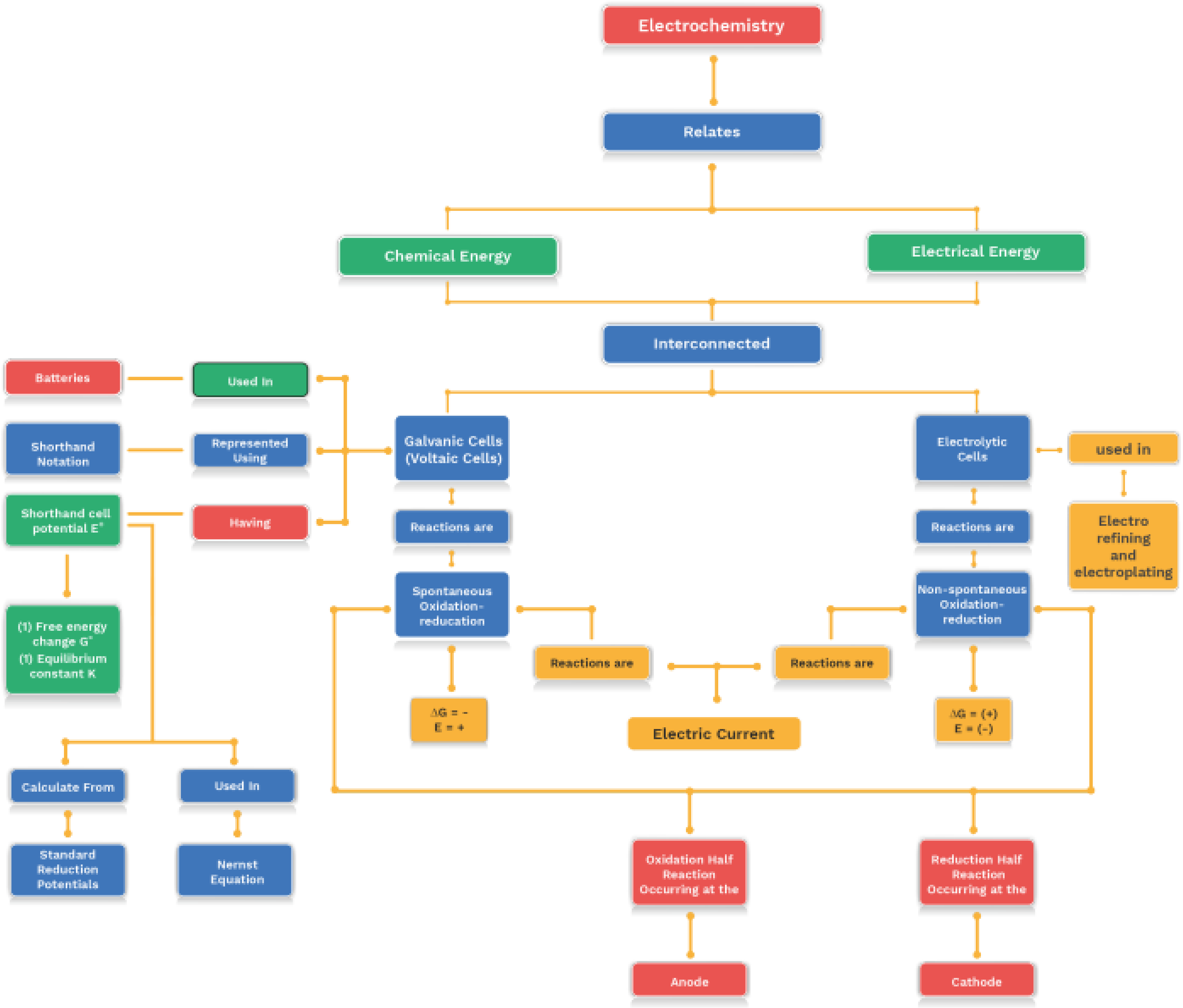
According to classical concept, oxidation is an addition of oxygen [or electronegative radical/ element] or removal of hydrogen [or electropositive radical/element

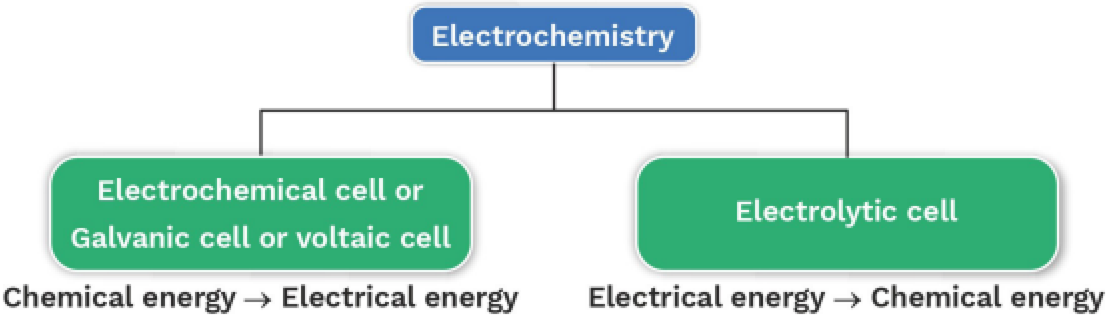
Rack your Brain

All redox reactions are exothermic. Why?

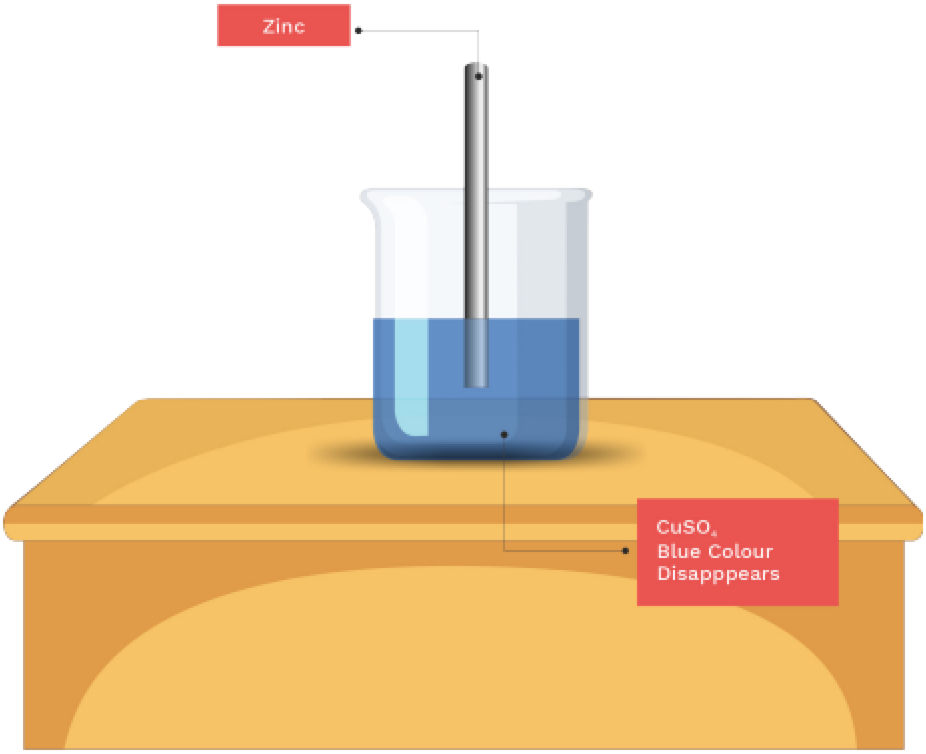
Definition

Electrochemistry deals with relationship between electrical and chemical energy


Electrochemistry
Relates
Chemical Energy
Electrical Energy
Interconnected
Galvanic Cells (Voltaic Cells)
Electrolytic Cells
used in
Electro refining and electroplating
Used In
Batteries
Represented Using
Shorthand Notation
Having
Shorthand cell potential E°
(1) Free energy change G°
(1) Equilibrium constant K
Calculate From
Standard Reduction Potentials
Used In
Nernst Equation
Reactions are
Spontaneous Oxidation-reducation
ΔG = -
E = +
Reactions are
Non-spontaneous Oxidation-reduction
ΔG = (+)
E = (-)
Reactions are
Reactions are
Electric Current
Oxidation Half Reaction Occurring at the
Anode
Reduction Half Reaction Occurring at the
Cathode



- Electro chemical cell concept came from the study of redox reaction



- This reaction happens by its own. Therefore its Gibb's free energy is negative.

  $\Delta G < 0$ (spontaneous)

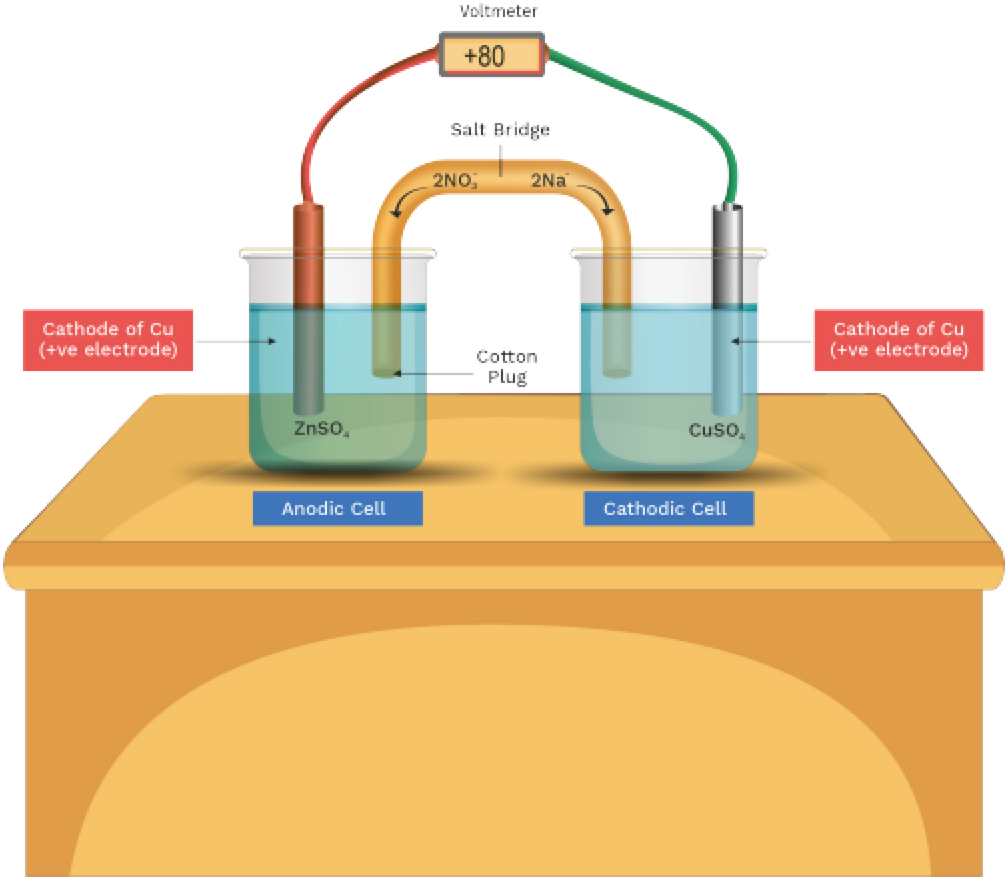
  $\Delta G > 0$ (Non spontaneous

- Work done by the system in electrochemical process Work done = $-\Delta G$
- Electrical work = Charge × potential Difference

Definition

The device in which chemical energy is converted into electrical energy by spontaneous redox reaction is called Galvanic cell Or Voltaic cell

Galvanic Cell Or Voltaic Cell



In the above cell, the zinc ion solution begins to build up a positive charge. Similarly, as copper ions plate on as copper, the solution builds up a negative charge. The half cell reactions will stop unless positive ions can move from the zinc half-cell to the copper half cell, and negative ions from the copper half-cell can move to the zinc half-cell. It is necessary that these ion flow occur without mixing of the zinc ion and copper ion solutions. If copper ion comes in contact with the zinc metal.

Concept Ladder

In a galvanic cell, reduction potential of reduction half cell reaction is always greater than oxidation half cell reaction.

Types of Conductors

	Electronic conductors or Metallic conductors	Electrolytic Conductors or Solution Conductors
1	It allows current to pass in metallic lattice by the movement of electron. e.g., Cu, Ag, etc.	It allows current to pass in molten state or in aq. solution of electrolytes by movement of ions. e.g., NaCl(aq) or NaCl (fused).
2	There is only physical change occur during passage of current.	There is physical as well as chemical changes occurs during passage of current.
3	It generally shows no transfer of matter.	It involves transfer of matter in form of ions.
4	During the passage of current, resistance increases due to increase in temperature. Thermal motion of metal ions which results in hindrance in the flow of electrons increases with increase in temperature.	During the passage of current, resistance generally decreases as there is decreases in degree of hydration of ions and viscosity of the medium with increase in temperature.
5	The conducting power of metal is usually high.	The conducting power of electrolytic conductors is relatively low.

Electrolytes and Electrolysis

(1) **Definition :** When current is passed through the aqueous solution of a substance and the substance decomposed of into its ions then the substance is termed as electrolyte and this process is known as electrolytic decomposition or electrolysis.

Examples of electrolytes are solutions of bases, acids, fused salts and salts in water etc. Electrolytes may be strong or weak. Solutions of alcohol, glycerine, cane sugar etc., are examples of non-electrolytes.

Strong and Weak Electrolytes

(i) The extent or degree of dissociation of different electrolytes in solution is different.

Rack your Brain

An aqueous solution and copper sulfate is electrolysed using platinum electrodes in another case. Will the products of electrolysis be same of different?

Concept Ladder

Higher is the value of dissociation constant greater is the degree of dissociation and stronger is the electrolyte.

(ii) Strong electrolytes are the substances which are largely dissociated and form a highly conducting liquid in water. e.g., All salt (except $CdBr_2$, $HgCl_2$), mineral acids like HCl, H_2SO_4, NHO_3, etc., and bases like KOH, NaOH, etc., are strong electrolytes. They are almost 100% ionized at normal dilution.

Rack your Brain

Mineral acids have covalent bond, still they are strong electrolytes. Why?

(iii) Weak electrolytes are the substances which are low conducting liquid formed to a small extent in aqueous solution, e.g., all organic acids (except sulfonic acids), inorganic acids like H3BO3, HCN etc., and bases like ammonia, amines etc., are weak electrolytes.

Concept Ladder

Dilution of solute follows ostwald's law of dilution for weak electrolytes.

Factors Influencing Degree of Dissociation

The degree of dissociation (α) of an electrolyte in solution is given by:

$$\alpha = \frac{\text{Mole dissoicated at any time}}{\text{Total mole present at t = 0 or dissolved initially}}$$

The variation of α of an electrolyte is directed by

(i) Nature of solute : All ionic compounds (strong electrolytes) have $\alpha \sim 1$ at normal dilution. Most of the polar covalent compounds (weak electrolytes) have $\alpha << 1$.

(ii) Nature of solvent : Solvent having high dielectric constants are themselves feebly ionized but an electrolyte in high dielectric constant solvent (say water) show higher degree of dissociation than in a solvent of low dielectric constant (say methanol).

(iii) Dilution : The extent of dissociation of an electrolyte increases with dilution of solution.

Rack your Brain

A solution of NaCl is initially at 50°C and temperature is increased to 100°C. would there be change in ionisation?

(iv) Temperature : the extent of dissocation of an electrolyte also increases with an increase in temperature.

(v) Addition of other species : Addition of another solute having an ion common to that of weak electrolyte shows a decrease in degree of dissociation of weak electrolyte (see common ion effect).

$$\text{Electrical energy} \xrightarrow{\text{Electrolysis}} \text{Chemical energy}$$

$$\text{Chemical energy} \xrightarrow[\text{Chemistry}]{\text{Electromotive}} \text{Electrical energy}$$

Concept Ladder

Common ion effect involves the presence of similer type of ions in two different compound present in the same solution only for weak electrolytes. Example may insicde the soltuion of CH_3COOH and CH_3COONa

(2) Electrolytic cell or Voltameter : The device which carries the process of electrolysis or electrolytic decomposition is known as electrolytic cell or voltameter.

(i) Voltameter convert electrical energy into chemical energy.

(ii) Anode (or +ve pole) is an electrode where reduction takes place whereas cathode (or –ve pole) is an electrode where oxidation takes place

(iii) Anions are discharged on anode and cations on cathode, during the electrolysis in voltameter.

(iv) In voltameter, flow of electrons is from anode to cathode and current will flow from cathode to anode outside the electrolyte.

$$\text{Anode} \xrightleftharpoons[\text{Flow of current}]{\text{Flow of electrons}} \text{Cathode}$$

For voltameter, E_{cell} = -ve and ΔG = +ve.

(v) Neutral atoms are converted from the anions after reaching the anode by giving up their electrons.

Concept Ladder

During Faraday's time, there were no devices available which could supply constant current Hence, the quantity of electrochemistry passed was measured by putting an apparatus called coulometer (Coulomb measures) in the cirrcuit which is simply a standard electrolytic cell.

At Anode :

$$A^{-} \longrightarrow A + e^{-} \text{(Oxidation)}$$

(vi) Neutral atoms can also be converted from cations when electrons supplied by the battery are reaching to the cathode.

At Cathode :

$$B^{+} + e^{-} \longrightarrow B \text{ (Reduction)}$$

Products formed in above reactions at cathode and anode are known as primary products and the overall change takes place is known as primary change.

Secondary products are the molecules or compounds formed due to furthur change in primary products and this further change is known as secondary change.

(3) Preferential discharge theory : According to this theory " The ion is discharged on one which occur low in the electrochemical series or which requires least energy or ions with lower discharge potential then at either electrode more than one type of ion is attracted".

The potential at which the ion is deposited or discharged on the appropriate electrode is defined as the discharge or deposition potential (D.P.). The values of discharge potential will be different for different ions.

The increase in order of deposition of some of the ions or the decrease in order of discharge potential is given below,

Concept Ladder

Voltage (v) supplied in an electrical circuit is obtained from the equation of emf.

$$E = V + Ir$$

$= V = E - Ir$

Where E = emf of cell

r = Internal resistance

Rack your Brain

On Electrolysis of brine, NaOH, H_2 and Cl_2 are obtained. H_2 is obtained at cathode and Cl_2 at anode. Why Na is not obtained at cathode?

Concept Ladder

To obtained the products of electrolysis from aqueous solution, the process is for more complicated in comparison to the electrolysis products from molten state.

For cations :

$Li^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+},$

$Fe^{2+}, Ni^{2+}, H^+, Cu^{2+}, Hg^{2+}, Ag^+, Au^{3+}$

For Anion :

$SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-$

(4) Application of electrolysis : It has wide applications in major industries. Given below are some of the important applications :

(i) Production of hydrogen by electrolysis of water.

(ii) Manufacture of heavy water (D_2O).

(iii) The metals like Al, Mg, K, Na, etc. are obtained by electrolysis of fused electrolytes.

(iv) Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.

(v) In this method the metal ions Ag, Cu etc. contained in the solution, pure metal is deposited at cathode.

(vi) Electroplating : It is the process in which superior metal is coated over an inferior metal by electrolysis. To prevent inferior metal from corrosion and making it more attractive in appearance electroplating is done. Cathode of an electrolytic cell is made by the object to be plated, the solution is made by the ions of the metal to be deposited.

Concept Ladder

Compounds like NaOH, KOH, Na_2CO_3, $KClO_3$ white lead, $KMnO_4$ etc. are synthesised by electrosynthesis method.

Rack your Brain

When will be the conducting power of strong electrolyte greater than weak electrolyte?

Concept Ladder

The techanique of electrolysis is used in the refining of Cu. The impure Cu(95%) is made anode and thin a sheet of pure Cu is made cathode, and electrolysis is carried out to get pure Cu. The electrolyte is $CuSO_4$ solution acidified with dilute H_2SO_4. Impurities fall down as anode mud.

Faraday's laws of electrolysis

These laws are given by Michael Faraday in 1833. The Faraday's laws of electrolysis governs that, during the process of electrolysis when the substances (in the form of ions) are depositaed on electrodes.

(1) **Faraday's first law :** It states that, "The mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed." i.e., $W \propto Q$

Where, W = Mass of ions liberated in gm,

Q = Quantity of electricity passed in Coulombs

= Current in Amperes (I) × Time in second (t)

$\therefore W \propto I \times t$ or $W = Z \times I \times t$

In case current efficiency (η) is given, then

$$W = Z \times I \times t \times \frac{\eta}{100}$$

where, Z is constant, called as electrochemical equivalent (ECE) of the ion deposited.

When a current of 1 A is passed for 1 sec. (i.e., Q = 1), then, W = Z

Therefore, electrochemical equivalent (ECE) may be defined as when a current of 1 amp. is passed through the mass of the ion deposited for a second.

It's unit is gram per coulomb.

Coulomb is the unit of electrical charge.

96500 Coulombs 6.023×10^{23} electrons = 1 mole electrons

$$1 \text{ coulomb} = \frac{6.023 \times 10^{23}}{96500} = 6.28 \times 18^{18} \text{ electrons}$$

or 1 electronic charge = 1.6×10^{-19} Coulomb

Rack your Brain

Mass of substance is deposited at electrode. Can this method be used to address corrosion?

Concept Ladder

Electr chemical Equivalent = Weight deposited by 1 colomb

$$= \frac{\text{Eq.wt of substance}}{96500}$$

Previous Year's Question

Calculate the quantity of electricity that would be required to reduce 12.3 gram of nitrobenzene to online if the current efficiency for the process is 50 percent. If the process drop across the cell is 3 volts, how much energy will be consumed?

[NEET-2014]

(1) 347kJ (2) 447kJ
(3) 397kJ (4) 497kJ

(2) **Faraday's second law :** It states that, "When the same quantity of electricity is passed through different electrolytes, the masses of different ions liberated at the electrodes are directly proportional to their chemical equivalents (Equivalent weights)." i.e

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \text{ or } \frac{Z_1 It}{Z_2 It} = \frac{E_1}{E_2} \text{ or } \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Therefore electrochemical equivalent (Z) of an element is proportional to its equivalent weight (E), i.e.,

$E \propto Z$ or $E = FZ$ or $E = 96500 \times Z$

where,

F = Faraday constant = 96500 C mol^{-1}

1F = Charge on an electron × Avogadro's number.

$$\text{If} = e^- \times N = (1.602 \times 10^{-19}\ c) \times (6.023 \times 10^{23}\ mol^{-1})$$

Number of Faraday

$$= \frac{\text{Number of electrons passed}}{6.023 \times 10^{23}}$$

(3) **Faraday's law for gaseous electrolytic product** For the gases, we use

$$V = \frac{It\ V_e}{96500}$$

where, V = Volume of gas evolved at an electrode at S.T.P.

V_e = Equivalent volume = Vol. of gas evolved at S.T.P. at an electrode by 1 Faraday charge

Concept Ladder

Magnitude of charge carried by 1 mole of electrons is 96487 C($6 \times 10^{23} \times 1.6 \times 10^{-19}$ = 96487C). It is also known as one faraday, i.e., 1F = 96500C.

Rack your Brain

Why oxidation potential of H_2O is greater than fluoride ion?

Concept Ladder

Reduction potential of H_2O > (×) Reduction potential of cations of 1, 2 and 13 groups of periodic table, e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, etc. so reduction of H_2O occurs at cathode.

Electrical Resistance and Conductance

- **Resistance (R) :-**

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

- **Conductance (G) :-**

  Conductance is the property of material by virtue of which it favours flow of current.

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

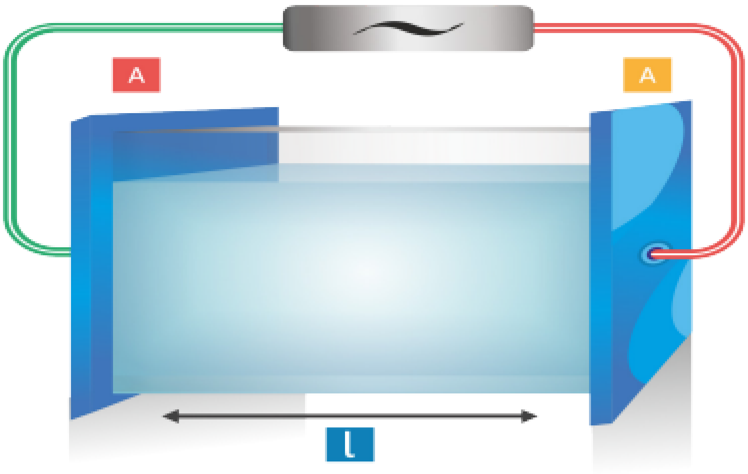
  [unit of G is **mho** or **ohm**$^{-1}$ or **Siemens** (S)]

- **Specific resistance/Resistivity (ρ) :-**

  The resistance (R) of a conductor is directly proportional to its length(l) and inversely proportional to its area of cross section (A).

$$R \propto \frac{\ell}{A}$$

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



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

If l = 1 cm, A= 1 cm^2, therefore ρ = R

Previous Year's Question

Zinc can be coated on iron to produce galvanised iron but the reverse is not possible. It is becasue. **[NEET 2016]**

(1) Zinc is lighter than iron
(2) Zinc has lower melting point than iron
(3) Znc has lower negative electrode potential than iron
(4) Zinc has higher electrode potential than iron

$\therefore V = A \times l = 1\ cm^3$

Therefore resistance offered by 1 cm^3 electrolytic solution is known as resistivity.

[Unit of $\rho \rightarrow$ ohm cm^{-1}]

(d) Specific conductance/ Conductivity (κ) :-

Conductivity is defined as the reciprocal of specific resistance, $\kappa = \dfrac{1}{\rho}$

$$R = \frac{\rho \ell}{A} \qquad \frac{1}{\rho} = \frac{1}{R}.\frac{\ell}{A}$$

$\kappa = G \times G^*$

Specific conductance = Conductance × Cell constant [Unit of K is $ohm^{-1}\ cm^{-1}$]

Hence specific conductivity of a solution is defined as the conductance offered by 1 cm^3 of electrolytic solution.

Cell constant :

$G^* = \dfrac{\ell}{A}$: its unit is cm^{-1}

(e) Molar conductivity or Molar conductance :

$\Lambda_m = \kappa \times V$

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

[Unit $\rightarrow$ $ohm^{-1}\ cm^2\ mol^{-1}$]

(f) Equivalent conductivity or Equivalent conductance (Λ_{eq} or λ_{eq})

$\Lambda_{eq} = \kappa \times V$

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N}$$

Relation between Λ_{eq} and Λ_m

$$\Lambda_m = \frac{\kappa \times 1000}{M} \text{ and } \Lambda_{eq} = \frac{\kappa \times 1000}{N}$$

Previous Year's Question

An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to

[NEET 2010]

(1) Increase in both i.e. number of ions and ionic mobility of ions
(2) Increase in ionic mobility of ions
(3) 100% ionisation of electrolyte at normal dilution.
(4) increase in number of ions

Concept Ladder

Resistivity is the measure of resisting power of a specified material to the flow of an electric current. It only depends only on nature of material

Q.1 1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq cm in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution.

A.1 Given l = 2.1 cm, a = 4.2 sq. cm, R = 50 ohm

Specific conductance,

Specific conductance, $\kappa = \frac{l}{a}.\frac{1}{R}$

Or $\kappa = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01 \text{ ohm}^{-1}$

Equivalent conductivity = $\kappa \times V$

V = the volume containing 1 g equivalent = 1000 ml

So Equivalent conductivity = 0.01 × 1000 = 10 $\text{ohm}^{-1}\text{ cm}^2\text{ equiv}^{-1}$

Q.2 At 298 K $\frac{1}{50N}$ KCl is field in a cell of Its specific conductance is 0.001735 ohm^{-1} cm^{-1} and resistance is 100 ohm then calculate

(i) Cell const.

(ii) Molar conductivity (or) Molar conductance

A.2 (i) $K = \frac{1}{R}.\frac{l}{A}$ $= 0.001735 = \frac{1}{100 \text{ ohm}} \times \frac{l}{A}$ $= 5 \text{ cm}^{-1}$

$= \frac{l}{A}$ $= 0.1735 \text{ cm}^{-1}$

(ii) $\Lambda_m = \frac{K \times 1000}{m} = \frac{0.001735 \times 1000}{\frac{1}{50}}$ $\left[\begin{array}{l} N = Mn_f \\ n_f = 1 \\ M \Rightarrow \frac{1}{50} \end{array}\right]$

$= 86.75 \text{ S cm}^2 \text{ mol}^{-1}$

Q.3 Specific conductance of an electrolyte is 3.825 S cm^{-1}. If limiting molar conductivity is 425 S $cm^2 mol^{-1}$, then calculate molarity of electrolyte of it is 90% dissociated :

A.3 K = 3.825 S cm^{-1}

Limiting molar conductivity = 425

$$\wedge_m = \frac{3.825 \times 1000}{M} \quad \left[\alpha = \frac{\wedge_m}{\wedge_m^0}\right]$$

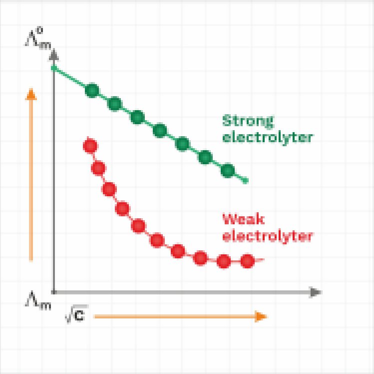
$$0.4 \times 425 = \Lambda_m$$
$$= 382.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$382.5 = \frac{3.825 \times 100}{M}$$

Molarity = 10 M

DETERMINATION OF Λ^0_m OR Λ^0

A plot of Λ_m vs $\sqrt{C}$ as found experimentally is as shown below graphically.



Debye Huckel Onsager equation -

$$\Lambda_m = \Lambda^\infty_m - b\sqrt{C} \text{ [only for strong electrolyte]}$$

- When values of Λ_m are plotted against C then a straight line is obtained. This induced to zero concentration. The point where the straight line intersects Λ^0_m axis is of the strong electrolyte.

Previous Year's Question

Molar conductivites (Λ^0_m) at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 425.9 and 91.0 S cm^2 mol^{-1} respectively for CH_3COOH will be

[NEET 2012]

(1) 425.5 S cm^2 mol^{-1}
(2) 180.5 S cm^2 mol^{-1}
(3) 290.8 S cm^2 mol^{-1}
(4) 390.5 S cm^2 mol^{-1}

Concept Ladder

There is avery large increase in conductance with dilution especially near infinite delution. As concentration of the weak electrolyte is Reduced, more of it ionizes.

- But the non linearity of curve in case of weak electrolyte shoots up suddenly for some low concentration and assumes the shape of straight line parallel to Λ_m axis. Hence extrapolation in this case is impossible. Thus, experimentally also the value of Λ_0 of a weak electrolyte cannot be determined. However, it can be done with the help of Kohlrausch's law to be discussed later.

Kohlrausch's Law of Independent Migration of Ions

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte regardless of the nature of the other ion which with it is associated and that the molar conduction at infinite dilution for any electrolyte is given by the sum of the contribution of the two ions. $\wedge_m^0 = \wedge_+^0 + \wedge_-^0$, $\wedge_+^0$ the contribution of the cation $\wedge_-^0$ is the contribution of the anion

APPLICATION OF KOHLRAUSCH'S LAW

- **Determination of $\wedge_m^0$ of a weak electrolyte:**

$$(CH_3COOH) = (HCl) + \wedge_m^0 (CH_3COONa) - \wedge_m^0 (NaCl)$$

- **Determination of degree of dissociation (α)**

$$\alpha = \frac{\text{No. of molecules ionised}}{\text{Total number of molecules dissolved}}$$

$$= \frac{\wedge_m}{\wedge^0}$$

- **Determination of solubility of sparingly soluble salt**

$$\wedge_m^0 = \frac{1000K}{C}$$

where C is termed as molarity of solution and hence the solubility.

Previous Year's Question

Which of the following expression correctly represent the equivalent conductance at of infinite dilution of $Al_2(SO_4)$?

Given that $\overset{\circ}{\wedge}_{SO_4^{2-}}$ and $\overset{\circ}{\lambda}_{Al^{3+}}$ are the equivalent conductances at infitite dilution of respective ions

[NEET 2010]

(1) $2\overset{0}{\Lambda}_{Al^{3+}} + 3\overset{0}{\Lambda}_{SO_4^{2-}}$

(2) $\overset{0}{\Lambda}_{Al^{3+}} + \overset{0}{\Lambda}_{SO_4^{2-}}$

(3) $\left(\overset{0}{\Lambda}_{Al^{3+}} + \overset{0}{\Lambda}_{SO_4^{2-}}\right) \times 6$

(4) $\frac{1}{3}\overset{0}{\Lambda}_{Al^{3+}} + \frac{1}{2}\overset{0}{\Lambda}_{SO_4^{2-}}$

Concept Ladder

Ionic mobility is defined as the speed of the ion cm/sec at infinite dilution under a potential gradient of 1 volt/cm.

$$\text{Ionic Mobility} = \frac{\text{Ionic conductance}}{96500}$$

Q.4 Compare the conductance in following

$Cl_3\,C\,CH_2\,COOH$ (a) $\qquad CH_3CH_2COOH$ (b)

A.4 a > b → degree of dissociation of a > degree of dissociation of b

Q.5 Calculate solubility product of $BaSO_4$ If its conductivity and molar conductance at saturation are 3.06×10^{-6} S cm^{-1} and 153 S cm^2 mol^{-1} respectively.

A.5 $BaSO_4 \rightleftharpoons \underset{s}{Ba^{2+}} + \underset{s}{SO_4^{2-}}$

$$K_{SP} = s^2$$

$$s = \frac{K \times 1000}{\wedge_m^0} = \left(\frac{3.06 \times 10^{-6} \times 1000}{153\ \ S\ cm^2 mol^{-1}}\right)$$

$$K_{sp} = (2 \times 10^{-5})^2 \quad = 2 \times 10^{-5}\ mol/lit \quad = 4 \times 10^{-10}$$

Q.6 The equivalent conductances of sodium chloride, hydrochloric acid and sodium acetate at infinite dilution are 126.45, 426.16 and 91.0 ohm^{-1} cm^2 equiv^{-1}, respectively at 25°C. Calculate the equivalent conductance of acetic acid at infinite dilution.

A.6 According to Kohlrausch's law

$$\wedge_{\propto CH_3COONa} = \wedge_{CH_3COO^-} + \wedge_{Na^+} = 91.0 \qquad .....1\ \cdot$$

$$\wedge_{\propto HCl} = \wedge_{H^+} + \wedge_{Cl^-} = 426.16 \qquad .....2$$

$$\wedge_{\propto NaCl} = \wedge_{Na^+} + \wedge_{Cl^-} = 126.45 \qquad .....3$$

By adding eq^n (1) and (2) and subtracting (3)

$$\wedge_{CH_3COO^-} + \wedge_{Na^+} + \wedge_{H^+} + \wedge_{Cl^-} - \wedge_{Na^+} - \wedge_{Cl^-} = 91.0 + 426.16 - 126.45$$

$$\wedge_{CH_3COO^-} + \wedge_{H^+} + \wedge_{\propto CH_3COOH} = 390.7\ ohm^{-1}cm^2equiv^{-1}$$

FACTORS AFFECTING ELECTROLYTIC CONDUCTANCE

- **Inter ionic attraction :-**
  inter ionic attraction between ions of solute is more, then the conductance will be less.
- **Polarity of solvent :-**
  If solvent has high-dielectric constant then the ionization and conductance will be higher.
- **Viscosity of medium :-**
  On increasing the viscosity of medium, the conductance decreases.
- **Temperature :-**
  As the temperature of electrolytic solution is increased, the conductance increases
- **Hydrated size :** Due to hydration of ions conductance decreases.
- **Dilution :-**
  (i) On increasing the dilution conductance (G) increases.
  For strong electrolyte on dilution interionic force of attraction decreases therefore conductance increases. For weak electrolyte with dilution degree of dissociation (α) increases therefore conductance increases.
  (ii) On dilution specific conductance decreases because on dilution number of ions in 1 ml solution decreases.
  (iii) On dilution equivalent and molar conductance increases because with dilution normality or molarity decreases.

Rack your Brain

Conductivity of solution dependes upon the polarity of solvent. Would the solution of benzene and toluene conduct electrolysis?

Concept Ladder

Transport number is the fraction of current carried by ion.

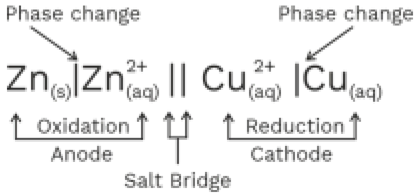
Transport number =

$$\frac{\text{Current carried by ion}}{\text{Total current carried}}$$

Rack your Brain

Is there any relationship between molar conductance and dilution?

Representation of a cell



Concept Ladder

In a galvanic cell, cathode is positive with respect to anode.

Net reaction

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

Q.7 Give the cell reaction from the cell notation

$$Zn_{(s)}\,|\,Zn^{2+}_{(aq)}\,||\,Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)}\,|\,Pt$$

A.7 The half cell reactions are

Anode

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

Cathode

$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$

and the cell reaction is :

$Zn_{(s)} + 2Fe^{3+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Fe^{2+}_{(aq)}$

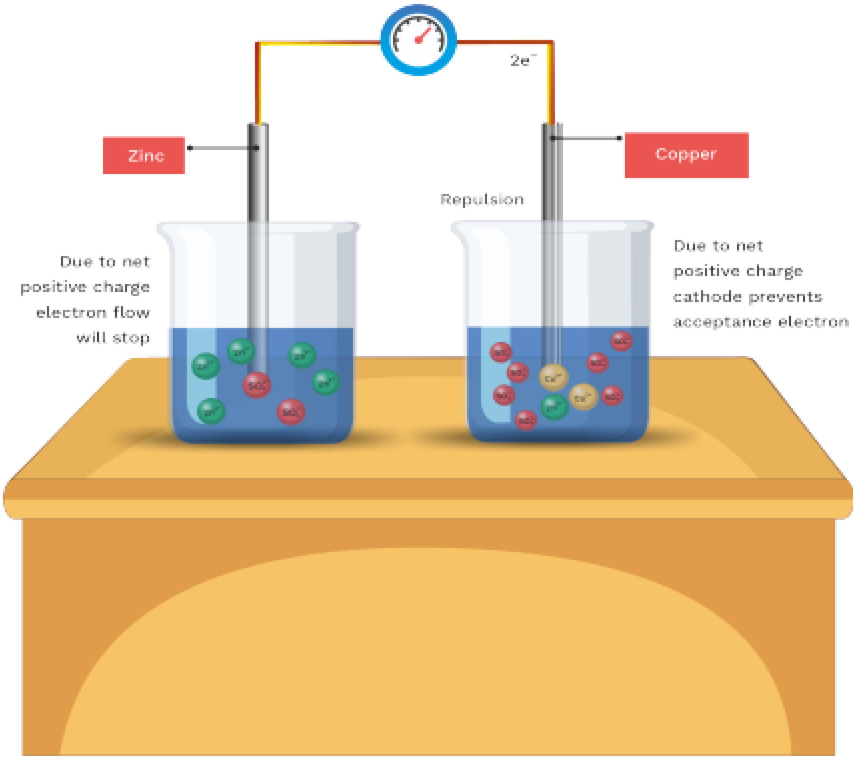
Electrode potential

Metal acquires either a negative or positive charge w.r.t. the solution when it is placed in a solution of its ions. By this a definite potential is developed between the metal and the solution. This difference in potential is known as electrode potential. It depends on the concentration of ions, nature of electrode and temperature.

Concept Ladder

Decreasing order of metallic character is given below:
K > Na > Ba > Ca > Mg > Al > Zn > Fe > Ni > Sn
H > Cu > Hg > Ag > Au > Pt

Condition in which the circuit stops working



- No current will flow. In this situation salt bridge is introduced.

Salt bridge construction :

1. It is inverted U–shaped tube
2. Contains inert electrolyte like KCl, KNO_3, NH_4Cl etc. in agar–agar gel & gelatin.
3. Ions of electrolyte do not react with ions of electrode solution.

Salt bridge functions :

1. To complete circuit.
2. To maintain electrical neutrality.

Standard Reduction Potential :

Conditions:

Rack your Brain

On what criteria the sign convention of electrodes is decided ?

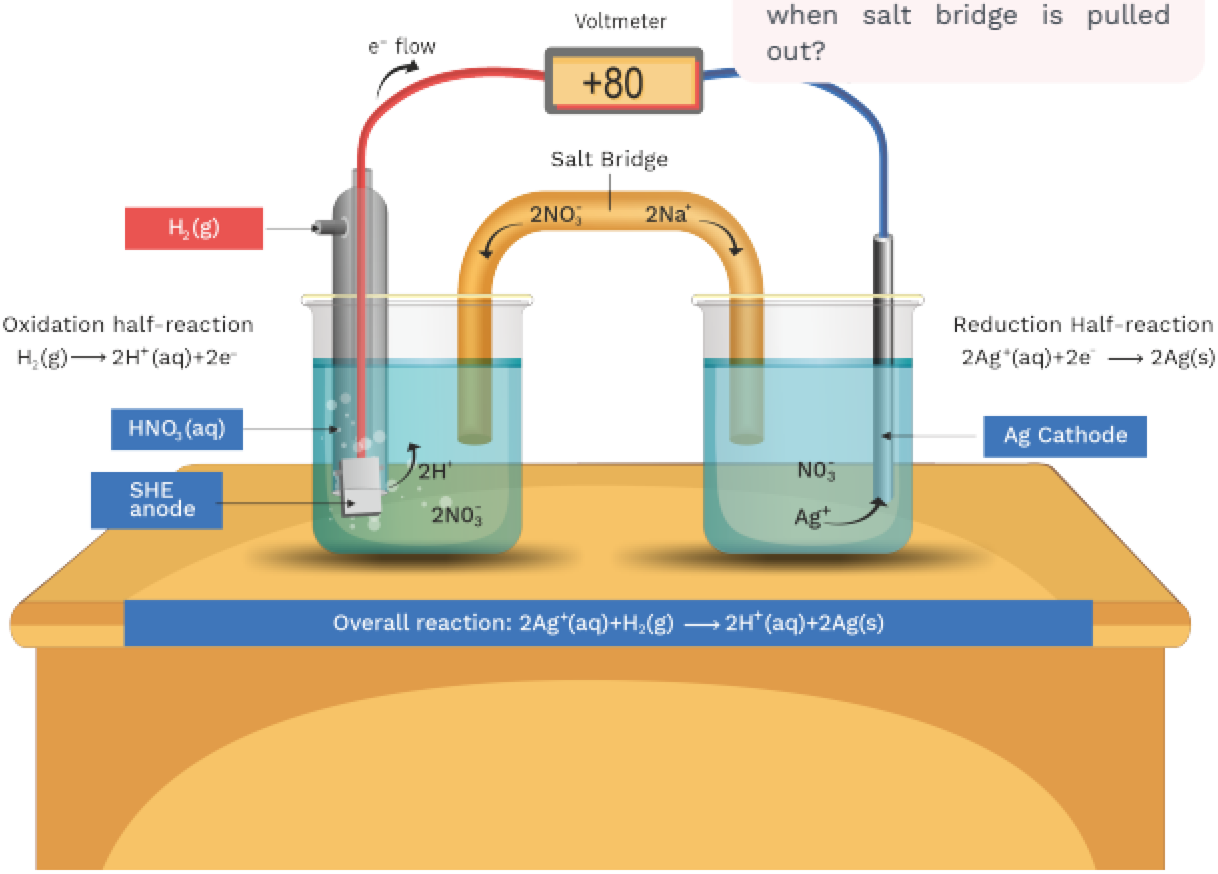
Concept Ladder

Another function of salt bridge is that it prevents liquid-liquid junction potential i.e., the potential difference that arises between the two solutions when they are directly in contact with each other

Concentration = 1 M

For gases pressure = 1 atm

Temperature = 298 K



According to the IUPAC conventions, Standard electrode potential = Standard reduction potential

Cell potential Or emf of the cell (E_{cell})

The difference between electrode potential of two half cells is known as cell potential

$$E_{cell} = (E_{OP})_A + (E_{RP})_C$$

$$E_{cell} = (E_{RP})_C - (E_{RP})_A$$

Q.8 For the cell reaction $2Ce^{4+} + Co \longrightarrow 2Ce^{3+}$

Rack your Brain

Why current drops to zero when salt bridge is pulled out?

Concept Ladder

Electrode an which oxidation occurs is called anode (-ve pole)

Electrode on which reduction occurs is called cathode (+ve pole)

+ Co^{2+}, E^0_{cell} is 1.89 V

$E^0_{CO^{2+}|CO}$ is 0.28 V, what is the value of $E^0_{Ce^{4+}|Ce^{3+}}$

A.8 $E^0_{cell} = E^0_{Ce^{4+}|Ce^{3+}} - E^0_{CO^{2+}|CO}$

$1.89 = E^0_{Ce^{4+}|Ce^{3+}} - (-.28)$

$E^0_{Ce^{4+}|Ce^{3+}} = 1.61$ V

Rack your Brain

Which electrode of a galvanic cell corresponds to the higher potential energy.

Q.9 Which of the following metal displaces hydrogen from H_2SO_4 solution or acidified water?

(1) Mg
(2) Al
(3) Fe
(4) All of these

A.9 **(4)**

Relationship between Gibb's free energy change and emf of cell

Work done = Decrease in free energy change

Charge on 1 mole e^- = $N_A \times e^-$

$= 6.023 \times 10^{23} \times 1.6 \times 10^{-19}$

= 96500 = 1 Faraday

[1 Faraday = charge on 1 mole of electron]

Charge of n moles of electron

$q = nF$

Work done = charge × cell potential

$\Delta G = -nFE_{cell}$

Reactions	ΔG	E
Spontaneous	(–)	(+)
Non- spontaneous	(+)	(–)
Equilibrium	0	0

Previous Year's Question

The pressure of H_2 required to make the potential of H_2 elctrode is zero in pure water at 298K is

(1) 10^{-10} atm
(2) 10^{-4} atm
(3) 10^{-14} atm
(4) 10^{-12} atm

Concept Ladder

Electron flow from anode to cathode in the external circuit. Inner circuit is completed by the flow of ions through the salt bridge.

Electrochemical Series

The elements arranged in the decreasing order of reduction potential, the series attained is known as Electrochemical series

Increasing strength of reducing agent

Electrode	Reaction	SRP(at 298K)
Li	$Li^+ + e^- \rightarrow Li(s)$	−3.05 V
K	$K^+ + e^- \rightarrow K(s)$	−2.93 V
Ba	$Ba^{+2} + 2e^- \rightarrow Ba$	−2.91 V
Ca	$Ca^{+2} + 2e^- \rightarrow Ca(s)$	−2.87 V
Na	$Na^+ + e^- \rightarrow Na(s)$	−2.71 V
Mg	$Mg^{+2} + 2e^- \rightarrow Mg(s)$	−2.36 V
Al	$Al^{3+} + 3e^- \rightarrow Al$	−1.66 V
Mn	$Mn^{+2} + 2e^- \rightarrow Mn$	−1.18 V
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	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44V
Cd	$Cd^{+2} + 2e^- \rightarrow Cd(s)$	−0.40 V
Co	$Co^{+2} + 2e^- \rightarrow Co$	−0.28 V
Ni	$Ni^+ + 2e^- \rightarrow Ni(s)$	−0.25 V
Sn	$Sn^{+2} + 2e^- \rightarrow Sn(s)$	−0.14 V
Pb	$Pb^{+2} + 2e^- \rightarrow Pb(s)$	−0.13 V
H_2	$2H^+ + 2e^- \rightarrow H_2(s)$	0.00 V
Cu	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.34 V
I_2	$I_2 + 2e^- \rightarrow 2I^-$	0.54 V
Fe	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77 V
Hg	$Hg_2^{2+} + 2e^- \rightarrow 2Hg(l)$	0.79 V
Ag	$Ag^+ + e^- \rightarrow Ag$	0.80 V
Hg	$Hg^{2+} + 2e^- \rightarrow Hg(l)$	0.85 V
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	1.09 V
Pt	$Pt^{+2} + 2e^- \rightarrow Pt$	1.20 V
O_2	$\frac{1}{2}O_2 + 2H^+ + 2^{e^-} \rightarrow H_2O(l)$	1.23 V
Cl_2	$Cl_2 + 2e^- \rightarrow 2\ Cl^-$	1.36 V
Au	$Au^{+3} + 3e^- \rightarrow Au(s)$	1.40 V
F_2	$F_2 + 2e^- \rightarrow 2F^-$	2.87 V

Increasing strength of oxidasing agent

Q.10 If E_0 for $Au^+ + e^- \longrightarrow Au\ (s)$ is 1.69 V & E_0 for $3e^- + Au^{+3} \longrightarrow Au$ is 1.40 V, then E_0 will be

(1) 0.19 V (2) 2.945 V

(3) 1.255 V (4) none

A.10 (3)

$Au^+ + e^- \rightarrow Au(s)$ $E° = 1.69$ V ..(1); ΔG_1^0

$Au^{3+} + 3e^- \rightarrow Au(s)$ $E° = 1.40$ V ..(2); ΔG_2^0 $\Delta G_3^\circ = \Delta G_2^\circ - \Delta G_1^\circ$

$-2 \times F \times E° = -3 \times F \times 1.40 + 1 \times 1.69 \times F$

$E° = 1.255$ V

Nernst equation:

When the concentration is not equal to 1 Molar.

Then we use Nernst equation

According to thermodynamics,

$\Delta G = \Delta G° + RT \ln Q$

$(\therefore -\Delta G = nFE \text{ and } -\Delta G° = nFE°)$

$-nFE = -nFE° + RT \ln Q$

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{nF} \log Q$$

where E^0 = standard electrode potential,

R = gas constant, T = temperature (in K)

F = Faraday (96500 coulomb mol^{-1}),

n = number of moles of e^- gained lost or transferred in balanced equation.

At 25°C, above equation may be written as

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log Q$$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

Concept Ladder

$E_{RP} \uparrow$ = Reduction tendency ↑

$E_{OP} \uparrow$ = Oxidation tendency ↑

If nothing is given

$E°_{RP} \uparrow$ = Reduction tendency ↑

$E°_{OP} \uparrow$ = Oxidation tendency ↑

Previous Year's Question

If the $E°_{Cell}$ for a given reaction has a negative value, which of the following gives the correct relationship for the value of ΔG^0 and K_{eq}?

[NEET 2016]

(1) $\Delta G^0 > 0; K_{eq} < 1$

(2) $\Delta G^0 > 0; K_{eq} > 1$

(3) $\Delta G^0 < 0; K_{eq} > 1$

(4) $\Delta G^0 < 0; K_{eq} < 1$

Q.11 Calculate the EMF of a Daniel cell when the concentration of $ZnSO_4$ and $CuSO_4$ are 0.001 M and 0.1 M respectively. The standard EMF of the cell is 1.1V

A.11 E = 1.159 V

$Zn(S) + CuSO_4 \rightarrow ZnSO_4 + Cu$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\left[\frac{Zn^{2+}}{Cu^{2+}}\right] = 1.1 - \frac{0.0591}{2}\log\frac{10^{03}}{10^7} = 1.159\,V$$

Q.12 Calculate E^0 and E for the cell Sn | Sn^{2+} (1M) || $Pb^{2+}(10^{-3}M)$ | Pb, E0 (Sn^{2+}| Sn) = -0.14V, E^0 (Pb^{2+}| Pb) = -0.13V. Is cell reaction is feasible?

A.12 No, E_{cell} = -0.078V

$$E_{cell} = -E^0_{Sn^{2+}/Sn} + E^0_{Pb^{2+}/Pb} - \frac{0.059}{2}\log\left[\frac{Sn^{2+}}{Pb^{2+}}\right] = +0.14 - 0.13 - \frac{0.059}{2}\log 10^{13}$$

$$\text{Take } = +0.01 - \frac{0.059}{2}\times = -0.078\ V$$

Applications of Nernst Equation

(i) Calculation of electrode potential (E_{RP} or E_{OP})

$$E_{RP} = E^0_{RP} - \frac{0.0591}{n}\log\frac{1}{[M^{+n}]}$$

If $[M^{+n}]$ increases, then E_{RP} increases

(ii) Calculation of electrode potential and pH of hydrogen electrode -

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

$$E_{RP} = E^0_{RP} - \frac{0.0591}{2}\log\frac{P_{H_2}}{[H^+]^2}$$

$$\therefore \quad E^0_{RP} = 0\ ;\ E_{RP} = E^0_{RP} - \frac{0.0591}{2}\log\frac{1}{[H^+]^2}$$

[P_{H_2} is taken 1 atm]

$E_{RP} = 0.0591 \log [H^+]$

$E_{RP} = -0.0591pH$ $\qquad$ $E_{OP} = +0.0591$ pH

Previous Year's Question

Consider the half-cell reduction reaction

$Mn^{2+} + 2e^- \rightarrow Mn$, E^0 = -1.18V

$Mn^{2+} \rightarrow Mn^{3+} + e^-$, E^0 = -1.51V

The E^0 for the reaction,

$3Mn^{2+} \rightarrow Mn^0 + 2Mn^{+3}$

and possibility of the forward reaction are respectively?

[NEET 2016]

(1) -4.18 V and yes
(2) +0.33 V and Yes
(3) +2.69 V and No
(4) -2.69 V and No

Rack your Brain

Why Cu^{2+} dispropostiones in aqueous solution?

(iii) Calculation of equilibrium constant (K_{eq}) and $\Delta G°$

From Nernst equation –

$$E_{cell} = E^{\circ}_{Cell} - \frac{0.0591}{n}\log\frac{[P]}{[R]}$$

At equilibrium, $E_{cell} = 0$ and $\frac{[P]}{[R]} = K_{eq}$

$$E^{\circ}_{Cell} = \frac{0.0591}{n}\log K_{eq}$$

$$E^{\circ}_{Cell} = \frac{2.303RT}{nF}\log K_{eq}$$

$$nF\ E^{\circ}_{Cell} = 2.303\ RT\ \log K_{eq}$$

$$\Delta G° = -2.303\ RT\ \log K_{eq}$$

Previous Year's Question

In the electrochemical cell; $Zn \mid ZnSO_4\ (0.01M) \parallel CuSO_4 (1.0M) \mid Cu$ the emf of this Daniell cell is E_1 when the concentration of $ZnSO_4$ is changed to 1.0M and that of $CuSO_4$ changed to 0.01 M the emf changes to E_0. From the followings, which one is the relationship between E_1 and E_2?

[NEET 2017]

(1) $E_1 < E_2$
(2) $E_1 > E_2$
(3) $E_2 = 0 \neq E_2$
(4) $E_1 = E_2$

Q.13 Calculate the equilibrium constant for the reaction

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3++},\ [E^0_{Ce^{4+}/Ce^{3+}} = 1.44V; E^0_{Fe^{3+}/Fe^{2+}} = 0.68V]$$

$$\frac{2.303\ RT}{F} = 0.06 \text{ at } 25°\ C, \log 4.68 = 0.67$$

A.13 $K_c = 4.68 \times 10^{12}$

$$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$$

$$E^0 = 1.44 - 0.68 = 0.76\ V = \frac{0.06}{1}\log K_c$$

$$K_c = 4.64 \times 10^{12}$$

CONCENTRATION CELL ($E°_{Cell} = 0$)

- **Electrode Gas concentration cell :**

  $Pt, H_2\ (P_1) \mid H^+\ (C) \mid H_2\ (P_2), Pt$

  At 25° C,

  [For spontaneity of such cell reaction, $p_1 > p_2$]

Rack your Brain

Will change in tempature affect E^0_{Cell}?

Q.14 Pt | Cl_2 (g, P_2) | Cl^- (aq,C) || Cl^- (aq, C) | Cl_2 (g, P_1) | Pt EMF of cell is positive if

(1) $P_1 > P_2$ (2) $P_2 > P_1$

(3) $P_1 = P_2$ (4) We cannot predict

A.14 For spontaneous reaction $P_1 > P_2$

Anode half cell

$$E_{OX} = E^{0}_{Ox} - \frac{0.0591}{2}\log\frac{P_2}{C} \quad .....(1)$$

Cathode half cell

$$E_{red} = E^{-}_{red} - \frac{0.0591}{2}\log\frac{C}{P_1} \quad ......(2)$$

$$E_{cell} = E_{OX} + E_{red}$$

$$= E^{-}_{OX} + E^{-}_{red} - \frac{0.0591}{2}\log\frac{P_2}{C}\cdot\frac{C}{P_1}$$

$$E_{cell} = \frac{0.0591}{2}\log\frac{P_1}{P_2}$$

- **Electrolyte concentration cells**

Zn(s) | $ZnSO_4$ (C_1) || $ZnSO_4$ (C_2) | Zn(s)

$$E = \frac{2.303RT}{2F}\log\left[\frac{C_1}{C_2}\right]$$

[For spontaneity of such cell reaction,$C_2 > C_1$]

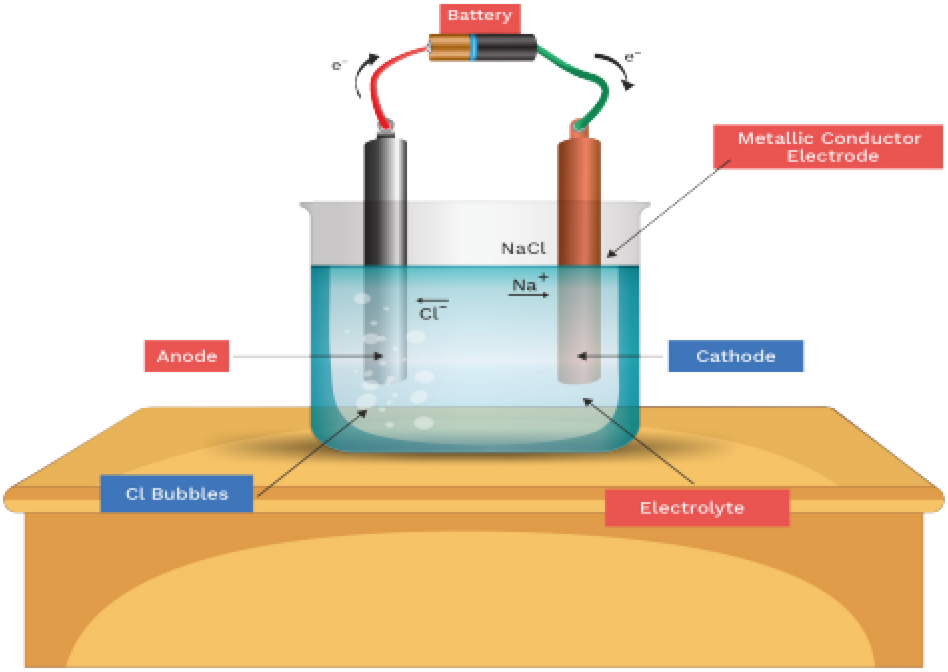
Rack your Brain

Why Pt electrodes are used with the combination of the gas when oxidised or reduced part is a gas?

Concept Ladder

A potential difference develops across the boundary of two solutions which is known has liquid junction potential of diffusion potential.

Electrolytic cell



$NaCl(molten) \rightarrow Na^+ + Cl^-$

Reactions at Anode (oxidation)

$2Cl^- \rightarrow Cl_2\,(g) + 2e^-$

Cathode (reduction)

$2Na^+ + 2e^- \rightarrow 2Na(l)$

Concept Ladder

The minimum voltage required for discharge of ions is called discharge potential

Q.15 By electrolysis of aq. $MgSO_4$ with the help of inert electrode calculate ratio of moler of substance deposited at cathode and anode

(1) 1 : 4 (2) 1 : 2 (3) 2 : 1 (4) 4 : 1

A.15 At cathode

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

$n_f = 2$

gm eq. H_2 = mol $H_2 \times 2$

$$\frac{\text{mol}\,H_2}{\text{mol}\ O_2} = \frac{4}{2} = \frac{2}{1}$$

At anode

$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$

$n_f = 2$

gm eq. H_2 = mol × 4

Q.16 Aq. Na_2SO_4 is electrolysed then after electrolysis pH will be

(1) increased (2) decreased

(3) unchanged (4) None of these

A.16 (3)

Quantitative aspects of Electrolysis

$Fe^{+2} + 2e^{-1} \rightarrow Fe$

2 mole of e^- $\rightarrow$ 1 mol Fe

1 mole of e^- $\rightarrow$ 1/2 mol Fe

$$\text{Equivalent weight of } Fe^{2+} = \frac{\text{Molecular weight}}{2}$$

1 Faraday will discharge 1 Equivalent.

Faraday's law

(a) First law of electrolysis :

Amount of substance liberated or deposited at an electrode is proportional to value of charge passed (utilized) through the solution.

$W \propto Q$

$W = ZQ$ where Z = electrochemical equivalent

then $W = Z$ (when Q = 1 coulomb)

Amount of substance deposited or liberated by 1 coulomb charge is called **electrochemical equivalent.**

Let I ampere current is passed till 't' seconds

$Q = It$

$W = ZIt.$

1 Faraday = 96500 coulomb = Charge on one mole electrons

Let 'E' is equivalent weight then 'E' gram will be liberated by 96500 coulombs.

$\therefore$ 1 Coulomb will liberate $\frac{E}{96500}$ gram;

Previous Year's Question

On electrolysis of dil. sulphuric acid using platinum (Pt) electrode, the product obtained at anode will be :

[NEET–2020]

(1) Hydrogen gas

(2) Oxygen gas

(3) H_2S gas

(4) SO_2 gas

Rack your Brain

Electrolysis of water is often done with a small amount of sulphuric acid added to water. Why?

Previous Year's Question

The weight of silver (at. wt = 108) displaced by a quantity of electricity which displaces 5600mL O_8O_2 at STP will be

[NEET–2014]

(1) 5.4 g (2) 10.8 g

(3) 54.0 g (4) 108.0 g

$Z = \frac{E}{96500}$ $\quad \therefore W = \frac{EIt}{96500}$

$\frac{W}{E} = \frac{It}{96500}$ = number of g eq = number of faraday's

Q.17 How long a current of 2 A has to be passed through a solution of $AgNO_3$ to coat a metal surface of 80 cm^2 with 5 μm thick layer? Density of silver = 10.8 g/cm^3.

A.17 $d = \frac{M}{V} \Rightarrow 10.8 = \frac{M}{80 \times 5 \times 10^{-4}} \Rightarrow M = 10.8 \times 400 \times 10^{-4}$

$W = \frac{E \times I \times t}{96500} \Rightarrow 10.8 \times 400 \times 10^{-4} = \frac{108 \times 2 \times t}{96500} \Rightarrow t = 193\ s$

(b) Second law of electrolysis:

The weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights, when same amount of charge is passed through different electrolyte solutions connected in series.

i.e. $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

Concept Ladder

Amount of substance deposited

$\left(\frac{Eq.\,wt \times Q}{96500}\right)$

Q.18 One ampere current for how much time should be passed through Aq. Soln of 2 molar, 200 ml $AgNO_3$, so that 1 mol of Ag can be deposited

A.18 $AgNO_3 \rightleftharpoons Ag^+$

$\frac{w}{E} = \frac{i.t}{96500}$ molarity $= \frac{W}{E} = \frac{1 \times t}{9600} \Rightarrow 10^{-3} \times 1 = \frac{1 \times t}{96500}$

T= 96.5 sec

Q.19 When 1 M 2L Aq. $AgNO_3$ and 1 M, 2L aq NaCl are connected in units If 10.8 gm Ag deposited on cathode, then calculated volume of Cl_2 (at NTP) collected at anode

A.19 gm aq. Of Ag = gm aq. Of Cl_2

$$\frac{w}{E}=\frac{V_{STP}}{22.4}\times n_f$$

concept $(Z)=\frac{Eq.wt}{96500}$

$AgNO_3 + e^- = Ag = 1$

$$\frac{\underline{10.8}}{\underset{1}{\underline{108}}}=\frac{V_{STP}}{22.4}\times 2$$

$2NaCl \rightarrow Cl_2 + 2e^- = n_f = 2$

Previous Year's Question

When 0.1 mole MnO_4^{2-} is oxidised the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is

[NEET–2014]

(1) 96500 C
(2) 2×96500C
(3) 9650C
(4) 96.50C

Commercial Voltaic Cell

Primary Batteries

Can be used only once and can't be recharged.
Ex.
Dry cells and alkaline batteries

Secondary Batteries

Can be used more than once and can be recharged
Ex.
Nickel - Cadmium ("Ni - Cad") batteries lead storage batteries

Deniell cell

Deniell cell converts chemical energy liberated during the redox reaction to electrical energy and has an electrical potential equal to 1.1V when the concentration or activity of Zn^{2+} and Cu^{2+} ions is unity (1 mol dm^{-3}).

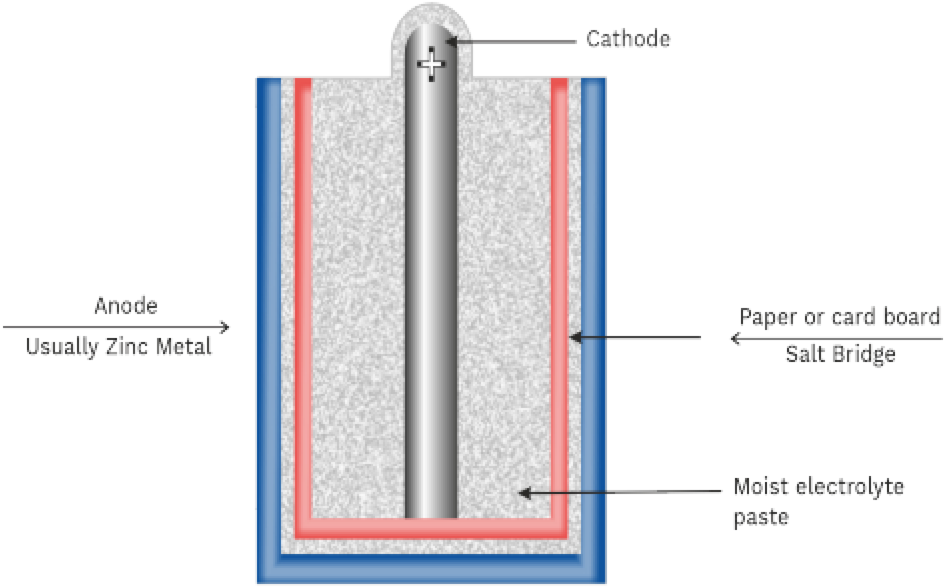
$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Concept Ladder

Electrochemical equivalent

$$(Z)=\frac{Eq.wt}{96500}$$

Primary Batteries
(Dry cells and alkaline batteries)



Cathode, reductions:

$$2NH_4^+(aq) + 2e^- \rightarrow 2NH_3(g) + H_2(g)$$

Anode Oxidation :

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

The pressure will be builded up and the cell is reptured by the formation of two gases at the cathode.

$$Zn^{2+}(aq) + 2NH_3(g) + 2Cl^-(aq) \rightarrow Zn(NH_3)_2Cl_2(s)$$

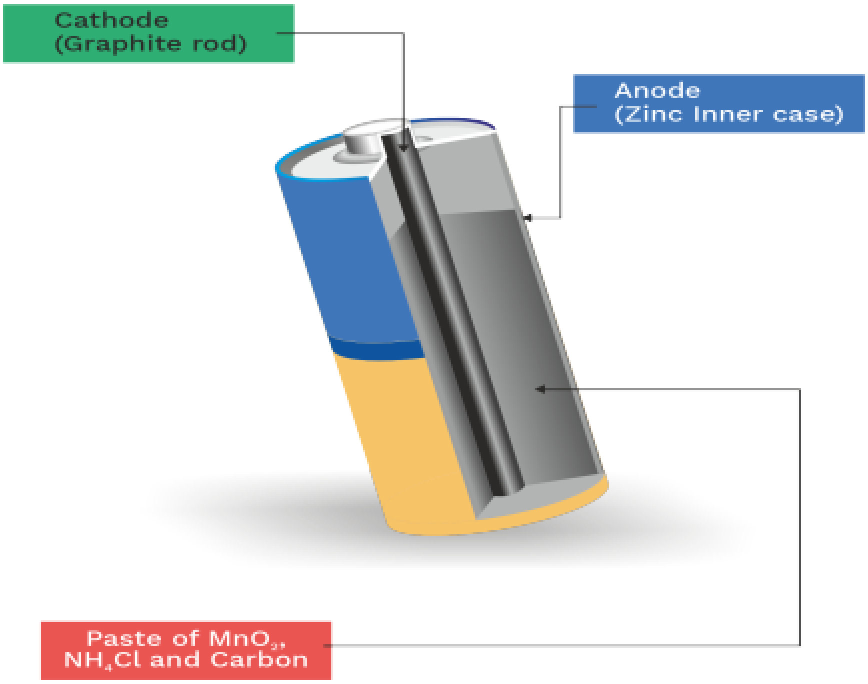
$$2MnO_2(s) + H_2(g) \rightarrow Mn_2O_3(s) + H_2O(l)$$

Rack your Brain

What is the most common Primary Battery?

Concept Ladder

Mecury cell suitable for low current devices like hearing acids, watches, etc. consists of zinc-mercury amalgam as anode and a paste of HgO and carbon as the cathode.



SECONDARY OR RECHARGABLE BATTERIES

The lead storage battery –

Discharging reaction :

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

Cathode reduction :

$$2MnO_2(s) + H_2(g) \rightarrow Mn_2O_3(s) + H_2O(l)$$

Anode Oxidation

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

Net Cell reaction

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

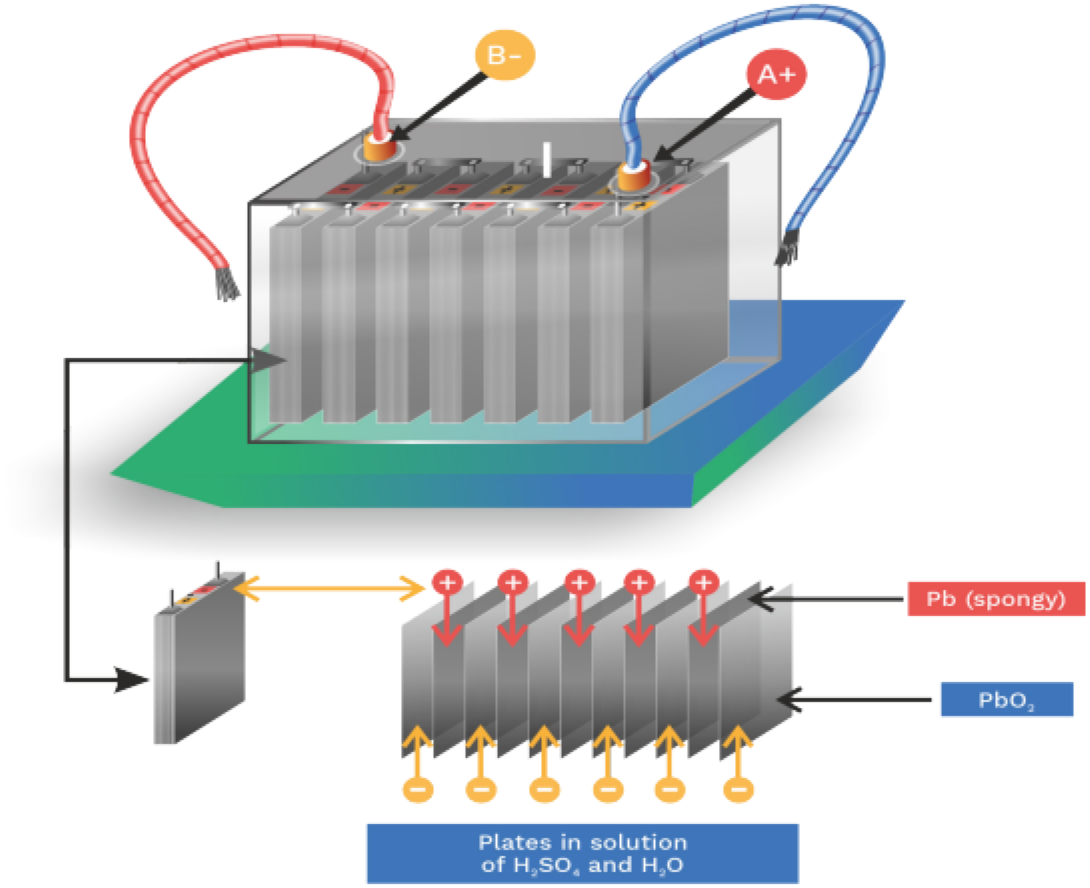
Charging reaction is reverse of discharging reaction with the reaction on anode will be written on cathode and vice versa

Concept Ladder

The discharging process of the storage cell is based on the principles of electrochemical cell, whereas the charging process is based upon the principles of electrolytic cells.

Rack your Brain

What is end life of the battery?



Nickel - Cadmium ("Ni - Cad") batteries

Cathode (Reduction) :

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

Anode (Oxidation):

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

Net cell reaction :

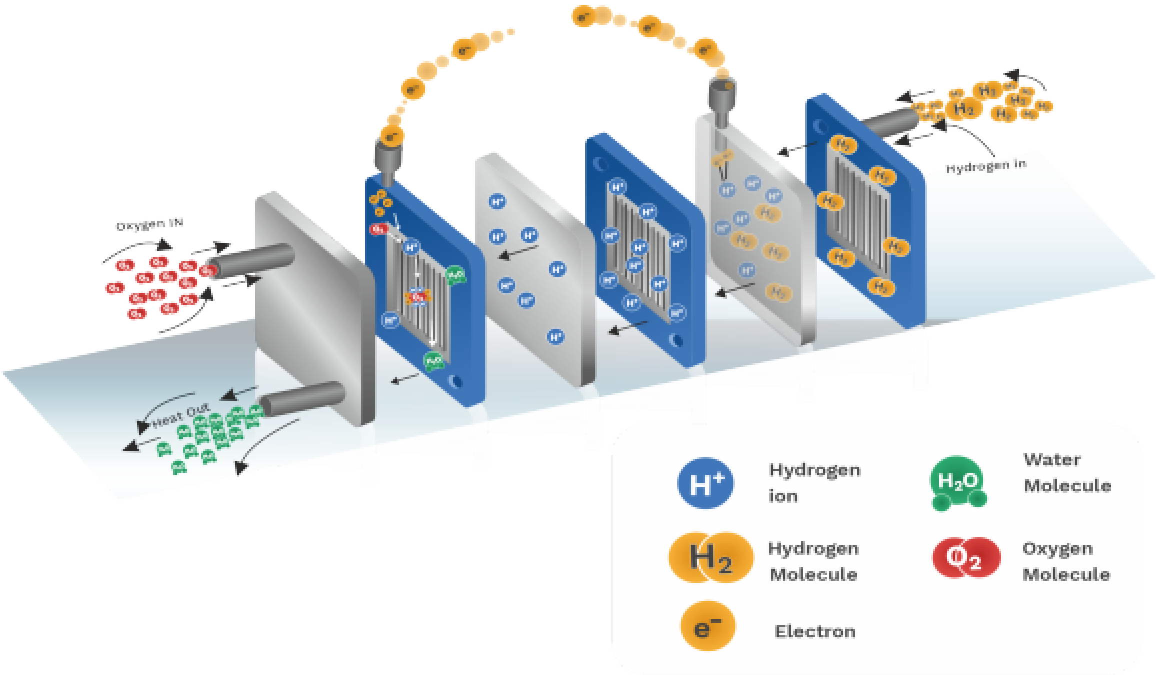
$$NiO_2(OH) + Cd + H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2$$

Concept Ladder

Discharge potential of negative ions is as follows

$$SO_4^{2-} < NO_3^- < OH^- < Br^- < I^-$$

Fuel Cell



Cathode, reduction :

$$O_2(g) + 2\,H_2O(l) + 4e^- \rightarrow 4OH^-\,(aq)$$

$E^\circ = 1.23$ V

Anode, Oxidation :

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

$E^\circ = 0$ V

Corrosion Cells and Reactions

A corrosion system can be regarded as a short-circuited electrochemical cell in which the anodic process is something like

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

and the cathodic steps can be given as

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

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

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

Concept Ladder

Efficiency of a Fuel Cell

$$\eta = \left|\frac{\Delta G}{\Delta H}\right| = \left|\frac{nFE}{\Delta H}\right|$$

Previous Year's Question

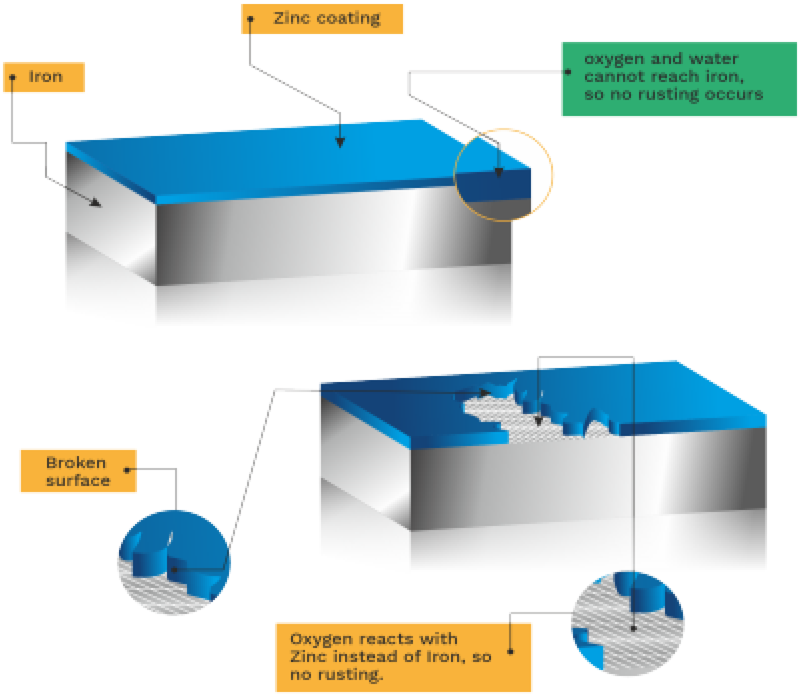
A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as **[2015, Cancelled]**

(1) Dynamo
(2) Ni-Cd cell
(3) Fuel cell
(4) Electrolytic cell

Control of Corrosion

- ### Sacrificial coatings

  When coating of more active metal is applied on another metal, negative charge is supplied to the metal.



Sacrificial protection of iron by zinc

Cathodic Production

By maintaining a continuous supply of negative electrical charge on a metal for inhabitation for dissolution of positive ions.

Concept Ladder

In a galvanic cell, cathode is positive with respect to anode.

Q.20 Compare the conductance in following Colour of KI solution containing starch turns blue when Cl_2 water is added. Explain.

A.20 Chlorine placed below iodine in electrochemical series having more reduction potential and thus shows reduction whereas I^- undergoes oxidation. The I_2 so formed get absorbed in starch to give blue colour.

$$\begin{array}{l} 2I^- \longrightarrow 2e^- \\ \underline{Cl_2 + 2e^- \longrightarrow 2Cl^-} \\ Cl^- + 2I^- \longrightarrow I_2 + 2Cl^- \end{array}$$

Q.21 How many moles of electrons are needed for the reduction of 20 mL of 0.5M solution of $KMnO_4$ in acid medium ?

A.21 Moles of $KMnO_4$ = M × V (L) = $0.5 \times 20 \times 10^{-3} = 10^{-2}$ [$\because$ $Mn7^+ + 5e^- \rightarrow Mn^{2+}$]

$\because$ 1 mol $KMnO_4$ required = 5 mol e^-

$\therefore$ 10^{-2} mol $KMnO_4$ required = 5×10^{-2} mol e^-

Q.22 Which cells were used in te Apollo space program? What was the product used for?

A.22 H_2—O_2 fuel cell. The product H_2O was used for drinking by the astronauts.

Q.23 An aqueous solution of NaCl is electrolysed with inert electrodes. Write the equations for the reactions taking place at cathode and anode. What happens if $NaNO_3$(aq.) is used instead of NaCl ?

A.23 For NaCl(aq.)anode : $2Cl^- \rightarrow Cl_2 + 2e^-$

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

For NaNO3 (aq.) anode : $2OH^- \rightarrow H_2O + 1/2\ O_2 + 2e^-$

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

Q.24 The value of μ^{∞} for NH_4Cl, NaOH and NaCl are 129.8, 248.1 and 126.4 $ohm^{-1}\ cm^2\ mol^{-1}$ respectively. Calculate μ^{∞} for NH_4OH solution.

A.24 $\mu^{\infty}_{NH_4OH} = \mu^{\infty}_{NH_4\,Cl} + \mu^{\infty}_{NaOH} - \mu^{\infty}_{NaCl} = 129.8 + 248.1 - 126.4 = 251.5\ ohm^{-1}cm^2mol^{-1}$

Q.25 Given the standard electrode potentials ; $K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V, $Hg^{2+}/Hg = 0.79$ V, $Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74$V.

Arrange these metals in their increasing order of reducing power.

A.25 More is E°RP, hence more is the oxidising power or more is the tendency to get reduced or lesser is reducing power. Ag < Hg < Cr < Mg < K

Q.26 Iron does not rust even if zinc coating on its surface is broken but the same is not true when coating is of tin.

A.26 Zn is more reactive than Fe, this implies that if a crack appears on the surface of Fe coated with Zn even then Zn will take part in the redox reaction and not Fe. In other words, Zn will be corroded in preference to Fe, but same is not in the case with Sn. It is less reactive than Fe, when a crack appears on the surface of Fe coated with Sn, then Fe will take part in the redox reaction and not Sn. Therefore, Fe will be corroded under these circumstances.

Q.27 How will show that Faraday's second law of electrolysis is simply corollary of the first law.

A.27 According to Faraday's first law of electrolysis. $w = Z \times Q$ If same quantity of electricity is passed through two electrolytes, i.e., $Q_1 = Q_2 = Q$, then In case of first electrolyte,

$w_1 = Z_1 \times Q$ and In case of second electrolyte, $w_2 = Z_2 \times Q$

On diving $\frac{w_1}{w_2} = \frac{Z_1}{Z_2} = \frac{E_1 / 96500}{E_2 / 96500} = \frac{E_1}{E_2}$

Where E_1 and E_2 are their equivalent masses

Q.28 Calculate the equilibrium constant for the reaction at 298 K

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

Given $E^0_{zn^{2+}/Zn} = -0.76V$ and $E^0_{Cu^{2+}/Cu} = +0.34V$

A.29 We know that log = $\frac{nE^0_{Cell}}{0.0591}$

$$E^0_{cell} = \left[E^0_{cathode} - E^0_{anode}\right] = [(+0.34\ V) - (-\ 0.76\ V)] = 1.10\ V,\ n = 2,$$

$$\log K_c = \frac{2 \times (1.10\ V)}{(0.0591\ V)} = 37.29 \Rightarrow \quad K_c = \text{Antilog } 37.29 = 1.95 \times 1037$$

Q.30 Given that, $Co^{3+} + e^- \longrightarrow Co^{2+}$ $E° = +1.82V$

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$; $E° = -1.23V$.

Explain why Co^{3+} is not stable in aqueous solutions

A.30 $4\,[Co^{+3} + e^- \longrightarrow Co^{2+}]$; $E° = +1.82V$

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$; $E° = -1.23\ V$

E° for first reaction is positive, hence cell reaction is spontaneous. This implies Co^{3+} ions will take part in the reaction. Therefore, Co^{3+} is not stable.

Q.31 The measured e.m.f. at 25°C for the cell reaction,

$Zn\ (s) + Cu^{2+}\ (1.0M) \xrightarrow{\quad} Cu\ (s) + Zn^{2+}\ (0.1\ M)$

is 1.3 volt Calculate E° for the cell reaction.

A.31 Using Nernst equation (at 298 K),

$$E_{cell} = E^{0}_{cell} - \frac{0.0591\ V}{2}\log\frac{\left[Zn^{2+}\ (aq)\right]}{\left[Cu^{2+}\ (aq)\right]}$$

Substituting the values

$$1.3V = E^{0}_{cell} - \frac{0.0591V}{2}\log\frac{0.1}{1.0} \Rightarrow 1.3V = E^{0}_{cell} - 0.02955\ V\log 10^{-1}$$

$$1.3V = E^{0}_{cell} + 0.02955\,V\ \log\ 10 \Rightarrow E^{0}_{cell} = 1.3\ V - 0.02955 = 1.27\ V$$

Q.32 The resistance of a 0.01 N solution of an electrolyte was found to 210 ohm at 298 K using a conductivity cell with a cell constant of 0.88 cm^{-1}. Calculate specific conductance and equivalent conductance of solution

A.32 Given for 0.01 N solution. R = 210 ohm

$$\frac{\ell}{A} = 0.88\ cm^{-1}$$

$$\therefore K = \frac{1}{R}\times\frac{\lambda}{A} \Rightarrow K = \frac{1}{210}\times 0.88 = 4.19\times 10^{-3}\,mho\ cm^{-1}$$

$$\lambda_{eq} = \frac{k\times 1000}{N} \Rightarrow \lambda_{eq} = \frac{4.19\times 10^{-3}\times 1000}{0.01} \Rightarrow \lambda_{eq} = 419\ mho\ cm^{2}eq^{-1}$$

Chapter Summary

- An electrochemical cell contains two electrodes (metallic conductors) in contact with an electrolyte.

  An electrode and its electrolyte comprise an Electrode Compartment. Electrochemical Cells can be classified as:

  (i) Electrolytic Cells in which external source of current drives a non-spontaneous reaction

  (ii) Galvanic Cells which generates electricity as a result of a spontaneous cell reaction

- A voltic cell is a cell in which a spontaneous reaction generates an electric current.

  In a galvanic cell, cathode is positive with respect to anode.

  The salt-bridge having solution of strong ionic salts like KNO3, KCl, NaNO3, , NaCl etc., which is soaked in a colloidal soln of agar-agar gel which permits the movement of ions of salts only.

  REPRESENTATION OF A CELL (IUPAC CONVENTIONS)

  Anodic half-cell is written on left and cathodic half-cell on R.H.S.

  $Zn(s) \mid ZnSO_4\ (sol) \parallel CuSO_4\ (sol) \mid Cu(s)$

  The net reaction that occurs in the galvanic cell, it is called the cell reaction..

  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

- A metal and the solution develops definite potential difference between them. This potential difference is called electrode potential.

  (i) Oxidation potential : When electrode is negatively charged w.r.t. solution, i.e., it acts as anode. Oxidation occurs. $M \rightarrow Mn^{+} + ne^{-}$

  (ii) Reduction potential : When electrode is positively charged w.r.t. solution. i.e., it acts as cathode. Reduction occurs. $Mn+ + ne^{-} \rightarrow M$

- The magnitude of potential depends on the given below factors :

  (i) Nature of the electrode

  (ii) Concentration of the ion in solution

  (iii) Temperature

- Concept for Electromotive force (EMF) of a

  $E_{Cel}l$ = R.P. (Cathode) – R.P. (Anode)

  = R.P. (Cathode) + O.P (Anode)

- Electrolytic Cell : This cell changes EE to chemical energy. Electrolytic cell is defined to be the entire setup except external battery.

  Electrolysis of molten sodium Chloride

  NaCl(molten) → Na+ + Cl–

rxns at anode (oxidation) : cathode (reduction)

$2Cl^- \rightarrow Cl^2 (g) + 2e^-$: $2Na^+ + 2e^- \rightarrow 2Na(l)$

- Relationship Between ΔG & Electrode Potential

	Reactions	**ΔG**	**E**
1	Spontaneous	(-)	(+)
2	Non-spontaneous	(+)	(-)
3	Equilibrium	0	0

- Nernst Equation :

  $aA + bB \rightarrow cC + dD$,

  $$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Concentration Cell :

  For such cell, $E°_{Cell} = 0$.

  Electrode Gas concentration cell :

  For spontaneity of such cell reaction, $p_1 > p_2$

  Electrolyte concentration cells:

  For spontaneity of such cell reaction, $C_2 > C_1$
- **Commercial Voltaic Cells :**

  After even recharging Primary batteries cannot be returned to their original state, so the battery is "dead" and must be discarded when the reactants are consumed,. Secondary batteries are also called rechargeable or storage batteries. The batteries can be recharged by reversing its reactions.
- The discharging process of the storage cell is based on the principles of electrochemical cell, whereas the charging process is based upon the principles of electrolytic cells.
- **Faraday's laws of Electrolysis :**
- **First law of electrolysis :** Amount of substance liberated or deposited at an electrode is proportional to value of charge passed (utilized) through the solution.
- **Second law of electrolysis :** The weight of substances deposited or dissolved at anode or cathode are in ratio of their equivalent weights, when same amount of charge is passed through different electrolyte solutions connected in series.
- i.e. $w_1 / w_2 = E_1 / E_2$
- **Conductance**

  Inverse of resistance is called as conductance and inverse of specific resistance is called as specific conductance.

E^0_{cell}

- **Equivalent Conductance**

$E^0_{co^{2+}|co}$

Molar Conductance

$E^0_{Ce^{4+}|Ce^{3+}}$

Relation between

- Kohlrausch's Law of Independent Migration of Ions

$E^0_{co^{2+}|co}$