ELECTROCHEMISTRY

CONTENTS

JEE (Advanced) Syllabus

Electrochemical cells and cell reactions; Electrode potentials; Nernst equation and its relation to ΔG; Electrochemical series, emf of galvanic cells; Faraday's laws of electrolysis; Electrolytic conductance, specific, equivalent and molar conductance, Kohlrausch's law; Concentration cells.

JEE (MAIN) Syllabus

Electrolytic and metallic conduction, conductance in electrolytic solutions, specific and molar conductivities and their variation with concentration: Kohlrausch's law and its applications. Electrochemical cells – Electrolytic and Galvanic cells, different types of electrodes, electrode potentials including standard electrode potential, half – cell and cell reactions, emf of a Galvanic cell and its measurement; Nernst equation and its applications; Relationship between cell potential and Gibbs' energy change; Dry cell and lead accumulator; Fuel cells; Corrosion and its prevention.

ELECTROCHEMISTRY

1. INTRODUCTION :

Electrochemistry deals with the study of electrical properties of solutions of electrolytes and the inter-relation of chemical phenomenon and electrical energies.

❖ **Electric Conductors are of two types :**

(i) Metallic conductors

(ii) Electrolytic conductors or electrolytes.

(i) **Metallic conductors :**

The conductors which conduct electric current by movement of free electrons without undergoing any chemical change are known as metallic conductors.

eg. Metals : Cu,Ag,Fe,Al etc., non metals : graphite and various alloys.

(ii) **Electrolytic conductors :**

Those substances whose aqueous solution conducts the electric current and which are decomposed by the passage of DC current are called electrolytes. In this case, conduction takes place by movement of ions.

Electrolytes also conduct electricity in fused state and undergo decomposition by passage the electric current.

❖ **Strong electrolyte :**

Electrolytes which are completely ionized in aqueous solution or in their molten state, are called ***strong electrolytes***. Their aqueous solutions are strongly conducting.

Ex : All salts, strong acids and strong bases.

❖ **Weak electrolyte :**

Electrolytes which are not completely ionized in aqueous solution are called ***Weak electrolytes.*** Their aqueous solutions are weakly conducting.

Ex: Carboxylic acids (RCOOH),HCN etc.

Organic base : Amines, Aniline etc.

Note : Ostwald's dilution law is only applicable for weak electrolytes according to which degree of dissociation(α) increases on dilution.

- For weak electrolyte : $\alpha << 1 \Rightarrow$ lesser ions $\Rightarrow$ weakly conducting
- For strong electrolyte : $\alpha = 1$ (always) $\Rightarrow$ more ions $\Rightarrow$ strongly conducting

❖ **Difference between metallic and electrolytic conduction :**

S.No.	Metallic conduction	Electrolytic conduction
(i)	Flow of electricity takes place due to free electrons without the decomposition of the substance.	Flow of electricity takes place by ions.
(ii)	No transfer of matter takes place.	Transfer of matter takes place.
(iii)	The resistance to the flow of current increases with the increase in temperature and hence the increase in temperature decreases the conduction.	The resistance to the flow of current decreases with the increase in temperature and hence increase in temperature increases the conduction.

2. ELECTROCHEMICAL CELL :

It is device for inter-converting chemical energy in to electrical energy or vice versa.

Electrochemical cells are of two types

Galvanic cell or Voltaic cell

- A spontaneous chemical reaction generates an electric current | EMF
- Chemical energy converted into electrical energy.

Electrolytic cell.

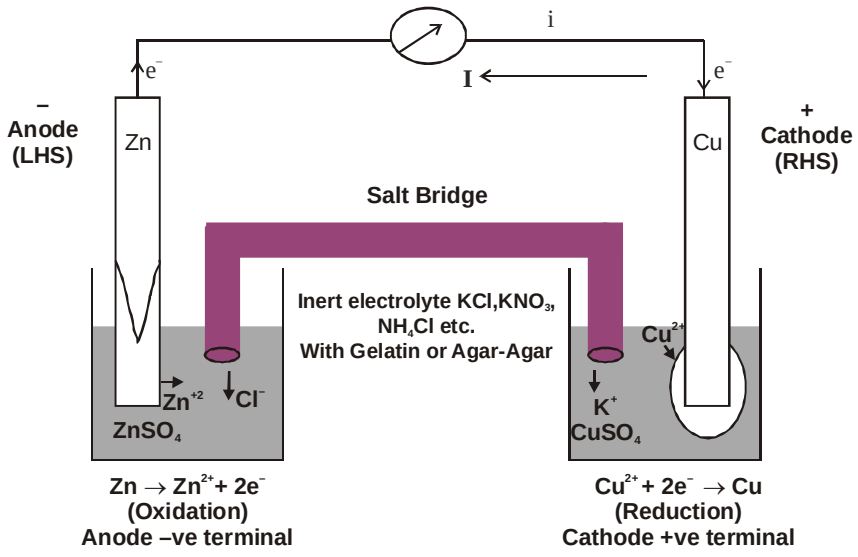
- An electric current drives a non-spontaneous reaction.
- Electrical energy converted into chemical energy.

3. GALVANIC CELL | VOLTAIC CELL

- A cell in which the chemical energy is transformed into electrical energy.
- The chemical reaction occurring in a galvanic cell is a spontaneous redox reaction.
- During the chemical process, the reduction in Gibbs free energy is converted in the form of electrical energy.

$$(\Delta G)_{T,P} = w_{Useful|max.} = -nF\,E_{cell.}$$

Galvanic cell is made up of two half cells i.e., anodic and cathodic. The cell reaction is of redox kind. Oxidation takes place at anode and reduction at cathode. It may be represented by Daniel cell which is a type of Galvanic cell. Zinc rod immersed in $ZnSO_4$ behaves as anode and copper rod immersed in $CuSO_4$ behaves as cathode.



❖ **Oxidation takes place at anode :**

$Zn(s) \longrightarrow Zn^{2+} + 2e^-$ (Loss of electron : Oxidation)

❖ **Reduction takes place at cathode :**

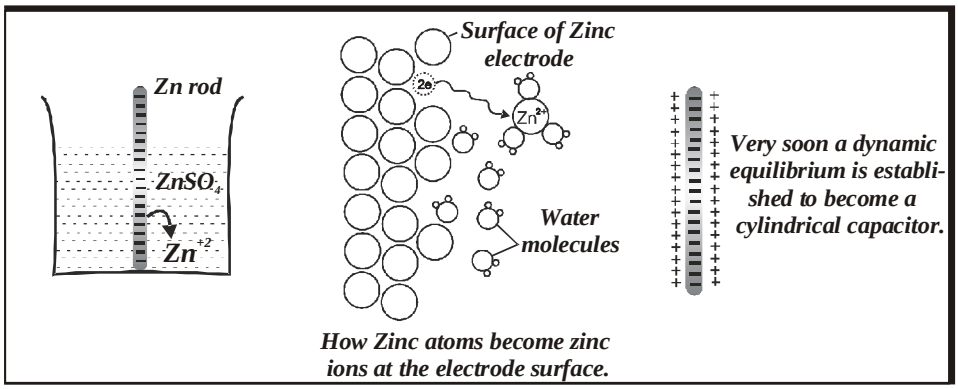
$Cu^{2+} + 2e^- \longrightarrow Cu(s)$ (Gain of electron ; Reduction)

3.1 Construction of Cell :

- It has two half–cells, each having a beaker containing a metal strip that dips in its aqueous solution.
- The metal strips are called ***electrodes*** and are connected by a conducting wire.
- Two solutions are connected by a ***salt bridge.***

3.2 Construction and Working principle of Daniel cell :

I. Anode of Daniel cell : Zn rod is placed in $ZnSO_4$ solution are found to have tendency to go into the solution phase when these are placed in contact with their ions or their salt solutions.



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

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

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

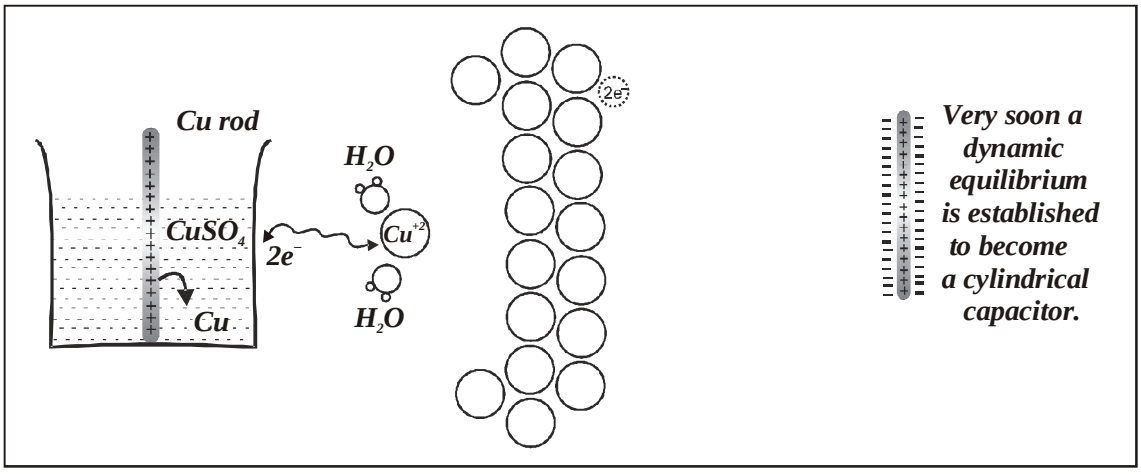
The positive charge will be more concentrated near the rod.

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

This particular electrode is known as anode :

- At anode oxidation will take place. (Release of electron).
- To act as source of electrons.
- It is of negative polarity.
- The electrode oxidation potential is represented by $E_{Zn(s)\,/\,Zn^{2+}_{(aq.)}}$ & reduction potential by $E_{Zn^{2+}/Zn}$.

II. Cathode of Daniel cell :



Cu, when placed in contact with their aqueous ions, the ions (Cu^{2+}) from the solution will get deposited on the metal rod.

The following equilibrium will be established :

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

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

- At cathode reduction will take place. (Gain of e^- will take place)
- Cathode acts as sink of electron.
- Positive polarity will be developed.
- Their electrode reduction potential can be represented by : $E_{Cu^{2+}(aq)|Cu(s)}$.
- **Anode :** { Is where oxidation occurs ; Has a negative sign } • **Cathode :** { Is where reduction occurs ; Has a positive sign }

❖ **Overall process :**

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

In Galvanic cell like Daniel cell ; electrons flow from anode (zinc rod) to the cathode (copper rod) through external circuit ; zinc dissolves as Zn^{2+} ; Cu^{2+} ion in the cathode cell picks up two electron and is deposited at cathode.

Note: The electrode potential will keep on decreasing with time as Zn^{2+} ions increase & Cu^{2+} ions decrease in solution therefore tendency of cell reaction decreases and cell attains equilibrium.

3.3 Functions of Salt Bridge :

- A **salt bridge** is a U-shaped inverted tube that contains a gel permeated with an inert electrolyte.
- It connects the solution of two half cell to complete the circuit.
- It minimise the liquid junction potential, the potential difference between the junction of two liquids)
- It maintains the electrical neutrality of the solution in order to give continuous flow or generation of current " The simultaneous electrical neutrality of the anodic oxidation chamber and cathodic reduction chamber is due to almost same mobility or velocity of K^+ and NO_3^- ions taken into salt bridge.
- If the salt bridge is removed then voltage drops to zero & cell stops working.
- The ions of the inert electrolyte should not react with other ions in the solution and the ions are not oxidised or reduced at the electrodes.
- Generally tube is filled with a paste of agar-agar powder with neutral electrolyte generally not common to anodic|cathodic compartment with porous plugs at each mouth of tube.
- It prevents mechanical mixing of two electrolytic solutions.

❖ **Liquid Junction Potential :**

The potential difference which arises between two solutions when in contact with each other. Salt bridge removes effects of junction potential by providing appropriate migration of ions.

❖ **Characteristics of electrolyte used in salt bridge :**

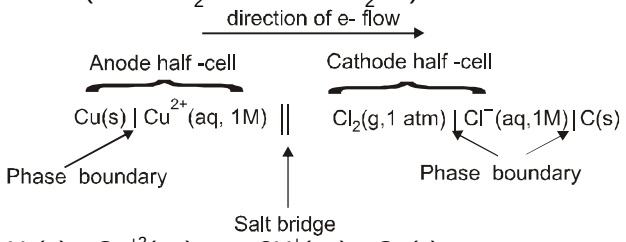
1. The electrolyte should be inert.
2. The cations and anions of the electrolyte used should be of ionic mobility.
3. Ions of electrolyte should not react with ions involved in cell reaction.

3.4 Representation of galvanic cell (IUPAC)

We require two half cells to produce an electrochemical cell, which can be represented by following few rules;

- ❍ The anode half-cell is always written on the left followed on the right by cathode half cell.
- ❍ The separation of two phases (state of matter) is shown by a vertical line.
- ❍ The various materials present in the same phase are shown together using commas.
- ❍ The salt bridge is represented by a double slash (||).
- ❍ The significant features of the substance viz. pressure of a gas, concentration of ions etc. are indicated in brackets immediately after writing the substance.
- ❍ For a gas electrode, the gas is indicated after the electrode for anode and before the electrode

in case of cathode. (i.e Pt H_2 / H^+ or H^+ /H_2 Pt)



- **Ex.** For cell reaction : $H_2(g) + Cu^{+2}(aq) \longrightarrow 2H^+(aq) + Cu(s)$

  $Pt \mid H_2(g) \mid H^+(aq) \parallel Cu^{2+}(aq.) \mid Cu(s)$.

SOLVED EXAMPLE

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

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

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

(a) $Zn \mid Zn^{2+} \parallel Br^-, Br_2 \mid Pt$ (b) $Cr \mid Cr^{3+} \parallel I^-, I_2 \mid Pt$

(c) $Pt \mid H_2, H^+ \parallel Cu^{2+} \mid Cu$ (d) $Cd \mid Cd^{2+} \parallel Cl^-, AgCl \mid Ag$

Solution

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

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

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

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

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

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

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

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

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

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

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

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

3.5 Electrode potential :

When a strip of metal is brought in contact with the solution containing its own ions then the strip of metal gets positively charged or negatively charged and results into a potential being developed between the metallic strip and its solution which is known as electrode potential.

- **At anode :** $M \rightarrow M^{+n} + ne^-$ (Oxidation Potential)
- **At cathode :** $M^{+n} + ne^- \rightarrow M$ (Reduction Potential)
- The value of electrode potential depends upon :

(i) the nature of electrode

(ii) the concentration of solution

(iii) the temperature

3.6 Standard electrode potential (E°) :

If the concentration of ions is unity, temperature is any constant temperature (generally 25ºC) and pressure is 1 bar (standard conditions), the potential of the electrode is called ***standard electrode potential.***

- The given value of electrode potential is regarded as reduction potential unless it is specifically mentioned that it is an oxidation potential.

3.7 Electromotive force of cell or cell voltage :

The difference in the electrode potentials of the two electrodes of the cell is termed as electro motive force [EMF] or cell voltage which causes current to flow.

$$E_{cell} = E_{red}\text{ (cathode)} - E_{red}\text{ (anode)} = E_{oxi.}\text{(anode)} - E_{oxi.}\text{(cathode)} = E_{oxi.}\text{(anode)} + E_{red}\text{(cathode)}$$

3.8 Concept of ΔG

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

  $\Delta G = -nFE$

  Where n = Number of moles of electron transferred in the reaction

  F = Faraday constant = 96485 C/mole e^- ($\approx$ 96500 C/mole e^-)
- **Calculation of Electrode Potential of unknown electrode with the help of given (two) electrode.**
- Obtain the reaction of the 3rd electrode with the help of some algebraic operations on reactions of the given electrodes.
- Then calculate ΔG^o of the 3rd reaction with the help of some algebaric operations of ΔG^0 of 1st and 2nd reactions.
- Use $\Delta G^0 = -nF\, E^0_{elec.}$ to calculate unknown E.P.
- E^0_{cell} is intensive property so if we multiply/Divide electrode reaction by any number the E^0_{cell} value would not changed

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

  Multiply by 2

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

SOLVED EXAMPLE

Example-3 Given that $E^0_{Cu^{2+}/Cu} = 0.337$ V and $E^0_{Cu^+/Cu^{2+}} = -0.153$ V. Then calculate $E^0_{Cu^+/Cu}$.

Solution

(i) $Cu^{2+} + 2e^- \rightarrow Cu$ ΔG_1

(ii) $Cu^+ \rightarrow Cu^{2+} + e^-$ ΔG_2

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

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

$-2F E^0_1 - F E^0_2 = -F E^0_3$

$E_3 = 2E^0_1 + E^0_2$

$= 2 \times 0.337 - 0.153$

$= 0.674 - 0.153 = 0.521$ V

Example-4 $E^0_{Mn^{2+}/MnO_4^-} = -1.51$ V

$E^0_{MnO_2/Mn^{+2}} = +1.23$ V

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

Solution

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

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

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

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

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

(i) + (ii) = (iii)

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

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

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

3.9 Electro chemical series: Standard aqueous electrode potentials at 298 K

Electrode Reduction Reaction	Standard electrode Reduction potential E°, Volts
$Li^+ + e \rightarrow Li$	– 3.05
$K^+ + e^- \rightarrow K$	– 2.93
$Ba^{+2} + 2e^- \rightarrow Ba$	– 2.90
$Ca^{+2} + 2e^- \rightarrow Ca$	– 2.87
$Na^+ + e^- \rightarrow Na$	– 2.71
$Mg^{+2} + 2e^- \rightarrow Mg$	– 2.37
$Al^{+3} + 3e^- \rightarrow Al$	– 1.66
$Mn^{+2} + 2e^- \rightarrow Mn$	– 1.18
$H_2O + e^- \rightarrow ½ H_2 + OH^-$	– 0.83
$Zn^{+2} + 2e^- \rightarrow Zn$	– 0.76
$Cr^{+3} + 3e^- \rightarrow Cr$	– 0.74
$Fe^{+2} + 2e^- \rightarrow Fe$	– 0.44
$Cd^{+2} + 2e^- \rightarrow Cd$	– 0.40
$Ni^{+2} + 2e^- \rightarrow Ni$	– 0.25
$Sn^{+2} + 2e^- \rightarrow Sn$	– 0.14
$Pb^{+2} + 2e^- \rightarrow Pb$	– 0.13
$2D^+ + e^- \rightarrow D_2$	– 0.01 V
$2H^+ + 2e^- \rightarrow H_2$	0
$AgBr(s) + e^- \rightarrow Ag(s) + Br^-$	+0.09 V
$AgCl + e^- \rightarrow Ag + Cl^-$	0.22 V
$Cu^{+2} + 2e^- \rightarrow Cu$	+ 0.34
$¼ O_2 + ½ H_2O + e^- \rightarrow OH^-$	+0.401 V
$I_2 + 2e^- \rightarrow 2I^-$	+ 0.54
$Q + 2H^+ + 2e^- \rightarrow H_2Q$	+ 0.70 (H_2Q : Hydroquinol)
$Hg_2^{+2} + 2e \rightarrow 2Hg$	+ 0.79
$Ag^+ + e^- \rightarrow Ag$	+ 0.80
$Hg^{+2} + 2e^- \rightarrow Hg$	+ 0.85
$Br_2 + 2e^- \rightarrow 2Br^-$	+ 1.08
$¼ O_2 + H^+ + e^- \rightarrow ½ H_2O$	+1.23 V
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.36
$Pt^{+2} + 2e^- \rightarrow Pt$	+ 1.20
$Au^{+3} + 3e \rightarrow Au$	+ 1.50
$Au^+ + e \rightarrow Au$	+ 1.69
$S_2O_8^{--} + 2e^- \rightarrow 2SO_4^{--}$	+2.0 V
$F_2 + 2e^- \rightarrow 2F^-$	+ 2.87

Application of electrochemical series :

(i) **Activity of metal :** From electrochemical series, the activity of any metal can easily be determined. All the metals which are placed above hydrogen are stronger reducing agents & can easily evolve H_2 gas whereas metals lying below hydrogen are weaker reducing agents cannot lose electrons to H^+ ions & hence can't evolve H_2 gas. For e.g. Na, K, Zn etc. can easily evolve H_2 whereas Cu, Hg, Ag etc. do not have tendency to evolve H_2 gas.

$$Na + H_2SO_4 \rightarrow Na_2SO_4 + H_2\uparrow$$

$$Na + H_2O \rightarrow NaOH + \frac{1}{2} H_2\uparrow$$

$$Cu + H_2SO_4 \not\longrightarrow CuSO_4 + H_2\uparrow$$

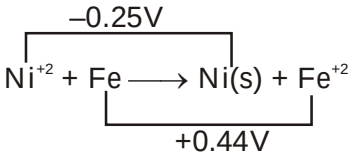
(ii) **Displacement reaction :** The active metal can easily displace less active metal from their aq. salt solution for e.g. Zn can replace Cu^{2+} from an aq. solution of $CuSO_4$. But Cu cannot displace Zn^{2+} from solution similarly,

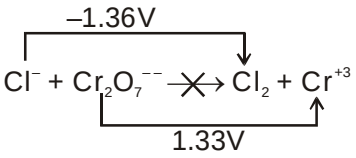
$$2AgNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2Ag,$$

$$CuSO_4 + Ag \not\longrightarrow Ag_2SO_4 + Cu$$

(iii) **Feasibility of redox reaction :** The feasibility of particular redox reaction can be easily find out from electrochemical series. The metal placed higher or have more reducing property can easily lose electrons to the metal ion present below in series, hence redox reaction become feasible i.e. cell will serve as source of electrical energy. For e.g. $NiSO_4$ solution cannot be placed in Fe vessel because, the redox reaction between them is feasible.

Note: If emf of the cell for redox reaction comes out to be positive , it suggest the redox reaction is spontaneous or feasible. Negative value indicate that redox reaction is not feasible.





(iv) **Oxidising & reducing powers :** The metals placed above hydrogen in the electrochemical series are strong reducing agents whereas non-metals placed after hydrogen, are strong oxidising agents.

(v) **Displacement of one non-metal from its salt solution by another non-metal :** A non metal lower in the series will have more reduction potential and will displace another non-metal with lower reduction potential. e.g. F_2 can displace all halide ion from solution.

$$F_2 + 2KCl \longrightarrow 2KF + Cl_2$$

$$Cl_2 + 2KI \longrightarrow 2KCl + I_2$$

3.10 NERNST EQUATION :

For a reaction $aA + bB \rightleftharpoons cC + dD$

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

$-nFE = -nFE^o + RT\ln Q$

With the help of Nernst equation, we can calculate the non-standard electrode potential of electrode or EMF of cell.

Nernst equation predicts effects of concentration, pressure or temperature changes on cell EMF. Nernst equation can be applied on half-cell as well as complete Galvanic cells reaction.

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

Where - E^0 = Standard electrode potential
R = Gas constant
T = Temperature (in K)
F = Faraday (96500 coulomb mol^{-1})
n = No. of e^- gained or lost in balanced equation.
Q = Reaction quotent

$$\frac{2.303 \times 8.314 \times 298}{96500} = 0.059 \text{ volt (At 298 K)}$$

Note: (i) For writing Nernst equation, first write balanced cell reaction.
(ii) Nernst equation can be applied on half-cell as well as complete Galvanic cells.

SOLVED EXAMPLE

Example-5 Calculate E^0_{cell} of (at 298 K), $Zn(s) / ZnSO_4(aq) \,||\, CuSO_4(aq) / Cu(s)$ given that $E^0_{Zn/Zn^{2+}(aq)} = 0.76$ V, $E^0_{Cu(s)/Cu^{2+}(aq)} = -0.34$ V

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

Example-6 Given the cell Ag AgCl(s) | NaCl (0.05 M) || Ag NO_3 (0.30 M) | Ag
(a) Write half reaction occurring at the anode.
(b) Write half reaction occurring at the cathode.
(c) Write the net ionic equation of the reaction.
(d) calculate $E°_{cell}$ at 25°C.
(e) Does the cell reaction go spontaneous as written ?

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

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

$$Ag^+ + Cl^- \longrightarrow AgCl(s) + e^- \quad \text{... (i)}$$

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

$$Ag + e \longrightarrow Ag(s) \quad \text{... (ii)}$$

(c) From equation (i) and (ii) cell reaction is : Cl^- (0.05 M) + Ag^+ (0.30 M) $\longrightarrow$ AgCl(s)
(d) $E°_{cell} = E°_{right} - E°_{left}$
$= (0.80 - 0.22$ volt $= 0.58$ volt
(e) Yes, the e.m.f. value is positive, the reaction will be spontaneous as written in the cell reaction.

3.11 DIFFERENT TYPES OF ELECTRODES

I. Metal - Metal ion electrode : Ex. - $M^{+n} \,|\, M$

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

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

II. Gas - ion Electrode :

Andoe : Pt , H_2 (P atm) | H^+ (cM)
Cathode : H^+(cM) | H_2 (P atm)| Pt

Cathodic raction : $H^+(aq) + e^- \longrightarrow \frac{1}{2} H_2$ (P atm)

$$E = E° - 0.0591 \log \frac{P_{H_2}^{\frac{1}{2}}}{[H^+]} = -0.0591 \text{ pH} \left[\because E^0_{H^+/H_2} = 0 \ \& \ P_{H_2} = 1\text{bar}\right]$$

III. Oxidation - reduction Electrode (or redox electrode) :

It has same metal (or element) in two different oxidation states in same solution.

$Pt \mid Fe^{2+}, Fe^{3+}$

As a reduction electrode

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$

$$E = E° - 0.0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Also, $Pt \mid Cr_2O_7^{-2}(aq.), Cr^{+3}(aq.), H^+$

$Pt \mid Mn^{+2}(aq.), MnO_4^-(aq.), H^+$

IV. Metal - metal insoluble salt-anion electrode :

In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell:

This half cell is represented as $Cl^-|AgCl|Ag$. The equilibrium reaction that occurs at the electrode is

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$$

$$E^0_{Cl^-/AgCl/Ag} = E^0_{Ag^+/Ag} + \frac{0.0591}{1} \log K_{sp}$$

$$E_{Cl^-/AgCl/Ag} = E^0_{Cl^-/AgCl/Ag} - \frac{0.0591}{1} \log\left[Cl^-\right]$$

potential of such cells depends upon the concentration of anions. Such cells can be used as Reference Electrode.

3.12 Reference Electrode :

Absolute values of electrode potentials can not be measured. Reference electrodes is an electrode used to measure the electrode potential of other electrodes.

(a) Standard Hydrogen Electrode (SHE) :

It consist of a platinum electrode over which H_2 gas (1 bar pressure) is bubbled and the electrode is immersed in a solution that is 1 M in H^+ at any specified temperature.

$2H^+(1\ M) + 2e^- \longrightarrow H_2(g)(1\ atm)$

The potential of this electrode at all temperature is taken as Zero volt.

[IUPAC convention : $E^\circ_{H^+/H_2} = E^\circ_{H_2/H^+} = 0$]

Calculation of electrode potential :

At Anode

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

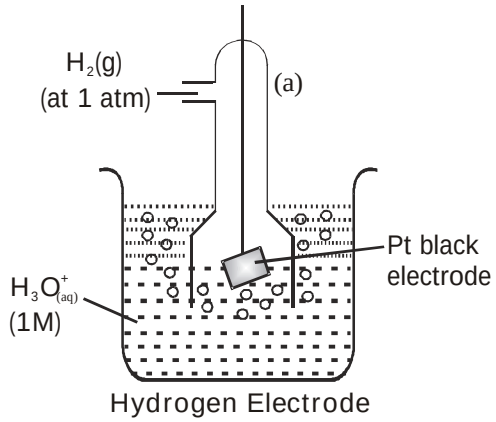
- Oxidation potential O.P. = $E_{H_2(g)/H^+(aq.)}$
- $E^0_{H_2(g)/H^+(aq.)}$ = SOP = 0
- $E_{H_2/H^+} \neq 0$

At Cathode

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

- Reduction Potential (R.P.)

  $E_{H^+/H_2(g)}$ = RP
- $E^0_{H^+/H_2(g)}$ = SRP = 0
- $E_{H^+/H_2} \neq 0$



Hydrogen Electrode

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

Ex. **Anode** : Zinc electrode
Cathode : SHE
Cell : Zinc electrode | | SHE

$E_{cell} = E_{H^+ / H_2(g)} - E°_{Zn2+ | Zn}$

= 0.76 V (at 298 K experimentally)

So, $E°_{Zn^{2+} | Zn} = -0.76$ V (SRP)

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

(b) Calomel Electrode :

Cathode : $Cl^-(c\ M) | Hg_2Cl_2(s) | Hg(l) | Pt(s)$

It is prepared by a Pt wire in contact with a paste of Hg and Hg_2Cl_2 present in a KCl solution.

reaction $Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-$; $E^0 = +0.27$ V

$\Rightarrow$ $\boxed{E_{Cl^- / Hg_2Cl_2 / Hg} = E^0_{Cl^- / Hg_2Cl_2 / Hg} - \frac{0.059}{2}\log[Cl^-]^2}$.

4. CONCENTRATION CELL

The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cells.

4.1 Electrode concentration cell :

$Pt | H_2(p_1) | H^+(C) | H_2(p_2) | Pt$

Here, hydrogen gas is bubbled at two different partial pressures at electrode dipped in the solution of same electrolyte.

Cell process :

$\frac{1}{2}H_2(p_1) \rightarrow H^+(c) + e^-$ (Anode process)

$H^+(c) + e^- \rightarrow \frac{1}{2}H_2(p_2)$ (Cathodic process)

$\frac{1}{2}H_2(p_1) \rightarrow \frac{1}{2}H_2(p_2)$ (Overall process)

$\therefore \quad E = -\frac{2.303RT}{F}\log\left[\frac{p_2}{p_1}\right]^{1/2}$

or $E = \left[\frac{2.303\,RT}{2F}\right]\log\left[\frac{p_2}{p_1}\right]$, At 25^0C , $E = \frac{0.059}{2F}\log\left[\frac{p_1}{p_2}\right]$

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

4.2 Electrolyte concentration cells:

$Zn(s) \mid ZnSO_4\,(C_1) \parallel ZnSO_4\,(C_2) \mid Zn(s)$

In such cells, concentration gradient arise in electrolyte solutions. Cell process may be given as,

$Zn(s) \rightarrow Zn^{2+}(C_1) + 2e^-$ (Anodic process)

$Zn^{2+}(C_2) + 2e^- \longrightarrow Zn(s)$ (Cathodic process)

$Zn^{2+}(C_2) \longrightarrow Zn^{2+}(C_1)$ (Overall process)

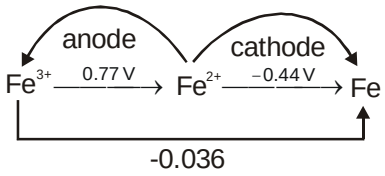
$\therefore$ From Nernst equation, we have

$$E = 0 - \frac{2.303RT}{2F}\log\left[\frac{C_1}{C_2}\right] \quad \text{or} \quad E = \frac{2.303RT}{2F}\log\left[\frac{C_2}{C_1}\right]$$

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

SOLVED EXAMPLE

Example-7 Will Fe^{2+} disproportionate or not



Ans. No

Solution This is known as latimer diagram.
S.R.P to right of the species greater than SRP of it's left species will undergo disproportionation.

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

Solution $[H^+] = \sqrt{K_a \times C} = \sqrt{1.8\times10^{-5}\times10^{-1}} = \sqrt{1.8\times10^{-6}}$

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

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

$E_{Red^n} = -\frac{0.059}{2}\log\left(\frac{1}{1.8\times10^{-6}}\right) = -\frac{0.059}{2}[6 - \log(1.8)]$

$E_{Red^n} = -\frac{0.059}{2} \times 5.74 = -0.169$ V

Example-9 Which is stronger oxidizing agent
(i) $K_2Cr_2O_7$ in solution in which
$[Cr_2O_7^{2-}] = 0.1$ M, $[Cr^{3+}] = 10^{-2}$ M and $[H^+] = 10^{-1}$ M
(ii) $KMnO_4$ in a solution in which
$[MnO_4^-] = 10^{-1}$M, $[Mn^{2+}] = 10^{-2}$M, $[H^+] = 10^{-2}$ M

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

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

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

$$E_{Red^n} = 1.33 - \frac{0.649}{6} = 1.330 - 0.108 = 1.222\ V$$

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

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

E_{Red^n} is more so, good oxidising agent

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

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

$E^0\ Cl^- \mid Cl_2 = -1.36\ V$

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

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

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

$E^0_{cell} = 1.33 - (+1.36) = -0.03$

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

$E_{cell} = -0.26\ V$

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

Solution We have the Nernst equation at equilibrium at 25°C

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

Since $E°_{Cell}$ for the given reaction is negative, therefore, the reverse reaction is feasible for which $E°_{cell}$ will be + 0.32 V, Thus for

Zn	+	Fe^{2+}	$\rightleftharpoons$	Fe	+	Zn^{2+}	;	$E°_{Cell}$ + 0.32 V
–		x		–		(1–x)		

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

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

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

Example-12 Calculate the maximum work that can be obtained from the Daniel cell given below -

$Zn(s) \mid Zn^{2+}(aq) \mid\mid Cu^{2+}(aq) \mid Cu(s)$. Given that $E°_{Zn^{2+}/Zn} = -0.76\ V$ and $E°_{Cu^{2+}/Cu} = +0.34\ V$.

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

$E°_{cell} = E°_{cathode} - E°_{anode}$ (On the basis of reduction potential)

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

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

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

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

5 CALCULATION OF THERMODYNAMIC PARAMETERS OF GALVANIC CELL

5.1 Determination of equilibrium constant : We know, that

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

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. E = 0 & Q = K_{eq}.

$\therefore$ From E (i), we have

$$0 = E^0 - \frac{0.0591}{n}\log K_{eq} \quad \text{or} \quad K_{eq} = \text{anti log}\left[\frac{nE^0}{0.0591}\right] = 10^{\frac{nE°}{0.591}}$$

5.2 Heat of Reaction inside the cell: Let n Faraday charge flows out of a cell of e.m.f. E, then

$-\Delta G = nFE$ (i)

Gibbs Helmholtz equation (from thermodynamics) may be given as,

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_p \qquad \text{(ii)}$$

From Eqs. (i) and (ii), we have

$$-nFE = \Delta H + T\left[\frac{\partial(-nFE)}{\partial T}\right]_p = \Delta H - nFT\left[\frac{\partial E}{\partial T}\right]_p$$

$\therefore$ $$\Delta H = -nFE + nFT\left[\frac{\partial E}{\partial T}\right]_p$$

5.3 Entropy change inside the cell : We know that G = H - TS or $\Delta G = \Delta H - T\Delta S$ ...(i)

where ΔG = Free energy change ; ΔH = Enthalpy change and ΔS = entropy change.

According to Gibbs Helmoholtz equation,

$$\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_p \qquad ....(ii)$$

From Eqs. (i) and (ii), we have

$$-T\Delta S = T\left[\frac{\partial \Delta G}{\partial T}\right]_p \quad \text{or} \quad \Delta S = -\left[\frac{\partial \Delta G}{\partial T}\right]_p$$

or $$\Delta S = nF\left[\frac{\partial E}{\partial T}\right]_p$$

where $\left[\frac{\partial E}{\partial T}\right]_p$ is called temperature coefficient of cell.

6. ELECTROLYSIS :

The process of decomposition of an electrolyte by the passage of electricity is called ***electrolysis*** or electrolytic dissociation. It is carried out in electrolytic cell where electrical energy is converted into chemical energy. For electrolysis to take place two suitable electrodes are immersed in the liquid or solution of an electrolyte containing ions. When an electric potential is applied between the electrodes, the positively charged ions move towards the negative cathode and negatively ions move towards the positive anode, when a cation reaches the cathode, its takes up electron(s) and thus gets its charge neutralised. Thus the gain of electrons(decrease in oxidation number) means reduction takes place at the cathode.

Similarly when an anion it reaches the anode, gives up electron(s) and thus gets discharged. Loss of electrons (Increase in oxidation number) means oxidation takes place at anode

- The tendency of an electrode to lose electrons is known as the ***oxidation potential***.
- The tendency of an electrode to gain electrons is known as the ***reduction potential***.
- ***Greater oxidation potential means stronger is tendency to get oxidised and act as a reducing agent or reductant.***
- ***Greater reduction potential means stronger is tendency to get reduced and act as an oxidising agent (oxidant)***.

(a) Electrolysis of fused sodium chloride :

When fused sodium chloride is electrolysed, Na^+ ions moves towards the cathode and Cl^- ions moves towards the anode. At cathode Na^+ ions accept electrons to form sodium metal. At anode each Cl^- ion loses an electron to form Cl_2 gas.

- **At anode :** $Cl^- \longrightarrow \frac{1}{2} Cl_2 + e^-$; $E^0_{OP} = -1.36V$
- **At cathode :** $Na^+ + e^- \longrightarrow Na(s)$; $E^0_{RP} = -2.71V$

(b) Electrolysis of aqueous solution of KBr

The solution of KBr contain K^+, Br^- & small amounts of H^+, OH^- (due to small dissociation of water)

- **At anode :** $2Br^-(aq.) \longrightarrow Br_2(g) + 2e^-$
- **At cathode :** $2H_2O(\ell) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)$
- If more than one types of ions are present at a given electrode, then the one ion is the liberated which requires least energy. The energy required to liberate an ion is provided by the applied potential between electrodes. This potential is called ***discharge or deposition potential***.

Note :

1. In aqueous solution most electropositive metal cations for eg. (s-block & Al^{3+}) will not discharg at cathode instead H_2O is reduced. $2H_2O(\ell) + 2e^- \longrightarrow H_2(g) - + 2OH^-(aq)$

2. In aqueous solution cations of moderately electropositive metals (Mn, Co, Fe, Zn etc.) and least electropositive metals (Cu, Hg, Au, Ag, Pt) get discharged at cathode first.

3. Active vs Inactive electrodes :

- Sometimes the metal electrodes in the cell are active and the metals themselves are components of the half reactions or influence the reaction of electrode.
- For many redox reactions, however, there are no reactants or products capable of serving as electrodes. Inactive electrodes are used, most commonly rods of graphite or platinum, materials that conduct electrons into or out of the cell but cannot take part in the half-reactions.
- Platinum is used ∵ highly conducting , unreactive.
  highly malleable and ductile.

❖ **Examples of Electrolysis :**

- **Electrolysis of aq. $PbBr_2$** (Using inert (Pt|graphite) electrodes).

Cathode :	$Pb^{2+} + 2e^- \rightarrow Pb(s)$	$E^0 = 0.126V$
Anode :	$2Br^- \rightarrow Br_2 + 2e^-$	$E^0 = -1.08$ V
	$E_{cell} = -0.126 - (0.108) \times 10 = -1.206$ V	
	$E_{ext} > 1.206$ V	

- **Electrolysis of aq. $CuSO_4$** (Using inert (Pt|graphite) electrodes).

Cathode :	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	$E^0 = 0.34$ V
	$2e + 2H_2O(\ell) \rightarrow H_2(g) + 2OH^-(aq)$	$E^0 = -0.83V$
Anode :	$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$	$E^0 = -2.05$ V
	$2H_2O(\ell) \rightarrow O_2 + 4H^+ + 4e^-$	$E^0 = -1.23$ V

∴ Cu discharged at cathode and O_2 at anode.

- **Electrolysis of aq. NaCl** (Using inert (Pt|graphite) electrodes).

Cathode :	$Na^+ + e^- \rightarrow Na$	$E^0 = -2.71$ V
	$2e^- + 2H_2O(\ell) \rightarrow H_2(g) + 2OH^-$	$E^0 = -0.83$ V

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

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

Rate of production of Cl_2 is more than rate of production of O_2 gas because of greater activation energy barrier for O_2 production, therefore Cl_2 is released at anode and H_2 at cathode.

Note:

(i) As observed from electrode potential values discharge potential for O_2 is less than for Cl_2. According to thermodynamics, oxidation of H_2O to produce O_2 should take place on anode but experimentally (experiment from chemical kinetics) the rate of oxidation of water is found to be very slow. To increase it's rate, the greater potential difference has to be is applied called over voltage or over potential. Because of this oxidation of Cl^- ions also become feasible and this takes place at anode.

(ii) Electrode potentials are thermodynamic intensive properties obtained experimentally under ideal & standard conditions. Sometimes in working conditions additional potentials are required for discharging. This difference is termed as overvoltage or overpotential.

❖ **Electrolysis using attackable (reactive) electrodes :**

• **Electrolysis of aq. $CuSO_4$ using Cu electrode.**

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

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

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

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

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

$\therefore$ Both oxidation and reduction of copper occurs and density of solution remains constant.

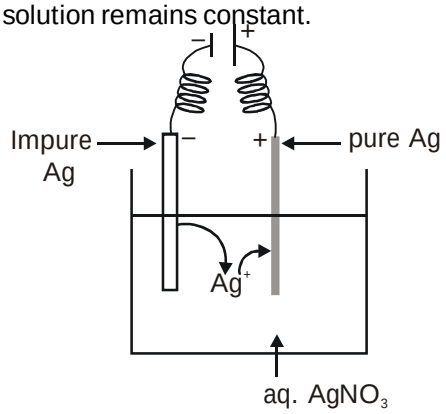
• **Electrolytic Refining**

Electrolysis of $AgNO_3$(aq) using Ag cathode & Ag anode.

Impure metal $\rightarrow$ Anode ;

Pure Metal $\rightarrow$ Cathode ;

Metal salt solution $\rightarrow$ Electrolyte



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

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

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

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

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

$\therefore$ Both oxidation and reduction of Ag occurs and mass transfer of Ag occurs from anode (impure Ag) to cathode (pure Ag). Electrical energy provided by battery is used for mass transfer of Ag from anode to cathode.

PRODUCTS OF ELECTROLYSIS OF SOME ELECTROLYTES

S.No.	Electrolyte	Electrode	Product obtained at anode	Product obtained at Cathode
(i)	Fused NaCl(molten)	Pt or Graphite	Cl_2	Na
(ii)	Aqueous NaCl(conc.)	Pt or Graphite	Cl_2	H_2
(iii)	dil.NaCl	Pt or Graphite	O_2	H_2
(iv)	Aqueous NaOH	Pt or Graphite	O_2	H_2
(v)	Fused NaOH	Pt or Graphite	O_2	Na
(vi)	Aqueous $CuSO_4$	Pt or Graphite	Cl_2	Cu
(vii)	Dilute HCl	Pt or Graphite	O_2	H_2
(viii)	Dilute H_2SO_4	Pt or Graphite	O_2	H_2
(ix)	Aqueous $AgNO_3$	Pt or Graphite	O_2	Ag
(x)	Aqueous CH_3COONa	Pt or Graphite	$CH_3–CH_3 + CO_2$	H_2

7 FARADAY'S LAWS OF ELECTROLYSIS :

Michael Faraday on basis of experiments deduced two important laws :

(a) **Faraday's first law of electrolysis :** This law states that ***"The amount of a substance deposited or discharged at an electrode is directly proportional to the charge passing through the electrolytic solution".***

If a current of **I** amperes is passed for **t** seconds, (the quantity of charge Q in coulombs). If W gram of substances is deposited by Q coulombs of electricity, then

$$W \propto Q \propto i \times t$$

$$W = Z \times i \times t = \frac{E}{96500} \times i \times t = \eta \times \frac{E}{F} \times i \times t$$

E = Equivalent mass of species discharged

η = current efficiency in fraction if current efficiency is not mentioned , by default it is assumed to be 1 (100%).

Z is constant of proportionality and is known as ***electrochemical equivalent***. Its value is different for different species, when Q = 1 coulomb , W = Z, thus electro chemical equivalent may be defined as the weight in grams of an element liberated by the passage of 1 coulomb of electricity.

Electrochemical equivalent of species (Z) = $\frac{E}{96500}$ gm | coulomb.

moles of $e^- = n_e = \frac{\eta \times i \times t}{F}$ = no. of equivalents of species discharged During electrolysis :

Where 1 Faraday (1F) is defined as charge of 1 mole electrons = $eN_A = 1\ F \cong 96500\ C$

Hence faraday (F) is the quantity of charge in coulombs required to deposit one g equivalent of any substance.

(b) **Faraday's second law :** This law states that the amounts of different substances deposited in different solutions connected in series at electrodes by passage of the same quantity of electricity are proportional to their equivalent masses(E).

W ∝ E (E = equivalent mass)

If W_1 and W_2 be the amounts of two different substances deposited at electrodes and E_1 and E_2 be the equivalent weights respectively then -

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

8. APPLICATION OF ELECTROLYSIS

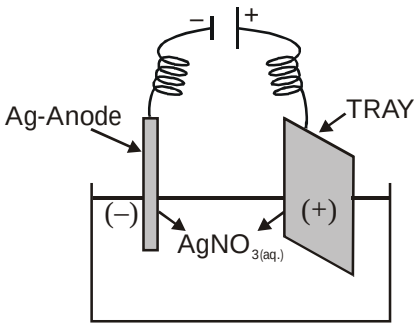
(i) **Electroplating :** Metal used for plating → ANODE

Object to be plated → CATHODE

(ii) **Electrorefining :** Impure metal → ANODE (see fig.)

Pure metal → CATHODE

Metal salt solution → electrolyte



(iii) **Electro-metallurgy :** (Electrolytic reduction)

Ex. Electrolysis of NaCl (from seawater) Using Hg-cathode.

Anode : $2Cl^- \longrightarrow Cl_{2(g)} + 2e$

Cathode : $Na^+ + e^- \xrightarrow{Hg} Na–Hg$

SOLVED EXAMPLE

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

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

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

0.2 mole 0.4 mole

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

0.2 mole of $e^- \rightarrow$ 0.1 mole of H_2 at S.T.P.

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

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

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

so, total moles = 0.25 mole

Total volume = 5.6 Ltr.

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

Solution According to Faraday's first law, W = Zit

W = 0.5 × 50 × 60 × 0.003296 = 0.4944 g

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

Solution ∵ Eq. of Cu = Eq. of Zn = Eq. of H_2

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

9. SOME COMMERCIAL BATTERIES

Any battery or cell that we use as a source of electrical energy is basically an electrochemical cell where oxidising and reducing agents are made to react by using a suitable device. In principle, any redox reaction can be used as the basis of an electrochemical cell, but there are limitations to the use of most reactions as the basis of practical batteries. A battery should be reasonably right and compact and its voltage should not vary appreciably during the use.

There are mainly two types of cells :

(i) primary cells and (ii) secondary cells.

In primary cells, the reaction occurs only once and the battery then becomes dead over a period of time and cannot be used again. (For example, dry cell, mercury cell.) Contrary to this, secondary cells can be recharged by passing a current through them so that they can be used again and again.(For example, lead storage battery, nickel- cadmium storage cell.)

9.1 Primary Batteries

9.1.1 Dry cell or Laclanche cell :

The most familiar type of battery is the dry cell which is a compact of Leclanche cell known after its discoverer Leclanche (fig.) : In this cell, the anode consists of a zinc container and the cathode is a graphite rod surrounded by powdered MnO_2 and carbon. The space between the electrodes is filled with a moist paste of NH_4Cl and $ZnCl_2$. The electrode reactions are complex, but they can be written approximately as follows.

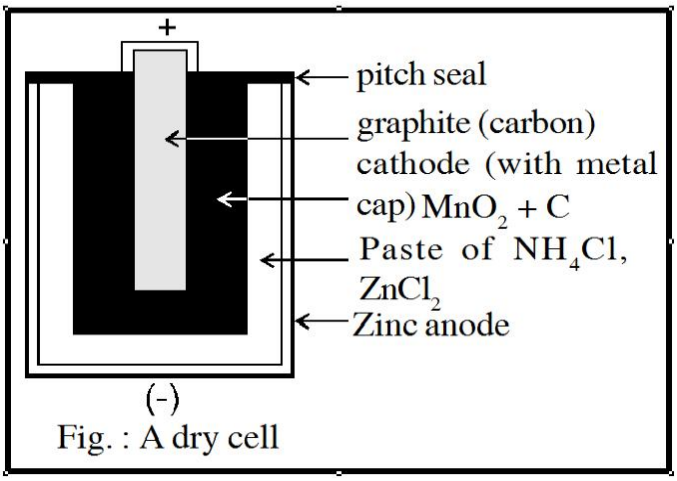


Fig. : A dry cell

- **Anode** $Zn(s) \longrightarrow Zn^{+2} + 2e^-$
- **Cathode** $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

In the cathode reaction, manganese is reduced from the +4 oxidation state to the +3 state. Ammonia is not liberated as a gas but combines with Zn^{2+} to form $Zn(NH_3)_4^{2+}$ ion. The cell has a potential of nearly 1.5 V.

9.1.2 Mercury cell :

Mercury cell, suitable for low current devices like hearing aids, watches, etc.consists of zinc & mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions for the cell are given below:

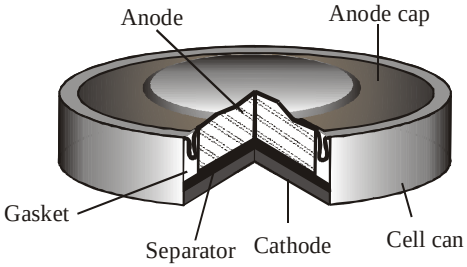
Anode : $Zn(Hg) + 2OH– \rightarrow ZnO(s) + H_2O + 2e–$

Cathode : $HgO + 2H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

The overall reaction is represented by

$$Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$$

The cell potential is approximately 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its life time.



Commonly used mercury cell. The reducing agent is zinc and the oxidising agent is mercury (II) oxide.

9.2 Secondary Batteries

A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles.

9.2.1 Lead storage cell :

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 (PbO_2) 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:

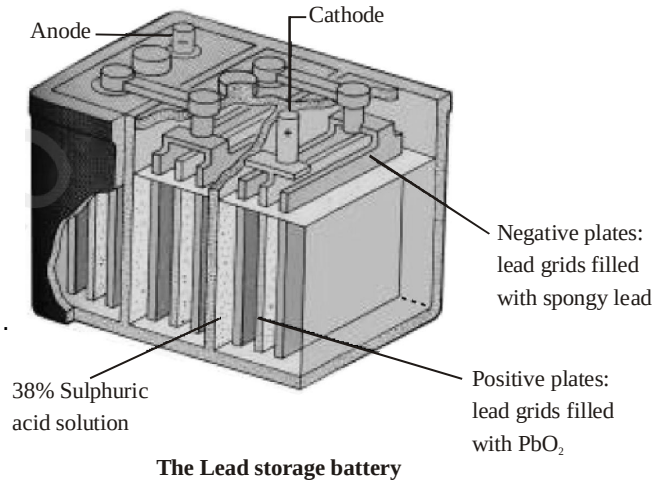
Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

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

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

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

On charging the battery the reaction is reversed and $PbSO_4(s)$ on anode and cathode is converted into Pb and PbO_2, respectively

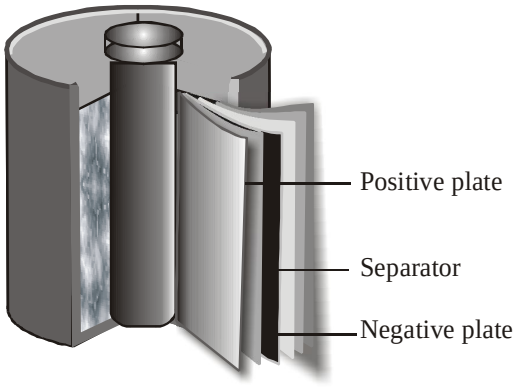


The Lead storage battery

9.2.2 Nickel-cadmium cell :

Another important secondary cell is the nickel-cadmium cell which has longer life than the lead storage cell but more expensive to manufacture. We shall not go into details of working of the cell and the electrode reactions during charging and discharging. The overall reaction during discharge is:

$$Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(\ell)$$



A rechargeable nickel-cadmium cell in a jelly roll arrangement and separated by a layer soaked in moist sodium or potassium hydroxide

9.3 FUEL CELLS

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. 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:

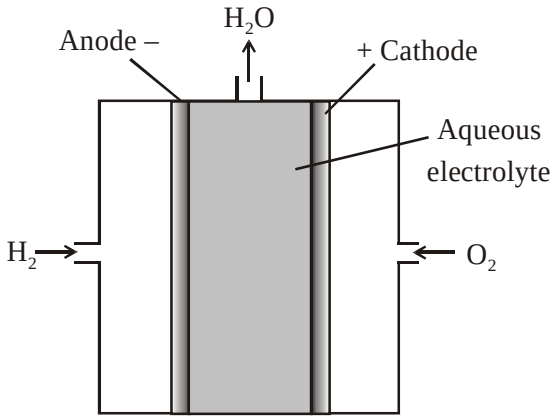
Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

Overall reaction being:

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

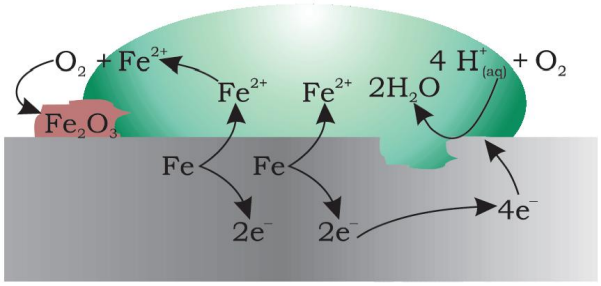
The cell runs continuously as long as the reactions are supplied Fuel cells produce electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes 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.



Fuel cell using H_2 and O_2 produces electricity

10. CORROSION :

Corrosion slowly coats the surfaces of metallic objects with oxides or other salts of the metal. The rusting of iron, tarnishing of silver, development of green coating on copper and bronze are some of the examples of corrosion. It causes enormous damage to buildings, bridges, ships and to all objects made of metals especially that of iron. We lose crores of rupees every year on account of corrosion. In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides. Corrosion of iron (commonly known as rusting) occurs in presence of water and air. The chemistry of corrosion is quite complex but it may be considered essentially as an electrochemical phenomenon. At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction



Oxidation : $Fe(s) \rightarrow Fe^{2+} + 2e^-$
Reduction : $O_2(g) + 4H^+(aq) + 4\ e^- \rightarrow 2H_2O(\ell)$
(Atomospheric)

Anode: $2Fe(s) \longrightarrow 2Fe^{2+} + 4e^{-1}$ $\qquad E^{\ominus}_{(Fe^{2+}/Fe)} = -0.44\ V$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(I)$ $\qquad E_{H^+|O_2|H_2O} = 1.23\ V$

The overall reaction being:

$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(I)$ $\qquad E^{\ominus}_{(Cell)} = 1.67\ V$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide ($Fe_2O_3 \cdot xH_2O$) and with further production of hydrogen ions.

Prevention of corrosion is of prime importance. It not only saves money but also helps in preventing accidents such as a bridge collapse or failure of a key component due to corrosion. One of the simplest methods of preventing corrosion is to prevent the surface of the metallic object to come in contact with atmoshphere. This can be done by covering the surface with paint or by some chemicals (e.g. bisphenol). Another simple method is to cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object. An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.). Which corrodes itself but saves the object.

SOLVED EXAMPLE

Example-16 During the discharge of a lead storage battery the density of H_2SO_4 falls from ρ_1 g/cc to ρ_2 g/C, H_2SO_4 of density of ρ_1 g/C. C is X% by weight and that of density of ρ_2 g/c.c is Y% by weight. The battery holds V litre of acid before discharging. Calculate the total charge released at anode of the battery. The reactions occurring during discharging are.

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

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

Solution Mass of acid solution before discharge of lead storage battery (LSB) = $(V \times 10^3 \times \rho_1)$ g
$= (1000 \times V\rho_1)$g

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

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

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

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

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

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

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

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

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

$\therefore$ Total charge released at cathode, Q = nF = xF.

Example-17 A lead storage cell is discharged which causes the H_2SO_4 electrolyte to change from a concentration of 34.6% by weight (density 1.261 g ml^{-1} at 25°C) to one of 27% by weight. The original volume of electrolyte is one litre. Calculate the total charge released at anode of the battery. Note that the water is produced by the cell reaction as H_2SO_4 is used up. Over all reaction is.

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

Solution Before the discharge of lead storage battery,

Mass of solution = 1000 x 1.261 = 1261 g

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

Mass of water = 1261 – 436.3 = 824.7 g

After the discharge of lead storage battery,

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

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

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

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

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

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

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

11 ELECTROLYTIC CONDUCTANCE

11.1 Resistance (R) :

Metallic and electrolytic conductors obey ohm's law according to which the resistance of a conductor is the ratio of the applied potential difference (V) to the current following(I).

$R = \frac{V}{I}$

- R is expressed in ohms.
- In the case of solution of electrolytes, the resistance offered by the solution to the flow of current is –

(a) Directly proportional to the distance between the electrodes

$R \propto \ell$

(b) Inversely proportional to the area of cross section of the electrodes

$R \propto \frac{1}{A}$

11.2 Conductance (G) :

The conductance of a conductor is equal to reciprocal of resistance.

$G = \frac{1}{R}$ • G is expressed in mho or Ω^{-1} or Siemen(S).

[1S = $1\ \Omega^{-1}$ S.I. unit]

11.3 Specific resistance or resistivity (ρ) :

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

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

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

When $\ell = 1$, $A = 1$, then $\rho = R$ thus the specific resistance may be defined as the resistance of a conductor of unit length and unit area of cross section.

- Unit of $\rho \rightarrow$ ohm.cm

11.4 Specific conductance or conductivity (κ) :

It is defined as the reciprocal of specific resistance

$$\kappa = \frac{1}{\rho} ,$$

$$G = \kappa / G^* , \quad G^* = \frac{l}{a} = \text{cell constant}$$

If ℓ = 1 cm & A = 1 cm^2 then κ = G

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

- Cell constant is a fixed quantity for a particular cell and is defined as the distance between two parallel electrodes of a cell divided by the area of cross section of the electrodes.
  κ = G × cell constant
- Unit of $\kappa \rightarrow ohm^{-1} cm^{-1}$
- SI unit of $\kappa \rightarrow S\ m^{-1}$
  $1\ S\ m^{-1} = 100\ ohm^{-1} cm^{-1}$

11.5 Molar conductance (λ_m or $\wedge_m$) : Conductance of a solution containing 1 mole of an electrolyte between 2 electrodes which are unit length apart.

$$\Lambda_m = \kappa \times v \quad \text{and} \quad \Lambda_m = \frac{\kappa \times 1000}{M}\ ohm^{-1} cm^2 mol^{-1} \qquad [\text{SI unit : } S\ m^2 mol^{-1}]$$

11.6 Equivalent conductance (λ_{eq} or Λ_{eq}) : Conductance of a solution containing 1 gm equivalent of an electrolyte between 2 electrodes which are unit length apart.

$$\Lambda_{eq} = \kappa \times v \quad \text{and} \quad \Lambda_{eq} = \frac{\kappa \times 1000}{N}\ ohm^{-1} cm^2 eq^{-1} \qquad [\text{SI unit : } S\ m^2 eq^{-1}]$$

Relation between $\Lambda_{eq.}$ and Λ_m :

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

We know that, ***Normality = Valency Factor × Molarity***

or $N = n \times M \Rightarrow \boxed{\lambda_{eq.} = \frac{\lambda_M}{n}}$

\# n = total cationic (or anionic) charge of salt.

Ex. $\Lambda_{eq[Al_2(SO_4)_3]} = \frac{\Lambda_{m[Al_2(SO_4)_3]}}{6}$, $\Lambda_{eq.\ NaCl} = \frac{\Lambda_{m\ NaCl}}{1}$, $\Lambda_{eq.CaCl_2} = \frac{\Lambda_{m\ CaCl_2}}{2}$

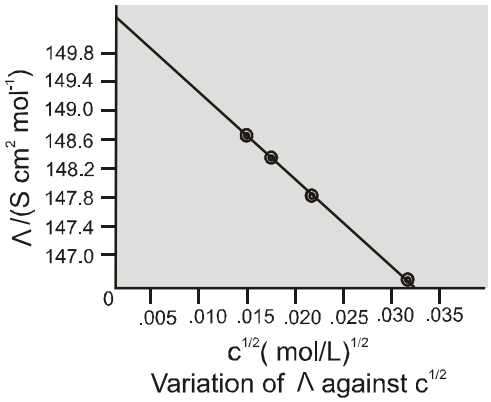
12 EFFECT OF DILUTION ON THE CONDUCTIVITY OF ELECTROLYTES

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

Strong Electrolytes :

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

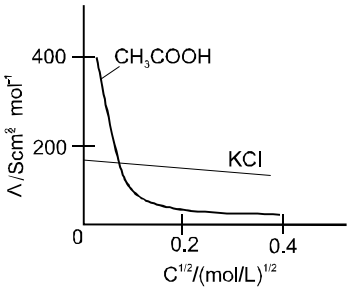
  Example : Thus NaCl, $CaCl_2$, $MgSO_4$ are known as 1-1 , 2-1 and 2-2 electrolyte respectively.
- All electrolytes of a particular type have the same value for 'A'.



Variation of 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 increases in the number of ions in total volume of solution that contains 1 mol of electrolyte.
- At infinite dilution (i.e. concentration c $\rightarrow$ zero) electrolyte dissociates completely (α = 1), but at such low concentration the conductivity of the solution is so low that it cannot be measured accurately.
- Molar conductivity versus $c^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte in aqueous solutions)



Note : (A) Weaker the electrolyte more sharp will be increase of Λ_m or $\Lambda_{eq.}$ on dilution.

(B) same plot is also observed for Λ_m vs. molarity of respective electrolytes.

13. KOHLRAUSCH'S LAW

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

i.e., for $A_{n+}B_{n-}$ $\boxed{\begin{array}{l}\Lambda^{\infty}_{eq.} = \Lambda^{\infty}_{eq.}(+) + \Lambda^{\infty}_{eq.}(-) \\ \Lambda^{\infty}_{m} = \nu_{+}\Lambda^{\infty}_{m}(+) + \nu_{-}\Lambda^{\infty}_{m}(-)\end{array}}$

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

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

Note : $\lambda^{\infty} = \lambda^{\circ}$

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

$$\lambda^{0}_{eq} = \frac{\lambda^{0}_{m}}{\text{chargeon the anion}} \qquad \lambda^{0}_{eq}, \text{electrolyte} = \frac{\lambda^{0}_{m}\ \text{electrolyte}}{\begin{array}{c}\text{total +ve charge on cations in electrolyte} \\ \text{or} \\ \text{total -ve charge on anions in electrolyte}\end{array}}$$

Observations of this kind were first made by **Kohlrausch (1879, 1885)** by comparing equivalent conductances at high dilutions; described them to the fact that under these conditions every ion makes a definite contribution towards the equivalent conductance of the electrolyte, irrespective of the nature of the other ion with which it is associated in the solution. The value of the equivalent conductance at infinite dilution may thus be regarded as made up of the sum of two independent factors, one characteristic of each ion; this result is known as Kohlrausch's law of independent migration of ions.

The ion conductance is a definite constant for each ion, in a given solvent, its value depending only on the temperature.

It will be seen later that the ion conductances at infinite dilution are related to the speeds with which the ions move under the influence of an applied potential gradient.

❖ **Applications of Kohlrausch's Law :**

- **Calculate Λ° for any electrolyte from the Λ° of individual ions.**

An important use of ion conductances is to determine the equivalent conductance at infinite dilution of certain electrolytes which cannot be, or have not been, evaluated from experimental data. For example, with a weak electrolyte the extrapolation to infinite dilution is very uncertain, and with sparingly soluble salts the number of measurements which can be made at appreciably different concentrations is very limited. The value of Λ° can, however, so obtained by adding the ion conductances. For example, the equivalent conductance of acetic acid at infinite dilution is the sum of the conductances of the hydrogen and acetate ions; the former is derived from a study of strong acids and the latter from measurements on acetates. It follows, therefore, that at 25°.

$$\Lambda^{\circ}_{(CH_3CO_2H)} = \Lambda^{0}_{H^+} + \Lambda^{0}_{CH_3CO_2^-} = 349.8 + 40.9 = 390.7 \text{ ohms}^{-1}\text{ cm}^2$$

The same result can be derived in another manner which is often convenient since it avoids the necessity of separating the conductance of an electrolyte into the contributions of its constituent ions. The equivalent conductance of any weak electrolyte MA at infinite dilution it follows, therefore, that

$\Lambda^{\circ}(MA) = \Lambda^{\circ}(MCl) + \Lambda^{\circ}(NaA) - \Lambda^{\circ}(NaCl)$, [MCl, NaA, NaCl are strong electrolytes]

where Λ° (MCl), Λ°(NaA) and Λ°(NaCl) are the equivalent conductances at infinite dilution of the chloride of the metal M, i.e., MCI, of the sodium salt of the anion A, i.e., NaA, and of sodium chloride, respectively. Any convenient anion may be used instead of the chloride ion, and similarly the sodium ion may be replaced by another metallic cation or by the hydrogen ion. For example, if M^+ is the hydrogen ion and A^- is the acetate ion, it follows that

$\Lambda°(CH_3COOH)$ $= \Lambda°(HCl) + \Lambda°(CH_3COONa) - \Lambda°(NaCl)$
$= 426.16 + 91.0 - 126.45$
$= 390.71$ ohms^{-1} cm^2 at 25.

Similarly :

$\Lambda_m°[BaSO_4] = \Lambda_m°[BaCl_2] + \Lambda_m°[Na_2SO_4] - 2\Lambda_m°[NaCl]$

- **Degree of dissociation :**

$\therefore$ Degree of dissociation

$$\frac{\text{equivalent conductance at a given concentration}}{\text{equivalent conductance at infinite dilution}}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{\Lambda_{eq}^c}{\Lambda_{eq}^0}$$

- **Dissociation constant** of weak electrolyte :

$$K_c = \frac{C\alpha^2}{1-\alpha} \quad \frac{C\left(\frac{\Lambda_m^c}{\Lambda_m^0}\right)^2}{1-\frac{\Lambda_m^c}{\Lambda_m^0}}$$

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

Sparingly soluble salt = Very small solubility

Solubility = molarity $\cong$ S $\to 0$

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

$$\Lambda_m^\circ \; \Lambda_m^s = \kappa = \frac{1000}{s}$$

$$s = \frac{\kappa \times 1000}{\Lambda_m^0}$$

SOLVED EXAMPLE

Example-18 If resistivity of 0.8 M KCl solution is 2.5 x 10^3 Ω cm calculate Λ_m of the solution.

Solution $\rho = 2.5 \times 10^{-3}$ Ω cm

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

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

Example-19 $\Lambda_m^0 \; Na^+ = 150 \, \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$; $\Lambda_{eq}^0 \; Ba^{2+} = 100 \, \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$

$\Lambda_{eq}^0 \; SO_4^{2-} = 125 \, \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$; $\Lambda_m^0 \; Al^{3+} = 300 \, \Omega^{-1} \text{ cm}^2 \text{ mole}^{-1}$

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

Then calculate

(a) Λ_{eq}^0, Al^{3+} (b) $\Lambda_{eq}^0 \; Al_2(SO_4)_3$ (c) $\Lambda_m^0 \; (NH_4)_2SO_4$

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

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

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

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

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

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

Example-20 To calculate Λ^0_m or Λ^0_{eq} of weak electrolyte

Sol. $\Lambda^0_{mCH_3COOH} = \Lambda^0_{mCH_3COO^-} + \Lambda^0_m\,H^+ = (\Lambda^0_{mCH_3COO^-} + \Lambda^0_{mNa^+}) - \Lambda^0_{mNa^+} + \Lambda^0_{mH^+} + \Lambda^0_{mCl^+} - \Lambda^0_{mCl^-}$

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

Example-21 Calculate Λ^0_m of oxalic acid, given that

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

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

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

Solution $\Lambda^0_m\,H_2C_2O_4 = 700 + 800 - 900 = 600\,\Omega^{-1}\,cm^2\,mole$

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

$\Lambda_m = 600$

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

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

calculate K_{SP} of AgCl

Solution $\Lambda^0_M\,AgCl = 140$

Total conductance = 10^{-5}

$S = \frac{140 \times 4 \times 10^{-5} \times 1000}{140} = \frac{1.4 \times 10^{-4}}{14}$

$S = 5.4 \times 10^{-4}$

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

Example-23 To calculate K_W of water

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

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

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

$molarity = [H^+] = [OH^-] = \frac{K \times 1000}{\lambda^\infty_M}$

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

❖ **Abnormal ion conductances of H^+ and OH^-:**

It is supposed, as already indicated, that the hydrogen ion in water is H_3O^+ with three hydrogen atoms attached to the central oxygen atom. When a potential gradient is applied to an aqueous solution containing hydrogen ions, the latter travel to some extent by the same mechanism as do other ions, but there is in addition another mechanism which permits of a more rapid ionic movement. This second process is believed to involve the transfer of a proton (H^+) from a H_3O^+ ion to an adjacent water molecule; thus

The resulting H_3O^+ ion can now transfer a proton to another water molecule, and in this way the positive charge will be transferred a considerable distance in a short time. The electrical conductance will thus be much greater than that due solely to the normal mechanism.

14. CONDUCTOMETRIC TITRATION :

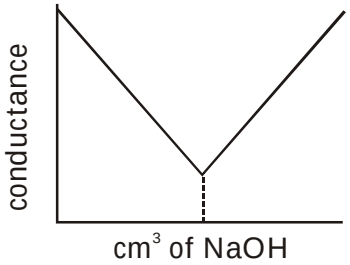
The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invari ably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point may be located graphically by plotting the change in conductance as a function of the volume of titrant added. In order to reduce the influence of errors in the c onductometric titration to a minimum, the angle between the two branches of the titration curve should be as small as possible (see Fig. 6.2). If the angle is very obtus e, a small error in the conductance data can cause a large deviation. The following app roximate rules will be found

- The smaller the conductivity of the ion which repla ces the reacting ion, the more accurate will be the result. Thus it is preferable C to titrate a silver salt with lithium chloride rather than with HCl. Generally, cations should be titrated with lithium salts and anions with acetates as these ion s have low conductivity
- The larger the conductivity of the anion of the reagent which reacts with the cation to be determined, or vice versa, the more acute is the angle of titration curve.
- The titration of a slightly ionized salt does not g ive good results, since the conductivity increases continuously from the commen cement. Hence, the salt present in the cell should be virtually completely dissociated; for a similar reason; the added reagent should also be as strong electrolyte. The main advantages to the conductometric titration are its applicability to very dilute, and coloured solutions and to system that involver elative incomplete reactions. For example, which neither a potentiometric, nor indica tor method can be used for the neutralization titration of phenol ($K_a \times 10^{-10}$) a conductometric endpoint can be successfully applied.

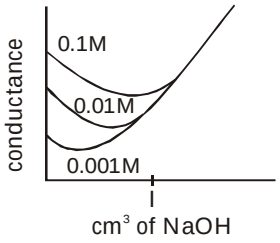
Cation	H_3O^+	NH_4^+	K^+	Na^+	Ag^+	Ca^{2+}	Mg^{2+}
$\lambda^\infty_m/(\Omega^{-1}cm^2mol^{-1})$	350.0	73.5	73.5	50.1	62.1	118.0	106.1
Anion	OH^-	Br	Cl^-	NO_3^-	CH_3COO^-	SO_4^{2-}	
$\lambda^\infty_m/(\Omega^{-1}cm^2mol^{-1})$	199.2	78.1	76.5	71.4	40.0	159.6	

Some Typical Conductometric Titration Curves are :

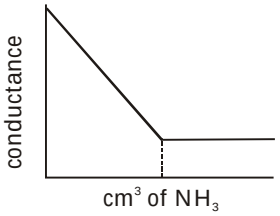
14.1 Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H^+ ions react with OH - ions to form undissociated water. This decrease in the conducta nce continues till the equivalence point. At the equivalence point, the so lution contains only NaCl. After the equivalence point, the conductance increases due to the large.



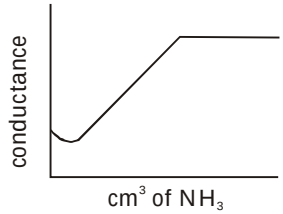
14.2 Weak Acid with a Strong Base, e.g. acetic acid with NaOH: Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH
neutralizes the un-dissociated CH_3 COOH to CH_3OONa which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH_3 COONa. Beyond the equivalence point, conductance in creases more rapidly with the addition of NaOH due to the highly conducting OH ions.



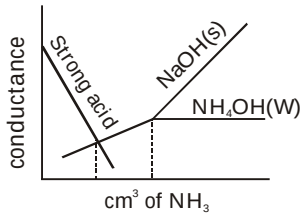
14.3 Strong Acid with a Weak Base, e.g. sulphuric acid with dilute ammonia : Initially the conductance is high and then it decre ases due to the replacement of H^+. But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate.



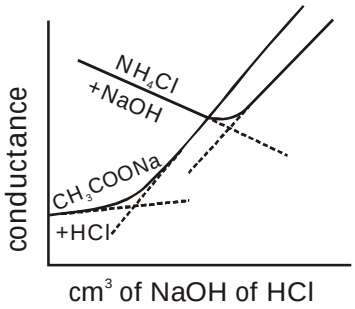
14.4. Weak Acid with a Weak Base : The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting



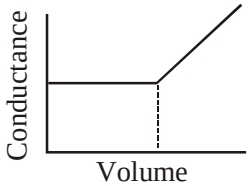
Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base : In this curve there are two break points. The first break point corresponds to the neutralization of strong acid. When the stro ng acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance
increases due to the excess of OH - ions in case of a strong base as the titrant. However, when the titrant is a weak base, it remain s almost constant after the end point similar to



Displacement (or Replacement) Titrations : When a salt of a weak acid is titrated with a strong acid, the anion of the weak acid is replaced by that of the strong acid and weak acid itself is liberated in the undissociated form. Similarly, in the addition of a strong base to the salt of a weak base, the cation of the weak base is replaced by that of the stronger one and the weak base itself is generated in the undissociated form. If for example, M-HCl is added to 0.1 M solution of sodium acetate, the curve shown in Fig.6.7 is obtai ned, the acetate ion is replaced by the chloride ion after the endpoint. The initial increase in conductivity is due to the fact that the conductivity of the chloride ion is slightly geater than that of acetate ion. Until the replace ment is nearly complete, the solution contains enough sodium acetate to suppress the ionization of the liberated acetic acid, so resulting a negligible increase in the conductivity of the solution. However, near the equivalent point, the acetic acid is sufficiently ionized to affect the conductivity and a rounded portion of the curve is obtained. Beyond the equivalence point, when excess of HCl is present (ionization of acetic acid is very much suppressed) therefore, the conductivity arises rapidly. Care must be taken that to titrate a 0.1 M-salt of a weak acid, the dissociation constant should not be more than 5×10^{-4}, for a 0.01 M -salt solution, $K_a < 5 \times 10^{-5}$ and for a 0.001 M-salt solution, $K_a < 5 \times 10^{-6}$, i.e., the ionization constant of the displace acid or base divided by the original concentration of the salt must not exceed above 5×10^{-3} . Fig. 6.6. Also includes the titrationof 0.01 M- ammonium chloride solution versus 0.1 M - sodium hydroxide solution. The decrease in conductivity during the displacement is caused by the displacement of ammonium ion of grater conductivity by sodium ion of smaller conductivity.



14.5 Precipitation Titration and Complex Formation Titration : : A reaction may be made the basis of a conductometric precipitation titration provided the reaction product is sparingly soluble or is a stable complex . The solubility of the precipitate (or the dissociation of the complex) should be less than 5%. The addition of ethanol is sometimes recommended to reduce the solubility in the precipitations. An experimental curve is given in F ig. 6.8 (ammonium sulphate in aqueous-ethanol solution with barium acetate). I f the solubility of the precipitate were negligibly small, the conductance at the equivalence point should be given by AB and not the observed AC. The addition of excess of the reagent depresses the solubility of the precipitate and, if the solubility is not too large, the position of the point B can be determine d by continuing the straight portion of the two arms of the curve until they intersect



$AgNO_3$(aq.) vs NaCl

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. Na-amalgam is prepared by electrolysis of NaCl solution using liquid Hg as cathode. How long should the current of 10 amp. is passed to produce 10% Na – Hg on a cathode of 10 g Hg. (atomic mass of Na = 23).
(A) 7.77 min (B) 9.44 min. (C) 5.24 min. (D) 11.39 min.

Sol. **(A)**

90 g Hg has 10 g Na

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

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

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

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

2. We have taken a saturated solution of AgBr. K_{sp} of AgBr is 12×10^{-14}. If 10^{-7} mole of $AgNO_3$ are added to 1 litre of this solution then the conductivity of this solution in terms of 10^{-7} Sm^{-1} units will be
[Given $\Lambda^o_{(Ag^+)} = 4 \times 10^{-3}$ Sm^2 mol^{-1}, $\Lambda^o_{(Br^-)} = 6 \times 10^{-3}$ S m^2 mol^{-1}, $\Lambda^o_{(NO_3^-)} = 5 \times 10^{-3}$ Sm^2 mol^{-1}]
(A) 39 (B) 55 (C) 15 (D) 41

Sol. **(A)**

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

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

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

Sol. **(B)**

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

$E_1 = 0 - .0591 \log \frac{1}{(H^+)_1}$

$E_1 = 0 + .0591 \log [H^+]_1 = - .0591\ pH_1$

$E_2 = - .0591\ pH_2$

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

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

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

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

Add (1) & (2)

$pH_1 + pH_2 = 2\ pk_a$

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

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

$Ag(s) \mid Ag_2CO_3(s) \mid Na_2CO_3(aq) \mid\mid KBr(aq) \mid AgBr(s) \mid Ag(s)$

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

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

Sol. **(B)**

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

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

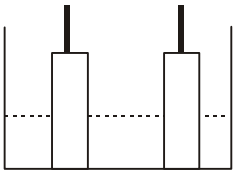
---

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

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

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

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



(A) 50 Ω (B) 100 Ω (C) 25 Ω (D) 200 Ω

Sol. **(A)**

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

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

6. Calculate the cell EMF in mV for

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

if $\Delta G_f°$ values are at 25°C

$-109.56 \frac{kJ}{mol}$ for AgCl(s) and $-130.79 \frac{kJ}{mol}$ for $(H^+ + Cl^-)(aq)$

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

Sol. **(A)**

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

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

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

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

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

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

Sol. **(A)**

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

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

Now cell reaction is

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

$$Br^- + AgCl \xrightarrow{1e^-} Cl^- + AgBr$$

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

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

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

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

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

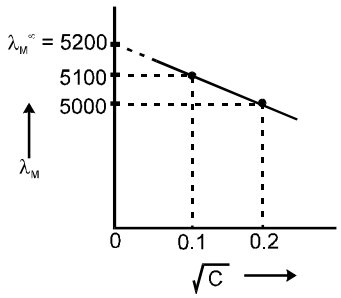
$\therefore$ $[ions]_{total} = 2\sqrt{50} \times 10^{-4}$ M

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

Ans. 29

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

Sol.



From the graph we can see the λ_M^∞ value of 5200 Ω^{-1} cm^2 mol^{-1}.

Hence

$$\alpha = \frac{5000}{5200} = 0.9615 \simeq 0.96$$

Ans. 96

Exercise # 1

PART - I : SUBJECTIVE QUESTIONS

Marked Questions may have for Revision Questions.

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

Commit to memory :

Notation for Galvanic cell :

Anode half cell | Cathode half cell

$M(s) \mid M^{2+}(aq, C_1) \,||\, N^{2+}(aq, C_2) \mid N(s)$

↓ Phase boundary ↓ Salt bridge ↓ Phase boundary

→ LOAN ≡ left oxidation- Anode-negative

A-1. In the galvanic cell $Zn \mid Zn^{2+} \,||\, Ag^{+} \mid Ag$, the electrons flow from Zn-electrode to Ag-electrode. Answer the following questions regarding this cell :
(a) Which is the anode ?
(b) Which is the cathode ?
(c) What happens at anode-reduction or oxidation ?
(d) What happens at cathode-oxidation or reduction ?
(e) Which electrode loses mass ?
(f) Which electrode gains mass ?
(g) Write the electrode reactions.
(h) Write the cell reaction
(i) Which metal has greater tendency to loss electron-Zn or Ag ?
(j) Which is the more reactive metal-Zn or Ag ?
(k) What is the function of salt bridge represented by the symbol || ?

A-2. Write cell representation for following cells.
(a) $Cd^{2+}(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Cd(s)$
(b) $2Ag^{+}(aq) + H_2(g) \longrightarrow 2H^{+}(aq) + 2Ag(s)$
(c) $Cr_2O_7^{2-}(a) + 14H^{+}(aq) + 6Fe^{2+}(aq) \longrightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

A-3. Write cell reaction of the following cells :
(a) $Cu\left|Cu^{2+}(aq)\right|\left|Ag^{+}(aq)\right|Ag$
(b) $Pt\left|Fe^{2+}, Fe^{3+}\right|\left|MnO_4^{-}, Mn^{2+}, H^{+}\right|Pt$
(c) $Pt, Cl_2\left|Cl^{-}(aq)\right|\left|Ag^{+}(aq)\right|Ag$
(d) $Cd\left|Cd^{2+}(aq)\right|\left|H^{+}(aq)\right|H_2\left|Pt\right.$

Section (B) : Concept of ΔG

Commit to memory :

E^{o}_{cell} is an intensive property, so on multiplying or dividing electrode reaction, E^{o}_{cell} remains same. Calcualte E^{o}_{cell} for 3rd reaction with the help of 1st and 2nd reaction using $\Delta G^{o} = -nF\,E^{o}_{cell}$.

$$E^{o}_{target} = \frac{n_1E_1 + n_2E_2}{n_{target}}$$

where n_1 = electrons participating in 1st reaction.
n_2 = electrons participating in 2nd reaction.
n_{target} = electrons participating in target reaction.

B-1. If for the half cell reactions $Cu^{2+} + e^- \longrightarrow Cu^+$ $E° = 0.15$ V
$Cu^{2+} + 2e^- \longrightarrow Cu$ $E° = 0.34$ V
Calculate E° of the half cell reaction
$Cu^+ + e^- \longrightarrow Cu$

B-2. If $E^\circ_{Fe^{2+}|Fe} = -0.44$ V, $E^\circ_{Fe^{3+}|Fe^{2+}} = 0.77$ V. Calculate $E^\circ_{Fe^{3+}|Fe}$

B-3. The standard oxidation potentials for Mn^{3+} ion acid solution are $Mn^{2+} \xrightarrow{-1.5\,V} Mn^{3+} \xrightarrow{-1.0\,V} MnO_2$. Is the reaction $2Mn^{3+} + 2H_2O \longrightarrow Mn^{2+} + MnO_2 + 4H^+$ spontaneous under conditions of unit activity ? What is the change in free energy ?

B-4. Consider the standard reduction potentials (in volts) as shown in Fig. Find E°.

$$SO_4^{2-} \xrightarrow{-0.936} SO_3^{2-} \xrightarrow{-0.576} \frac{1}{2}S_2O_3^{2-}$$
$$\underbrace{\qquad\qquad}_{E° = ?}\uparrow$$

Section (C) : Electrochemical series & its Applications

Commit to memory :

$$SRP \propto \text{Oxidising power} \propto \frac{1}{\text{reducing power}} \propto \text{Non-metallic character} \propto \frac{1}{\text{Metallic character}}$$

C-1. The reduction potential values are given below
$Al^{3+}/Al = -1.67$ volt, $Mg^{2+}/Mg = -2.34$ volt, $Cu^{2+}/Cu = +0.34$ volt
$I_2 / I^- = +0.53$ volt. Which one is the best reducing agent ?

C-2. The standard reduction potential value of the three metallic cations X, Y and Z are 0.52, – 3.03 and – 1.18 V respectively. Write the decreasing order of reducing power of the corresponding metals :

C-3. **(i)** Which of the following oxides is reduced by hydrogen ?
MgO, CuO and Na_2O
(ii) Which of the following oxides will decompose most easily on heating ?
ZnO, CuO, MgO, and Ag_2O
(iii) The value of E^o_{OX} for electrode reactions,
$Fe \longrightarrow Fe^{2+} + 2e^-$ $Cu \longrightarrow Cu^{2+} + 2e^-$ and $Zn \longrightarrow Zn^{2+} + 2e^-$
are 0.444, –0.337 and 0.763 volt respectively. State which of these metals can replace the other two from the solution of their salts ?

C-4. For the cell reaction $2Ce^{4+} + Co \rightarrow 2Ce^{3+} + Co^{2+}$
E°_{Cell} is 1.89 V. If $E^\circ_{Co^{2+}|Co}$ is – 0.28 V, what is the value of $E^\circ_{Ce^{4+}|Ce^{3+}}$?

C-5. Determine the standard reduction potential for the half reaction :
$Cl_2 + 2e^- \rightarrow 2Cl^-$
Given $Pt^{2+} + 2Cl^- \rightarrow Pt + Cl_2$, $E^\circ_{Cell} = -0.15$ V
$Pt^{2+} + 2e^- \rightarrow Pt$ $E° = 1.20$ V

C-6. What is E°_{Cell} if :
$2Cr + 3H_2O + 3OCl^- \rightarrow 2Cr^{3+} + 3Cl^- + 6\,OH^-$
$Cr^{3+} + 3e^- \rightarrow Cr$, $E° = -0.74$ V
$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ $E° = 0.94$ V

Section (D) : Nernst equation & its Applications (Including Concentration Cell)

Commit to memory :

Nernst equation : $E_{cell} = E^{o}_{cell} - \frac{RT}{nf} \ln Q$

At 25°C, $E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log Q$

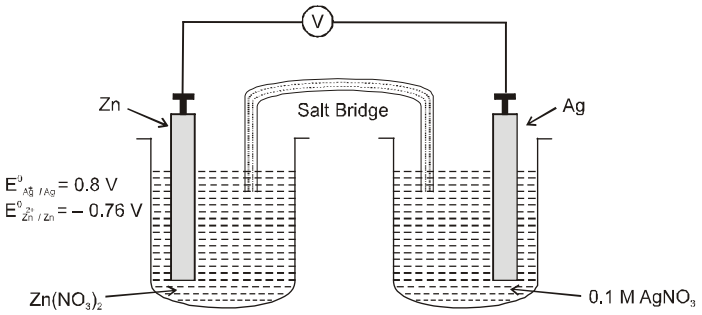
where, n = number of transferred electron, Q = reaction quotient.
For concentration cell $E^{o}_{cell} = 0$

D-1. For a cell Mg(s) | Mg^{2+}(aq) || Ag^{+} (aq) | Ag,
(i) Calculate the equilibrium constant at 25°C of
$Mg(s) + 2Ag^{+}(aq) \rightleftharpoons 2Ag(s) + Mg^{2+}(aq)$
(ii) Also find the maximum work per mole Mg that can be obtained by operating the cell in standard condition.
$E^{0}_{(Mg^{2+}|Mg)} = -2.37V$, $E^{0}_{(Ag+|Ag)} = 0.8$ V.

D-2. Calculate the equilibrium constant for the reaction :

$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$, [Given : $E^{0}_{Ce^{4+}/Ce^{3+}} = 1.61$ V; $E^{0}_{Fe^{3+}/Fe^{2+}} = 0.77$V]

D-3. Consider the following electrochemical cell :



(a) Write a balanced net ionic equation for the spontaneous reaction that take place in the cell.
(b) Calculte the standard cell potential E^{o} for the cell reaction.
(c) If the cell emf is 1.6 V, what is the concentration of Zn^{2+} ?
(d) How will the cell potential be affected if KI is added to Ag^{+} half-cell ?

D-4. A zinc electrode is placed in a 0.1M solution at 25°C. Assuming that the salt (ZnX) is 20% dissociated at this dilutions calculate the electrode reduction potential. $E^{0}(Zn^{2+}|Zn) = -0.76$V.

D-5. Calculate EMF of a concentration cell consisting of two zinc electrodes, one dipping into $\frac{M}{4}$ sol. of zinc sulphate & the other into $\frac{M}{16}$ sol. of the same salt at 25^{0} C .

D-6. Calculate pH using the following cell :
Pt (H_2) | H^{+} (x M) | | H^{+} (1 M) | Pt (H_2) if $E_{cell} = 0.2364$ V.
1 atm 1 atm

Section (E) : Metal-metal insoluble salt electrode :

Commit to memory :

$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$

$$E^0_{Cl^-/AgCl/Ag} = E^0_{Ag^+/Ag} + \frac{0.0591}{1}\log K_{sp}$$

$$E_{Cl^-/AgCl/Ag} = E^0_{Cl^-/AgCl/Ag} - \frac{0.0591}{1}\log\left[Cl^-\right]$$

E-1. Given, E° = –0.27 V for the Cl^- | $PbCl_2$ |Pb couple and – 0.12 V for the Pb^{2+} | Pb couple, determine K_{sp} for $PbCl_2$ at 25°C ? (Take $\frac{2.303RT}{F}$ = 0.06)

E-2. The pK_{sp} of AgI is 16. if the E° value for Ag+ | Ag is 0.8 V. Find the E° for the half cell reaction $AgI(s) + e^- \rightarrow Ag + I^-$? (Take $\frac{2.303RT}{F}$ = 0.06)

Section (F) : Calculation of Thermodynamic parameters of Galvanic cell

Commit to memory :

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

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

$$\Delta S = +nF\frac{dE_{cell}}{dT}$$

$\frac{dE_{cell}}{dT}$ = temperature cofficient of cell reaction.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = -nF E_{cell} + nFT\frac{dE_{cell}}{dT}$$

F-1. The standard electromotive force of the cell :
$Fe \mid Fe^{2+}(aq) \mid\mid Cd^{2+} \mid Cd$ is 0.0372 V
The temperature coefficient of e.m.f. is –0.125 V K^{-1}. Calculate the quantities ΔG^o, ΔH^o and ΔS^o at 25ºC.

F-2. ΔH for the reaction $Ag(s) + \frac{1}{2}Hg_2Cl_2(s) \longrightarrow AgCl(s) + Hg(\ell)$ is +1280 cal at 25°C. This reaction can be conducted in a cell for which the emf = 0.0455 volt at this temperature. Calculate the temperature coefficient of the emf.

F-3. The voltage of a certain cell has standred potential at 25ºC and 20ºC are 0.3525 V and 0.3533 V respectively. If the number of electrons involved in the overall reactions are two, calculate ΔG^o, ΔS^o and ΔH^o at 25ºC.

Section (G) : Electrolysis

Commit to memory :

Higher SOP means higher tendency of oxidation.
Higher SRP means higher tendency of reduction.
SOP order : $SO_4^{2-} < NO_3^- < Cl^- < H_2O < Br^- < Ag < I^- < OH^- < Cu.....< Li$
SRP order : Follow ECS

G-1.

	ELECTROLYTE	ANODE Product	CATHODE Product
1	$AgNO_3$ (aq) with Pt electrode		
2	$NaNO_3$ (aq) with Pt electrode		
3	Na_2SO_4 (aq) with Pt electrode		
4	NaCl (Molten) with Pt electrode		
5	$CuSO_4$ (aq) with Copper electrode		
6	NaCl (aq) with Pt electrode		
7	$CuSO_4$ (aq) with Inert electrode		

Section (H) : Faraday laws & its Applictions

Commit to memory :

Faraday's law of electrolysis :

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

$Q = it$

2nd law $\frac{W_1}{W_2} = \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$ (Q = same)

Current efficiency (η) = $\frac{\text{actual amount of product}}{\text{theortical amount of product}} \times 100$

$W_{actual} = \left(\frac{E \times Q}{96500}\right)\frac{\eta}{100}$

H-1. Calculate the no. of electrons lost or gained during electrolysis of
(a) 3.55 gm of Cl^- ions (b) 1 gm Cu^{2+} ions (c) 2.7 gm of Al^{3+} ions

H-2. How many faradays of electricity are involved in each of the case
(a) 0.25 mole Al^{3+} is converted to Al.
(b) 27.6 gm of SO_3 is convered to SO_3^{2-}
(c) The Cu^{2+} in 1100 ml of 0.5 M Cu^{2+} is converted to Cu.

H-3. A certain metal salt solution is electrolysed in series with a silver coulometer. The weights of silver and the metal deposited are 0.5094 g and 0.2653g. Calculate the valency of the metal if its atomic weight is nearly that of silver.

H-4. 3A current was passed through an aqueous solution of an unknown salt of Pd for 1Hr. 2.977g of Pd^{+n} was deposited at cathode. Find n. (Given Atomic mass of Pd = 106.4)

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

H-6. A certain electricity deposited 0.54g of Ag from $AgNO_3$ Solution. What volume of hydrogen will the same quantity of electricity liberate at at 1atm, 0ºC (V_m = 22.4 L/mol).

H-7. A current of 3.7A is passed for 6hrs. between Ni electrodes in 0.5L of 2M solution of $Ni(NO_3)_2$. What will be the molarity of solution at the end of electrolysis?

Section (I) : Commercial Cells & Corrosion

Commit to memory :

At STP, V_m (molar volume of the gas) = 22.4 L/mol
Volume of gas required at STP = moles of gas × 22.4

I-1._ Write cell reaction of Dry Cell.

I-2._ Write cell reaction of Nickel-Cadmium Cell.

I-3._ Write cell reaction of Hydrogen fuel Cell.

I-4._ Write cell reaction of Corrosion.

Section (J) : Electrical Conductance

Commit to memory :

Conductivity (κ) = $C \times \frac{\ell}{A} = \frac{1}{R} \times \frac{\ell}{A}$

where, $\frac{\ell}{A}$ = cell constant, C = conductance, R = resistance.

A = surface area of electrodes, ℓ = distance between electrodes.

Molar conductance (Λ_m) = $\frac{\kappa \times 1000}{M}$ S cm^2 mol^{-1}

Equivalent conductance (Λ_{eq}) = $\frac{\kappa \times 1000}{N}$ S cm^2 eq^{-1}

where, M = molarity, N = normality and N = M × valence factor

J-1. The resistance of a conductivity cell filled with 0.01N solution of NaCl is 200 ohm at18ºC.Calculate the equivalent conductivity of the solution. The cell constant of the conductivity cell is 0.88 cm^{-1}.

J-2. The resistance of a solution 'A' is 50 ohms and that of solution 'B' is 100 ohms, both solutions being taken in the same conductivity cell. If equal volumes of solution A. and B are mixed, what will be the resistance of the mixture using the same cell. (Assume that there is no increase in the degree of dissociation of A and B on mixing & Both solutions containing same strong electrolyte)

J-3. The molar conductivity of 0.1 M CH_3COOH solution is 4 S cm^2 mole^{-1} . What is the specific conductivity and resistivity of the solution ?

J-4. The specific conductance of a N/10 KCl solution at 18°C is 1.12 × 10^{-2} mho cm^{-1}. The resistance of the solution contained in the cell is found to be 65 ohms. Calculate the cell constant.

J-5. In a conductivity cell the two platinum electrodes, each of area 10 sq, cm, are fixed 1.5 cm apart. The cell contained 0.05 M solution of a salt. If the two electrodes are just half dipped into the solution which has a resistance of 50 ohms, find molar conductance of the salt solution.

Section (K) : Kohlrausch law and its applications

Commit to memory :

Kohlrausch law : At infinite dilution, $\Lambda^o_{m,\text{ electrolyte}} = \nu_+\Lambda^o_{m^+} + \nu_-\Lambda^o_{m^-}$

where, ν_+ = number of cations in one formula unit of electrolyte.

ν_- = number of anions in one formula unit of electrolyte.

At infinite dilution equivalent conductance : $\Lambda^o_{eq,\text{ electrolyte}} = \Lambda^o_{eq^+} + \Lambda^o_{eq^-}$

Degree of dissociation (D.O.D.) = $\alpha = \frac{\Lambda_m}{\Lambda^o_m} = \frac{\Lambda_{eq}}{\Lambda^0_{eq}}$

For weak electrolyte, dissociation constant (K_a) = $\frac{C\alpha^2}{1-\alpha}$, where, C = concentration of electrolyte.

Solubility (s) = $\frac{\kappa \times 1000}{\Lambda^o_m}$ and $K_{sp} = S^2$ for AB type salt.

K-1. For the strong electroytes NaOH, NaCl and $BaCl_2$ the molar ionic conductivities at infinite dilution are 240×10^{-4}, 125×10^{-4} and 280.0×10^{-4} mho cm^2 mol^{-1} respectively. Calculate the molar conductivity of $Ba(OH)_2$ at infinite dilution.

K-2. The value of Λ^∞_m for HCl, NaCl and CH_3CO_2Na are 425, 125 and 100 S cm^2 mol^{-1} respectively. Calculate the value of Λ^∞_m for acetic acid. If the equivalent conductivity of the given acetic acid is 48 at 25° C, calculate its degree of dissociation.

K-3. The specific conductance of a saturated solution of AgCl at 25°C after subtracting the specific conductance of conductivity of water is 2.28×10^{-6} mho cm^{-1}. Find the solubility product of AgCl at 25°C.

($\lambda^\infty_{AgCl} = 138.3$ mho cm^2)

K-4. Calculate K_a of acetic acid if its 0.05 N solution has equivalent conductance of 7.36 mho cm^2 at 25°C.

($\lambda^\infty_{CH_3COOH} = 390.7$) .

Section (L) : Conductometric Titration

Commit to memory :

H^+ and OH^- ions are highly conducting.

L-1. Draw approximate titration curve for following –

(1) HCl(aq) is titrated with NaOH
(2) CH_3COOH(aq) is titrated with NaOH
(3) Equimolar mixture of HCl and HCN titrated withNaOH
(4) NH_4Cl(aq) is titrated with NaOH
(5) H_2SO_4 is titrated with dilute NH_3
(6) CH_3COOH is titrated with dilute NH_3
(7) $AgNO_3$ is titrated with NaCl

PART- II : OBJECTIVE QUESTIONS

*** Marked Questions are having more than one correct option.**

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

A-1. Which of the following statement is wrong about galvanic cell ?

(A) cathode is positive charged

(B) anode is negatively charged

(C) reduction takes place at the anode

(D) reduction takes place at the cathode

A-2. Which of the following is/are function(s) of salt - bridge ?
(A) It completes the electrical circuit with electrons flowing from one electrode to the other through external wires and a flow of ions between the two compartments through salt - bridge
(B) it minimises the liquid - liquid junction potential
(C) both correct
(D) none of these

A-3. The emf of the cell, Ni | Ni^{2+} (1.0 M) || Ag^+ (1.0M) | Ag [E° for Ni^{2+} / Ni = – 0.25 volt, E° for Ag^+/Ag = 0.80 volt] is given by -
(A) –0.25 + 0.80 = 0.55 volt (B) –0.25 – (+0.80) = –1.05 volt
(C) 0 + 0.80 – (–0.25) = + 1.05 volt (D) –0.80 – (–0.25) = – 0.55 volt

A-4. Salt bridge contains :
(A) calomel (B) sugar (C) H_2O (D) agar-agar paste

Section (B) : Concept of ΔG

B-1. Which of the following statements about the spontaneous reaction occurring in a galvanic cell is always true?
(A) $E^o_{cell} > 0$, $\Delta G^o < 0$, and Q < K (B) $E^o_{cell} > 0$, $\Delta G^o < 0$, and Q > K
(C) $E^o_{cell} > 0$, $\Delta G^o > 0$, and Q > K (D) $E_{cell} > 0$, $\Delta G < 0$, and Q < K

B-2. Given standard electrode potentials :
$Fe^{3+} + 3e^- \longrightarrow Fe$; E° = –0.036 volt

$Fe^{2+} + 2e^- \longrightarrow Fe$; E° = –0.440 volt

The standard electrode potential E° for $Fe^{3+} + e^- \longrightarrow Fe^{2+}$
(A) –0.476 volt (B) –0.404 volt (C) 0.440 volt (D) 0.772 volt

B-3. $Cu^+ + e^- \longrightarrow Cu$, E° = x_1 volt ;

$Cu^{2+} + 2e^- \longrightarrow Cu$, E° = x_2 volt, then for

$Cu^{2+} + e^- \longrightarrow Cu^+$, E° (volt) will be -
(A) $x_1 - 2x_2$ (B) $x_1 + 2x_2$ (C) $x_1 - x_2$ (D) $2x_2 - x_1$

B-4. If $\Delta G°$ of the cell reaction, $AgCl(s) + \frac{1}{2} H_2(g) \rightarrow Ag(s) + H^+ + Cl^-$ is –21.52 KJ

then $\Delta G°$ of $2AgCl(s) + H_2(g) \rightarrow 2Ag(s) + 2H^+ + 2Cl^-$ is :
(A) –21.52 KJ (B) –10.76 KJ (C) –43.04 KJ (D) 43.04 KJ

Section (C) : Electrochemical series & its Applications

C-1. The reduction potential values are given below:
Al^{3+} | Al = –1.67 volt, Mg^{2+} | Mg = –2.34 volt
Cu^{2+} | Cu = + 0.34 volt, I_2 | $2I^-$ = + 0.53 volt
Which one is the best reducing agent ?
(A) Al (B) Mg (C) Cu (D) I_2

C-2. A standard reduction electrode potentials of four metal cations are -
A^+ = – 0.250 V , B^+ = – 0.140 V C^+ = – 0.126 V , D^+ = – 0.402 V
The metal that displaces A^+ from its aqueous solution is :–
(A) B (B) C (C) D (D) None of the above

C-3. E^0 for $F_2 + 2e \longrightarrow 2F^-$ is 2.8 V, E^0 for $\frac{1}{2}F_2 + e \longrightarrow F^-$ is

(A) 2.8 V (B) 1.4 V (C) – 2.8 V (D) – 1.4 V

C-4. If a spoon of copper metal is placed in a solution of ferrous sulphate -

(A) Cu will precipitate out (B) iron will precipitate

(C) Cu and Fe will precipitate (D) no reaction will take place

C-5. Standard reduction electrode potentials of three metals A, B and C are respectively + 0.5V, – 3.0V and –1.2 V. The reducing powers of these metals are :

(A) C > B > A (B) A > C > B (C) B > C > A (D) A > B > C

C-6. For Zn^{2+} / Zn, E° = –0.76 V, for Ag^+/Ag E° = 0.799 V. The correct statement is -

(A) the reaction Zn getting reduced Ag getting oxidized is spontaneous

(B) Zn undergoes reduction and Ag is oxidized

(C) Zn undergoes oxidation Ag^+ gets reduced

(D) No suitable answer

C-7. Electrode potential data are given below.

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$; $E^0 = + 0.77$

$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$; $E^0 = – 1.66$ V

$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$; $E^0 = + 1.08$ V

Based one the data given above, reducing power of Fe^{2+}, Al and Br^- will increase in the order :

(A) $Br^- < Fe^{2+} < Al$ (B) $Fe^{2+} < Al < Br^-$ (C) $Al < Br^- < Fe^{2+}$ (D) $Al < Fe^{2+} < Br^-$

C-8. Consider the following E^o values :

$E^0_{Fe^{3+}/Fe^{2+}} = + 0.77$ V ; $E^0_{Sn^{2+}/Sn} = – 0.14$ V

Under standard conditions the potential for the reaction is

$Sn(s) + 2Fe^{3+}(aq) \rightarrow 2Fe^{2+}(aq) + Sn^{2+}(aq)$

(A) 1.68 V (B) 1.40 V (C) 0.91 V (D) 0.63 V

C-9. KCl can be used in salt bridge as electrolyte in which of the following cells?

(A) $Zn \mid ZnCl_2 \mid\mid AgNO_3 \mid Ag$ (B) $Pb \mid Pb(NO_3)_2 \mid\mid Cu(NO_3)_2 \mid Cu$

(C) $Cu \mid CuSO_4 \mid\mid AuCl_3 \mid Au$ (D) $Fe \mid FeSO_4 \mid\mid Pb(NO_3)_2 \mid Pb$

C-10. The position of some metals in the electrochemical series in decreasing electropositive character is given as Mg > Al > Zn > Cu > Ag. What will happen if a copper spoon is used to stir a solution of aluminium nitrate ?

(A) The spoon will get coated with aluminium (B) An alloy of aluminium and copper is formed

(C) The solution becomes blue (D) There is no reaction

Section (D) : Nernst equation & its Applications (Including Concentration Cell)

D-1. Which of the following represents the reduction potential of silver wire dipped into 0.1 M $AgNO_3$ solution at 25° C ?

(A) $E°_{red}$ (B) $(E°_{red} + 0.059)$ (C) $(E°_{oxi} – 0.059)$ (D) $(E°_{red} – 0.059)$

D-2. The reduction potential of hydrogen electrode (P_{H_2} = 1 atms; $[H^+]$ = 0.1 M) at 25°C will be -

(A) 0.00 V (B) –0.059 V (C) 0.118 V (D) 0.059 V

D-3. The standard emf for the cell reaction $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ is 1.10 volt at 25°C. The emf for the cell reaction when 0.1 M Cu^{2+} and 0.1 M Zn^{2+} solutions are used at 25°C is

(A) 1.10 volt (B) 0.110 volt (C) –1.10 volt (D) –0.110 volt

D-4. Consider the cell $\begin{matrix} H_2(Pt) \\ 1\ atm \end{matrix}\left|\begin{matrix} H_3O^+(aq.) \\ pH = 19/3 \end{matrix}\right|\left|\begin{matrix} Ag^+ \\ x\ M \end{matrix}\right| Ag$ The measured EMF of the cell is 1.0 V. What is the value of x ? $E^0_{Ag^+|Ag}$ = + 0.8 V. [T = 25°C] $\left(\frac{2.303 \times 8.314 \times 298}{96500} = 0.06\right)$

(A) 2×10^{-3} M (B) 1×10^{-3} M (C) 1.5×10^{-3} M (D) 1.5×10^{-2} M

D-5. For the cell reaction
$Mg_{(s)} + Zn^{2+}_{(aq)}(1M) \longrightarrow Zn(s) + Mg^{2+}_{(aq)}(1M)$
The emf has been found to be 1.60 V, E° of the cell is :
(A) –1.60 V (B) 1.60 V (C) 0.0 V (D) 0.16 V

D-6. $Zn \mid Zn^{2+}(C_1) \| Zn^{2+}(C_2) \mid Zn$. for this cell ΔG is negative if -
(A) $C_1 = C_2$ (B) $C_1 > C_2$ (C) $C_2 > C_1$ (D) None

D-7. $Pt\left|\begin{matrix} H_2 \\ (p_1) \end{matrix}\right|\begin{matrix} H^+ \\ (1M) \end{matrix}\Bigg\|\begin{matrix} H^+ \\ (1M) \end{matrix}\left|\begin{matrix} H_2 \\ (p_2) \end{matrix}\right|Pt$ (where p_1 and p_2 are pressures) cell reaction will be spontaneous if :
(A) $p_1 = p_2$ (B) $p_1 > p_2$ (C) $p_2 > p_1$ (D) p_1 = 1 atm

Section (E) : Metal - Metal insoluble salt electrode

E-1. The solubility product of silver iodide is 8.3×10^{-17} and the standard reduction potential of Ag, Ag^+ electrode is + 0.8 volts at 25° C. The standard reduction potential of Ag,AgI/I^- electrode from these data is
(A) – 0.30 V (B) + 0.15 V
(C) + 0.10 V (D) – 0.15 V

E-2. Given the data at 25°C,
$Ag_{(s)} + I^-_{(aq)} \rightarrow AgI_{(s)} + e^-$, E° = 0.152V
$Ag_{(s)} \rightarrow Ag^+_{(aq)} + e^-$, E° = – 0.800 V
What is the value of log K_{sp} for AgI ?
(Where K_{sp}= solubility product)
$\left(2.303\frac{RT}{F} = 0.059V\right)$
(A) –8.12 (B) +8.612 (C) –37.83 (D) –16.13

E-3. A silver wire dipped in 0.1 M HCl solution saturated with AgCl develops oxidation potential of –0.209 V. If E°_{Ag/Ag^+} = – 0.799 V, the K_{sp} of AgCl in pure water will be
(A) 3×10^{-11} (B) 10^{-11}
(C) 4×10^{-11} (D) 3×10^{-11}

E-4. If K_{sp} values of AgCl, AgBr & AgI at 298 K are 10^{-10}, 10^{-13} & 10^{-17} respectively,
Compare $E^o_{Cl^-/AgCl/Ag}$, $E^o_{Br^-/AgBr/Ag}$ & $E^o_{I^-/AgBr/Ag}$:
(A) $E^o_{Cl^-/AgCl/Ag}$ will have the least value and its value will be less than $E^o_{Ag^+/Ag}$
(B) $E^o_{I^-/AgBr/Ag}$ will have the least value and its value will be more than $E^o_{Ag^+/Ag}$
(C) $E^o_{Cl^-/AgCl/Ag}$ will have the least value and its value will be more than $E^o_{Ag^+/Ag}$
(D) $E^o_{I^-/AgBr/Ag}$ will have the least value and its value will be less than $E^o_{Ag^+/Ag}$

Section (F) : Thermodynamics of Cell potential

F-1. $\Delta G = \Delta H - T\Delta S$ and $\Delta G = \Delta H + T\left[\frac{d(\Delta G)}{dT}\right]_p$ then $\left(\frac{dEcell}{dT}\right)$ is :

(A) $\frac{\Delta S}{nF}$ (B) $\frac{nE}{\Delta S}$ (C) $-nFE^{cell}$ (D) $+nEF_{cell}$

F-2. The standard emf of the cell, Cd(s) $|CdCl_2(aq)\ (0.1\ M)||AgCl(s)|$ Ag(s) in which the cell reaction is, $Cd(s) + 2AgCl(s) \longrightarrow 2Ag(s) + Cd^{+2}(aq) + 2Cl^{-}(aq)$ is 0.6915 V at 0°C and 0.6753 V at 25°C. The ΔH^{o} of the reaction at 25°C is :

(A) – 176 kJ (B) – 234.7 kJ (C) + 123.5 kJ (D) – 167.26 kJ

F-3. The potential of the Daniell cell, Zn $\left|\begin{matrix}ZnSO_4\\(1M)\end{matrix}\right|\left|\begin{matrix}CuSO_4\\(1M)\end{matrix}\right|$ Cu was reported by Buckbee, Surdzial and Metz as $E° = 1.1028 - 0.641 \times 10^{-3}\,T + 0.72 \times 10^{-5}\,T^2$, where T is the temperature in degree celsius. Calculate $\Delta S°$ for the cell reaction at 25°C : (EU – Entropy unit)

(A) – 45.32 EU (B) – 34.52 EU (C) – 25.43 EU (D) – 54.23 EU

Section (G) : Electrolysis

G-1. The products formed when an aqueous solution of NaBr is electrolyzed in a cell having inert electrodes are :

(A) Na and Br_2 (B) Na and O_2 (C) H_2, Br_2 and NaOH (D) H_2 and O_2

G-2. In an electrolytic cell of $Ag/AgNO_3/Ag$, when current is passed, the concentration of $AgNO_3$

(A) Increases (B) Decreases (C) Remains same (D) None of these

G-3. The two aqueous solutions, A ($AgNO_3$) and B (LiCl) were electrolysed using Pt electrodes. The pH of the resulting solutions will

(A) increase in A and decrease in B (B) decrease in both

(C) increase in both (D) decrease in A and increase in B.

G-4. During electrolysis of $CuSO_4$ using Pt-electrodes, the pH of solution

(A) increases (B) decreases (C) remains unchanged (D) cannot be predicted

G-5. In the electrolysis of aqueous $CuBr_2$ using Pt electrodes :

(A) Br_2 gas is not evolved at the anode

(B) Cu (s) is deposited at the cathode

(C) Br_2 gas is evolved at anode and H_2 gas at cathode

(D) H_2 gas is evolved at anode.

Section (H) : Faraday laws & its Applictions

H-1. If 0.224 L of H_2 gas is formed at the cathode, the volume of O_2 gas formed at the anode under identical conditions, is

(A) 0.224 L (B) 0.448 L (C) 0.112 L (D) 1.12 L

H-2. Number of electrons involved in the electrodeposition of 63.5 g of Cu from a solution of $CuSO_4$ is : ($N_A = 6 \times 10^{23}$)

(A) 6×10^{23} (B) 3×10^{23} (C) 12×10^{23} (D) 6×10^{22}

H-3. How many faradays are required to reduce one mol of MnO_4^{-} to Mn^{2+} -

(A) 1 (B) 2 (C) 3 (D) 5

H-4. Three faradays of electricity was passed through an aqueous solution of iron (II) bromide. The mass of iron metal (at. mass 56) deposited at the cathode is -

(A) 56 g (B) 84 g (C) 112 g (D) 168 g

H-5. A current of 9.65 ampere is passed through the aqueous solution NaCl using suitable electrodes for 1000 s. The amount of NaOH formed during electrolysis is

(A) 2.0 g (B) 4.0 g (C) 6.0 g (D) 8.0 g

Section (I) : Commercial Cells & Corrosion

I-1. Which is not correct method for prevention of iron from Rusting -

(A) Galvanisation (B) Connecting to sacrificial electrode of Mg
(C) Making medium alkaline (D) Making medium acidic

I-2. During discharge of a lead storage cell the density of sulphuric acid in the cell :

(A) Increasing (B) decreasing
(C) remians unchanged (D) initially increases but decrease subsequently

I-3. Correct combination for Mercury cell is -

	Anode	**Cathode**
(A)	Paste of HgO	Zn-Hg Amalgam
(B)	Zn-Hg Amalgam	Paste of HgO
(C)	Mercury	Graphite
(D)	Graphite	Mercury

Section (J) : Electrical Conductance

J-1. Electrolytic conduction differs from metallic conduction from the fact that in the former

(A) The resistance increases with increasing temperature
(B) The resistance decreases with increasing temperature
(C) The resistance remains constant with increasing temperature
(D) The resistance is independent of the length of the conductor

J-2. If x is specific resistance of the electrolyte solution and y is the molarity of the solution, then Λ_m is given by

(A) $\frac{1000\,x}{y}$ (B) $1000\,\frac{y}{x}$ (C) $\frac{1000}{xy}$ (D) $\frac{xy}{1000}$

J-3. Resistance of decimolar solution is 50 ohm. If electrodes of surface area 0.0004 m^2 each are placed at a distance of 0.02 m then conductivity of solution is :

(A) 1 s cm^{-} (B) 0.01 s cm^{-} (C) 0.001 s cm^{-} (D) 10 s cm^{-}

J-4. Which of the following solution of KCl has the lowest value of specific conductance :

(A) 1 M (B) 0.1 M (C) 0.01 M (D) 0.001 M

J-5. The resistance of 0.1 N solution of a acetic acid is 250 ohm. When measured in a cell of cell constant 1.15 cm^{-1}. The equivalent conductance (in $ohm^{-1}\,cm^2\,equiv.^{-1}$) of 0.1 N acetic acid is

(A) 46 (B) 9.2 (C) 18.4 (D) 0.023

Section (K) : Kohlrausch law and its applications

K-1. The molar conductance at infinite dilution of $AgNO_3$, AgCl and NaCl are 115, 120 and 110 respectively. The molar conductance of $NaNO_3$ is :–

(A) 110 (B) 105 (C) 130 (D) 150

K-2. The ionization constant of a weak electrolyte (HA) is 25×10^{-6} while the equivalent conductance of its 0.01 M solution is 19.6 S cm^2 eq^{-1}. The equivalent conductance of the electrolyte at infinite dilution (in S cm^2 eq^{-1}) will be

(A) 250 (B) 196 (C) 392 (D) 384

K-3. The conductivity of a saturated solution of $BaSO_4$ is 3.06×10^{-6} ohm^{-1} cm^{-1} and its equivalent conductance is 1.53 ohm^{-1} cm^2 $equiv^{-1}$. The K_{sp} for $BaSO_4$ will be

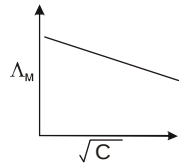
(A) 4×10^{-12} (B) 2.5×10^{-13}

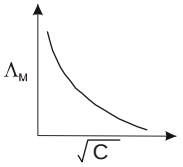
(C) 25×10^{-9} (D) 10^{-6}

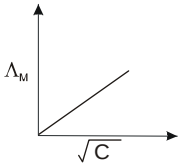
K-4. Molar conductances of $BaCl_2$, H_2SO_4 and HCl at infinite dilutions are x_1, x_2 and x_3, respectively. Equivalent conductance of $BaSO_4$ at infinite dilution will be :

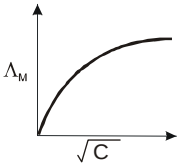
(A) $\frac{[x_1 + x_2 - x_3]}{2}$ (B) $\frac{[x_1 - x_2 - x_3]}{2}$ (C) $2\,(x_1 + x_2 - 2x_3)$ (D) $\frac{[x_1 + x_2 - 2x_3]}{2}$

K-5. Which of the following curve represents the variation of Λ_M with $\sqrt{C}$ for $AgNO_3$?

(A) 

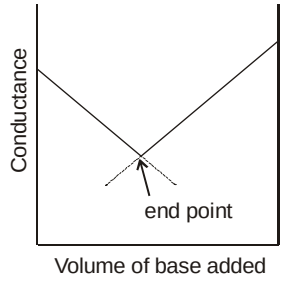
(B) 

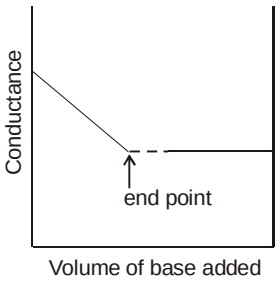
(C) 

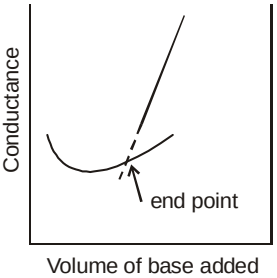
(D) 

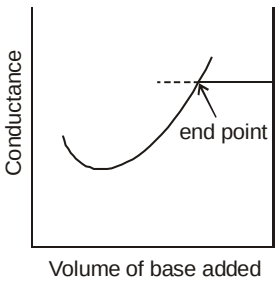
Section (L) : Conductometric Titration

L-3. Conductance measurements can be used to detect the end point of acid-base titrations. Which of the following plots correctly represent the end point of the titration of strong acid and a strong base ?

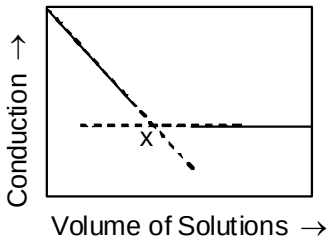
(A) 

(B) 

(C) 

(D) 

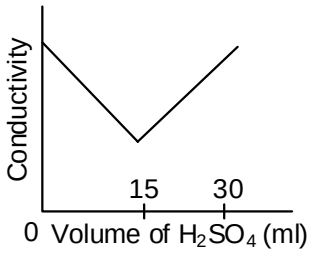
L-2. Following curve for conductometric titration is obtained when –



x = Equivalence point

(A) NaOH solution is added in to HCl solution
(B) NaOH solution is added in to CH_3COOH solution
(C) NH_4OH solution is added in to HCl solution
(D) NH_4OH solution is added in to CH_3COOH solution

L-3. 20 ml KOH solution was titrated with 0.2 mol/l H_2SO_4 solution in conductivity cell



Concentration of KOH solution was –
(A) 0.3 M (B) 0.15 (C) 0.12 (D) None of these

PART - III : MATCH THE COLUMN

1.

Column I	**Column II** **(Major Electrolysis product using inert electrode)**
(A) Dilute solution of HCl	(P) O_2 evolved at anode
(B) Dilute solution of Na_2SO_4	(Q) H_2 evolved at cathode
(C) Concentrated solution of NaCl	(R) Cl_2 evolved at anode
(D) $AgNO_3$ solution	(S) Ag deposition at cathode

2. Match Matrix ($E^0_{Ag^+/Ag}$ = 0.8).

Column – I	**Column – II**
(A) Pt | H_2 (0.1 bar) | HCl (0.1 M) || H^+ (1 M) | H_2 (0.01 bar) | Pt	(p) Concentration cell
(B) Ag | Ag^+ (10^{-9} M) || Ag^+ (10^{-2} M) | Ag	(q) $E_{cell} > 0$
(C) Zn | Zn^{2+} (0.1 M) || Zn^{2+} (0.01 M) | Zn	(r) $E^o_{cell} = 0$ but cell is working.
(D) Pt | Cl_2 (1bar) | HCl (0.1 M) || NaCl (0.1M) | Cl_2 | Pt (1 bar)	(s) non working condition

Exercise # 2

PART - I : OBJECTIVE QUESTIONS

1. From the following E° values of half cells,

(i) $A + e \rightarrow A^{-}$; E° = –0.24 V (ii) $B^{-} + e \rightarrow B^{2-}$; E° = +1.25 V

(iii) $C^{-} + 2e \rightarrow C^{3-}$; E° = –1.25 V (iv) $D + 2e \rightarrow D^{2-}$; E° = +0.68 V

What combination of two half cells would result in a cell with the largest potential ?

(A) (ii) & (iii) (B) (ii) & (iv) (C) (i) & (iii) (D) (i) & (iv)

2. A hydrogen electrode placed in a buffer solution of CH_3COONa and CH_3COOH in the ratios of x : y and y : x has electrode potential values E_1 volts and E_2 volts, respectively at 25ºC. The pK_a values of acetic acid is (E_1 and E_2 are oxidation potentials)

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

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

3. What is the emf at 25° C for the cell, $Ag \left| \begin{matrix} AgBr(s), Br^{-} \\ c = 0.34M \end{matrix} \right\| \left| \begin{matrix} Fe^{3+} , Fe^{2+} \\ c = 0.1M \; c = 0.02M \end{matrix} \right| Pt$

The standard reduction potentials for the half-reactions $AgBr + e^{-} \rightarrow Ag + Br^{-}$ and $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$ are + 0.0713 V and + 0.770 V respectively.

(A) 0.474 volt (B) 0.529 volt

(C) 0.356 volt (D) 0.713 volt

4. Which of the following will increase the voltage of the cell with following cell reaction

$Sn_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Sn^{+2}_{(aq)} + 2Ag_{(s)}$

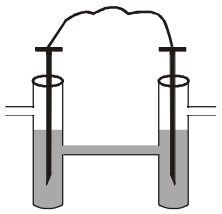
(A) Decrease in the concentration of Ag^{+} ions (B) Increase in the concentration of Sn^{+2} ions

(C) Increase in the concentration of Ag^{+} ions (D) (A) & (B) both

5. During the preparation of $H_2S_2O_8$ (per disulphuric acid) O_2 gas also releases at anode as byproduct, When 9.72 L of H_2 releases at cathode and 2.35 L O_2 at anode at 1 atm and 0ºC, the weight of $H_2S_2O_8$ produced in gram is

(A) 87.12 (B) 43.56 (C) 83.42 (D) 51.74

6. Two weak acid solutions HA_1 and HA_2 each with the same concentration and having pK_a values 3 and 5 are placed in contact with hydrogen electrode (1 atm, 25ºC) and are interconnected through a salt bridge. The emf of the cell is :



(A) 0.21 V (B) 0.059 V (C) 0.018 V (D) 0.021 V

7. When the sample of copper with zinc impurity is to be purified by electolysis, the appropriate electrode are
(A) pure zinc as cathode and pure copper as anode
(B) impure sample as cathode and pure copper as anode
(C) impure zinc as cathode and impure sample as anode
(D) pure copper as cathode and impure sample as anode

8. What is the potential of the cell containing two hydrogen electrodes as represented below

$Pt \mid H_2(g) \mid H^+_{(aq)}(10^{-8}\ M) \parallel H^+_{(aq)}(0.001\ M) \mid H_2(g) \mid Pt$

(A) – 0.295 V (B) – 0.0591 V (C) 0.295 V (D) 0.0591 V

9. Which statement is correct.
(A) In SHE, the pressure of dihydrogen gas should be low and pH of solution should be zero.
(B) In the reaction $H_2O_2 + O_3 \longrightarrow 2H_2O + 2O_2$, H_2O_2 is oxidised to H_2O.
(C) The absolute value of electrode potential cannot be determined.
(D) According to IUPAC conventions, the standard electrode potential pertains to oxidation reactions only.

10. When iron is rusted, it is :
(A) reduced (B) oxidised (C) evaporated (D) decomposed

11. Using the standard potential values given below, decide which of the statements I, II, III, IV are correct. Choose the right answer from (a), (b), (c) and (d)

$Fe^{2+} + 2e^- = Fe, \quad E^o = -0.44\ V$

$Cu^{2+} + 2e^- = Cu, \quad E^o = +0.34\ V$

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

I. Copper can displace iron from $FeSO_4$ solution
II. Iron can displace copper from $CuSO_4$ solution
III. Silver can displace Cu from $CuSO_4$ solution
IV. Iron can displace silver from $AgNO_3$ solution
(A) I and II (B) II and III (C) II and IV (D) I and IV

12. When the electric current is passed through a cell having an electrolyte, the positive ions move towards cathode and negative ions towards the anode. If the cathode is pulled out of the solution
(A) the positive and negative ions will move towards anode
(B) the positive ions will start moving towards the anode while negative ions will stop moving
(C) the negative ions will continue to move towards anode while positive ions will stop moving
(D) the positive and negative ions will start moving randomly

13. Four moles of electrons were transferred from anode to cathode in an experiment on electrolysis of water. The total volume of the two gases (dry and at 1atm, 0°C) produced will be approximately (in litres)
(A) 22.4 (B) 44.8 (C) 67.2 (D) 89.4

14. The following facts are available :–

$2X^- + Y_2 \rightarrow 2Y^- + X_2$

$2W^- + Y_2 \rightarrow$ NO reaction

$2Z^- + X_2 \rightarrow 2X^- + Z_2$

Which of the following statements is correct :–

(A) $E^\circ_{W^-/W_2} > E^\circ_{Y^-/Y_2} > E^\circ_{X^-/X_2} > E^\circ_{Z^-/Z_2}$

(B) $E^\circ_{W^-/W_2} < E^\circ_{Y^-/Y_2} < E^\circ_{X^-/X_2} < E^\circ_{Z^-/Z_2}$

(C) $E^\circ_{W^-/W_2} < E^\circ_{Y^-/Y_2} > E^\circ_{X^-/X_2} > E^\circ_{Z^-/Z_2}$

(D) $E^\circ_{W^-/W_2} > E^\circ_{Y^-/Y_2} < E^\circ_{X^-/X_2} < E^\circ_{Z^-/Z_2}$

PART - II : NUMERICAL TYPE QUESTIONS

1. How many of the following comparisons are correct with respect to their Λ_m^∞ ?

(A) $K^+ > Na^+$ (B) $K^+ > H_3O^+$ (C) $Ca^{2+} > Na^+$

(D) $Mg^{2+} > NH_4^+$ (E) $H_3O^+ > Mg^{2+}$ (F) $K^+ > Mg^{2+}$

2. The conductivity of a solution which is 10^{-4} M in $Ba(NO_3)_2$ and 2×10^{-4} M in $AgNO_3$ is 5.3×10^{-3} Sm^{-1}. If $\lambda^o_{(Ag^+)} = 6 \times 10^{-3}$ Sm^2 mol^{-1} & $\lambda^o_{(Ba^{2+})} = 13 \times 10^{-3}$ Sm^2 mol^{-1}, determine $\lambda^o_{(NO_3^-)}$ in same unit. Report your answer after multiplying by 1000.

3. The standard reduction potential of Cu^{2+} / Cu couple is 0.34 V at 25°C. Calculate the reduction potential at pH = 14 for this couple.
(Given : K_{sp}, $Cu(OH)_2 = 1.0 \times 10^{-19}$).

4.

$H_4XeO_6 + 2H^+ + 2e^- \longrightarrow XeO_3 + 3H_2O$	E^o = 3 V
$F_2 + 2e^- \longrightarrow 2F^-$	E^o = 2.87 V
$O_3 + 2H^+ + 2e^- \longrightarrow O_2 + H_2O$	E^o = 2.07 V
$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	E^o = 1.67 V
$2HClO + 2H^+ + 2e^- \longrightarrow Cl_2 + 2H_2O$	E^o = 1.63 V
$ClO_4^- + 2H^+ + 2e^- \longrightarrow ClO_3^- + H_2O$	E^o = 1.23 V
$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^-$	E^o = 0.89 V
$BrO^- + H_2O + 2e^- \longrightarrow Br^- + 2OH^-$	E^o = 0.76 V
$ClO_4^- + H_2O + 2e^- \longrightarrow ClO_3^- + 2OH^-$	E^o = 0.36 V
$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$	E^o = 0.36 V

Based on the above data, how many of the following statements are correct ?

(A) F_2 is better oxidizing agent than H_4XeO_6.

(B) Ozone can oxidize Cl_2

(C) ClO_4^- is better oxidizing agent in basic medium than in acidic medium

(D) Ferrocyanide ion can be easily oxidized by ClO^-, Ce^{4+}, Li^+, BrO^-

(E) ClO^- can oxidize Br^- and ClO_3^- in basic medium

(F) Ce^{4+} can oxidize Cl_2 in acidic medium under standard conditions.

5. Estimate the cell potential of a Daniel cell having 1.0M Zn^{++} and originally having 1.0M Cu^{++} after sufficient NH_3 has been added to the cathode compartment to make NH_3 concentration 2.0M at equilibrium. Given K_f for $[Cu(NH_3)_4]^{2+} = 1 \times 10^{12}$, E° for the reaction, $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ 1.1V. (Take $\frac{2.303RT}{F}$ = 0.06, log 6.25 = 0.8) Respond as 10 × your answer.

6. $NO_3^- \longrightarrow NO_2$ (acid medium), $E^0 = 0.790$ V

$NO_3^- \longrightarrow NH_3OH^+$ (acid medium), $E^0 = 0.731$ V.
At what pH, the above two will have same E value? Assume the concentration of all other species NH_3OH^+ except $[H^+]$ to be unity.

7. The emf of the cell Ag(s)|AgI(s)|KI(0.05M) || $AgNO_3$(0.05M) |Ag(s) is 0.788V. Calculate the solubility product of AgI.

8. Molar conductivity of 0.04 M $MgCl_2$ solution at 298 k is 200 Scm^2mole^{-1}. A conductivity cell which is filled with $MgCl_2$ have area of cross-section of electrode $4cm^2$ & distance between electrode is 8 cm. If potential difference between electrode is 10V then find current flow in miliampere.

9. Hydrofluoric acid is weak acid. At 25°C, the molar conductivity of 0.002M HF is 200 ohm^{-1} cm^2 $mole^{-1}$. If its Λ_m^∞ = 400 ohm^{-1} cm^2 $mole^{-1}$, calculate its degree of dissociation and equilibrium constant at the given concentration.

10. The standard reduction potential values, E^o (Bi^{3+} / Bi) and E^o (Cu^{2+}/Cu) are 0.226V and 0.344V respectively. A mixture of salts of bismuth and copper at unit concentration each is electrolysed at 25°C. To what value can $[Cu^{2+}]$ be brought down before bismuth starts to deposit, in electrolysis.

11. A hydrogen gas electrode is made by dipping platinum wire in a solution of NaOH of pH = 10 and by passing hydrogen gas around the platinum wire at one atm pressure. The oxidation potential of electrode is 10x milivolt. Find x ? (Take $\frac{2.303\ RT}{F}$ = 0.059)

12. Calculate the emf of the cell in mV

$$Ag\ (s)\ \Big|\ AgIO_3\ (s)\ \Big|\ Ag^+(xM), HIO_3\ (1M)\ \Big|\ \Big|\ Zn^{+2}(1M)\ \Big|\ Zn(s)$$

If $K_{sp} = 3 \times 10^{-8}$ for $AgIO_3$ and $K_a = \frac{1}{6}$ for HIO_3 and E^0_{cell} for $2Ag + Zn^{+2} \longrightarrow 2Ag^+ + Zn$ is – 1.56 V.

(log 3 = 0.48) (Take $\frac{2.303RT}{F}$ = 0.06) (Write magnitude of first two digits of your answer)

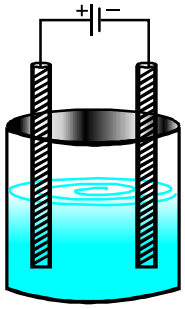
13. A fuel cell uses $CH_4(g)$ and forms CO_3^{2-} at the anode. It is used to power a car with 80 Amp. for 0.96 hr. How many litres of $CH_4(g)$ (at 1 atm, 0ºC) would be required ? (V_m = 22.4 L/mol) (F = 96500). Assume 100% efficiency.

14. Cd amalgam is prepared by electrolysis of a solution of $CdCl_2$ using a mercury cathode. How long should a current of 5A be passed in order to prepare 12% Cd-Hg amalgam when 2 g Hg is used as cathode (atomic weight of Cd = 112.4)

15. Find the volume of gases evolved by passing 0.965 A current for 1 hr through an aqueous solution of CH_3COONa at 25^0C and 1 atm.

PART - III : ONE OR MORE THAN ONE CORRECT OPTIONS

1. Consider an electrolytic cell E being powered by a galvenic cell G, as shown in the figure. Then :



(A) Anode of E is connected to cathode of G
(B) Anode of E is connected to anode of G
(C) Cathode of E is connected to anode of G
(D) Cathode of E is connected to cathode of G

2. Given $E^{\circ}_{Ag^{+}/Ag}$ = 0.80V, $E^{\circ}_{Mg^{2+}/Mg}$ = –2.37V, $E^{\circ}_{Cu^{2+}/Cu}$ = 0.34V, $E^{\circ}_{Hg^{2+}/Hg}$ = 0.79 V.

Which of the following statements is/are correct
(A) $AgNO_3$ can be stored in copper vessel
(B) $Mg(NO_3)_2$ can be stored in copper vessel
(C) $CuCl_2$ can be stored in silver vessel
(D) $HgCl_2$ can be stored in copper vessel

3. Pick out the correct statements among the following from inspection of standard reduction potentials (Assume standard state conditions).

$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$ $E^{o}_{Cl_2/Cl^-}$ = + 1.36 volt

$Br_2(\ell) + 2e^- \longrightarrow 2Br^-(aq)$ $E^{o}_{Br_2/Br^-}$ = + 1.09 volt

$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$ $E^{o}_{I_2/I^-}$ = + 0.54 volt

$S_2O_8^{2-}(aq) + 2e^- \longrightarrow 2SO_4^{2-}(aq)$ $E^{o}_{S_2O_8^{2-}/SO_4^{2-}}$ = + 2.00 volt

(A) Cl_2 can oxidise SO_4^{2-} from solution
(B) Cl_2 can oxidise Br^- and I^- from aqueous solution
(C) $S_2O_8^{2-}$ can oxidise Cl^-, Br^- and I^- from aqueous solution
(D) $S_2O_8^{2-}$ is added slowly, Br^- can be reduce in presence of Cl^-

4. The EMF of the following cell is 0.22 volt.
Ag(s) | AgCl(s) | KCl (1M) | H^+(1M) | H_2(g) (1atm) ; Pt(s).
Which of the following will decrease the EMF of cell.
(A) increasing pressure of H_2(g) from 1 atm to 2 atm
(B) increasing Cl^- concentration in Anodic compartment
(C) increasing H^+ concentration in cathodic compartment
(D) decreasing KCl concentration in Anodic compartment.

5. Which of the following arrangement will produce oxygen at anode during electrolysis ?
(A) Dilute H_2SO_4 solution with Cu electrodes.
(B) Dilute H_2SO_4 solution with inert electrodes.
(C) Fused NaOH with inert electrodes.
(D) Dilute NaCl solution with inert electrodes.

6. A current of 2.68 A is passed for one hour through an aqueous solution of $CuSO_4$ using copper electrodes. Select the correct statement(s) from the following :
(A) increase in mass of cathode = 3.174 g
(B) decrease in mass of anode = 3.174 g
(C) no change in masses of electrodes
(D) the ratio between the change of masses of cathode and anode is 1 : 2 .

7. Three moles of electrons are passed through three solutions in succession containing $AgNO_3$, $CuSO_4$, and $AuCl_3$, respectively. The molar ratio of amounts of cations reduced at cathode will be

(A) 1 : 2 : 3 (B) $\frac{1}{1} : \frac{1}{2} : \frac{1}{3}$ (C) 3 : 2 : 1 (D) 6 : 3 : 2

8. Mark out the correct statement(s) regarding electrolytic molar conductivity.
(A) It increase as temperature increases.
(B) It experiences resistance due to vibration of ion at the mean position.
(C) Increase in concentration decreases the electrolytic molar conductivity of both the strong as well as the weak electrolyte.
(D) Greater the polarity of solvent, greater is the electrolytic molar conduction.

9. If same quantity of electricity is passed through three electrolytic cells containing $FeSO_4$, $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$, then
(A) the amount of iron deposited in $FeSO_4$ and $Fe_2(SO_4)_3$ are equal
(B) the amount of iron deposited in $FeSO_4$ is 1.5 times of the amount of iron deposited in $Fe(NO_3)_3$.
(C) the amount of iron deposited in $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$ are equal
(D) the same amount of gas is evolved in all three cases at the anode.

10. During discharging of lead storage battery, which of the following is|are true ?
(A) H_2SO_4 is produced (B) H_2O is consumed
(C) $PbSO_4$ is formed at both electrodes (D) Density of electrolytic solution decreases

11. The resistances of following solutions of KCl were measured using conductivity cells of different cell con stants, at same temperature. (Consider that at concentration less than 0.1 M, the specific conductivity of solution is directly proportional to the concentration of solution.)

	Concentration of Solution	**Cell Constant**
1.	0.1 M	1 cm^{-1}
2.	0.01 M	10 cm^{-1}
3.	0.005 M	5 cm^{-1}
4.	0.0025 M	25 cm^{-1}

Which of the following comparisons between their conductances (G) is/are correct ?
(A) G_1 is maximum (B) G_4 is minimum (C) $G_3 >> G_2$ (D) G_4 is maximum

12. Identify correct statements :
(A) Kohlraush law is applicable only on weak electrolyte.
(B) On increasing dilution conductance, molar conductivity, equivalent conductivity increases but conductiv ity decreases.

(C) $\Lambda_m = \frac{K}{C}$ following formula has units $\Lambda_m : \Omega^{-} dm^2/mol$ K : $\Omega^{-} dm^{-1}$ C : mol/ℓ

(D) equation $\Lambda_m = \Lambda_m^{\infty} - b\sqrt{C}$ is applicable on weak as well as strong electrolyte.

13. Select the correct option(s):

(A) $\frac{\lambda^{\circ}_{eq\ (Al^{3+})}}{3} = \lambda^{\circ}_{m}\left(Al^{3+}\right)$ & $\frac{\lambda^{\circ}_{eq\ (SO_4^{2-})}}{2} = \lambda^{\circ}_{m\ (SO_4^{2-})}$

(B) $\lambda^{\circ}_{eq\ (Al^{3+})} = \frac{\lambda^{\circ}_{m\ (Al^{3+})}}{3}$ & $\lambda^{\circ}_{eq\ (SO_4^{2-})} = \frac{\lambda^{\circ}_{m\ (SO_4^{2-})}}{2}$

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

(D) $\lambda^{\circ}_{m\ Al_2(SO_4)_3} = 6 \times \lambda^{\circ}_{eq\ Al_2(SO_4)_3}$

14. For strong electrolyte Λ_M increases slow with dilution and can be represented by the equation

$\wedge_M = \wedge_M^o - AC^{½}$

Select correct statement

(A) Plot of $\wedge_M$ against $C^{½}$ is obtain a straight line with intercept $\wedge_M^o$ & and slope '–A'

(B) Value of A depends upon temperature solvent and nature of electrolyte.

(C) NaCl and KCl have different value of constant 'A'

(D) NaCl and $MgSO_4$ have different value of constant 'A'

15. If 270.0 g of water is electrolysed during an experiment performed by a student with 75% current efficiency then

(A) 168 L of O_2 (g) will be evolved at anode at 1 atm & 273 K

(B) Total 504 L gases will be produced at 1 atm & 273 K.

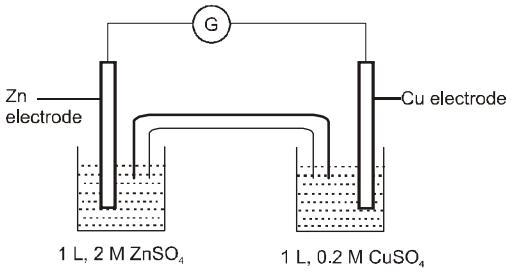
(C) 336 L of H_2 (g) will be evolved at anode at 1 atm & 273 K

(D) 45 F electricity will be consumed

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1



Given $E^{\circ}_{Zn^{+2}|Zn} = -0.76$ V $K_f\ [Cu(NH_3)_4]^{+2} = 4 \times 10^{11}$

$E^{\circ}_{Cu^{+2}|Cu} = 0.34$ V

Answer the following.

1. The emf of cell at 200 k is [Given : $\frac{2.303 \times R}{F} = 2 \times 10^{-4}$ and assume that E^0 values are independent on temperature.]

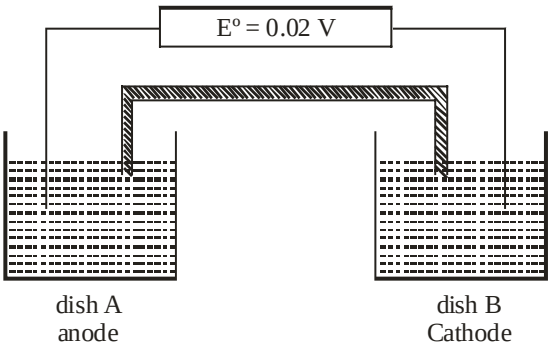
(A) 1.7 V (B) 1.08 V (C) 1.09 V (D) 1.10 V

2. When 1 mole NH_3 added to cathode compartment than emf of cell is (at 298K)
(A) 0.81 V (B) 1.91 V (C) 1.1 V (D) 0.72 V

3. At what conc of Cu^{+2} emf of the cell will be zero (at 298K) and conc. of Zn^{+2} is remain same
(A) 1.19×10^{-37} (B) 1.19×10^{-20} (C) 3.78×10^{-4} (D) 0.0068

Comprehension # 2

The cell potential for the balanced chemical reaction :
$Hg_2^{2+}(aq) + NO_3^-(aq) + 3H_3O^+(aq) \rightarrow 2Hg^{2+}(aq) + HNO_2(aq) + 4H_2O(\ell)$
is measured under standard conditions in the electrochemical cell shown in the accompanying diagram



4. In which dish, the solution is acidic ?
(A) Dish A (B) Dish B (C) Both (D) None

5. How many moles of electrons pass through the circuit when 0.60 mole of Hg^{2+} and 0.30 mole of HNO_2 are produced in the cell that contains 0.50 mole of Hg_2^{2+} and 0.40 mole of NO_3^- at the beginning of the reactions?
(A) 0.30 (B) 0.60 (C) 0.15 (D) 1.20

6. How long will it take to produce 0.10 mole of HNO_2 by the reaction if a current of 10 A passes through the cell ?
(A) 965 s (B) 193 s (C) 1930 s (D) 482.5 s

Comprehension # 3

Answer Q. 7 to Q.9 by appropriately matching the information given in the three columns of the following table.

The curves in Column-1 shows the variation of conductivity during different titrations. The analyte and titrants has been listed in Column 2 and column 3 respectively

(**Given** Titrate : Solution consisting of substance to be estimated, it is generally taken in a beaker.
Titrant : It is a solution whose concentration is known and is taken in burette.)

Column-1		**Column-2 (Titrate)**		**Column-3(Titrant)**	
(I)	Conductivity decreases initially then increases slowly then increases rapidly	(i)	$(C_2H_5)_2NH$	(P)	HCl
(II)	Conductivity decreases initially then increases	(ii)	CH_3COOH	(Q)	NaOH
(III)	Conductivity decreases initially then remains approximately same	(iii)	HBr	(R)	CH_3COOH
(IV)	Conductivity increases initially then remains approximately same	(iv)	NaOH	(S)	NH_4OH

7. Which of the followin is an incorrect conbination of curves jn column-1.
(A) (II) (iii) (Q) (B) (I) (i) (P) (C) (I) (iii) (S) (D) (I) (ii) (Q)

8. The correct combination for the titration in which conductance at equivalent point is lower than initial
(A) (I) (ii) (Q) (B) (I) (iii) (S) (C) (III) (iv) (R) (D) (IV) (ii) (S)

9. Select the correct combination
(A) (I) (iii) (Q) (B) (IV) (ii) (S) (C) (I) (iii) (S) (D) (I) (iv) (R)

Exercise # 3

PART - I : JEE ADVANCE PROBLEMS (PREVIOUS YEARS)

1. For the reduction of NO_3^- ion in an aqueous solution, E^o is +0.96 V. Values of E^o for some metal ions are given below :

$V^{2+}(aq) + 2e^- \longrightarrow V$ $\quad E^o = -1.19$ V

$Fe^{3+}(aq) + 3e^- \longrightarrow Fe$ $\quad E^o = -0.04$ V

$Au^{3+}(aq) + 3e^- \longrightarrow Au$ $\quad E^o = +1.40$ V

$Hg^{2+}(aq) + 2e^- \longrightarrow Hg$ $\quad E^o = +0.86$ V

The pair(s) of metals that is(are) oxidized by NO_3^- in aqueous solution is(are) : **[JEE 2009, 4/160]**

(A) V and Hg (B) Hg and Fe

(C) Fe and Au (D) Fe and V

Comprehension # 1

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is :

$M(s) \mid M^+(aq ; 0.05 \text{ molar}) \parallel M^+(aq ; 1 \text{ molar}) \mid M(s)$

For the above electrolytic cell, the magnitude of the cell potential is $|E_{cell}| = 70$ mV.

Now answer the following two questions :

2. For the above cell : **[JEE 2010, 3/163]**

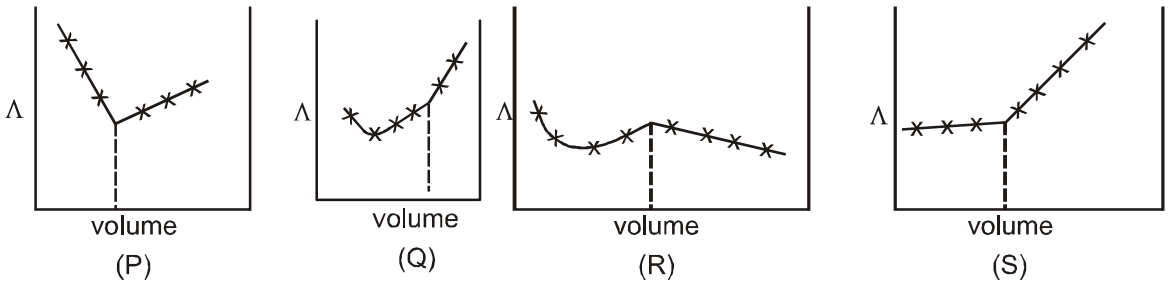
(A) $E_{cell} < 0 ; \Delta G > 0$ (B) $E_{cell} > 0 ; \Delta G < 0$

(C) $E_{cell} < 0 ; \Delta G^o > 0$ (D) $E_{cell} > 0 ; \Delta G^o < 0$

3. If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitude of the cell potential would be : **[JEE 2010, 3/163]**

(A) 35 mV (B) 70 mV (C) 140 mV (D) 700 mV

4. $AgNO_3$(aq.) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) versus the volume of $AgNO_3$ is : **[JEE 2011, 3/180]**



(A) (P) (B) Q (C) (R) (D) (S)

5. Consider the following cell reaction : **[JEE 2011, 3/180]**

$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$ $\quad E^o = 1.67$ V

At $[Fe^{2+}] = 10^{-3}$ M, $P(O_2) = 0.1$ atm and pH = 3, the cell potential at 25°C is : (Take $\frac{2.303R(298)}{F} = 0.06$)

(A) 1.47 V (B) 1.77 V

(C) 1.87 V (D) 1.57 V

Comprehension # 2

The electrochemical cell shown below is a concentration cell.

$M|M^{2+}$ (saturated solution of a sparingly soluble salt,MX_2)|| M^{2+} (0.001 mol dm^{-3}) |M

The emf of the cell depends on the difference in concetration of M^{2+} ions at the two electrodes. The emf of the cell at 298 is 0.059 V

6. The solubility product (K_{sp} ; in $mol^3\ dm^{-9}$) of MX_2 at 298 K based on the information available in the given concentration cell is : (Take 2.303× R × 298/F = 0.059 V) **[IIT-JEE 2012, 3/66]**

(A) 1×10^{-15} (B) 4×10^{-15} (C) 1×10^{-12} (D) 4×10^{-12}

7. The value of ΔG (in kJ mol^{-1}) for the given cell is : (Take 1F = 96500 C mol^{-1}) **[IIT-JEE 2012, 3/136]**

(A) – 5.7 (B) 5.7 (C) 11.4 (D) –11.4

8. An aqueous solution of **X** is added slowly to an aqueous solution of **Y** as shown in list I. The variation in conductivity of these reactions is given in List II. Match List I with List II and select the correct answer using the code given below the lists : **[JEE(Advanced) 2013, 3/120]**

	List I		**List II**
P.	$(C_2H_5)_3N$ + CH_3COOH (X Y)	1.	Conductivity decreases and then increases
Q.	KI (0.1M) + $AgNO_3$(0.01M) (X Y)	2.	Conductivity decreases and then does not change much
R.	CH_3COOH + KOH (X Y)	3.	Conductivity increases and then does not change much
S.	NaOH + HI (X Y)	4.	Conductivity does not change much and then increases

Codes :

	P	Q	R	S		P	Q	R	S
(A)	3	4	2	1	(B)	4	3	2	1
(C)	2	3	4	1	(D)	1	4	3	2

9. The standard reduction potential data at 25ºC is given below. **[JEE(Advanced) 2013, 3/120]**

$E^o\ (Fe^{3+}.Fe^{2+})$ = + 0.77 V ;

$E^o\ (Fe^{2+}.Fe)$ = – 0.44 V ;

$E^o\ (Cu^{2+}.Cu)$ = + 0.34 V ;

$E^o\ (Cu^{+}.Cu)$ = + 0.52 V ;

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

$E^o\ (O_2(g) + 2H_2O + 4e^- \rightarrow 4OH)$ = + 0.40 V

$E^o\ (Cr^{3+}.Cr)$ = – 0.74 V ;

$E^o\ (Cr^{2+}.Cr)$ = – 0.91 V

Match E^o of the rebox pair in List I with the values given in List II and select the correct answer using the code given below the lists :

	List I		**List II**
P.	$E^o\ (Fe^{3+}, Fe)$	1.	– 0.36 V
Q.	$E^o\ (4H_2O \rightleftharpoons 4H^+ + 4OH^-)$	2.	–0.4 V
R.	$E^o\ (Cu^{2+} + Cu \rightarrow 2Cu^+)$	3.	–0.04 V
S.	$E^o(Cr^{3+}, Cr^{+2})$	4.	–0.83 V

Codes :

	P	Q	R	S		P	Q	R	S
(A)	4	1	2	3	(B)	2	3	4	1
(C)	1	2	3	4	(D)	3	4	1	2

10. In a galvanic cell, the salt bridge **[JEE(Advanced) 2014, 3/120]**

(A) does not participate chemically in the cell reaction.
(B) stops the diffusion of ions from one electrode to another.
(C) is necessary for the occurrence of the cell reaction.
(D) ensures mixing of the two electrolytic solutions.

11. All the energy released from the reaction $X \rightarrow Y$, $\Delta_r G^o = -193$ kJ mol^{-1} is used for oxidizing M^+ as $M^+ \rightarrow M^{3+} + 2e^-$, $E^o = -0.25$ V.

Under standard conditions, the number of moles of M^+ oxidized when one mole of X is converted to Y is

[F = 96500 C mol^{-1}] **[JEE(Advanced) 2015, 4/168]**

12. The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\lambda^0_{X^-} \approx \lambda^0_{Y^-}$, the difference in their pK_a values, pK_a (HX) – pK_a (HY), is (consider degree of ionization of both acids to be <<1) **[JEE(Advanced) 2015, 4/168]**

13. For the following electrochemical cell at 298K, **[JEE-Adv. 2016]**

Pt(s) | H_2(g, 1bar) | H^+ (aq, 1M) || M^{4+}(a), M^{2+}(a) | Pt(s)

E_{cell} = 0.092 V when $\frac{[M^{2+}(aq.)]}{[M^{4+}(aq.)]} = 10^x$

Given : $E^0_{M^{4+}/M^{2+}}$ = 0.151V ; 2.303 $\frac{RT}{F} = 0.059\,V$

The value of x is -

(A) –2 (B) –1 (C) 1 (D) 2

14. The conductance of a 0.0015 M aqueous solution of a weak monobasic acid was determined by using a conductivity cell consisting of platinized Pt electrodes. The distance between the electrodes is 120 cm with an area of cross section of 1 cm^2. The conductance of this solution was found to be 5×10^{-7}S. The pH of the solution is 4. The value of limiting molar conductivity $\left(\Lambda^0_m\right)$ of this weak monobasic acid in aqueous solution is $Z \times 10^2$S $cm^{-1}mol^{-1}$. The value of Z is. **[JEE-Adv. 2017]**

15. For the following cell : **[JEE-Adv. 2017]**

Zn(s) | $ZnSO_4$ (aq.) || $CuSO_4$ (aq.) | Cu(s)

when the concentration of Zn^{2+} is 10 times the concentration of Cu^{2+}, the expression for ΔG (in J mol^{-1}) is

[F is Faraday constant , R is gas constant, T is temperature , E^o(cell) = 1.1V]

(A) 2.303 RT + 1.1F (B) 2.303 RT – 2.2F

(C) 1.1 F (D) –2.2 F

16. Consider an electrochemical cell: A(s) | A^{n+} (aq, 2M) || B^{2n+} (aq, 1M) | B(s). The value of ΔH^θ for the cell reaction is twice that of ΔG^θ at 300 K. If the emf of the cell is zero, the ΔS^θ (in JK^{-1} mol^{-1}) of the cell reaction per mole of B formed at 300 K is___. **[JEE-Adv. 2018]**

(Given : ln (2) = 0.7, R (universal gas constant) = 8.3 J K^{-1} mol^{-1}. H, S and G are enthalpy, entropy and Gibbs energy, respectively.)

17. For the electrochemical cell,

$Mg(s)|Mg^{2+}(aq, 1M)||Cu^{2+}(aq, 1M)|Cu(s)$

the standard emf of the cell is 2.70 V at 300 K. When the concentration of Mg^{2+} is changed to x M, the cell potential changes to 2.67 V at 300 K. The value of x is____. **[JEE-Adv. 2018]**

(Given, $\frac{F}{R}$ = 11500 KV^{-1}, where F is the Faraday constant and R is the gas constant, ln(10) = 2.30)

PART - II : JEE MAIN PROBLEMS (PREVIOUS YEARS)

1. Given: $E^0_{Fe^{3+}/Fe} = -0.036$ V, $E^0_{Fe^{2+}/Fe} = -0.439$ V **[AIEEE–2009, 8/144]**

The value of standard electrode potential for the change, $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$ will be :

(1) 0.385V (2) 0.770V (3) –0.270V (4) –0.072V

2. The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows : **[AIEEE–2010, 4/144]**

$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$; $\Delta_rG = +966$ kJmol^{-1}. The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least :

(1) 4.5 V (2) 3.0 V (3) 2.5 V (4) 5.0 V

3. The reduction potential of hydrogen half-cell will be negative, if : **[AIEEE–2011(1), 4/120]**

(1) $p(H_2)$ = 1 atm and $[H^+]$ = 2.0 M (2) $p(H_2)$ = 1 atm and $[H^+]$ = 1.0 M

(3) $p(H_2)$ = 2 atm and $[H^+]$ = 1.0 M (4) $p(H_2)$ = 2 atm and $[H^+]$ = 2.0 M

4. The standard reduction potentials for Zn^{2+}/Zn, Ni^{2+}/Ni and Fe^{2+}/Fe are –0.76, – 0.23 and –0.44 V respectively. The reaction $X + Y^{2+} \rightarrow X^{2+} + Y$ will be spontaneous, when : **[AIEEE 2012, 4/120]**

(1) X = Ni, Y = Fe (2) X = Ni, Y = Zn (3) X= Fe, Y = Zn (4) X= Zn, Y = Ni

5. Given: $E^0_{Cr^{3+}/Cr} = -0.74$ V ; $E^0_{MnO_4^-/Mn^{2+}} = 1.51$ V

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

Based on the data given above, strongest oxidising agent will be : **[JEE(Main) 2013, 4/120]**

(1) Cl (2) Cr^{3+} (3) Mn^{2+} (4) MnO_4^-

6. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.4 S m^{-1}. The resistance of 0.5 M solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in S m^2 mol^{-1} is : **[JEE(Main) 2014, 4/120]**

(1) 5×10^{-4} (2) 5×10^{-3} (3) 5×10^3 (4) 5×10^2

7. The equivalent conductance of NaCl at concentration C and at infinite dilution are Λ_C and Λ_∞, respectively. The correct relationship between Λ_C and Λ_∞ is given as : (where the constant B is positive) **[JEE(Main) 2014, 4/120]**

(1) $\Lambda_C = \Lambda_\infty + (B)C$ (2) $\Lambda_C = \Lambda_\infty - (B)C$ (3) $\Lambda_C = \Lambda_\infty - (B)\sqrt{C}$ (4) $\Lambda_C = \Lambda_\infty + (B)\sqrt{C}$

8. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is :

[JEE(Main) 2014, 4/120]

(1) Ag (2) Ca (3) Cu (4) Cr

9. Given below are the half-cell reactions : **[JEE(Main) 2014, 4/120]**

$Mn^{2+} + 2e^- \longrightarrow Mn$; $E^o = -1.18$ V

$2(Mn^{3+} + e^- \longrightarrow Mn^{2+})$; $E^o = +1.51$ V

The E^o for $3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$ will be :

(1) –2.69 V ; the reaction will not occur (2) –2.69 V ; the reaction will occur

(3) –0.33 V ; the reaction will not occur (4) –0.33 V ; the reaction will occur

10. At 298 K, the standard reduction potentials are 1.51 V for $MnO_4^-|Mn^{2+}$, 1.36 V for $Cl_2|Cl^-$, 1.07 V for $Br_2|Br^-$, and 0.54 V for $I_2|I^-$ .At pH = 3, permanganate is expected to oxidize $\left(\frac{RT}{F} = 0.059\,V\right)$:-

[JEE-MAINS (ONLINE) 2015]

(1) Cl^- and Br^- (2) Cl^-, Br^- and I^-

(3) Br^- and I^- (4) I^- only

11. A variable, opposite external potential (E_{ext}) is applied to the cell $Zn|Zn^{2+}$ (1 M) || Cu^{2+} (1 M) | Cu, of potential 1.1 V. When $E_{ext} < 1.1$ V and $E_{ext} > 1.1$ V, respectively electrons flow from : **[JEE-MAINS (ONLINE) 2015]**

(1) anode to cathode in both cases

(2) anode to cathode and cathode to anode

(3) cathode to anode in both cases

(4) cathode to anode and anode to cathode

12. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1M $ZnSO_4$

(1) The copper metal will dissolve and zinc metal will be deposited

(2) No reaction will occur **[JEE-MAINS (ONLINE) 2016]**

(3) The copper metal will dissolve with evolution of oxygen gas

(4) The copper metal will dissolve with evolution of hydrogen gas

13. Oxidation of succinate ion produces ethylene and carbon dioxide gases. On passing 0.2 Faraday electricity through on aqueous solution of potassium succinate, the total volume of gases (at both cathode and anode) at STP (1 atm and 273 K) is : **[JEE-MAINS (ONLINE) 2016]**

(1) 8.96 L (2) 2.24 L (3) 4.48 L (4) 6.72 L

14. Given **[JEE-MAINS - 2017]**

$E^o_{Cl_2/Cl^-} = 1.36\,V, E^o_{Cr^{3+}/Cr} = -0.74\,V$

$E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\,V, E^o_{MnO_4^-/Mn^{2+}} = 1.51\,V$.

Among the following, the strongest reducing agent is

(1) Cr (2) Mn^{2+} (3) Cr^{3+} (4) Cl^-

15. What is the standard reduction potential (E°) for $Fe^{3+} \rightarrow Fe$? **[JEE-MAINS (ONLINE) 2017]**
Given that :

$Fe^{2+} + 2e^- \rightarrow Fe$; $E^{o}_{Fe^{2+}/Fe} = -0.47\ V$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$; $E^{o}_{Fe^{3+}/Fe^{2+}} = +0.77\ V$

(1) +0.30 V (2) +0.057 V
(3) –0.057 V (4) –0.30 V

16. To find the standard potential of $M^{3+}|M$ electrode, the following cell is constituted: $Pt|M|M^{3+}(0.001\ mol\ L^{-1})|Ag^{+}(0.01\ mol\ L^{-1})|Ag$ **[JEE-MAINS (ONLINE) 2017]**
The emf of the cell is found to be 0.421 volt at 298 K. The standard potential of half reaction $M^{3+} + 3e^- \rightarrow M$ at 298 K will be : (Given $E^{\ominus}_{Ag^{+}/Ag}$ at 298 K = 0.80 Volt)

(1) +0.30 V (2) +0.057 V (3) –0.057 V (4) –0.30 V

17. How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane ? **[JEE-MAINS (OFFLINE) 2017]**
(Atomic weight of B = 10.8 u)
(1) 0.8 hours (2) 3.2 hours (3) 1.6 hours (4) 6.4 hours

18. When an electric current is passed through acidified water, 112 mL of hydrogen gas at N.T.P. was collected at the catode in 965 seconds. The current passed, in ampere, is : **[JEE-MAINS (ONLINE) 2018]**
(1) 2.0 (2) 1.0 (3) 0.1 (4) 0.5

19. When 9.65 ampere current was passed for 1.0 hour into nitrobenzene in acidic medium, the amount of p-aminophenol produced is :- **[JEE-MAINS (ONLINE) 2018]**
(1) 10.9 g (2) 98.1 g (3) 109.0 g (4) 9.81 g

20. The anodic half-cell of lead-acid battery is recharged unsing electricity of 0.05 Faraday. The amount of $PbSO_4$ electrolyzed in g during the process in : **[JEE-MAINS (ONLINE) JAN. 2019]**
(Molar mass of $PbSO_4$ = 303 g mol^{-1})
(1) 22.8 (2) 15.2 (3) 7.6 (4) 11.4

21. If the standard electrode potential for a cell is 2 V at 300 K, the equilibrium constant (K) for the reaction
$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$ **[JEE-MAINS (ONLINE) JAN. 2019]**
at 300 K is approximately.
(R = 8 $JK^{-1}\ mol^{-1}$, F = 96000 C mol^{-1})
(1) e^{160} (2) e^{320} (3) e^{-160} (4) e^{-80}

22. Given that : $E^0_{O_2/H_2O} = +1.23V$, **[JEE-MAINS (ONLINE) APRIL. 2019]**

$E^0_{S_2O_8^{2-}/SO_4^{2-}} = +2.05V$

$E^0_{Br_2/Br^-} = +1.09V$

$E^0_{Au^{3+}/Au} = +1.4V$

The strongest oxidizing agent is -

(1) O_2 (2) Br_2 (3) $S_2O_8^{2-}$ (4) Au^{3+}

23. Calculate the standard cell potential in(V) of the cell in which following reaction takes place :

$Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$ **[JEE-MAINS (ONLINE) APRIL. 2019]**

Given that

$E^o_{Ag^+/Ag} = xV$

$E^o_{Fe^{2+}/Fe} = yV$

$E^o_{Fe^{3+}/Fe} = zV$

(1) x + 2y – 3z (2) x – z (3) x – y (4) x + y – z

24. Given that the standard potentials (E°) of **[JEE-MAINS (ONLINE) JAN. 2020]**
Cu^{2+}/Cu and Cu^+/Cu are 0.34 V and 0.522 V respectively, the E° of Cu^{2+}/Cu^+ is :

(1) +0.158 V (2) 0.182 V (3) –0.182 V (4) –0.158 V

25. The equation that is incorrect is - **[JEE-MAINS (ONLINE) JAN. 2020]**

(1) $\left(\Lambda^0_m\right)_{NaBr} - \left(\Lambda^0_m\right)_{NaI} = \left(\Lambda^0_m\right)_{KBr} - \left(\Lambda^0_m\right)_{NaBr}$

(2) $\left(\Lambda^0_m\right)_{H_2O} = \left(\Lambda^0_m\right)_{HCl} + \left(\Lambda^0_m\right)_{NaOH} - \left(\Lambda^0_m\right)_{NaCl}$

(3) $\left(\Lambda^0_m\right)_{KCl} - \left(\Lambda^0_m\right)_{NaCl} = \left(\Lambda^0_m\right)_{KBr} - \left(\Lambda^0_m\right)_{NaBr}$

(4) $\left(\Lambda^0_m\right)_{NaBr} - \left(\Lambda^0_m\right)_{NaCl} = \left(\Lambda^0_m\right)_{KBr} - \left(\Lambda^0_m\right)_{KCl}$

ANSWER KEY

EXERCISE # 1

PART-I

A-1. (a) Zn (b) Ag
(c) oxidation (d) reduction
(e) Zn (f) Ag
(g) anode-$Zn \longrightarrow Zn^{2+} + 2e^-$; cathode-$Ag^+ + e^- \longrightarrow$ Ag
(h) $Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag$ (i) Zn
(j) Zn (k) to complete circuit and maintain electrical neutrality in solution

A-2. (a) $Zn \mid Zn^{2+} \mid\mid Cd^{2+} \mid Cd$, (b) $Pt, H_2 \mid H^+ \mid\mid Ag^+ \mid Ag$,
(c) $Pt \mid Fe^{2+}, Fe^{3+} \mid\mid Cr_2O_7^{2-}, H^+, Cr^{3+} \mid Pt$

A-3. (a) $2Ag^+ + Cu \longrightarrow 2Ag + Cu^{2+}$ (b) $8H^+ + MnO_4^- + 5Fe^{2+} \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$
(c) $2Ag^+ + 2Cl^- \longrightarrow 2Ag + Cl_2$ (d) $Cd + 2H^+ \longrightarrow Cd^{2+} + H_2$

B-1. 0.53 V **B-2.** – 0.036 V **B-3.** Spontaneous, – 48250 J

B-4. –0.756 V **C-1.** Mg **C-2.** Y > Z > X

C-3. **(i)** CuO **:** Cu is below hydrogen in series, so it can reduce from CuO to Cu.
(ii) Ag_2O **:** Lower in series stability of oxide become lesser.
(iii) Lower S.R.P. metal can displace higher S.R.P. metals ions from solution.

C-4. 1.61 V **C-5.** 1.35 V **C-6.** 1.68 V

D-1. $K_C = 2.868 \times 10^{107}$, $\Delta G° = -611.8$ kJ **D-2.** 10^{14}

D-3. (a) The spontaneous cell reaction : $Zn + 2Ag^+ (aq) \rightleftharpoons Zn^{2+} (aq) + 2Ag (s)$
(b) 1.56 V (c) $[Zn^{2+}] = 4 \times 10^{-4}$ M
(d) As we add KI to cathode chamber, some Ag^+ will precipitate out as :
$Ag^+ + I^- \longrightarrow AgI$
The above reaction reducing $[Ag^+]$ from cathode chamber. This will reduce E_{cell} according to Nernst's equation.

D-4. E = – 0.81 V **D-5.** 0.0178 V **D-6.** pH = 4 **E-1.** $K_{SP} = 10^{-5}$

E-2. –0.16V

F-1. $\Delta S^o = -24.125$ kJ K^{-1} $\Delta G^o = -7179.6$ J
$\Delta H^o = -7196.43$ kJ

F-2. 3.389×10^{-4} volt deg^{-1}

F-3. $\Delta S^o = -30.88$ JK^{-1} $\Delta H^o = -77.23$ kJ $\Delta G^o = -68.03$ kJ

G-1.

	ELECTROLYTE	ANODE Product	CATHODE Product
1	$AgNO_3$ (aq) with Pt electrode	$O_2(g)$	Ag
2	$NaNO_3$ (aq) with Pt electrode	$O_2(g)$	$H_2(g)$
3	Na_2SO_4 (aq) with Pt electrode	$O_2(g)$	$H_2(g)$
4	NaCl (Molten) with Pt electrode	$Cl_2(g)$	Na
5	$CuSO_4$ (aq) with Copper electrode	Cu dissolve	Cu
6	NaCl (aq) with Pt electrode	$Cl_2(g)$	$H_2(g)$
7	$CuSO_4$ (aq) with Inert electrode	$O_2(g)$	Cu

H-1. (a) 6.02×10^{22} electrons lost (b) 1.89×10^{22} electrons gained. (c) 1.80×10^{23} electrons gained.

H-2. (a) 0.75 F (b) 0.69 F (c) 1.1 F

H-3. 2 **H-4.** n = 4 **H-5.** t = 193 sec. **H-6.** $v_{(H_2)}$ = 56.0 mL.

H-7. Ni^{2+} = 2M

I-1. Anode $Zn(s) \longrightarrow Zn^{+2} + 2e^-$

Cathode $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

I-2. $Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(\ell)$

I-3. Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Anode: $2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-$

Overall reaction being:

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

I-4. Anode: $2Fe(s) \longrightarrow 2Fe^{2+} + 4e^{-1}$ $E^{\ominus}_{(Fe^{2+}/Fe)} = -0.44$ V

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(I)$ $E_{H^+|O_2|H_2O} = 1.23$ V

The overall reaction being:

$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(I)$ $E^{\ominus}_{(Cell)} = 1.67$ V

J-1. 442 Scm^2 $equivalent^{-1}$.

J-2. R = 66.67 ohms

J-3. 0.00040 Scm^{-1}; 2500 ohm cm.

J-4. 0.728 cm^{-1}.

J-5. 120 mho cm^2 mol^{-1}

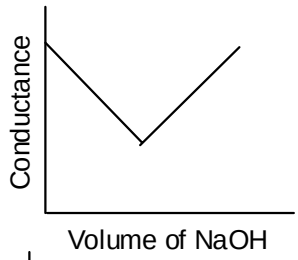
K-1. 510×10^{-4} mho cm^2 mol^{-1}

K-2. (i) 400 S cm^{-2} mol^{-1} (ii) 12 %

K-3. 2.70×10^{-10} $(mole/litre)^2$.

K-4. 1.76×10^{-5} mole/litre.

L-1. (1)



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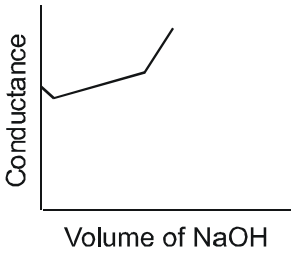

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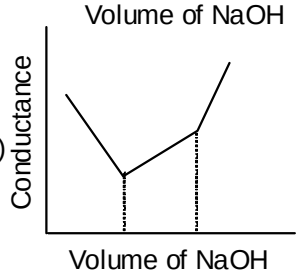

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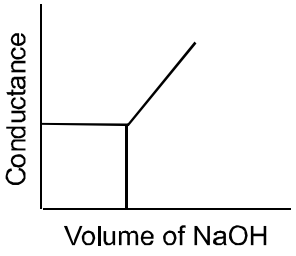

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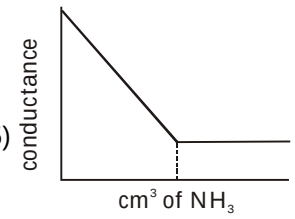

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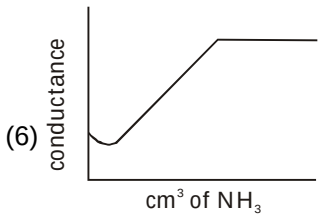

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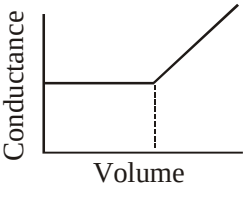


$AgNO_3$(aq.) vs NaCl

PART-II

A-1.	(C)	**A-2.**	(C)	**A-3.**	(C)	**A-4.**	(D)	**B-1.**	(D)	**B-2.**	(D)	**B-3.**	(D)
B-4.	(C)	**C-1.**	(B)	**C-2.**	(C)	**C-3.**	(A)	**C-4.**	(D)	**C-5.**	(C)	**C-6.**	(C)
C-7.	(A)	**C-8.**	(C)	**C-9.**	(C)	**C-10.**	(D)	**D-1.**	(D)	**D-2.**	(B)	**D-3.**	(A)
D-4.	(B)	**D-5.**	(B)	**D-6.**	(C)	**D-7.**	(B)	**E-1.**	(D)	**E-2.**	(D)	**E-3.**	(B)
E-4.	(D)	**F-1.**	(A)	**F-2.**	(D)	**F-3.**	(D)	**G-1.**	(C)	**G-2.**	(C)	**G-3.**	(D)
G-4.	(B)	**G-5.**	(B)	**H-1.**	(C)	**H-2.**	(C)	**H-3.**	(D)	**H-4.**	(B)	**H-5.**	(B)
I-1.	(D)	**I-2.**	(B)	**I-3.**	(B)	**J-1.**	(B)	**J-2.**	(C)	**J-3.**	(B)	**J-4.**	(D)
J-5.	(A)	**K-1.**	(B)	**K-2.**	(C)	**K-3.**	(D)	**K-4.**	(D)	**K-5.**	(A)	**L-3.**	(A)
L-2.	(C)	**L-3.**	(A)										

PART-III

1. (A - P, Q) ; (B - P, Q) ; (C - Q, R) ; (D - P, S) **2.** (A - p, q, r) ; (B - p, q, r) ; (C - p, s) ; (D - p, s)

EXERCISE # 2

PART-I

1.	(A)	**2.**	(A)	**3.**	(D)	**4.**	(C)	**5.**	(B)	**6.**	(B)	**7.**	(D)
8.	(C)	**9.**	(C)	**10.**	(B)	**11.**	(C)	**12.**	(D)	**13.**	(C)	**14.**	(B)

PART-II

1. 4

2. $K_{sol} = K_{Ba^{2+}} + K_{Ag^+} + K_{NO_3^-}$

$$5.3 \times 10^{-3} = \frac{\lambda^o_{Ba^{2+}} \times [Ba^{2+}]}{10^{-3}} + \frac{\lambda^o_{Ag^+} \times [Ag^+]}{10^{-3}} + \frac{\lambda^o_{NO_3^-} \times [NO_3^-]}{10^{-3}}$$

$$5.3 \times 10^{-3} = \frac{13\times10^{-3}\times10^{-4}}{10^{-3}} + \frac{6\times10^{-3}\times2\times10^{-4}}{10^{-3}} + \frac{\lambda^0_{NO_3^-}\times4\times10^{-4}}{10^{-3}}$$

$\therefore \lambda^o_{(NO_3^-)} = 7 \times 10^{-3} \times 1000\ Sm^2mol^{-1} = 7\ Sm^2\ mol^{-1}$

3. – 0.2214 V **4.** 3 [B, E & F] **5.** E° = 7 V. **6.** pH = 1.5.

7. $K_{sp} = 1.1 \times 10^{-16}$ **8.** 40 **9.** α = 0.5, k = 10×10^{-4}

10. $[Cu^{2+}] = 10^{-4}$ M. **11.** 59 **12.** 11 **13.** 8

14. t = 93.65 sec. **15.** V = 1.76 L

PART - III

1. (AC) **2.** (BC) **3.** (BC) **4.** (AD) **5.** (BCD) **6.** (AB) **7.** (BD)

8. (ACD) **9.** (BCD) **10.** (CD) **11.** (AB) **12.** (BC) **13.** (BCD) **14.** (ABD)

15. (AB)

PART - IV

1. (B) **2.** (A) **3.** (A) **4.** (B) **5.** (B) **6.** (C) **7.** (C)

8. (C) **9.** (B)

EXERCISE # 3

PART- I

1.* (ABD) **2.** (B) **3.** (C) **4.** (D) **5.** (D) **6.** (B) **7.** (D)

8. (A) **9.** (D) **10.** (A) **11.** 4 **12.** 3 **13.** (D) **14.** 6

15. (B) **16.** –11.62 **17.** 10

PART - II

1. (2) **2.** (3) **3.** (3) **4.** (4) **5.** (4) **6.** (1) **7.** (3)

8. (2) **9.** (1) **10.** (3) **11.** (2) **12.** (2) **13.** (1) **14.** (1)

15. (3) **16.** (2) **17.** (2) **18.** (2) **19.** (4) **20.** (3) **21.** (1)

22. (3) **23.** (1) **24.** (1) **25.** (1)

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Reliable students.

Self Assessment Test

PART- 1 : PAPER JEE (MAIN) PATTERN

SECTION–I : (Maximum Marks : 80)

- This section contains **TWENTY** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :
  Full Marks : +4If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0 If none of the bubbles is darkened.
  Negative Marks : –1 In all other cases

1. The standard electrode potentials (reduction) of Pt/Fe^{3+}, Fe^{2+} and Pt/Sn^{4+}, Sn^{2+} are + 0.77 V and 0.15 V respectively at 25° C. The standard EMF of the reaction $Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$ is

(A) – 0.62 V (B) – 0.92 V (C) + 0.31 V (D) + 0.85 V

2. The standard oxidation potentials, E^o, for the half reactions are as

$Zn \longrightarrow Zn^{2+} + 2e^-$; E^0 = + 0.76 V $\quad$ $Fe \longrightarrow Fe^{2+} + 2e^-$; E^0 = + 0.41 V

The EMF for the cell : $Fe^{2+} + Zn \longrightarrow Zn^{2+} + Fe$

(A) –0.35 V (B) + 0.35 V (C) + 1.17 V (D) – 1.17 V

3. Which is/are correct among the following ?

Given, the half cell emf's $E^0_{Cu^{+2}|Cu} = 0.337$, $E^0_{Cu^{+1}|Cu} = 0.521$

(A) Cu^{+1} disproportionates (B) Cu and Cu^{2+} comproportionates.

(C) $E^0_{Cu\,|\,Cu^{+2}} + E^0_{Cu^{+1}\,|\,Cu}$ is positive (D) (A) and (C) Both

4. How many g of silver will be displaced from a solution of $AgNO_3$ by 4 g of magnesium?

(A) 18 g (B) 4 g (C) 36 g (D) 16 g

5. The standard reduction potential for Zn^{+2}/Zn ; Ni^{+2}/Ni ; and Fe^{+2}/Fe are –0.76V, –0.23V, –0.44V respectively. The reaction $X + Y^{+2} \longrightarrow X^{+2} + Y$ will be non-spontaneous when :

	X	Y
(I)	Ni	Fe
(II)	Ni	Zn
(III)	Fe	Zn
(VI)	Zn	Ni

(A) I, II, IV (B) I, II, III (C) II, III, IV (D) all of these

6. The electrode potentials for

$Cu^{2+}_{(aq)} + e^- \longrightarrow Cu^+_{(aq)}$ and $Cu^+_{(aq)} + e^- \longrightarrow Cu_{(s)}$

are +0.15 V and + 0.50V respectively. The value of $E^o_{Cu^{2+}/Cu}$ will be :

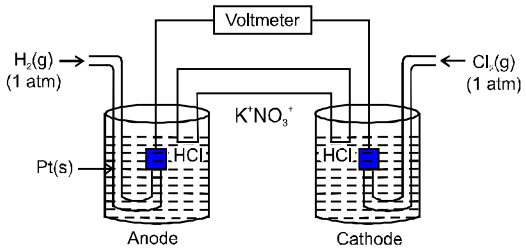
(A) 0.500 V (B) 0.325 V (C) 0.650 V (D) 0.150 V

7. How much will the reduction potential of a hydrogen electrode change when its solution initially at pH = 0 is neutralised to pH = 7 at 25º C ?

(A) Increases by 0.059 V (B) Decreases by 0.059 V

(C) Increases by 0.41 V (D) Decreases by 0.41 V

8. Consider the following Galvanic cell as shown in figure. By what will value the cell voltage change when concentration of ions in anodic and cathodic compartments are both increased by factor of 10 at 298 K



(A) + 0.591 V (B) – 0.0591 V

(C) – 0.1182 V (D) 0 V

9. In a cell that utilise the reaction : $Zn(s) + 2H^+(0.1M) \longrightarrow Zn^{2+}(aq) + H_2(g)$ addition of 0.1 M H_2SO_4 to cathode compartment will :

(A) increase the cell emf and shift equilibrium to the left.

(B) lower the cell emf and shift equilibrium to the right.

(C) increase the cell emf and shift equilibrium to the right.

(D) lower the cell emf and shift equilibrium to the left.

10. In the galvanic cell : $Pt(s) \mid I_2(g) \mid I^-(aq) \parallel Fe^{3+}(aq) \mid Fe^{2+}(aq) \mid Pt(s)$

(A) Representation of anode is incorrect and cell will not work

(B) $[Fe^{3+}] = [Fe^{2+}] = [I^-] = 1$ M is sufficient for $E_{cell} = E^o_{cell}$

(C) I^- gets oxidized to I_2 and Fe^{3+} gets reduced to Fe^{2+}.

(D) None of these

11. For the cell, $Pt \mid H_2(g) \mid H^+(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

$E^o_{Cu/\,Cu^{2+}} = -0.34$ V

Then calculate approximate value of K_{eq} ?

(A) 5×10^{12} (B) 2×10^{11} (C) 2×10^{-11} (D) 5×10^{-12}

12. Cost of electricity for the production of 'X' litre H_2 at NTP at cathode is Rs. X. Then cost of electricity for the production 'X' litre O_2 gas at NTP at anode will : (assume 1 mole of electrons as one unit of electricity)

(A) 2X (B) 4X (C) 16X (D) 32X

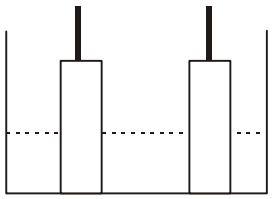
13. A current is passed through 2 voltameters connected in series. The first voltameter contains XSO_4 (aq.) and second has Y_2SO_4 (aq.). The relative atomic masses of X and Y are in the ratio of 2 : 1. The ratio of the mass of X liberated to the mass of Y liberated is

(A) 1 : 1 (B) 1 : 2 (C) 2 : 1 (D) None of the above

14. Charge produced in butane – O_2 Fuel cell if 2 mol butane is consumed, will be :

(A) 26 F (B) 49 F (C) 21 F (D) 52 F

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



(A) 50 Ω (B) 100 Ω (C) 25 Ω (D) 200 Ω

16. The equivalent conductance of a N/10 NaCl solution at 25ºC is 10^{-2} Sm^2eq^{-1}. Resistance of solution contained in the cell is 50 Ω. Cell constant is :

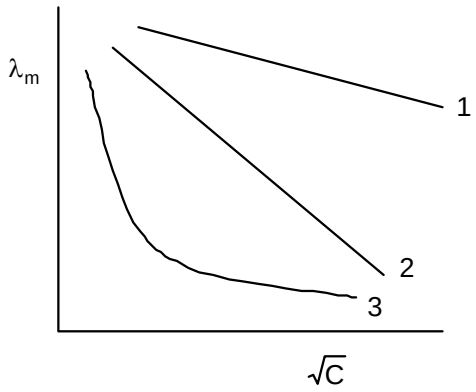
(A) 50 m^{-1} (B) 50 × 10^{-6} m^{-1} (C) 50 × 10^{-3} m^{-1} (D) 50 × 10^{3} m^{-1}

17. Find the value of λ^{α}_{eq} for potashalum.

Given : $\lambda^{\alpha}_{m(K^+)}$ = 73.5 $\Omega^{-1}cm^2\ mol^{-1}$, $\lambda^{\alpha}_{m(Al^{+3})}$ = 198 $\Omega^{-1}cm^2\ mol^{-1}$, $\lambda^{\alpha}_{m(SO_4^{-2})}$ = 160 $\Omega^{-1}cm^2\ mol^{-1}$

(A) 145.6 $\Omega^{-1}cm^2\ eq^{-1}$ (B) 1165 $\Omega^{-1}cm^2\ eq^{-1}$ (C) 532 $\Omega^{-1}cm^2\ eq^{-1}$ (D) 195.5 $\Omega^{-1}cm^2\ eq^{-1}$

18. A graph of molar conductivity of three electrolytes (NaCl, HCl and NH_4OH) is plotted against $\sqrt{C}$



Which of the following options is correct ?

	(1)	**(2)**	**(3)**
(A)	NaCl	HCl	NH_4OH
(B)	NH_4OH	NaCl	HCl
(C)	HCl	NaCl	NH_4OH
(D)	NH_4OH	HCl	NaCl

19. 0.1 molar solution NaCl filled in different conductivity cell. Order of equivalent conductance of NaCl solution is :

	Cell – 1	**Cell – 2**	**Cell – 3**
A	5 cm^2	6 cm^2	10 cm^2
l	2 cm	3 cm	4 cm^2
Equivalents :	a	b	c
conductance	A = Area of cross section		
	l = distance between two electrode.		

(A) Cell – 1 > Cell – 2 > Cell – 3 (B) Cell – 1 = Cell – 2 = Cell – 3

(C) Cell – 1 > Cell – 3 < Cell – 2 (D) None of these

20. Acetic acid is titrated with NaOH solution. Which of the following statement is correct for this titration?
(A) conductance increases upto equivalence point, then it decreases
(B) conductance increases upto equivalence point, then it increases
(C) first conductance increases slowly upto equivalence point and then increases rapidly
(D) first conductance increases slowly upto equivalence point and then drops rapidly .

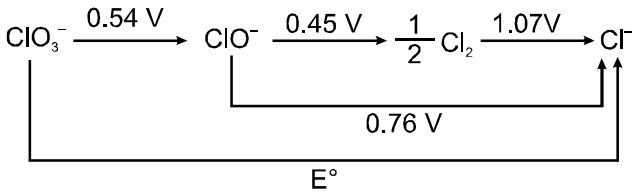
Section-II

Instructions.

1. This section contains Five (05) questions. The answer to each question is Numerical Value with two digit integer and decimal upto one digit.

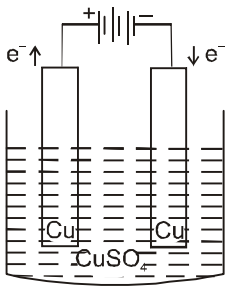
2. If the numerical value has more than two decimal places Truncate/Round-off the value upto Two decimal places.
Full Marks : +4 If Only the correct option is chosen.
Zero Marks : - 0 in all other cases

21.



Calculate the E° (in volt) in the given figure.

22. In the given figure, the electrolytic cell contains 1 L of an aqueous 1 M Copper (II) sulphate solution. If 0.4 mole of electrons are passed through cell, the concentration of copper ion after passage of the charge will be



23. A current of 0.1 A was passed for 965 second through a solution of Cu^+ solution and 0.03175 g of copper was deposited on the cathode. Calculate the current efficiency for the copper deposition. (Cu – 63.5)

24. A current of 9.95 amp following for 10 minutes, deposits 3 g of a metal. Equivalent weight of the metal is

25. The specific conductance of a N/10 KCl at 25°C is 0.0112 ohm^{-1} cm^{-1}. The resistance of cell containing solution at the same temperature was found to be 55 ohms. The cell constant (cm^{-1}) will be

PART 2 : PAPER JEE (ADVANCED) PATTERN

SECTION-I : (Maximum Marks : 12)

- This section contains **FOUR** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

Full Marks	:	+3	If only the bubble corresponding to the correct option is darkened.
Zero Marks	:	0	If none of the bubbles is darkened.
Negative Marks	:	–1	In all other cases

1. An initial solution of x M, 1L Fe^{+2} was reduced to Fe(s) on passage of 1 A current for 965 seconds. If after electrolysis 0.1M, 10 ml acidified $KMnO_4$ solution was required to oxidize remaining Fe^{+2} solution then the value of 'x' is -

(A) 10^{-2} (B) 10^{-3} (C) 5×10^{-3} (D) 5×10^{-2}

2. A solution of 100 mL, 0.2 M CH_3COOH is mixed with 100 mL, 0.2 M NaOH solution. The molar conductance for 0.1 M CH_3COOH at infinite dilution is 200 S cm^2 mol^{-1} and at given concentration is 2.0 S cm^2 mol^{-1}. Then calculate pH of the solution?

(A) 7 (B) 8 (C) 5 (D) 9

3. The conductance ratio $\frac{\lambda}{\lambda^\circ}$ = 0.936 given this for a certain solution of KCl and λ = 122 $\Omega^{-1}cm^2$ eq^{-1} and $\frac{\lambda^\circ_+}{\lambda^\circ}$ = $\frac{0.98}{1.98}$. Calculate the limiting values of Ionic conductance of $K^\oplus$ and Cl^- ions in $\Omega^{-1}cm^2$ eq^{-1}.

(A) 64.51 , 65.83 (B) 74.60, 26.40 (C) 30.31, 69.69 (D) 70.12, 29.88

4. A saturated solution of $Fe(OH)_3$ is present in a solution of pH = 12, what is the reduction potential of Fe^{3+}/ Fe in solution ($E^0_{Fe^{3+}/Fe}$ = –0.036V, K_{sp} of $Fe(OH)_3 = 10^{-26}$), [$\frac{2.303 \times RT}{F}$ = 0.06]

(A) –0.436V (B) 0.39V (C) + 0.36V (D) – 1.2 V

SECTION - II : (Maximum Marks: 32)

- This section contains **EIGHT** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks	:	+4	If only (all) the correct option(s) is (are) chosen.
Partial Marks	:	+3	If all the four options are correct but ONLY three options are chosen.
Partial Marks	:	+2	If three or more options are correct but ONLY two options are chosen, both of which are correct options.
Partial Marks	:	+1	If two or more options are correct but ONLY one option is chosen and it is a correct option.
Zero Marks	:	0	If none of the options is chosen (i.e. the question is unanswered).
Negative Marks	:	–1	In all other cases.

- **For Example :** If first, third and fourth are the **ONLY** three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in –1 marks.

5. Two test tubes I & II contain solutions of sodium salts of halide in water. When Br_2 was added to both the solutions then following observations were noted.

Test Tube	Observation
I	Violet vapous emerged
II	No reaction occurred

If halides in the tubes I & II are X^- and Y^- (and their molecular forms being X_2 & Y_2 respectively) then the true options would be :

(A) SRP of Br_2 is more than the SRP of X_2

(B) SRP of Br_2 is more than the SRP of Y_2

(C) Y_2 can oxidize X^- into X_2

(D) Y_2 can oxidize Br^- into Br_2.

6. In the concentration cell

$$Pt \left| H_2(g) \right| \begin{matrix} HA \\ NaA \end{matrix} \Bigg|\Bigg| \begin{matrix} HA \\ NaA \end{matrix} \left| H_2(g) \right| Pt$$

Value of cell potential will depend on –

(A) Value of pKa of HA

(B) Temperature

(C) Concentration of HA in two electrodes

(D) Concentration of NaA in two electrodes

7. 20 millimolar solution of aq. $CuSO_4$ (500 ml) is electrolysed with sufficient amount and a total of 0.04 faraday of electricity is supplied. Then :

(A) Total volume of gases evolved at STP = 224 ml

(B) Total volume of gases evolved at STP = 448 ml

(C) Total volume of gases evolved at STP = 672 ml

(D) Resulting solution after electrolysis becomes acidic

8. Emf of cell $Ag|Ag^+$ (saturated solution of Ag_2CrO_4) $||$ $Ag^+(0.1\ M)$ | Ag is 0.164 volt at 298 K. Then

(A) K_{sp} of Ag_2CrO_4 in water is nearly 2.3×10^{-12}

(B) Given cell is a concentration cell

(C) K_{sp} of Ag_2CrO_4 can't be determined by given data.

(D) Concentration of Ag^+ ion in anode compartment when EMF is 0.164 volt is nearly 1.66×10^{-4} M

9. $E^o_{Mg^{2+}/Mg} = -2.4V$, $E^o_{Sn^{4+}/Sn^{2+}} = 0.1\ V$, $E^o_{MnO_4^-, H^+/Mn^{2+}} = 1.5\ V$, $E^o_{I_2/I^-} = 0.5\ V$

Here,

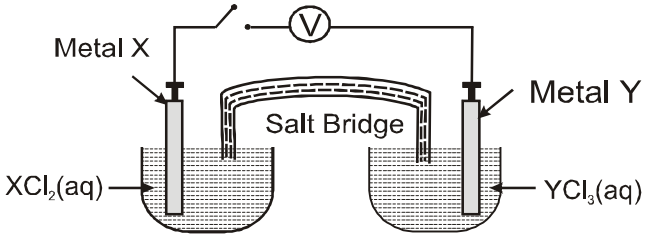
(A) MnO_4^- is the strongest Oxidizing Agent and Mg is the strongest Reducing Agent.

(B) $Sn^{4+} + 2I^- \longrightarrow Sn^{2+} + I_2$ is a nonspontaneous reaction.

(C) $Mg^{2+} + Sn^{2+} \longrightarrow Mg + Sn^{4+}$ is a spontaneous reaction.

(D) Here, Weakest oxidizing agent is Sn^{4+} and weakest reducing agent is Mn^{2+}

10. The following diagram shows an electrochemical cell in which the respective half cells contain aqueous 1.0 M solutions of the salts XCl_2 and YCl_3. Given that :
$3X(s) + 2Y^{3+}(aq) \longrightarrow 3X^{2+}(aq) + 2Y(s)$ $E_{cell} > 0$



Which of the following statements are correct?
(A) The electrode made from metal X has positive polarity.
(B) Electrode Y is the cathod
(C) The flow of electrons is from Y to X
(D) The reaction at electrode X is an oxidation

11. 0.1 molar solution of NaBr solution is electrolysed by passing 965 column charge. After electrolysis which statement is correct for resulting solution.
(A) Specific conductance increases (B) molar conductance increases
(C) No change in molar conductance. (D) Specific resistance increases.

12. A beaker contains a small amount of iron Fe(s). Which of the following aqueous solution, when added to the beaker, would dissolve the iron i.e. convert Fe(s) to Fe^{2+} (aq) ?

Half cells	E^o at 25°C
$Zn^{2+} + 2e^- \longrightarrow Zn$	–0.76
$Fe^{2+} + 2e^- \longrightarrow Fe$	–0.41
$Al^{3+} + 3e^- \longrightarrow Al$	–1.66
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	0.70
$Cr_2O_7^{2-} + 6e^- + H^+ \longrightarrow 2Cr^{3+}$	1.23
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.30

(A) $Cr_2O_7^{2-}$ (acidic solution) (B) H_2O_2 (acidic solution)
(C) Al^{3+} (D) Zn^{2+}

SECTION-III : (Maximum Marks: 18)

- This section contains **SIX** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.
  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:
  Full Marks : +3 If ONLY the correct numerical value is entered as answer.
  Zero Marks : 0 In all other cases.

13. By how many of the following actions, can the E_{cell} be increased (ΔS = + ve) for the cell reaction
$A \mid A^+(aq) \parallel Cl^- \mid Cl_2(g) \mid Pt$
(a) By dilution of anodic solution.
(b) By dilution of cathodic soltuion.
(c) By decreasing temperature.
(d) By increasing pressure of Cl_2 in cathodic compartment.
(e) By increasing the mass of anode (A(s))
(f) By increasing temperature

14. At infinite dilution the molar conductance for CH_3COONa is 150 S cm^2 mol^{-1}, for HCl is 200 S cm^2 mol^{-1} and for NaCl is 125 S cm^2 mol^{-1}. Then calculate pH of 0.001 M CH_3COOH ?
(Given : Molar conductance of CH_3COOH at 0.001 M concentration is 2.25 S cm^2 mol^{-1}).

15. The conductivity of an aqueous solution of a weak monoprotic acid is 0.000032 $ohm^{-1}cm^{-1}$ at a concentration, 0.2 M. If at this concentration the degree of dissociation is 0.02, calculate the value of Λ_0 (ohm^{-1} cm^2 /eqt).

16. Pt, $H_2(g)$ | 2 M $CH_3COONH_4(aq)$ || 2 M NaCl(aq) | $H_2(g)$, Pt
20 atm 0.2 atm
Given $pK_a(CH_3COOH) = 4.74$ $pK_b = (NH_4OH) = 4.74$

If E is emf of the cell in volt, calculate 1000 E. [Take : $\frac{2.303\ RT}{F} = 0.059$]

Pt, $H_2(g)$ | 2 M $CH_3COONH_4(aq)$ || 2 M NaCl(aq) | $H_2(g)$, Pt
20 atm 0.2 atm

17. EMF of the following cell is 0.634 volt at 298 K Pt | H_2 (1 atm) | H^+ (aq) || Hg_2^{2+}(aq.,1N) | Hg(ℓ). The pH of anode compartment is :

Given $E^0_{Hg_2^{2+}|Hg} = 0.28$ V and $\frac{2.303\ RT}{F} = 0.059$

18. Osmotic pressure of 0.1 M weak acid HA at 300 K is 3 atm. If molar conductance of 0.1 M HA is 30 $\Omega^{-1}cm^2$ mol^{-1}. than molar conductance ($\Omega^{-1}cm^2$ $mole^{-1}$) at infinite dilution is :

PART - 3 : OLYMPIAD (PREVIOUS YEARS)

STAGE - I (NATION STANDARD EXAMINATION IN CHEMISTRY (NSEC))

1. The increase in the equivalent conductance of a salt solution on dilution is due to increase in the **[NSEC-2000]**
(A) attraction between the ions (B) degree of ionization of the salt
(C) molecular attraction (D) association of the salt

2. When 96500 coulombs of electricity are passed through a nickel sulphate solution, the amount of nickel deposited will be **[NSEC-2000]**
(A) 1.0 mol (B) 0.5 mol (C) 0.1 mol (D) 2.0 mol

3. When a piece of copper wire is immersed in a silver nitrate solution, the colour of the solution turns blue due to **[NSEC-2000]**
(A) oxidation of silver (B) reduction of copper
(C) oxidation of copper (D) formation of soluble complex

4. The reduction potentials of Zn, Cu, Fe and Ag are in the order : **[NSEC-2001]**
(A) Zn,Cu,Fe,Ag (B) Cu,Ag,Fe,Zn (C) Ag,Cu,Fe,Zn (D) Fe,Zn,Cu, Ag

5. The standard reduction potentials of Cu^{2+}/Cu and Cu^+/Cu are 0.339 V and 0.518 V respectively. The standard electrode potential of Cu^+/Cu half cell is : **[NSEC-2001]**
(A) – 0.179 V (B) 0.827 V (C) 0.184 V (D) 0.490 V

6. How many coulombs are required for oxidation of 1 mole of H_2O to O_2 ? **[NSEC-2001]**
(A) 3.86 × 105C (B) 9.65 × 104C (C) 1.93 × 105C (D) 4.825 × 104C

7. The metal which can not be obtained by electrolysis of its aqueous salt solution is : **[NSEC-2001]**
(A) Au (B) Al (C) Ag (D) Cu

8. The units of conductivity are : **[NSEC-2001]**
(A) $Siemen^{-1}.cm^{-1}$. (B) Siemen.cm (C) $Siemen.cm^{-1}$ (D) $Semen.cm^{-2}.mol^{-1}$

9. The calomel electrode used a reference elecrode contains : **[NSEC-2001]**
(A) PbO_2-$PbSO_4$ mixture (B) $HgCl_2$
(C) Hg_2Cl_2 (D) $ZnCl_2$

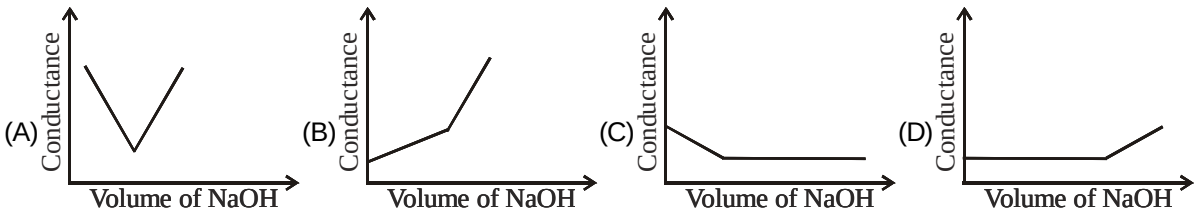
10. KCl is used in a salt bridge because : **[NSEC-2001]**
(A) it forms a good jelly with agar-agar
(B) it is strong electrolyte
(C) it is a good conductor of elelctric current
(D) the transference number of K^+ and Cl^- ions are almost equal

11. During the electrolysis of fused NaCl, the reaction occurring at the anode is : **[NSEC-2001]**
(A) reduction of Na^+ ions (B) oxidation of Cl^- ions
(C) oxidation of Na^+ ions (D) reduction of Cl^- ions

12. On electrolysis, one mole of chromium ions will be deposited by : **[NSEC-2001]**
(A) three moles of electrons (B) two moles of electrons
(C) one mole of electrons (D) six moles of electrons

13. The quantity of electricity which deposits 1.08 g of silver from $AgNO_3$ solution is : **[NSEC-2002]**
(A) 96500 coulombs (B) 9650 coulombs (C) 965 coulombs (D) 96.5 coulombs.

14. In the conductometric titration of CH_3COOH vs NaOH, the titration curve obtained will be of the type **[NSEC-2002]**



15. The standared reduction potentials at 298 K for the half reactions are : **[NSEC-2002]**
(a) $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$; –0.762 V (b) $Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$; – 0.740 V
(c) $2H^+(aq) + 2e^- \rightarrow H_2(g)$; 0.000 V (d) $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$; 0.770 V
Which is the strongest reducing agent ?
(A) $Zn_{(s)}$ (B) $Cr_{(s)}$ (C) $H_{2(g)}$ (D) $Fe^{2+}_{(aq).}$

16. The molar conductivities of H^+, Li^+ and Na^+ ions in aqueous solutions at infinite dilution are in the order : **[NSEC-2003]**
(A) $H^+ > Li^+ > Na^+$ (B) $H^+ < Li^+ < Na^+$ (C) $H^+ > Na^+ > Li^+$ (D) $Na^+ > H^+ > Li^+$

17. $Fe^{2+} + 2e \rightarrow Fe$ .....
(i) $Fe^{3+} + e \rightarrow Fe^{2+}$ ..... **[NSEC-2003]**
(ii) The standard potentials (in volt) corresponding to the reactions (i) and (ii) are E_1 and E_2 respec tively.
The value (in volt) of the standard potential corresponding to the reaction $Fe^{3+} + 3e \rightarrow Fe$ is (i) rFkk
(A) (E_1+E_2) (B) $(2E_1+E_2)/3$ (C) $(E_1+2E_2)/2$ (D) $(E_1+E_2)/3$

18. The standard reduction potentials of Cu^{2+} , Zn^{2+}, Sn^{2+} and Ag^{+} are 0.34, –0.76, –0.14 and 0.80 V respectively. The storage that is possible without any reaction is for **[NSEC-2003]**
(A) $CuSO_4$ solution in a zinc vessel (B) $AgNO_3$ solution in a zinc vessel
(C) $AgNO_3$ solution in a tin vessel (D) $CuSO_4$ solution in a silver vessel.

19. A certain current passed through $CuSO_4$ solution for 100 seconds deposits 0.3175 g of copper. The current passed (in A) is **[NSEC-2004]**
(A) 4.83 (B) 9.65 (C) 0.963 (D) 0.483

20. The salt that can be used in the salt bridge of an electrochemical cell is **[NSEC-2004]**
(A) $FeCl_3$ (B) AgCl (C) CH_3COONa (D) KNO_3

21. In an alkaline energy cell the overall cell reaction is as follows :
$Zn(s) + 2MnO_2(s) + 2H_2O \rightarrow Zn(OH)_2(s) + 2MnO(OH)$
Which of the following reactions is taking place at the cathode? **[NSEC-2005]**
(A) $2MnO_2(s) + 2H_2O + 2e \rightarrow Zn(OH)2(s) + 2MnO(OH)(s)$
(B) $2MnO_2(s) + 2H_2O + 2e \rightarrow 2MnO(OH)(s) + 2OH^{-}(aq)$
(C) $Zn(s) + 2OH^{-}(aq) \rightarrow Zn(OH)_2(s) + 2e$
(D) $Zn(OH)_2(s) + 2e \rightarrow Zn(s) + 2OH^{-}(aq)$.

22. What is the charge on an ion of tin if 7.42 g of metallic tin is deposited by passage of 24125 coulombs through a solution containing the ion ? **[NSEC-2005]**
(A) +1 (B) +3 (C) +2 (D) +4.

23. The cell potential (E) and free energy change (ΔG) accompanying an electrochemical reaction, are related by **[NSEC-2005]**
(A) $\Delta G = nFE$ (B) $\Delta G = nFE$ (C) $\Delta G = nF\log E$ (D) $\Delta G = nF \log E$. .

24. The mass of the copper, in grams, deposited during the passage of 2.5 ampere current through a Cu(II) sulphate solution for 1 hour is **[NSEC-2006]**
(A) 5.96 (B) 29.8 (C) 2.98 (D) 59.6

25. The standard reduction potentials of Fe^{2+}/Fe and Cu^{2+}/Cu electrodes are –0.44 and 0.34 volts,respectively. The following reaction would occur **[NSEC-2006]**
(A) copper will reduce Fe^{2+} ions (B) iron will reduce Cu^{2+} ions
(C) iron will oxidise copper metal (D) Cu^{2+} ions will reduce Fe^{2+}

26. Rusting of iron is due to the formation of **[NSEC-2006]**
(A) hydrated ferrous oxide (B) hydrated ferric oxide
(C) only ferric oxide (D) a mixture of ferric oxide and $Fe(OH)_3$

27. If the equilibrium constant of the disproportionation reaction
$Hg_2^{2+} = Hg^0 + Hg^{2+}$
at 298 K is 0.0795, the standard e.m.f. of the reaction is **[NSEC-2006]**
(A) –0.065 V (B) –0.212 V (C) 0.125 V (D) 0.110 V

28. The voltage for the cell: $Fe/Fe^{2+}(0.001M)$ // $Cu^{2+}(0.10M)/Cu^{2+}$ (0.10 M) / Cu^{2+} (0.10 M) / Cu is 0.807 V at 25°C. What is the value of E° ? **[NSEC-2007]**
(A) 0.629 V (B) 0.689 V (C) 0.748 V (D) 0.866 V

29. A current of 2.0 A is used to plate Ni(s) from 500mL of a 1.0 M Ni^{2+} aqueous solution. What is the $[Ni^{2+}]$ after 3.0 hours ? **[NSEC-2007]**
(A) 0.39 M (B) 0.46 M (C) 0.78 M (D) 0.89 M

30. Nickel metal is added to a solution containing1.0 M Pb^{2+}(aq) and 1.0 M Cd^{2+}(aq). Use the standard reduction potential to determine which of the following reaction (s) will occur. **[NSEC-2008]**
Reaction 1 : $Ni(s) + Pb^{2+}(aq) \rightarrow Pb(s) + Ni^{2+}(aq)$
Reaction 2 : $Ni(s) + Cd^{2+}(aq) \rightarrow Cd(s) + Ni^{2+}(aq)$
Reactions : $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$ $E° = –0.13$ V
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $E° = –0.23$ V
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$ $E° = –0.40$ V
(A) 1 only (B) 2 only (C) both 1 and 2 (D) neither 1 nor 2

31. An electrochemical cell constructed for the reaction :
$Cu^{2+}(aq) + M(s) \rightarrow Cu(s) + M^{2+}(aq)$ has an $E° = 0.75$ V. The standard reduction potential for $Cu^{2+}(aq)$ is 0.34 V. What is the standard reduction potential for $M^{2+}(aq)$? **[NSEC-2008]**
(A) 1.09 V (B) 0.410 V (C) – 0410 V (D) – 1.09 V

32. An electric current is passed through a silver voltameter connected to a water voltameter. 0.324 g of silver was deposited on the cathode of the silver voltameter. The volume of oxygen evolved at NTP is :
(A) 5.6 cm^3 (B) 16.8 cm^3 (C) 11.2 cm^3 (D) 22.4 cm^3

33. The amount of copper (At. wt. 63.54) deposited by passing 0.2 faraday of electricity through copper sulphate is **[NSEC-2009]**
(A) 5.6 cm^3 (B) 16.8 cm^3 (C) 11.2 cm^3 (D) 22.4 cm^3

34. When aqueous solution of sodum chloride is electrolysed using platinum electrode the cathode reaction is, **[NSEC-2009]**
(A) $Na^+ + e^- \rightarrow Na$ (B) $H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^-$
(C) $Na^+ + OH^- \rightarrow Na^+ + OH– + e^-$ (D) $Na^+ + H_2O + e^- \rightarrow Na + H^+ + OH^-$

35. The standard electrode potential values for four metals K, L, M and N are respectively, –3.05, –1.66, – 0.40 and +0.80V. The best reducing agent is – **[NSEC-2009]**
(A) L (B) K (C) N (D) M

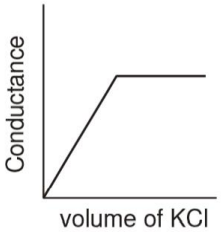
36. $10Cl^-(aq) + 2MnO_4^-(aq) + 16H^+(aq) \rightarrow 5Cl_2(g) + 2Mn^{2+}(aq) + 8H_2O(\ell)$
The value of E^o for the above reaction at 25°C is 0.15V. Hence, the value of K for this reaction is: **[NSEC-2009]**
(A) 2.4×10^{25} (B) 4.9×10^{12} (C) 1.2×10^5 (D) 3.4×10^2

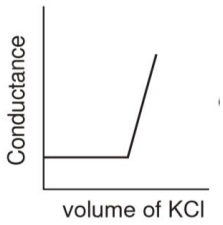
37. Adding powdered Pb and Fe to a solution containing 1 M each of Pb^{2+} and Fe^{2+} ions would result in the formation of $-(E^\circ_{Pb^{2+}/Pb} = -0.126\,V$ and $E^\circ_{Fe^{2+}/Fe} = -0.44\,V)$ **[NSEC-2010]**
(A) more of Pb and Fe^{2+} ions (B) more of Fe and Pb^{2+} ions
(C) more of Pb and Fe (D) more of Pb^{2+} and Fe^{2+} ions

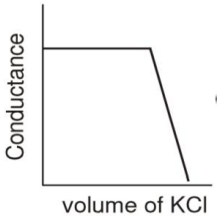
38. The cell $Al_{(s)}|Al^{3+}_{(aq)}$ (0.001 M) | | $Cu^{2+}_{(aq)}$ (0.10 M) | $Cu_{(s)}$ has a standard cell potential $E^0 = 2.00$ V at 25°C. The cell potential at the given concentration will be : **[NSEC-2010]**
(A) 2.07 V (B) 2.03 V (C) 1.97 V (D) 1.94 V

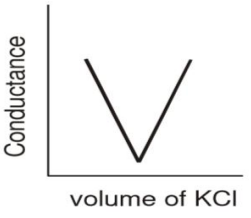
39. The mass of copper deposited when a current of 10A is passed through a solution of copper(II) nitrate for 30.6s is **[NSEC-2010]**
(A) 0.101 g (B) 0.201 g (C) 0.403 g (D) 6.04 g

40. In the conductometric titration of silver nitrate against KCl, the graph obtained is **[NSEC-2011]**

A) 

(B) 

(C) 

(D) 

41. Th emf of the cell (Zn | $ZnSO_4$(0.1M) || $CdSO_4$ (0.01M) | Cd) is **[NSEC-2011]**

($E^{\circ}_{Zn^{2+}/Zn} = -0.76V$ $E^{\circ}_{Cd^{2+}/Cd} = 0.40V$ at 298 K)

(A) +0.33 V (B) +0.36 V (C) +1.13 V (D) –0.36 V

42. The conductivity of a metal decreases with increase in temperature because : **[NSEC-2012]**

(A) the kinetic energy of the electrons increases
(B) the movement of electrons becomes haphazard
(C) the ions start vibrating
(D) the metal becomes hot and starts emiting radiation

43. The amount of electricity required to deposit 1.0 mole of aluminium from a solution of $AlCl_3$ will be: **[NSEC-2012]**

(A) 1 faraday (B) 3 faradays
(C) 0.33 faraday (D) 1.33 faraday

44. Which is the strongest oxidising agent among the species given below? **[NSEC-2013]**

(i) In^{3+} E^0 = – 1.34V (ii) Au^{3+} E^0 = 1.40V
(iii) Hg^{2+} E^0 = 0.867V (iv) Cr^{3+} E^0 = – 0.786V
(A) Cr^{3+} (B) Au^{3+} (C) Hg^{2+} (D) In^{3+}

45. Which of the following aqueous solution has the lowest electrical conductance ? **[NSEC-2013]**
(A) 0.01M $CaCl_2$ (B) 0.01M KNO_2 (C) 0.01M CH_3COOH (D) 0.01M CH_3COCH_3

46. The value of the constant in Nernst equation

$E = E^{o} - \frac{Constant}{n} \ln Q$ at 25°C is : **[NSEC-2013]**

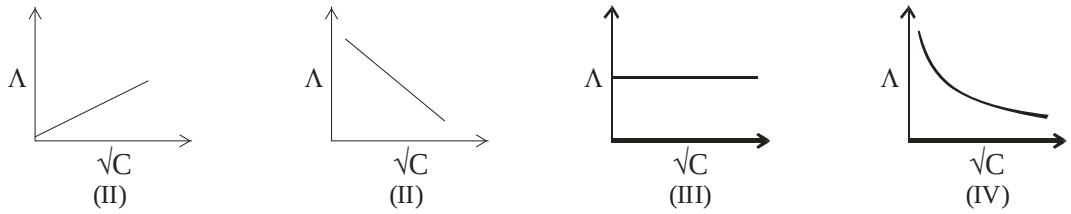
(A) 0.592 (B) 0.0592 (C) 0.296 (D) 0.0296

47. When zinc rod is directly placed in copper sulphate solution **[NSEC-2013]**
(A) the blue colour of the solution starts intensifying
(B) the solution remains electrically neutral
(C) the temperature of the solution falls
(D) the weight of zinc rod starts increasing

48. For the following cell at 25°C the E.M.F. is : [If $E^{\circ}_{M^{2+}/M} = 0.347V$] **[NSEC-2014]**

$M_{(s)}$ I M^{2+}(1M) II M^{2+} (0.01M) I $M_{(s)}$
(A) 0.089V (B) 0.598V (C) 0.251V (D) 0.764V

49. For a strong electrolyte, the change in the molar conductance with concentration is represented by : **[NSEC-2014]**



(A) I (B) II (C) III (D) IV

50. The specific conductance of 0.01M solution of the weak monobasic acid is 0.20×10^{-3} Scm^{-1}. The dissociation constant of the acid is [Given: λ^{o} HA = 400 Scm^2mol^{-1}] **[NSEC-2014]**
(A) 5×10^{-2} (B) 2.5×10^{-5} (C) 5×10^{-4} (D) 2.5×10^{-11}

51. The reaction given below is the cell reaction in a galvanic cell.
$Cd(s) + Sn^{2+}(aq) \rightarrow Cd^{2+}(aq) + Sn(s)$
Where,

Given: $E^0_{Cd^{2+}/Cd} = -0.403$ $E^0_{Sn^{2+}/Sn} = -0.136$, $F = 96485 C mol^{-1}$

At 25ºC, the free energy change for this reaction is : **[NSEC-2014]**

(A) –48.05 KJ (B) –54.96 KJ (C) –100.58 KJ (D) –107.46 KJ

52. A current of 5.0 A flows for 4.0 h through an electrolytic cell containing a molten salt of metal M. This results in deposition of 0.25 mol of the metal M at the cathode. The oxidation state of M in the molten salt is (1 Faraday = 96485 C mol–1) **[NSEC-2015]**

(A) +1 (B) +2 (C) +3 (D) +4

53. The limiting molar conductivities of KCl, KNO_3, and $AgNO_3$ are 149.9, 145.0 and 133.4 S $cm^2 mol^{-1}$, respectively, at 25ºC. The limiting molar conductivity of AgCl at the same temperature in S cm^2 mol^{-1} is: **[NSEC-2015]**

(A) 128.5 (B) 138.3 (C) 161.5 (D) 283.3

54. The emf of a cell corresponding to the following reaction is 0.199 V at 298 K.

$Zn(S) + 2H^+(aq) \rightarrow Zn^{2+}(0.1\ M) + H_2(g)$ ($E^{\circ}_{Zn/Zn^{+2}} = 0.76V$)

The approximate pH of the solution at electrode where hydrogen is being produced is (p_{H2} = 1 atm) **[NSEC-2015]**

(A) 3 (B) 9 (C) 10 (D) 11

55. The standard electrode potentials, Eº of Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe at 300 K are +0.77 V and –0.44 V, respectively. The Eº of Fe^{3+}/Fe at the same temperature is **[NSEC-2015]**

(A) 1.21 V (B) 0.33 V (C) –0.036 V (D) 0.036 V

56. Three Faradays of electricity are passed through aqueous solutions of $AgNO_3$, $NiSO_4$ and $CrCl_3$ kept in three vessels using inert electrodes. The ratio (in moles) in which the metals Ag, Ni and Cr are deposited is : **[NSEC-2016]**

(A) 1 : 2 : 3 (B) 3 : 2 : 1 (C) 6 : 3 : 2 (D) 2 : 3 : 6

57. The standard potentials (E°) of MnO_4^-/Mn^{2+} and MnO_2/Mn^{2+} half cells in acidic medium are 1.51 V and 1.23 V respectively at 298 K. The standard potential of MnO_4^-/MnO_2 half-cell in acidic medium at the same temperature is : **[NSEC-2016]**

(A) 5.09 V (B) 1.70 V (C) 0.28 V (D) 3.34 V

58. Given the E^0 values for the half reactions : **[NSEC-2016]**
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$, 0.15 V
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$, 0.92 V
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$, 1.45 V
Which of the following statements is true?
(A) Sn^{2+} is a stronger oxidizing agent than Pb^{4+}
(B) Sn^{2+} is a stronger reducing agent than Hg_2^{2+}
(C) Hg^{2+} is a stronger oxidizing agent than Pb^{4+}
(D) Pb^{2+} is a stronger reducing agent than Sn^{2+}

59. The conductivity of 0.10 M KCl solution at 298 K is 1.29×10^{-2} Scm^{-1}. The resistance of this solution is found to be 28.44 Ω. Using the same cell, the resistance of 0.10 M NH_4Cl solution is found to be 28.50 Ω. The molar conductivity of NH_4Cl solution in S cm^2 mol^{-1} is : **[NSEC-2016]**

(A) 0.130 (B) 13 (C) 130 (D) 1300

60. Which of the following statements is not correct regarding the galvanic cells ? **[NSEC-2016]**
(A) Oxidation occurs at the anode.
(B) Ions carry current inside the cell.
(C) Electrons flow in the external circuit from cathode to anode.
(D) When the cell potential is positive, the cell reaction is spontaneous.

61. When a medal is electroplated with silver (Ag) **[NSEC-2017]**
(A) The medal is the anode (B) Ag metal is the cathode
(C) The solution contains Ag^+ ions (D) The reaction at the anode is $Ag^+ + e^- \rightarrow Ag$

Use the table given below to answer questions 62 and 63

Reaction	E_0/V
$Ag \rightarrow Ag^+ + e^-$	–0.80
$Cr^{3+} + e^- \rightarrow 3Cr$	–0.74
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76
$I_2(s) + 2e^- \rightarrow 2I^-$	0.54
$Co^{2+} + 2e^- \rightarrow Co$	–0.28
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.26

62. The best reducing agent among the following is **[NSEC-2017]**
(A) Ag^+ (B) Zn^{2+} (C) Cr^{3+} (D) I^-

63. E^o of the given cell is : **[NSEC-2017]**
Ni | (Ni^{+2}, 1.0 M) || (Co^{+2}, 1.0 M) | Co
(A) +0.02V (B) –0.02V (C) –0.54V (D) +0.54V

64. The reduction of O_2 to H_2O in acidic solution has a standard reduction potential of 1.23 V. If the pH of the acid solution is increased by one unit, half cell potential will **[NSEC-2017]**
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(\ell)$
(A) decrease by 59 mV (B) increase by 59 mV
(C) decrease by 236 mV (D) increase by 236 mV

65. From the given standard electrode potentials
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ $E^o = 0.15V$
$Br_2(\ell) + 2e^- \rightarrow 2Br^-(aq)$ $E^o = 1.07V$
The approximate free energy change of the process
$2Br^-(aq) + Sn^{4+}(aq) \rightarrow Br_2(\ell) + Sn^{2+}(aq)$ is : **[NSEC-2018]**
(A) 117.6 kJ (B) 355 kJ (C) –177.6 kJ (D) –355 kJ

66. Concentration of K^+ ions inside a biological cell was found to be 25 times higher than that outside. The magnitude of the potential difference between the two sides of the cell is close to (2.303 RT/F- can be taken as 59 mV; difference in concentrations of other ions can be taken as negligible) **[NSEC-2018]**
(A) 4.2 mV (B) 195 mV (C) 82 mV (D) –82 mV

67. The standard redox potential for the reaction $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ is –1.23V. If the same reaction is carried out at 25ºC and at pH = 7, the potential will be **[NSEC-2018]**
(A) –0.82 V (B) –3.28V (C) 0.82V (D) –1.18V

68. The standard electrode potential (E°) of the Daniel cell is 1.1 V and the overall cell reaction can be represented as $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ Under which of the following conditions will the cell potential be higher than 1.1 V ? **[NSEC-2018]**
(A) 1.0 M Zn^{2+}, 1.0 M Cu^{2+} (B) 1.2 M Zn^{2+}, 1.2 M Cu^{2+}
(C) 0.1 M Zn^{2+}, 1.0 M Cu^{2+} (D) 1.0 M Zn^{2+}, 0.01 M Cu^{2+}

68. An electrochemical cell was constructed with Fe^{2+} /Fe and Cd^{2+} at 25ºC with initial concentration of $[Fe^{2+}]$ = 0.800 M and $[Cd^{2+}]$ = 0.250 M. The EMF of the cell when $[Cd^{2+}]$ becomes 0.100 M is -

Half Cell	E°(V)
Fe^{2+}(aq.)/Fe(s)	–0.44
Cd^{2+}(aq.)/Cd(s)	0.40

(A) 0.013 V (B) 0.011 M (C) 0.051 M (D) 0.002 M

69. If the standard electrode potentials of Fe^{3+}/Fe and Fe^{2+}/Fe are –0.04 V and –0.44 V respectively then that of Fe^{3+}/Fe^{2+} is :
(A) 0.76 V (B) –0.76 V (C) 0.40 V (D) –0.40 V

70. Molten NaCl is electrolysed for 35 minutes with a current of 3.50 Amp. at 40ºC and 1 bar pressure. Volume of chlorine gas evolved in this electrolysis is
(A) 0.016 L (B) 0.98 L (C) 9.8 L (D) 1.96 L

PART-4 : ADDITIONAL PROBLEMS

ONLY ONE OPTION CORRECT TYPE

1. Red hot carbon will remove oxygen from the oxide AO and BO but not from MO, while B will remove oxygen from AO. The activity of metals A, B and M in decreasing order is
(A) A > B > M (B) B > A > M (C) M > B > A (D) M > A > B

2. Salts of A (atomic mass 15), B (atomic mass 27) and C (atomic mass 48) were electrolysed using same amount of charge. It was found that when 4.5 g of A was deposited, the mass of B and C deposited were 2.7g and 9.6 g. The valencies of A, B and C respectively.
(A) 1, 3 and 2 (B) 3, 1 and 3 (C) 2, 6 and 3 (D) 3, 1 and 2

3. The standard potential of the reaction $H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-$ at 298 K by using K_w (H_2O) = 10^{-14}, is :
(A) – 0.828 V (B) 0.828 V (C) 0 V (D) – 0.5 V

4. Given : $Hg_2^{2+} + 2e \longrightarrow 2Hg$, $E^0 = 0.789$ V & $Hg^{2+} + 2e \longrightarrow Hg$, $E^0 = 0.854$ V,
calculate the equilibrium constant for $Hg_2^{2+} \longrightarrow Hg + Hg^{2+}$.
(A) 3.13×10^{-3} (B) 3.13×10^{-4} (C) 6.26×10^{-3} (D) 6.26×10^{-4}

5. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$,
If H^+ concentration is decreased from 1 M to 10^{-4} M at 25ºC, where as concentration of Mn^{2+} and MnO_4^- remain 1 M.
(A) the potential decreases by 0.38 V with decrease in oxidising power
(B) the potential increases by 0.38 V with increase in oxidising power
(C) the potential decreases by 0.25 V with decrease in oxidising power
(D) the potential decreases by 0.38 V without affecting oxidising power

6. The cell Pt (H_2) (1 atm) | H^+(pH = ?) || I^-(a = 1) | AgI(s), Ag(s) | Pt has emf, $E_{298K} = 0$. The standard electrode potential for the reaction $AgI + e^- \rightarrow Ag + I^\ominus$ is – 0.151 volt. Calculate the pH value.
(A) 3.37 (B) 5.26 (C) 2.56 (D) 4.62

7. Using the information in the preceding problem, calculate the solubility product of AgI in water at 25°C [$E^\circ_{(Ag^+, Ag)} = + 0.799$ volt]
(A) 1.97×10^{-17} (B) 8.43×10^{-17} (C) 1.79×10^{-17} (D) 9.17×10^{-17}

8. The efficiency of an hypothetical cell is about 84% which involves the following reaction :
$A(s) + B^{2+}(aq) \longrightarrow A^{2+}(aq) + B(s)$: $\Delta H = -285$ kJ
Then, the standard electrode potential of the cell will be (Assume as $\Delta S = 0$)
(A) 1.20 (B) 2.40 V (C) 1.10 V (D) 1.24 V

9. The temperature coefficient, of the emf i.e. $\frac{dE}{dT} = -0.00065$ volt. deg^{-1} for the cell Cd | $CdCl_2$ (1M) || AgCl (s) | Ag at 25°C. Calculate the entropy changes ΔS_{298K} for the cell reaction, $Cd + 2AgCl \rightarrow Cd^{++} + 2Cl^- + 2Ag$
(A) – 105.5 JK^{-1} (B) – 150.2 JK^{-1} (C) – 75.7 JK^{-1} (D) – 125.5 JK^{-1}

10. One g equivalent of Na metal is formed from electrolysis of fused NaCl. No. of mole of Al from the fused Na_3AlF_6 with the same current passed is :

(A) 1 (B) 3 (C) 1/3 (D) 2

11.

List-1	**List-II**
(P) Conductivity does not change much then increases	(1) NH_3 is added in C_6H_5COOH
(Q) Conductivity increases then does not change much	(2) CH_3COOH is added in NaOH
(R) Conductivity decreases then does not change much	(3) KOH is added in HCl
(S) Conductivity decreases then increases	(4) Conc. KCl is added in dilute $AgNO_3$
(T) Conductivity tends to zero at the end point	(5) $MgSO_4$ is added in $Ba(OH)_2$

	(P)	(Q)	(R)	(S)	(T)
(A)	4	2	1	5	3
(B)	1	2	3	4	5
(C)	5	4	3	2	1
(D)	4	1	2	3	5

12. The standard reduction potentials E° of the following systems are

	System	E° (volts)
(i)	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	1.51
(ii)	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	0.15
(iii)	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	1.33
(iv)	$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	1.61

The oxidising power of the various species decreases in the order

(A) $Ce^{4+} > Cr_2O_7^{2-} > Sn^{4+} > MnO_4^-$ (B) $Ce^{4+} > MnO_4^- > Cr_2O_7^{2-} > Sn^{4+}$

(C) $Cr_2O_7^{2-} > Sn^{4+} > Ce^{4+} > MnO_4^-$ (D) $MnO_4^- > Ce^{4+} > Sn^{4+} > Cr_2O_7^{2-}$

13. Consider the reaction : (T = 298 K)

$Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq.)$

The emf of the cell, when $[Cl^-] = [Br_2] = [Br^-] = 0.01M$ and Cl_2 gas is at 1 atm pressure, will be :
(E° for the above reaction is = 0.29 volt)

(A) 0.54 volt (B) 0.35 volt (C) 0.24 volt (D) –0.29 volt

14. $2Ce^{4+} + Co \longrightarrow 2Ce^{3+} + Co^{2+}$ $E^o_{cell} = 1.89$ V, $E^o_{Co^{2+}/Co} = -0.277$ V hence, $E^o_{Ce^{4+}/Ce^{3+}}$ is :

(A) 0.805 V (B) 1.62 V (C) – 0.805 V (D) – 1.61 V

15. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$; $E^o = 1.51$ V ; $\Delta G_1^0 = -5 \times 1.51 \times F$

$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$; $E^o = 1.23$ V ; $\Delta G_2^0 = -2 \times 1.23 \times F$

$E^o_{MnO_4^-|MnO_2}$ is

(A) 1.70 V (B) 0.91 V (C) 1.37 V (D) 0.548 V

16. A gas Cl_2 at 1 atm is bubbled through a solution containing a mixture of 1 M Br^{-1} and 1 M F^{-1} at 25°C. If the reduction potential is F > Cl > Br, then :

(A) Cl will oxidise Br and not F (B) Cl will oxidise F and not Br.

(C) Cl will oxidise both Br and F (D) Cl will reduce both Br and F

17. The oxidation potentials of Zn, Cu, Ag, H_2 and Ni are 0.76, –0.34, –0.80, 0.00, 0.25 volt, respectively. Which of the following reactions will provide maximum voltage ?

(A) $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$ (B) $Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$

(C) $H_2 + Cu^{2+} \longrightarrow 2H^+ + Cu$ (D) $H_2 + Ni^{2+} \longrightarrow 2H^+ + Ni$

18. Pure water is saturated with pure solid AgCl, a silver rod is placed in the solution and the potential is measured against normal calomel electrode at 25°C. This experiment is then repeated with a saturated solution of AgI. If the difference in potential in the two cases is 0.177 V, what is the ratio of solubilty product (K_{sp}) of AgCl and AgI at the temperature of the experiment ? (In both cases normal calomel electrode is cathod)

(A) 10^3 (B) 10^6 (C) 10^{-3} (D) 10^{-6}

19. Which one of the following will increase the voltage of the cell ? (T = 298 K)

$$Sn + 2Ag^+ \longrightarrow Sn^{2+} + 2Ag$$

(A) increase in the size of silver rod (B) increase in the concentration of Sn^{+2} ions

(C) increase in the concentration of Ag^+ ions (D) none of the above

20. In a $H_2 - O_2$ fuel cell, 6.72 L of hydrogen at NTP reacts in 15 minutes, the average current produced in amperes is

(A) 64.3 amp (B) 643.3 amp (C) 6.43 amp (D) 0.643 amp

21. The standard reduction potential of a silver chloride electrode is 0.2 V and that of a silver electrode is 0.79 V. The maximum amount of AgCl that can dissolve in 10^6 L of a 0.1 M $AgNO_3$ solution is

(A) 0.5 mmol (B) 1.0 mmol (C) 2.0 mmol (D) 2.5 mmol

22. A cell Cu | Cu^{++} || Ag^+ | Ag initially contains 2M Ag^+ and 2M Cu^{++} ions in 1 L electrolyte. The change in cell potential after the passage of 10 amp current for 4825 sec during usage of cell is: (Take $\frac{2.303RT}{F} = 0.06$)

(A) – 0.009 V (B) – 1.00738 V (C) – 0.0038 V (D) –1.2 V

23. At 27ºC $\left(\frac{\partial E^o}{\partial T}\right)_P = -1.45 \times 10^{-3}$ V K^{-1} and $E^o = 1.36$ V

For the cell Pt | H_2 (g) | HCl (aq) | Cl_2 | Pt.
Calculate entropy and enthalpy change in this standard state.

(A) –962.48 JK^{-1}, –346.435 KJ (B) –279.85 JK^{-1}, –346.453 KJ

(C) –1326.23 JK^{-1}, –346.435 KJ (D) –280.24 KJK^{-1}, –346.435 KJ.

NUMERICAL TYPE QUESTION

24. Determine range of E° values for this reaction $X^{2+}_{aq.} + 2e^- \longrightarrow X(s)$ for given conditions :

(a) If the metal X dissolve in HNO_3 but not in HCl it can displace Ag^+ ion but not Cu^{2+} ion.
(b) If the metal X in HCl acid producing H_2(g) but does not displace either Zn^{2+} or Fe^{2+}.

Given : $E^0_{Ag^+/Ag} = 0.8$ V , $E^0_{Fe^{2+}/Fe} = -0.44$ V ,

$E^0_{Cu^{2+}/Cu} = 0.34$ V , $E^0_{NO_3^-/NO} = 0.96$ V , $E^0_{Zn^{2+}/Zn} = -0.76$V

25. The standard reduction potential of TiO^{2+} and Ti^{3+} are given by

$TiO^{2+} + 2H^+ + e^- \longrightarrow Ti^{3+} + H_2O$ $E^0 = 0.10$ V

$Ti^{3+} + 3e^- \longrightarrow Ti$ $E^0 = -1.21$ V

Find the standard reduction potential of TiO^{2+} to Ti .

26. Calculate the electrode potential at 25^{0}C of Cr^{3+}, $Cr_2O_7^{2-}$ electrode at pOH = 11 in a solution of 0.01 M both in Cr^{3+} and $Cr_2O_7^{2-}$.

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O \qquad E^0 = 1.33 \text{ V.}$$

27. In two vessels each containing 500ml water, 0.5m mol of aniline ($K_b = 10^{-9}$) and 25 m mol of HCl are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately.

28. Write cell reaction from given cell diagrams

(A) $Cu \mid Cu^{2+} \parallel Cl^- \mid Hg_2Cl_2 \mid Hg \mid Pt$

(B) $Ag\ (s) \mid AgIO_3\ (s) \mid Ag^+, HIO_3 \parallel Zn^{2+} \mid Zn\ (s)$

(C) $Mn\ (s) \mid Mn(OH)_2\ (s)\ Mn^{2+}, OH^- \parallel Cu^{2+} \mid Cu\ (s)$

29. For the galvanic cell : $Ag \mid AgCl\ (s) \mid KCl\ (0.2M) \parallel KBr\ (0.001M) \mid AgBr\ (s) \mid Ag$,

Calculate the EMF generated? (Take $\frac{2.303RT}{F} = 0.06$)

[$K_{sp(AgCl)} = 10^{-10}$; $K_{sp(AgBr)} = 10^{-13}$]

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

31. The EMF of the standard weston cadmium cell Cd (12.5%) in Hg | $3CdSO_4, 8H_2O$ (solid) | saturated solution of $CdSO_4$ || $Hg_2SO_4(s)$ | Hg is 1.0180 volts at 25° C and the temperature coefficient of the cell, $\left(\frac{\partial E}{\partial T}\right)_P = -4.0 \times 10^{-5}$ V/degree. Calculate ΔG, ΔH and ΔS for the reaction in the cell when n = 2.

32. ΔH for the reaction $Ag(s) + \frac{1}{2}Hg_2Cl_2(s) \longrightarrow AgCl(s) + Hg(\ell)$ is +1280 cal at 25°C. This reaction can be conducted in a cell for which the emf = 0.0455 volt at this temperature. Calculate the temperature coefficient of the emf.

33. The standard electromotive force of the cell :
$Fe \mid Fe^{2+}(aq) \mid\mid Cd^{2+} \mid Cd$ is 0.0372 V
The temperature coefficient of e.m.f. is -0.125 V K^{-1}. Calculate the quantities ΔG^o, ΔH^o and ΔS^o at 25ºC.

34. A metal is known to form fluoride MF_2. When 10A of electricity is passed through a molten salt for 330 sec., 1.95g of metal is deposited. Find the atomic weight of M. What will be the quantity electricity required to deposit the same mass of Cu from $CuSO_4$?

35. Electrolysis of a solution of HSO_4^- ions produces $S_2O_8^{2-}$. Assuming 75% current efficiency, what current should be employed to achieve a production rate of 1 mole of $S_2O_8^{2-}$ per hour ?

36. **(a)** Calculate ΔG^o of the following reaction :

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

Given : $\Delta G^o(AgCl) = -109$ kJ/mole, $\Delta G^o(Cl^-) = -129$ kJ/mole, $\Delta G^o(Ag^+) = 77$ kJ/mole.
Represent the above reaction in form of a cell.
Calculate E^o of the cell. Find $\log_{10}K_{sp}$ of AgCl at 25ºC.
(b) 6.539×10^{-2} g of metallic Zn (atomic mass = 65.39 amu) was added to 100 mL of saturated solution of AgCl.

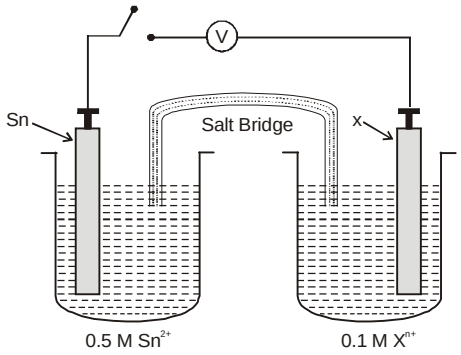
Calculate $\log_{10}\frac{[Zn^{2+}]}{[Ag^+]^2}$ at equilibrium at 25ºC, given that :

$Ag^+ + e^- \longrightarrow Ag$ $\qquad E^o = 0.80$ V

$Zn^{2+} + 2e^- \longrightarrow Zn$ $\qquad E^o = -0.76$ V

Also find how many moles of Ag will be formed. (Take $\frac{114}{193} = 0.59$, $\frac{1.56}{0.059} = 26.44$)

37. An electrochemical cell is constructed with an open switch as shown below :



When the switch is closed, mass of tin-electrode increase. If E^o (Sn^{2+} / Sn) = – 0.14 V and for E^o (X^{n+} / X) = – 0.78 V and initial emf of the cell is 0.65 V, determine n and indicate the direction of electron flow in the external circuit.

38. At 298 K, the conductivity of pure water is 5.5×10^{-6} S m^{-1}. Calculate the ionic product of water using the following data :

λ°_m values (in S m^2 mol^{-1}) : $Ba(OH)_2 = 5.3 \times 10^{-2}$, $HCl = 4.25 \times 10^{-2}$, $BaCl_2 = 2.8 \times 10^{-2}$.

Does your answer match with experimental value. Write 20 for yes & 40 for No.

39. The equivalent conductance of 0.10 N solution of $MgCl_2$ is 97.1 mho cm^2 $eq.^{-1}$ at 25°C. A cell with electrodes that are 1.50 cm^2 in surface area and 0.50 cm apart is filled with 0.1N $MgCl_2$ solution. How much current will flow when the potential difference between the electrodes is 5 volts ?

40. A current 0.5 ampere when passed through $AgNO_3$ solution for 193 sec. deposited 0.108 g of Ag . Find the equivalent weight of Ag :

41. The EMF of the cell $M|M^{n+}$ (0.02 M) $||$ H^+ (1M) | H_2 (g) (1 atm) , Pt at 25°C is 0.81V. Calculate the valency of the metal if the standard oxidation potential of the metal is 0.76V.

42. Using the ΔG^0 for the reactions

$C + O_2 \rightarrow CO_2$ $\Delta G^0 = -395$ kJ / mole,

$2Al(l) + 3/2O_2 \rightarrow Al_2O_3(s)$ $\Delta G^0 = -1269$ kJ/mole

$Al_2O_3(s) \rightarrow Al_2O_3$ (melt) $\Delta G^0 = 16$ kJ/mole

Calculate the EMF for the cell reaction

$2Al_2O_3$ (melt) $+ 3C \rightarrow 4Al(\ell) + 3CO_2(g)$

The number of electrons involved in the reaction is 12.

43. A silver coulom meter is in series with a cell electrolyzing water. In a time of 1 minute at a constant current, 1.08 g silver got deposited on the cathode of the coulometer. What total volume **(in mL)** of the gases would have produced in other cell if in this cell the anodic and cathodic efficiencies were 90% and 80% respectively. Assume STP conditions and the gases collected are dry. (Ag – 108) (Molar volume of any ideal gas at STP = 22.4 L). Report as (your answer $\div 10$)

44. A saturated solution of MX is prepared K_{SP} of MX is $a \times 10^{-b}$. If 10^{-7} mol of MNO_3 are added in 1 ℓ of this solution conductivity of this solution is 55×10^{-7} S m^{-1} :

$\lambda^{\circ}_{m^+} = 6 \times 10^{-3}$ S m^2 mol^{-1}

$\lambda^{\circ}_{x^-} = 8 \times 10^{-3}$

$\lambda^{\circ}_{NO_3^-} = 7 \times 10^{-3}$

Find the value of (a + b) ? Given that $10 < a < 100$

45. $Zn^{2+}(aq) + 4OH^{-}(aq) \longrightarrow Zn(OH)_4^{2-}(aq)$

Value of equilibrium constant (K_f) for above reaction is 10^x then find x:

Given : $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$; $E^o = -0.76V$

$Zn(OH)_4^{2-}(aq) + 2e^{-} \rightarrow Zn(s) + 4OH^{-}(aq)$; $E^o = -1.36V$

$2.303\frac{RT}{F} = 0.06$

$Zn^{2+}(aq) + 4OH^{-}(aq) \longrightarrow Zn(OH)_4^{2-}(aq)$

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

46. Which of the following statements is wrong about galvanic cells ?
(A) Cathode is the positive electrode
(B) Cathode is the negative electrode
(C) Electrons flow from cathode to anode in the external circuit
(D) Reduction occures at cathode

47. When a cleaned strip of zinc metal is placed in a solution of $CuSO_4$, a spontaneous reaction occurs. Which of the following observation(s) is/are made ?
(A) the mass of zinc metal decreases gradually
(B) the copper metal starts depositing on either zinc plate or settles down to the vessel
(C) the solution remains electrically neutral
(D) the temperature of the solution decreases as it is an endothermic reaction.

48. Mark out the correct statement(s)
(A) Copper metal cannot reduce iron (II) ions in acidic solutions.
(B) Sodium can be obtained by the electrolysis of aqueous solution of NaCl using Pt electrodes.
(C) The current carrying ions in an electrolytic cell are not necessarily discharged at the electrodes.
(D) Cations having more negative oxidation potential than – 0.828 V are reduced in preference to water.

49. When a lead storage battery is recharged
(A) $PbSO_4$ is formed (B) Pb is formed (C) SO_2 is consumed (D) H_2SO_4 is formed

50. Which of the following statements is / are correct ?
(A) The conductance of one cm^3 (or 1 $unit^3$) of a solution is called conductivity.
(B) Specific conductance increases while molar conductivity decreases on progressive dilution.
(C) The limiting equivalent conductivity of weak electrolyte cannot be determine exactly by extraplotation of the plot of Λ_{eq} against $\sqrt{c}$.
(D) The conductance of metals is due to the movement of free electrons.

51. Peroxodisulphate salts ($Na_2S_2O_8$) are strong oxidizing agents used as bleaching agents for fats, oil etc.
Given
$O_2(g) + 4H^{\oplus}(aq) + 4e^{-} \longrightarrow 2H_2O(\ell)$ $E^o = 1.23$ V
$S_2O_8^{-2} + 2e^{-} \longrightarrow 2SO_4^{-2}$ (aq) $E^o = 2.01$ V
Which of the following statements is (are) correct ?
(A) Oxygen gas can oxidize sulphate ion to per-oxo disulphate ion ($S_2O_8^{-2}$) in acidic solution.
(B) $O_2(g)$ is reduced to water
(C) Water is oxidised to O_2
(D) $S_2O_8^{-2}$ ions are reduced to SO_4^{-2} ions.

COMPREHENSION

Comprehension # 1

The molar conductance of NaCl varies with the concentration as shown in the following table . and all values follows the equation

$\lambda_m^C = \lambda_m^\infty - b\sqrt{C}$

Where λ_m^C = molar specific conductance

λ_m^∞ = molar specific conductance at infinite dilution

C = molar concentration

Molar Concentration of NaCl	Molar Conductance in $ohm^{-1}\ cm^2\ mole^{-1}$
4×10^{-4}	107
9×10^{-4}	97
16×10^{-4}	87

When a certain conductivity cell (C) was filled with 25×10^{-4} (M) NaCl solution. The resistance of the cell was found to be 1000 ohm. At Infinite dilution, conductance of Cl^- and SO_4^{-2} are 80 $ohm^{-1}\ cm^2\ mole^{-1}$ and 160 $ohm^{-1}\ cm^2\ mole^{-1}$ respectively.

52. What is the molar conductance of NaCl at infinite dilution ?

(A) 147 $ohm^{-1}\ cm^2\ mole^{-1}$ (B) 107 $ohm^{-1}\ cm^2 s\ mole^{-1}$

(C) 127 $ohm^{-1}\ cm^2\ mole^{-1}$ (D) 157 $ohm^{-1}\ cm^2\ mole^{-1}$

53. What is the cell constant of the conductivity cell (C)

(A) 0.385 cm^{-1} (B) 3.85 cm^{-1} (C) 38.5 cm^{-1} (D) 0.1925 cm^{-1}

54. If the cell (C) is filled with 5×10^{-3} (N) Na_2SO_4 the observed resistance was 400 ohm. What is the molar conductance of Na_2SO_4.

(A) 19.25 $ohm^{-1}\ cm^2\ mole^{-1}$ (B) 96.25 $ohm^{-1}\ cm^2\ mole^{-1}$

(C) 385 $ohm^{-1}\ cm^2\ mole^{-1}$ (D) 192.5 $ohm^{-1}\ cm^2 s\ mole^{-1}$

55. If a 100 mL solution of 0.1M HBr is titrated using a very concentrated solution of NaOH, then the conductivity (specific conductance) of this solution at the equivalence point will be (assume volume change is negligible due to addition of NaOH) . Report your answer after multipling it with 10 in Sm^{-1}.

[Given $\lambda^\circ_{(Na^+)} = 8 \times 10^{-3}\ Sm^2\ mol^{-1}$, $\lambda^\circ_{(Br^-)} = 4 \times 10^{-3}\ S\ m^2\ mol^{-1}$]

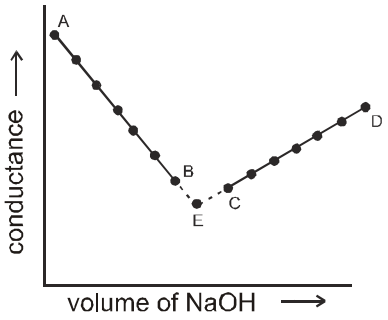
(A) 6 (B) 12 (C) 15 (D) 24

Comprehension # 2

Strong Acid Versus Strong Base

The principle of conductometric titrations is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that the conductivity of the solution varies during the course of the titration. Take, for example, the titration between a strong acid, say HCl, and a strong base, say NaOH. Before NaOH is added, the conductance of HCl solution has a high value due to the presence of highly mobile hydrogen ions. As NaOH is added, H^+ ions are replaced by relatively slower moving Na^+ ions. Consequently, the conductance of the solution decreases and this continues right upto the equivalence point where the solution contains only NaCl. Beyond the equivalence point, if more of NaOH is added, then the solution contains an excess of the fast moving OH^- ions with the result that its conductance is increased and it continues to increase as more and more of NaOH is added.

If we plot the conductance value versus the amount of NaOH added, we get a curve of the type shown in **Fig**.



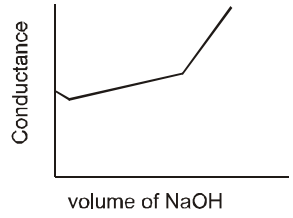
The descending portion AB represents the conductances before the euivalence point (solution contains a mixture of acid HCl and the salt NaCl) and the ascending portion CD represents the conductances after the equivalence point (solution contains the salt NaCl and the excess of NaOH). The point E which represents the minium conductance is due to the solution containing only NaCl with no free acid or alkali and thus represents the equivalence point. This point can, however, be obtained by the extrapolation of the lines AB and DC, and therefore, one is not very particular in locating this point experimentally as it is in the case of ordinary acid-base titrations involving the acid-base indicators.

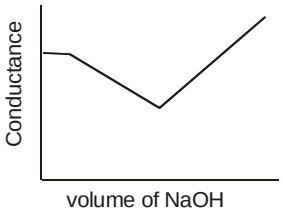
Weak Acid versus Strong Base

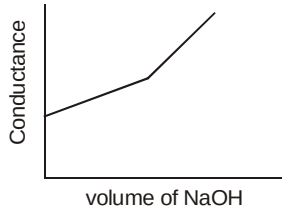
Let us take the specific example of acetic acid being titrated against NaOH. Before the addition of alkali, the solution shows poor conductance due to feeble ionization of acetic acid. Initially the addition of alkali casuse not only the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to the common ion Ac^- and thus the conductance of the solution decreases in the beginning. But very soon the conductance starts increasing as addition of NaOH neutralizes the undissociated HAc to Na^+Ac^- thus causing the replacement of non-conducting HAc with strong-conducting electrolyte Na^+Ac^-. The increase in conductance continunes right up to the equivalence point. Beyond this point conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions. The graph near the equivalence point is curved due to the hydrolysis of the salt NaAc. The actual equivalence point can, as usual, be obtained by the extrapolation method.

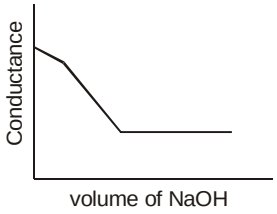
In all these graphs it has been assumed that the volume change due addition of solution from burrette is negligible, hence volume change of the solution in beaker the conductance of which is measured is almost constant throughout the measurement.

56. The nature of curve obtained for the titration **between weak acid versus strong base as described in the above passage will be :**

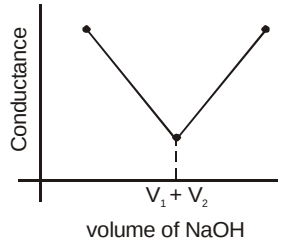
(A) 

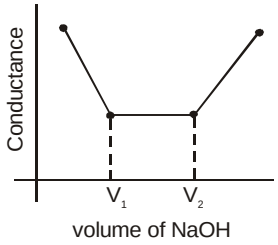
(B) 

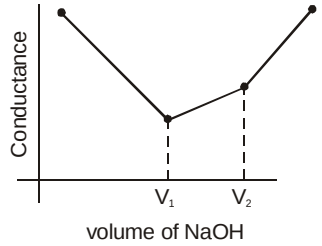
(C) 

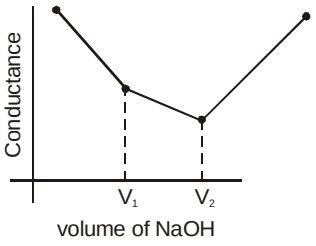
(D) 

57. The most appropriate titration curve obtained when a mixture of a strong acid (say HCl) and a weak acid (say CH_3COOH) is titrated with a strong base(say NaOH) will be

(A) 

(B) 

(C) 

(D) 

RRP ANSWER KEY

PART- 1

1.	(A)	**2.**	(B)	**3.**	(D)	**4.**	(C)	**5.**	(B)	**6.**	(B)	**7.**	(D)
8.	(C)	**9.**	(C)	**10.**	(C)	**11.**	(B)	**12.**	(A)	**13.**	(A)	**14.**	(D)
15.	(A)	**16.**	(A)	**17.**	(A)	**18.**	(C)	**19.**	(B)	**20.**	(C)	**21.**	0.6
22.	(1 M)	**23.**	50%	**24.**	**(48.5)**	**25.**	0.0616						

PART - 2

1.	(A)	**2.**	(D)	**3.**	(A)	**4.**	(A)	**5.**	(ACD)	**6.**	(BCD)	**7.**	(BD)
8.	(AD)	**9.**	(AB)	**10.**	(BD)	**11.**	(AB)	**12.**	(AB)	**13.**	4 (a, b, d, f)		
14.	5	**15.**	8	**16.**	59	**17.**	6	**18.**	$150\ \Omega^{-1}cm^2\ mole^{-1}$				

PART - 3

1.	(B)	**2.**	(B)	**3.**	(C)	**4.**	(C)	**5.**	(A)	**6.**	(C)	**7.**	(B)
8.	(C)	**9.**	(C)	**10.**	(D)	**11.**	(B)	**12.**	(A)	**13.**	(C)	**14.**	(B)
15.	(A)	**16.**	(C)	**17.**	(B)	**18.**	(D)	**19.**	(A)	**20.**	(D)	**21.**	(B)
22.	(D)	**23.**	(A)	**24.**	(C)	**25.**	(B)	**26.**	(D)	**27.**	(A)	**28.**	(C)
29.	(C)	**30.**	(A)	**31.**	(C)	**32.**	(B)	**33.**	(B)	**34.**	(B)	**35.**	(B)
36.	(A)	**37.**	(A)	**38.**	(B)	**39.**	(A)	**40.**	(B)	**41.**	(C)	**42.**	(B)
43.	(B)	**44.**	(B)	**45.**	(D)	**46.**	(D)	**47.**	(B)	**48.**	(C)	**49.**	(B)
50.	(B)	**51.**	(A)	**52.**	(C)	**53.**	(B)	**54.**	(C)	**55.**	(C)	**56.**	(C)
57.	(B)	**58.**	(B)	**59.**	(C)	**60.**	(C)	**61.**	(C)	**62.**	(D)	**63.**	(B)
64.	(A)	**65.**	(A)	**66.**	(C)	**67.**	(A)	**68.**	(C)	**68.**	(B)	**69.**	(A)
70.	(B)												

PART - 4

1. (C) **2.** (C) **3.** (A) **4.** (C) **5.** (A) **6.** (C) **7.** (B)

8. (D) **9.** (D) **10.** (C) **11.** (D) **12.** (B) **13.** (B) **14.** (B)

15. (A) **16.** (A) **17.** (B) **18.** (B) **19.** (C) **20.** (A) **21.** (B)

22. (A) **23.** (B)

24. (a) $0.34 < E° < 0.8$; (b) $-0.44 < E° < 0$

25. –0.8825 volt **26.** 0.936V **27.** E = 0.395 V

28. (A) $Hg_2Cl_2(s) + Cu(s) \longrightarrow Cu^{2+}(aq) + 2Cl^-(aq) + 2Hg(l)$

(B) $2Ag_{(s)} + 2IO_3^- + Zn^{2+} \longrightarrow 2AgIO_{3_{(s)}} + Zn_{(s)}$

(C) $Mn_{(s)} + 2OH^- + Cu^{2+} \longrightarrow Mn(OH)_{2_{(s)}} + Cu_{(s)}$

29. –0.42 V **30.** $[Br^-] : [Cl^-] = 1 : 200$

31. $\Delta G = -196.5$ kJ ; $\Delta H = 198.8$ kJ ; $\Delta S = -7.72$ J d_{eg-1} **32.** 3.389×10^{-4} volt deg^{-1}

33. $\Delta S^o = -24.125$ kJ K^{-1} $\Delta G^o = -7179.6$ J

$\Delta H^o = -7196.43$ kJ

34. A = 114 , Q = 5926.8C. **35.** + 71.5 amp

36. (a) $E^o = 0.59$ V, $\log_{10}K_{sp} = -10$; (b) 52.88, 10^{-6} mole.

37. n = 3, Since mass of Sn increasing, Sn - electrode is working as cathode and X - metal electrode anode and electrons are flowing from X-electrode to Sn-electrode in the external circuit.

38. 20 **39.** 0.1456 amp **40.** 108. **41.** n = 2

42. –1.14 volt **43.** 14 **44.** 26 **45.** 20

46. (BC) **47.** (ABC) **48.** (ACD) **49.** (BD) **50.** (ACD)

51. (CD) **52.** (C) **53.** (D) **54.** (D) **55.** (B) **56.** (A) **57.** (C)

RRP SOLUTIONS

PART- 1

1. $E_{cell} \Rightarrow E^0_{Sn^{4+}/Sn^{2+}} + E^0_{Fe^{2+}/Fe^{3+}} \Rightarrow 0.15 — 0.77 = -0.62$ V

2. EMF = $E^o_{cathode} - E^o_{anode} = 0.76 - 0.41 = 0.35$.

3. $2Cu^{+1} \longrightarrow Cu + Cu^{+2}$

$2Cu^{+1} + 2e \longrightarrow 2Cu$

$Cu - 2e \longrightarrow Cu^{+2}$

———————————

$2Cu^{+1} \longrightarrow Cu^{+2} + Cu$

———————————

$\therefore \quad E° = \frac{2 \times 0.521 + 2(-0.337)}{2} = 0.184$

4. $\frac{W_1}{E_1} = \frac{W_2}{E_2}$; $\frac{4}{12} = \frac{W_{Ag}}{108}$; $W_{Ag} = 36$

5. $Zn + Ni^{+2} \longrightarrow Zn^{+2} + Ni$

$E^o = E^o_{Ni^{+2}/Ni} - E^o_{Zn^{+2}/Zn}$

$= -0.23 - (-0.76) = + 0.53$ V

Positive value shows that the process is spontaneous.

Rest of all (I) (II) (III) combination have negative E^o value.

(I) $E^o = -0.44 - (-0.23) = -0.21$ V

(II) $E^o = -0.76 - (-0.23) = -0.53$ V

(III) $E^o = -0.76 - (-0.44) = -0.32$ V

6. $Cu^{2+} + 1e^- \rightarrow Cu^+ \quad E^0_1 = 0.15$ v $\Delta G^0_1 = -n_1 E^0_1 F$

$Cu^+ + 1e^- \rightarrow Cu \quad E^0_2 = 0.50$ v $\Delta G^0_2 = -n_2 E^0_2 F$

$Cu^{2+} + 2e^- \rightarrow Cu \quad \Delta G^o = \Delta G^o_1 + \Delta G^o_2$

$(-1)\, n E^0 F = (-1)\, n_1 E^0_1 F + (-1)\, n_2 E^0_2 F$

$E^0 = \frac{n_1 E^0_1 + n_2 E^0_2}{n} = \frac{0.15 \times 1 + 0.50 \times 1}{2} = 0.325$V

7. $H^+ + e^- \longrightarrow \frac{1}{2} H_2$. $\quad E = 0 - \frac{.0591}{1} \log_{10} \frac{1}{[H^+]} = + 0.0591 \log_{10}[H^+]$.

$E_1 = 0$ {pH = 0}.

$E_2 = + 0.0591 \log_{10}[10^{-7}] = - .0591 \times 7$ {at pH = 7} $= -0.41$ V.

8. $E_{cell} = E^0_{cell} - \frac{0.0591}{1} \log_{10}[H^+]\,[Cl^-]$ and $E'_{cell} = E^0_{cell} - \frac{0.0591}{1} \log_{10} 100[H^+]\,[Cl^-]$.

$E'_{cell} - E_{cell} = -2 \times 0.0591 = -0.1182$.

10. Cell representation is correct, however working of cell will depend upon SRP values of both electrodes as well as concentration/partial pressure of species involved in cell reaction.

For $E_{cell} = E^{o}_{cell}$, $[Fe^{3+}] = [Fe^{2+}] = [I^-] = 1$ M & $P_{I_2} = 1$ bar.

Cell reaction : $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(g)$ [I^- oxidized & Fe^{3+} reduced].

11. $0.34 = \frac{0.06}{2} \log K_{eq}$

$\log K_{eq} = 11.3$ or $K_{eq} = 2 \times 10^{11}$

12. For same charge passed mole of H_2 produced = 2 × moles of O_2 produced.

13. $\frac{m_X}{m_Y} = \frac{\frac{A_X}{2} \times Q}{\frac{A_Y}{1} \times Q} \quad \Rightarrow \quad \frac{m_X}{m_Y} = 1 \quad \because \quad A_X = 2A_Y$

14. $C_4H_{10} + \frac{13}{2}O_2 \longrightarrow 4CO_2 + 5H_2O$

2 mol 13 mol O_2

$\Downarrow$

52 mol electron transfer

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

Dilution upto twice of initial volume just complete submerge of electrodes, k becomes half and A becomes double. Hence R remains 50 Ω.

16. $\lambda_{eq} = \frac{\left(\frac{1}{R} \times G^*\right) \times 10^{-3}}{N}$

$\therefore 10^{-2} = \frac{\left(\frac{1}{50} \times G^*\right) \times 10^{-3}}{1/10}$

$\therefore G^* = 50\ m^{-1}$

17. **(i)** $K_2SO_4 . Al_2(SO_4) . 24\ H_2O \Rightarrow 2\ K^+_{aq} + 2\ Al^{+3}_{aq} + 4\ SO^{-2}_{aq}$.

$\lambda^{\alpha}_{m(\text{Potash alum})} = 2\lambda^{\alpha}_{m(K^+)} + 2\lambda^{\alpha}_{m(Al^{+3})} + 4\lambda^{\alpha}_{m(SO_4^{-2})}$

$= 2 \times 73.5 + 2 \times 189 + 4 \times 160$

$= 1165\ r^-.cm^2.mol^{-1}$

V.F. for Potash alum = 8 . (total Positive charge)

$\lambda^{\alpha}_{eq(\text{Potash alum})} = \frac{\lambda^{\alpha}_{eq(\text{Potash alum})}}{8} = \frac{1165}{8} = 145.6\ \Omega^{-}\ cm^2\ eq^{-1}$

$\frac{\lambda^{\alpha}_{m(\text{Potash alume})}}{\lambda^{\alpha}_{eq(\text{Potash alume})}} = \frac{1165}{145.6} = 8 : 1$

(ii) $\frac{\lambda^{\alpha}_{m}}{\lambda^{\alpha}_{eq}}$ = V.F. of Compound, V.F. of Potash alume = 8.

18. $\underset{(SA)}{HCl} \rightarrow H^{\oplus} + Cl^{-}$ $\underset{(SASB)}{NaCl} \rightarrow Na^{\oplus} + Cl^{-}$

H^+ have highest mobility in comparison with $Na^{\oplus}$, both compound 100% dissociate.

because Molar mass of H^+ is less than $Na^{\oplus}$ ion and NH_4OH is weak basic.

19. Equivalent conductance in different cell is equal :

$\lambda_{eq} = \frac{K \times 1000}{N}$ K and N are constant

20. $CH_3COOH + NaOH \longrightarrow Na^+ + CH_3COO^- + H_2O$ Conductance Ist increases slowly since no. of ions increases. After end point it increases sharply due to OH^- ions.

21. $ClO_3^- + 2H_2O + 4e \longrightarrow ClO^- + 4OH^-$; $\Delta G_1°$

$ClO^- + H_2O + e \longrightarrow \frac{1}{2} Cl_2 + 2OH^-$; $\Delta G_2°$

$\frac{1}{2} Cl_2 + e \longrightarrow Cl^-$; $\Delta G_3°$

$ClO_3^- + 3H_2O + 3e \longrightarrow Cl^- + 6OH^-$; $\Delta G°$

$\therefore \quad \Delta G° = \Delta G_1° + \Delta G_2° + \Delta G_3°$

$-6FE° = -4F \times 0.54 - 1F \times 0.45 - 1F \times 1.07$

$\therefore \quad E° = + \frac{3.68}{6} = + 0.61\ V$

22. Number of moles of Cu^{2+} produced from anode = number of moles of Cu^{2+} deposited at cathode.

24. $\frac{W}{E} = \frac{it}{96500} \Rightarrow \frac{3}{E} = \frac{9.95 \times 10 \times 60}{96500} \Rightarrow E = 48.5$

25. $K = \frac{1}{R}\left(\frac{\ell}{a}\right) \Rightarrow 0.0112 = \frac{1}{55}\left(\frac{\ell}{a}\right) \Rightarrow \frac{\ell}{a} = 0.616$

PART - 2

1. $Fe^{+2} + 2e^- \longrightarrow Fe$

Number of milimoles of e^- passed = $\frac{(965)(1)}{96500} \times 1000 = 10$

$\therefore$ Milimoles of Fe^{+2} reduced = 5

$\therefore$ Milimoles of Fe^{+2} left = 1000 x – 5

$\therefore$ By equating mili equivalent = $(1000x - 5) \times 1 = (0.1)(10)(5)$

$\Rightarrow$ $x = 10^{-2}$

2.

	CH_3COOH	+ NaOH	$\rightleftharpoons$	CH_3COONa	+ H_2O
milli moles	100×0.2	100×0.2		–	–
	0	0		100×0.2	

Then,

$[CH_3COONa] = \frac{100 \times 0.2 \times 10^{-3}}{200} \times 1000 = 0.1$

D.O.D (α) for $CH_3COOH = \frac{\Lambda_m}{\Lambda_m^0} = \frac{2.0}{200} = 10^{-2}$

Then,

K_a of $CH_3COOH = C\alpha^2 = 0.1 \times (10^{-2})^2 = 10^{-5}$

$\Rightarrow$ pKa = 5 for CH_3COOH.

So, pH of CH_3COONa salt is :

$$pH = 7 + \frac{1}{2}pKa + \frac{1}{2}\log C.$$

$$= 7 + \frac{1}{2} \times 5 + \frac{1}{2}\log 0.1 = 9.$$

3. $\frac{\lambda}{\lambda^\circ} = \frac{122}{\lambda^\circ} = 0.936$

$\lambda^\circ = 130.34\ \Omega^{-1}\ cm^2\ eq^{-1}$

$\frac{\lambda_+^\circ}{\lambda^\circ} = \frac{0.98}{1.98}$

$\frac{\lambda_+^\circ}{130.34} = \frac{0.98}{1.98}$

$\lambda_{K+}^\circ = \lambda_+^\circ = 64.51\ \Omega^{-1}\ cm^2\ eq^{-1}$

And

$$\frac{\lambda_-^\circ}{\lambda^\circ} = 1 - \frac{\lambda_+^\circ}{\lambda^\circ}$$

$$\frac{\lambda_+^\circ}{\lambda^\circ} = 1 - \frac{0.98}{1.98}$$

$$\frac{\lambda_-^\circ}{130.34} = \frac{1}{1.98}$$

$$\lambda_-^\circ = \frac{130.34}{1.98}$$

$$= 65.83\ \Omega^{-1}\ cm^2\ eq^{-1}$$

4. $Fe(OH)_3 \rightleftharpoons Fe^{+3} + 3OH^-$; $[Fe^{+3}] = \frac{K_{sp}}{[OH^-]^3} = \frac{10^{-26}}{(10^{-2})^3} = 10^{-20}$

$$E_{Fe^{+3}/Fe} = E^0_{Fe^{+3}/Fe} - \frac{0.06}{3}\log\frac{1}{[Fe^{+3}]}$$

$$= -0.036 - \frac{0.06}{3} \times 20 = -0.036 - 0.4 = -0.436$$

5. X^- is I^-

Y^- is Cl^-

SRP $Cl_2 > Br_2 > I_2$

6. $E_{cell} = -\frac{RT}{nF}\ell n\frac{[H^+]_{anode}}{[H^+]_{cathode}} = -\frac{RT}{nF}\ell n\frac{\frac{K_a[HA]_{anode}}{[NaA]_{anode}}}{\frac{K_a[HA]_{cathode}}{[NaA]_{cathode}}}$

7. Anode : $2H_2O \longrightarrow O_2\uparrow + 4OH^- + 4e^-$

0.01 mol 0.04 F

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

$20\times10^{-3}\times0.5$ 0.04 faraday

$= 10^{-2}$ mol –0.02

= 0.01 mol = 0.02 F

$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-$

0.02F 0.01 mol

Total volume of gases evolved at STP = (0.01 + 0.01) × 22.4 = 448 ml

8. $0.164 = 0 + \frac{0.0591}{1}\log_{10}\frac{0.1}{[Ag^+]_{anode}}$

$\Rightarrow [Ag^+]_{anode} = 1.66 \times 10^{-4}$ M.

$K_{sp} = [Ag^+]^2 \times [CrO_4^{2-}] = 1.66 \times 10^{-4} \times \left(\frac{1.66\times10^{-4}}{2}\right)$

9. [Hint : Reverse of (B) & (C) is spontaneous ; weakest Oxidizing Agent here is Mg^{2+}]

11. Electrolysis of NaBr Solution

at $\frac{\text{anode C}}{2Br^- \rightarrow Br_2 + 2e^-}$

at cathode

$2H_2O \xrightarrow{+2e^-} H_2 + 2OH^-$

It is clear that Br^- ion are replaced by OH^-. hence molar conductance & specific conductance increases.

12. (A) For $Cr_2O_7^{2-}$ (acidic solution)

E^o = 1.23 which is greater than $E^o_{(Fe^{2+}/Fe)}$ hence it can oxidize Fe

(B) $H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$ E^o = –0.70 V

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ E^o = 1.30 V

$H_2O_2 + 2H^+ \longrightarrow 2H_2O$ $E^o = \frac{(-0.70\times2)+(4\times1.30)}{2} = 1.9$

Here E^o is grater than $E^o_{(Fe^{2+}/Fe)}$ hence H_2O_2 in acidic medium can oxides Fe.

13. **(a, b, d, f)** $E = E^o - \frac{0.6}{n}\log\frac{[A^+][Cl^-]}{P_{Cl_2}}$

14. $\Lambda^o_{CH_3COOH} = \Lambda^o_{CH_3COONa} + \Lambda^o_{HCl} - \Lambda^o_{NaCl}$

$= 150 + 200 - 125 = 225 \text{ S cm}^2 \text{ mol}^{-1}$.

$\Lambda^c_{CH_3COOH} = 2.25 \text{ S cm}^2 \text{ mol}^{-1}$.

$$\alpha = \frac{\Lambda^c_{CH_3COOH}}{\Lambda^0_{CH_3COOH}} = \frac{2.25}{225} = 10^{-2}$$

Then $[H^+]$ for $CH_3COOH = C\alpha = 0.001 \times 10^{-2} = 10^{-5}$

$\Rightarrow$ $pH = -\log[H^+] = -\log(10^{-5}) = 5$

15. $K = 3.2 \times 10^{-5} \ \Omega^{-1}.\text{cm}^{-1}$

$$\Lambda = \frac{10^3 K}{C}$$

$$\Lambda = \frac{3.2 \times 10^{-2}}{0.2} = 16 \times 10^{-2}$$

$$\alpha = \frac{\Lambda}{\Lambda_\infty}$$

$$\therefore \quad \Lambda_\infty = \frac{\Lambda}{\alpha} = \frac{16 \times 10^{-2}}{0.02} = 8$$

16. $E = E^o_{cell} - \frac{0.059}{2} . \log Q$

$$Q = \frac{(10^{-7})^2}{20} \times \frac{0.2}{(10^{-7})^2} = \frac{1}{100}$$

$$E = 0 - \frac{0.059}{2} . \log \frac{1}{100} = \frac{0.059}{2} \times 2 = 0.059$$

$1000E = 1000 \times 0.059 = 59$

17. At cathode :

$$\frac{1}{2} Hg_2^{2+} + e^- \longrightarrow Hg(l)$$

At anode :

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

$$\frac{1}{2} Hg_2^{2+} + \frac{1}{2} H_2(g) \longrightarrow Hg(l) + H^+(aq)$$

$$E_{cell} = E^0_{cell} - \frac{0.059}{1} \log [H^+]$$

or $0.634 = (0.28 - 0) + 0.059 \text{ pH}$

$$\text{or pH} = \frac{0.634 - 0.28}{0.059} = 6$$

18. $\Pi = iCRT$

$3 = i \times 0.1 \times \frac{1}{12} \times 300$

$i = 1.2$

$i = 1 + \alpha (n-1)$

$1.2 = 1 + \alpha (2-1)$

$\alpha = 0.2$

$0.2 = \frac{30}{\lambda_m^\infty}$; $\lambda_m^\infty = 150\ \Omega^{-1} cm^2 mol^{-1}$

PART - 4

1. (C) M is more reactive than carbon and B is more reaitive than A. Also both B and A are less reactive than C.

2. According to Faraday's second law

$$\frac{\text{mass of A}}{\text{equivalent mass of A}} = \frac{\text{mass of B}}{\text{equivalent mass of B}} = \frac{\text{mass of C}}{\text{equivalent mass of C}}$$

$\frac{4.5}{15/n_1} = \frac{2.7}{27/n_2} = \frac{9.6}{48/n_3}$

$0.3n_1 = 0.1n_2 = 0.2n_3 = k$

$n_1 = \frac{10}{3}k$

$n_2 = 10k$

$n_3 = 5k$

$n_1 : n_2 : n_3 = \frac{10}{3} : 10 : 5 = \frac{1}{3} : 1 : \frac{1}{2} = 2 : 6 : 3$

$0.3 : 0.1 : 0.2$

$3 : 1 : 2$

3. $H^+ + e^- \longrightarrow \frac{1}{2} H_2$, $E° = 0$, $\Delta G° = 0$

$H_2O \rightleftharpoons H^+ + OH^-$, $\Delta G° = -8.314 \times 298 \ln 10^{-14}$

$H_2O + e^- \longrightarrow \frac{1}{2} H_2 + OH^-$, $-1 \times E° \times 96500 = -8.314 \times 298 \ln 10^{-14}$ **$E° = -0.828$ Volt.**

4. $Hg_2^{2+} + 2e^- \longrightarrow 2Hg$, *0.789 Volt*

$Hg \longrightarrow Hg^{2+} + 2e^-$, –0.854 Volt

$Hg_2^{2+} \longrightarrow Hg + Hg^{2+}$, –0.065 Volt

$\Delta G = -2 \times (-0.065) \times 96500 = -8.314 \times 298 \ln K_{eq.}$; **$K_{eq.} = 6.3 \times 10^{-3}$**

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

$E_1 = E° - \frac{0.0591}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-] \times 1^8}$

$E_2 = E° - \frac{0.0591}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-] \times \left(10^{-4}\right)^8} = -\frac{0.0591}{5} \times 32 = -0.37824$ **$E_1 - E_2 = 0.38$ Volt**.

6. $0 = (-0.151 - 0) - \frac{0.0591}{1} \log [H^+]$.

$0.0591 \times \log[H^+] = -0.151$; $pH = \frac{0.151}{0.0591} = \mathbf{2.56}$

7. $E^0_{Ag|AgI|I^-} = E^0_{Ag^+|Ag} - \frac{0.0591}{1} \log \frac{1}{K_{SP}}$

$-0.151 = 0.799 - \frac{0.0591}{1} \log \frac{1}{K_{sp}}$

$0.0591 \log K_{sp} = -0.151 - 0.799$

$\log K_{sp} = -16.074$

$\mathbf{K_{sp} = 8.43 \times 10^{-17}}$

8. $A_{(s)} + B^{2+}_{aq.} \longrightarrow A^{2+}_{aq.} + B_{(s)}$, $DH° = -285$ KJ

Assuming Δs to negligible , $\Delta G° = \Delta H° = -285 \times 10^3 \times 0.84 = -2 \times E° \times 96500$

$E° = 1.24$ Volt

9. $\frac{d\varepsilon}{dt} = -0.00065$ Vol deg^{-1}

$\Delta S_{298} = n.F. \frac{dE}{dT} = 2 \times 96500 \times (-0.00065)$ **= – 125.5 J/K.**

10. $Na^+ + e^- \longrightarrow Na(s)$

1mole 1 Faraday

$Al^{3+} + 3e^- \longrightarrow Al(s)$

1 Faraday

No. of mole of Al = $\frac{1}{3}$ mole.

12. Higher the std. reduction potential, higher is the oxidising power.

13. $E_{cell} = 0.29 - \frac{0.059}{2} \log \frac{0.01 \times (0.01)^2}{(0.01)^2 \times 1}$ or E_{cell} **= 0.35 volt**

14. $E^o_{cell} = 1.89$; $E^o_{Ce4+/Ce3+} + E^o_{Co/Co2+} = E + 0.277$ Þ E = **1.62 V**

15. $E^o_{MnO_4^-/MnO_2} = \frac{5 \times 1.5 - 2 \times 1.23}{3} = 1.7$ volt

16. $Z > Y > X$ (Non metals like $F_2 > Cl_2 > Br_2$)

So, Y will oxidise X^- but not Z^-

Z will oxidise both X^- and Y^-

X can't oxidise Y^- or Z^- .

17. $E^o_{cell} = 0.8 - (-0.76) =$ **1.56 V**

18. $Ag \longrightarrow Ag^+ + e^-$

$E_1 = E_{oxid} + E_{calomel}$

$= E' - \frac{0.0591}{1} \log \sqrt{K_{sp_1}} + E_{calomel}$

$E_2 = E' - \frac{0.0591}{1} \log \sqrt{K_{sp_2}} + E_{calomel}$

$E_2 - E_1 = 0.177 = 0.0591 \log \sqrt{\frac{K_{sp_1}}{K_{sp_2}}}$

$\frac{K_{sp_1}}{K_{sp_2}} = 10^6$.

19. $E_{cell} = E^o_{cell} - \frac{0.059}{2} \log \frac{[Sn^{2+}]}{[Ag^+]^2}$ Ag^+ increase, E_{cell} increase.

20. $\frac{i \times 15 \times 60}{96500} = \frac{6.72}{22.4} \times 2 \quad \Rightarrow i = 64.3$ amp.

21. $AgCl + e^- \longrightarrow Ag + Cl^-$ $E° = 0.2$ V

$Ag \longrightarrow Ag^+ + e^-$ $E° = -0.79$ V

$AgCl \xrightarrow{e^-} Ag^+ + Cl^-$ $E° = -0.59$ V

$E° = \frac{0.059}{n} \log K \quad \Rightarrow \quad -0.59 = \frac{0.059}{1} \log K_{SP} \quad \Rightarrow \quad K_{SP} = 10^{-10}$

Now solubility of AgCl in 0.1 M $AgNO_3$

$S(S + 0.1) = 10^{-10} \quad \Rightarrow \quad S = 10^{-9}$ mol/L

Hence 1 mole dissolves in 10^9 L solution

hence in 10^6 L amount that dissolves in 1 m mol.

22. $Q = 10 \times 4825 = 48250$ C

no. of faraday $= \frac{48250}{96500} = 0.5$

$Ag + \frac{1}{2}Cu^{++} \longrightarrow Ag^+ + \frac{1}{2}Cu$

2.00 2.00

2–0.25 2 + 0.50

$E_{cell} = E^o_{Cell} - \frac{0.0591}{1} \log \frac{[Ag^+]}{[Cu^{++}]^{1/2}}$

$E_1 = E^o_{Cell} - \frac{0.0591}{1} \log \frac{2.00}{(2.00)^{1/2}}$

$E_2 = E^o_{Cell} - \frac{0.0591}{1} \log \frac{2.50}{(1.75)^{1/2}}$

$\Delta E = E_2 - E_1 = \frac{0.0591}{1}\left[\log\sqrt{2} - \log\frac{2.50}{\sqrt{1.75}}\right] = \frac{0.0591}{1}[\log 1.41 - \log 1.88]$

$= \frac{0.0591}{1}[0.1492 - 0.2742] = -\frac{0.0591}{1} \times 0.125 = -0.00738$ V.

23. $nF\left(\frac{\partial E^o}{\partial T}\right) = \Delta S^o = -2 \times 96500 \times 1.45 \times 10^{-3} = -279.85\ JK^{-1}$

$\Delta G^o = -nFE^o = -2 \times 1.36 \times 96500 = -262.48$ KJ.

$\Delta H^o = \Delta G^o + T\Delta S^o$

$= -262.48 \times 10^3 - 300 \times 279.85$

$= -262480 - 83955 = -346.435$ KJ

24. (a) Metal should below hydrogen and Cu^{2+} but should above Ag^+ in series.

(b) Metal should above hydrogen but should below from Zn^{2+} and Fe^{2+} both.

25. $TiO^{2+} + 2H^+ + e^- \longrightarrow Ti^{3+} + H_2O$, 0.1 V $\quad \Delta G_1^o = -2 \times F \times 0.1$

$Ti^{3+} + 3e^- \longrightarrow Ti - 1.21$ V $\quad \Delta G_2^o = -3 \times (-1.21) \times F$

$TiO^{2+} + 2H^+ + 4e^- \longrightarrow Ti + H_2O$

$-4 \times E^o \times F = -1 \times 0.1 \times F + -3 \times (-1.21) \times F$

$E^o = -0.8825$ volt

26. $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2\,Cr^{3+}\ 7\,H_2O$, 1.33 volt

$$E = 1.33 - \frac{0.0591}{6} \log \frac{(0.01)^2}{(0.01)\times(10.^{-3})^{14}} = 1.33 - \frac{0.0591}{6} \log 10^{-2} \times 10^{42}$$

$$= 1.33 - \frac{0.0591}{6} \times \log 10^{40} \qquad = 1.33 - \frac{0.0591}{6} \times 40 = 0.936 \text{ volt}$$

27. $Pt / H_2 / H^+ (C_6H_5NH_{2(C)}\ //\ H^+_{(HCl)} / H_2 / Pt$

$H_2 \longrightarrow 2H^+_{(10^{-8}M)} + 2e^-$, $\qquad C_6H_5NH_2 + H_2O \longrightarrow C_6H_5NH_3^+ + OH^-$

$2H^+ + 2e^- \longrightarrow H_2 \qquad K_b = \frac{(OH^-)^2}{\frac{5\times10^{-4}}{0.5}}$

$2H^+_{(5\times10^{-2})} \longrightarrow 2H^+_{(10^{-8})}$

$$E = 0 - \frac{0.0591}{2} \log \frac{(10^{-8})^2}{(5\times10^{-2})^2} = -\frac{0.0591}{2} \log 10^{-14} \times 4 = \frac{0.0591}{2} . [\log 4 - 14] = 0.396 \text{ volt}$$

28. (A) $Hg_2Cl_2(s) + Cu(s) \longrightarrow Cu^{2+}(aq) + 2Cl^-(aq) + 2Hg(l)$

(B) $2Ag_{(s)} + 2IO_3^- + Zn^{2+} \longrightarrow 2AgIO_{3_{(s)}} + Zn_{(s)}$

(C) $Mn_{(s)} + 2OH^- + Cu^{2+} \longrightarrow Mn(OH)_{2_{(s)}} + Cu_{(s)}$

29. $$E = 0 - \frac{.06}{1} \log \frac{10^{-10}/0.2}{10^{-13}/10^{-3}}$$

$= 0.42$ V

30. $[Br^-] : [Cl^-] = 1 : 200$

31. Cd (12.5%) in Hg / $3CdSO_4$, $8H_2O$ (solid) / satd sol of $CdSO_4$ || $Hg_2SO_{4(s)}$ | Hg, E = 1.018 volt

$\left(\frac{dE}{dT}\right)_P = -4 \times 10^{-5}$ volt $d_{eg-1.}$

$\Delta G = -nEF = -2\ 1.018 \times 96500 = -196.474$ kJ

$\Delta S = nF. \left(\frac{dE}{dT}\right)_P = 2 \times 96500 \times (-4 \times 10^{-5}) = -7.72\ JK^{-1}$.

$\Delta G = \Delta H - T\Delta S$

$\Delta H = -196.474 + \frac{298 \times (-7.72)}{1000} = -196.474 - 2.3 = 198.774$ kJ

32. $Ag(s) + \frac{1}{2} Hg_2Cl_2(s) \longrightarrow AgCl_{(s)} + Hg(l)$, $\Delta H = 1280$ cal.

$E = 0.0455$ volt

$\Delta H = -nEF + nF.T. \frac{dE}{dT}$

$1280 \times 4.18 = -1 \times 0.0455 \times 96500 + 1 \times 96500 \times 298 \times \frac{dE}{dT}$.

$\frac{dE}{dT} = 3.387 \times 10^{-4}$ volt deg^{-1}.

33. $\frac{dE}{dT} = -0.125\ VK^{-1}$. $E^o = 0.0372$ volt

$\Delta G^o = -nEF = -2 \times 0.0372 \times 96500 = -7.1796$ kJ.

$\Delta S^o = nF \times \left(\frac{dE}{dT}\right)_P = 2 \times 96500 \times (-0.125) = -24.125$ kJ K^{-1}.

$\Delta H^o = \Delta G^o + T\,\Delta S^o = -7.1796 - 298 \times 24.125 = -7196.43$ kJ

34. v.f. of metal = 2.
w = Zit.

$1.95 = \frac{E}{96500} it = \frac{M \times it}{v.f. \times 96500} \Rightarrow M = 114$ g.

Now for Cu, $w = \frac{63.5 \times (it)}{2 \times 96500} \Rightarrow 1.95 = \frac{63.5 \times (it)}{2 \times 96500} \Rightarrow it = 5926.77$ C.

35. $2HSO_4^- \longrightarrow S_2O_8^{2-} + 2e^- + 2H^+$ $i = \frac{2 \times 96500}{60 \times 60 \times 0.75}$ $i = 71.48$ Amp.

36. **(a)** $\Delta G^o_r = -109 + 129 - 77 = -57$ kJ/mol
Cell representation : $Ag \mid AgCl \mid\mid Cl^- \mid Ag^+ \mid Ag$.
$-1 \times 96500 \times E^o = -57 \times 10^3$.
$E^o = 0.59$ volt.

$0 = 0.59 - \frac{0.059}{1} \log \frac{1}{K_{SP}}$.

$\log K_{SP} =$ **-10.**

(b) $Zn \longrightarrow Zn^{2+} + 2e^-$, 0.76 volt.
$2Ag^+ + 2e^- \longrightarrow 2Ag$, 0.80 volt.

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37. $0.65 = E_{oxid} + E_{red} = \left\{0.78 - \frac{0.0591}{n} \log (0.1)\right\} + \left\{0 - 0.14 - \frac{0.0591}{2} \log \frac{1}{0.5}\right\}$

$0.01 = -\frac{0.0591}{n} \times (-1) - \frac{0.0591}{2} \times 0.301 = 0.0591 \left(\frac{1}{n} - \frac{0.301}{2}\right)$ $n = 3$

Electrons flow from X electrode to Zn electrode.

38. $\lambda^{\circ}_{m}\ (H_2O) = \dfrac{\lambda^{\circ}_{m(Ba(OH)_2)} + 2\,\lambda^{\circ}_{m(HCl)} - \lambda^{\circ}_{m(BaCl_2)}}{2}$

$= 5.5 \times 10^{-2}\ S\ m^2\ mol^{-1}$.

Now, in SI units,

$\lambda^{\circ}_{m} = \dfrac{K \times 10^{-3}}{M}$ $\quad\therefore\ \lambda^{\circ}_{m\ (H2}O) = \dfrac{K \times 10^{-3}}{[H_2O]\,diss}$

$\therefore\ 5.5 \times 10^{-2} = \dfrac{5.5 \times 10^{-6} \times 10^{-3}}{[H_2O]\,diss}$

$\therefore\ [H_2O]\ diss = [H^+] = [OH^-] = 10^{-7}\ M$

For equilibrium : $H_2O \rightleftharpoons H^+ + OH^-$

Dissociation constant $K = \dfrac{[H^+][OH^-]}{[H_2O]} = \dfrac{10^{-7} \times 10^{-7}}{\left(\dfrac{1000}{18}\right)}$

$= 1.8 \times 10^{-16}$

$\therefore$ Reported answer = 18

39. $\Lambda_{eq} = 97.1\ Scm^2\ eq^{-1}$, $C = 0.1\ N$

$A = 1.5\ cm^2$, $l = 0.5\ cm$

$\Lambda_{eq} = \dfrac{1000 \times \left(\frac{1}{R} \times \frac{\ell}{A}\right)}{C}$ $\Rightarrow$ $97.1 = \dfrac{1000}{0.1} \times \dfrac{1}{R} \times \dfrac{0.5}{1.5}$

$R = 34.33\ \Omega$ $\Rightarrow$ $i = \dfrac{V}{R} = \dfrac{5}{34.33} = 0.1456\ amp$

40. $0.108 = \dfrac{E}{96500} \times 0.5 \times 193$ $\quad E = 108\ g/eq.$

41. $(M \longrightarrow M^{n+}_{(0.02M)} + ne^-) \times 2$

$(2H^+ + 2e^- \longrightarrow H_2) \times n$

$2M + 2nH^+ \longrightarrow 2M^{n+} + nH_2$

$0.81 = (0.76 + 0) - \dfrac{0.0591}{2n} \log \dfrac{(0.02)^2}{(1)^{2n}}$ $\Rightarrow$ $(0.81 - 0.76) = \dfrac{0.0591}{2n} \log 4 \times 10^{-4}$

$n = -\dfrac{0.0591}{2 \times 0.5} \times \log 4 \times 10^{-4} = -0.591\ (-4 + 0.6) = 2.$

42. $2Al_2O_3\ (melt) \longrightarrow 2Al_2O_3(s)$, $\quad \Delta G_1^{o} = -2 \times 16$

$2Al_2O_3(s) \longrightarrow 4Al(l) + 3O_2(g)$, $\quad \Delta G_2^{o} = 2 \times 1269$

$3C + 3O_2 \longrightarrow 3CO_2$, $\quad \Delta G_3^{o} = -3 \times 395$

$2Al_2O_3\ (melt) + 3C \longrightarrow 4Al\ (l) + 3CO_2(g)$,

$\Delta G^{o} = \Delta G_1^{o} + \Delta G_2^{o} + \Delta G_3^{o} = -32 + 2 \times 1269 - 3 \times 395 = 1321\ kJ$

$\Delta G^{o} = -nFE^{o}$ $\Rightarrow$ $1321 \times 10^3 = -12 \times E^{o} \times 96500$

$E^{o} = -1.14\ volt$

43. Charge passed = 0.01 Faraday

At the anode $\left(H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-\right)$ with 90 % efficientcy 0.01 × 0.9 F have been used and will

produce $\frac{1}{4}$ × 0.01 × 0.9 mole of O_2 i.e. 0.00225 mol O_2.

At the cathode $2H_2O \xrightarrow{+2e^-} H_2 + 2OH^-$

moles of H_2 produced = $\frac{0.01\times 0.8}{2}$ mol = 0.004 mol

Total moles produced of gases = 0.004 + 0.00225 = 0.00625 mol
vol. at STP = 0.00625 × 22400 mL = 140 mL

44. $MX \rightleftharpoons M^+ + X^-$
$a + 10^{-7}$ a
$K_{SP} = (a + 10^{-7})\, a$

$\frac{55\times 10^{-7}}{1000} = (6 \times 10^{-3}\,(a + 10^{-7}) + 8 \times 10^{-3}\, a + 7 \times 10^{-3} \times 10^{-7})$
$55 \times 10^{-10} = 6 \times 10^{-3} a + 6 \times 10^{-10} + 8 \times 10^{-3}\, a + 7 \times 10^{-10}$
$42 \times 10^{-10} = 14 \times 10^{-3}\, a$
$a = 3 \times 10^{-7}$
$K_{SP} = 12 \times 10^{-14}$

45. $E^o_{cell} = E^o_{RP(RHS)} - E^o_{RP(LHS)}$
$= -0.76 - (-1.36) = 0.6$

$\Delta_r G^o = -RT \ln K_{eq}$;

or $\log K_{eq} = \frac{nFE^o}{RT \times 2.303} = \frac{2\times 0.6}{0.06} = 20$

$\Rightarrow \frac{2\times 0.6}{0.06} \Rightarrow 20;\ K_f = 10^{20}$

46. Reduction and electronation take place at cathode elctrode, so it become positive electrode.

47. (A, B, C) Reduction Potential of Ce is higher than that of Zn.

48. (A) because $E^o_{Cu^{2+}/Cu} > E^o_{Fe^{2+}/Fe}$.

49. Recharging reaction

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

50. On dilution specific conductance decreases while molar conductivity increases.

51. Create a cell with required cell reaction

$O_2 + SO_4^{-2} \longrightarrow S_2O_8^{-2} + H_2O$ $\qquad E^o_{cell} = 1.23 - 2.01 < 0$
$\Rightarrow$ Nonspontaneous cell reaction

52. $\lambda_m^C = \lambda_m^\infty - b\sqrt{C}$

when $C_1 = 4 \times 10^{-4}$ $\lambda_m^C = 107$

and when $C_2 = 9 \times 10^{-4}$ $\Lambda_m = 97$

so $107 = \lambda_m^\infty - b \times 2 \times 10^{-2}$ ... (1)

$97 = \lambda_m^\infty - b \times 3 \times 10^{-2}$ ... (2)

$b = 1000$

$\Lambda_m = \lambda_m^\infty - b\sqrt{C}$

$\lambda_m^\infty = \Lambda_m + b\sqrt{C}$

$= 107 + 10^3 \times 2 \times 10^{-2}$

$\lambda_m^\infty = 127 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$

53. For 25×10^{-4} (M) NaCl solution

$\Lambda_m = \lambda_m^\infty - b\sqrt{C}$

$\Lambda_m = 127 - 10^3 (25 \times 10^{-4})^{1/2}$

$\Lambda_m = 127 - 10^3 \times 5 \times 10^{-2}$

$\Lambda_m = 77$

But $\Lambda_m = \dfrac{K \times 1000}{M}$ $\qquad K = \left(\dfrac{\ell}{a}\right) \times \dfrac{1}{R}$

$\Lambda_m = \left(\dfrac{\ell}{a}\right) \times \dfrac{1}{R} \times \dfrac{1000}{M}$

$\Lambda_m = [\text{Cell constant}] \times \dfrac{1000}{R \times M}$

$\Rightarrow 77 = [\text{Cell constant}] \times \dfrac{1000}{1000 \times 25 \times 10^{-4}}$

Cell constant $= 77 \times 25 \times 10^{-4} = 0.1925 \text{ cm}^{-1}$

54. For Na_2SO_4 solution

$K = \left(\dfrac{\ell}{a}\right) \times \dfrac{1}{R} = \dfrac{0.1925}{400} = 4.81 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$

$\Lambda_m = \dfrac{K \times 1000}{M} = \dfrac{4.81 \times 10^{-4} \times 1000}{\frac{5}{2} \times 10^{-3}}$

$\Lambda_m (Na_2SO_4) = 192.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$

55. At the equivalence point the concentrations will be $[Br^-] = 100 \text{ mol/m}^3$, $[Na^+] = 100 \text{ mol/m}^3$

Therefore $\kappa_{total} = \kappa_{Br^-} + \kappa_{Na^+} = 1.2 \text{ Sm}^{-1} = \mathbf{12} \times 10^{-1} \text{ Sm}^{-1}$.

56. First conductance decreases due to nutralisation of free H^+ ions of weak acid, then it increases due to formation of salt and after equivalence point it increases more fastly due to increasing of OH^- ions.

57. First conductance decreases due to nutralisation of strong acid H^+ ion then after it increases due to nutralisation of weak acid and after equivalence point it increases more fastly.