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: Organic acids CH_3COOH, HCN (Except : Alkyl sulphonic acids, RSO_3H)

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 :**

	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

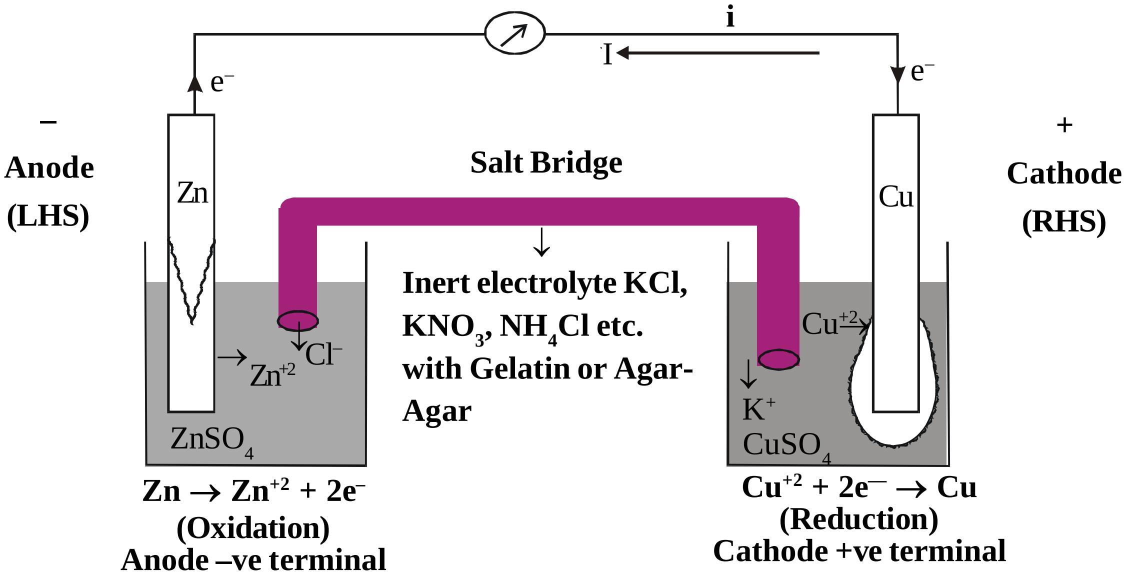
Galvanic cell or Voltaic cell	**Electrolytic cell.**
• A spontaneous chemical reaction generates an electric current | EMF	• An electric current drives a non-spontaneous reaction.
• Chemical energy converted into electrical energy.	• Electrical energy converted into chemical energy.

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 :**

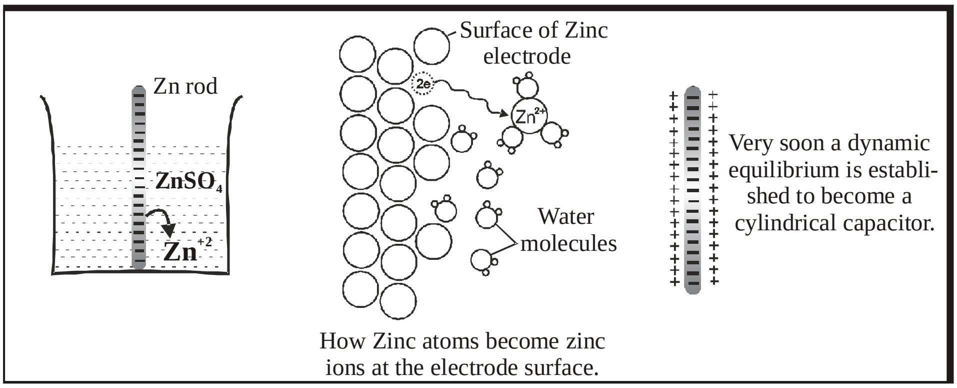
$Cu^{2+} + 2e^- \longrightarrow Cu(s)$ (Gain of electron ; Reduction)

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 | 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.



How Zinc atoms become zinc ions at the electrode surface.

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.

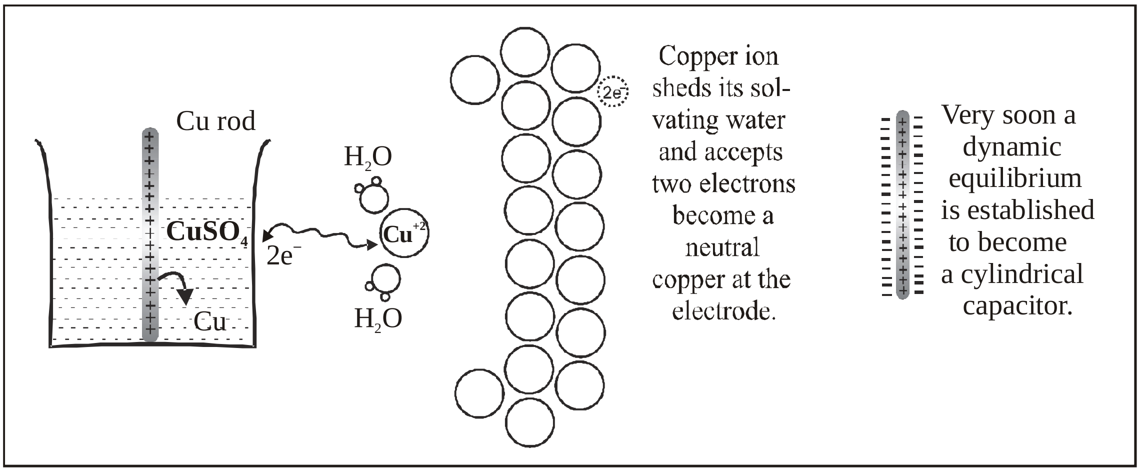
The positive charge will be more concentrated near the rod.

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 :** $\begin{cases}\text{Is where oxidation occurs}\\ \text{Has a negative sign}\end{cases}$ • **Cathode :** $\begin{cases}\text{Is where reduction occurs}\\ \text{Has a positive sign}\end{cases}$

❖ **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)

The anode is written on the LHS & cathode on the RHS.

we denote salt bridge by two vertical parallel lines (||), if used, in between anode & cathode.

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

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

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 25°C (or any constant temperature) 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.

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

3.8 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
$Q + 2H^+ + 1e^- \rightarrow H_2Q$	+ 0.70
$Hg_2^{+2} + 2e \rightarrow 2Hg$	+ 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.

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

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

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

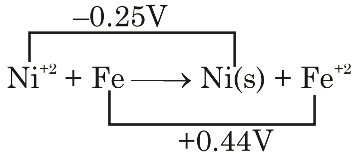
(ii) **Displacement reaction :** The active metal can easily displace less active metal from their aq. salt solution for e.g. Zn can replace Cu^{2+} from an aq. solution of $CuSO_4$. But Cu cannot displace Zn^{2+} from solution similarly,

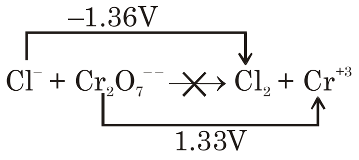
$$2AgNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2Ag,$$

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

(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.

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

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

EXERCISE # I

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

   E^o_{cell} is 1.89 V. If $E^o_{Co^{2+}|Co}$ is – 0.28 V, what is the value of $E^o_{Ce^{4+}|Ce^{3+}}$?

2. Determine the standard reduction potential for the half reaction :

   $Cl_2 + 2e^- \longrightarrow 2Cl^-$

   Given $Pt^{2+} + 2Cl^- \longrightarrow Pt + Cl_2$, $E^o_{Cell} = -0.15$ V

   $Pt^{2+} + 2e^- \longrightarrow Pt$ $E° = 1.20$ V

3. Is 1.0 M H^+ solution under H_2SO_4 at 1.0 atm capable of oxidising silver metal in the presence of 1.0 M Ag^+ ion?

   $E^o_{Ag^+|Ag} = 0.80$ V, $E^o_{H^+|H_2(Pt)} = 0.0$ V

4. If $E^o_{Fe^{2+}|Fe} = -0.44$ V, $E^o_{Fe^{3+}|Fe^{2+}} = 0.77$ V. Calculate $E^o_{Fe^{3+}|Fe}$.

5. 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

6. 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

7. The standard reduction potentials for two half-cell reactions are given below,

   $Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$, $E° = -0.40V$

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

   The standard free energy change for the reaction

   $2Ag^+(aq) + Cd(s) \rightarrow 2Ag(s) + Cd^{2+}(aq)$ is given by :

   (A) 115.8 KJ (B) –115.8 KJ (C) –231.6 KJ (D) 231.6KJ

8. 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

9. 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 : **[AIEEE 2003]**

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

10. The $E^0_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are –0.41, + 1.57, +0.77 and + 1.97V respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest ?

    (A) Fe (B) Mn (C) Cr (D) Co **[AIEEE 2004]**

11. Consider the following E^0 values, **[AIEEE 2004]**

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

Under standard conditions the potential for the reaction,

$Sn(s) + 2Fe^{3+}(aq) \longrightarrow 2Fe^{2+}(aq) + Sn^{2+}(aq)$ is:

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

12. For a spontaneous reaction the ΔG, equilibrium constant (K) and E^0_{Cell} will be respectively **[AIEEE 2005]**

(A) –ve, < 1, –ve (B) –ve, >1, –ve (C) –ve, >1, +ve (D) +ve, >1, –ve

13. Given : $E^\circ_{Fe^{+3}/Fe} = -0.036V$, $E^\circ_{Fe^{+2}/Fe} = -0.439V$

The value of standard electrode potential for the change.

$Fe^{+3}_{(aq)} + e^- \longrightarrow Fe^{+2}_{(aq)}$ will be :- **[AIEEE 2009]**

(A) 0.770 V (B) –0.27 V (C) –0.072 V (D) 0.385 V

14. The Gibbs energy for the decomposition of Al_2O_3 at 500 °C is as follows **[AIEEE 2010]**

$$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2,\ \Delta_rG = +966\ KJ\ mol^{-1}$$

The potential difference needed for electrolytic reduction of Al_2O_3 at 500 °C is at least :-

(A) 5.0 V (B) 4.5 V (C) 3.0 V (D) 2.5 V

15. A standard hydrogen electrode has zero electrode potential because

(A) hydrogen is easier to oxidise (B) electrode potential is assumed to be zero

(C) hydrogen atom has only one electron (D) hydrogen is the lighest element.

16. E° for $F_2 + 2e^- = 2F^-$ is 2.8 V, E° for $\frac{1}{2}F_2 + e^- = F^-$ is ?

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

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

18. Given electrode potentials :

$Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$; E° = 0.771 volts $I_{2(g)} + 2e^- \longrightarrow 2I^-_{(aq)}$; E° = 0.536 volts

E°_{cell} for the cell reaction, $2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(g)}$ is -

(A) (2 × 0.771 – 0.536) = 1.006 volts (B) (0.771 – 0.5 × 0.536) = 0.503 volts

(C) 0.771 – 0.536 = 0.235 volts (D) 0.536 – 0.771 = –0.235 volts

3.9 NERNST EQUATION :

For a reaction aA + bB = cC + dD

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

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

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.

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

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

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.

3.10 THERMODYNAMIC TREATMENT OF CELL :

(i) Determination of equilibrium constant : We know, that

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

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

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

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

$$-\Delta G = nFE \qquad \text{(i)}$$

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

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

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

(iii) 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.

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)

$$E = E° - 0.0591 \log \frac{P_{H_2}^{\frac{1}{2}}}{[H^+]} = -0.0591\ pH \left[\because E^0_{H^+/H_2} = 0 \,\&\, pH_2 = 1bar\right]$$

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

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

Pt | 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.

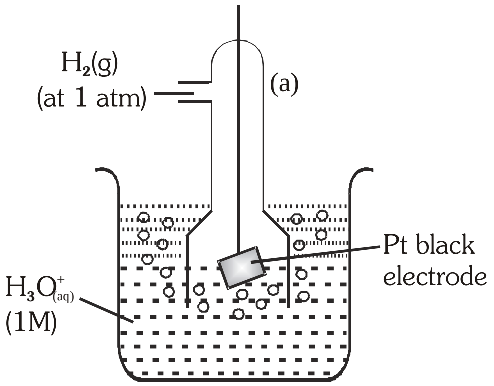
$2H^+(1\ M) + 2e^- \longrightarrow H_2(g)(1\ atm)$

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



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

$E_{cell} = E_{H^+/H_2(g)} - E^\circ_{Zn2+\,|\,Zn}$

$= 0.76\ V$ (at 298 K experimentally)

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

$E^\circ_{Zn\,|\,Zn^{2+}(aq)} = 0.76\ V$ (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 $Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-$; $E^0 = +0.27\ V$

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

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 : $1/2H_2(p_1) \to H^+(c) + e^-$ (Anode process)

$$\frac{H^+(c) + e^- \to 1/2H_2(p_2)}{1/2H_2(p_1) \rightleftharpoons 1/2H_2(p_2)} \qquad \therefore \qquad E = -\frac{2.303RT}{F}\log\left[\frac{p_2}{p_1}\right]^{1/2}$$

or $$E = \left[\frac{2.303RT}{2F}\right]\log\left[\frac{p_2}{p_1}\right]$$, 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)

$$\frac{Zn^{2+}(C_2) + 2e \longrightarrow Zn(s)}{Zn^{2+}(C_2) \rightleftharpoons Zn^{2+}(C_1)}$$ (Cathodic process , Over all 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 spontanity of such cell reaction, $C_2 > C_1$

EXERCISE # II

Representation of Cell diagrams, complete and half cell reactions :

19. Write cell reaction of the following cells :

(a) $Ag \mid Ag^+\,(aq) \mid\mid Cu^{2+}\,(aq) \mid Cu$ (b) $Pt \mid Fe^{2+}, Fe^{3+} \mid\mid MnO_4^-, Mn^{2+}, H^+ \mid Pt$

(c) $Pt, Cl_2 \mid Cl^-\,(aq) \mid\mid Ag^+\,(aq) \mid Ag$ (d) $Pt, H_2 \mid H^+\,(aq) \mid\mid Cd^{2+}\,(aq) \mid Cd$

20. 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) $Cr_2O_7^{2-}\,(a) + 14H^+\,(aq) + 6Fe^{2+}\,(aq) \longrightarrow 6Fe^{3+}\,(aq) + 2Cr^{3+}\,(aq) + 7H_2O\,(l)$

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

22. Calculate E^0 and E for the cell $Sn \mid Sn^{2+}\,(1M) \parallel Pb^{2+}(10^{-3}M) \mid Pb$, $E^0\,(Sn^{2+} \mid Sn) = -0.14V$, $E^0\,(Pb^{2+} \mid Pb) = -0.13V$. Is cell representation is correct?

23. At what concentration of Cu^{2+} in a solution of $CuSO_4$ will the electrode potential be zero at 25°C? Given : $E^0\,(Cu \mid Cu^{2+}) = -0.34$ V.

24. Calculate the equilibrium constant for the reaction

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

25. Calculate the equilibrium constant for the reaction

$Fe + CuSO_4 \rightleftharpoons FeSO_4 + Cu$ at 25°C.

Given $E^0\ (Fe|Fe^{2+}) = 0.44V$, $E^0\ (Cu|Cu^{2+}) = -0.337V$.

26. At 25^0C the value of K for the equilibrium $Fe^{3+} + Ag \rightleftharpoons Fe^{2+} + Ag^+$ is 0.531mol|litre. The standard electrode potential for $Ag^+ + e^- \rightleftharpoons Ag$ is 0.799V. What is the standard potential for $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$?

27. The reduction potential of hydrogen electrode when placed in a buffer solution is found to be – 0.413V. The pH of the buffer is -

28. Calculate the EMF of the following cell

$Zn\ |\ Zn^{2+}\ (0.01M)\ ||\ Zn^{2+}\ (0.1\ M)\ |\ Zn$

at 298 K.

29. 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

30. A standard hydrogen electrode has zero electrode potential because

(A) hydrogen is easier to oxidise

(B) electrode potential is assumed to be zero

(C) hydrogen atom has only one electron

(D) hydrogen is the lighest element.

31. The standard electrode potentials for the reactions

$Ag^+\ (a) + e^- \longrightarrow Ag(s)$ $Sn^{2+}\ (a) + 2e^- \longrightarrow Sn\ (s)$

at 25 °C are 0.80 volt and –0.14 volt, respectively. The standard emf of the cell.

$Sn_{(s)}|Sn^{2+}_{(aq)}(1M)||Ag^+_{(aq)}(1M)|Ag_{(s)}$ is :

(A) 0.66 volt (B) 0.80 volt (C) 1.08 volt (D) 0.94 volt

32. $E°(Ni^{2+}|Ni) = -0.25$ volt, $E°\ (Au^{3+}\ |\ Au) = 1.50$ volt.

The standard emf of the voltaic cell.

$Ni_{(s)}\ |\ Ni^{2+}_{(aq)}\ (1.0\ M)\ ||\ Au^{3+}_{(aq)}\ (1.0\ M)\ |\ Au_{(s)}$ is :

(A) 1.25 volt (B) –1.75 volt (C) 1.75 volt (D) 4.0 volt

33. E° for $F_2 + 2e^- = 2F^-$ is 2.8 V, E° for $\frac{1}{2}F_2 + e^- = F^-$ is ?

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

34. 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

35. 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

36. 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) $(E°_{red} - 0.059)$

37. For a reaction - $A(s) + 2B^{+}_{(aq)} \rightarrow A^{2+}_{(aq)} + 2B_{(s)}$ K_C has been found to be 10^{12}. The E°cell is:
(A) 0.354 V (B) 0.708 V (C) 0.0098 V (D) 1.36 V

38. At 25°C the standard emf of cell having reactions involving two electrons change is found to be 0.295V. The equilibrium constant of the reaction is -
(A) 29.5×10^{-2} (B) 10 (C) 10^{10} (D) 29.5×10^{10}

39. 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

40. The emf of the cell in which the following reaction,
$Zn(s) + Ni^{2+}_{(aq)}\ (a = 0.1) \rightarrow Zn^{2+}_{(aq)}\ (a = 1.0) + Ni(s)$
occurs, is found to be 0.5105 V at 298 K. The standard e.m.f. of the cell is :-
(A) –0.5105 V (B) 0.5400 V (C) 0.4810 V (D) 0.5696 V

41. Given electrode potentials :
$Fe^{3+}_{(aq)} + e^{-} \longrightarrow Fe^{2+}_{(aq)}$; E° = 0.771 volts $I_{2(g)} + 2e^{-} \longrightarrow 2I^{-}_{(aq)}$; E° = 0.536 volts
E°_{cell} for the cell reaction,
$2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(g)}$ is -
(A) (2 × 0.771 – 0.536) = 1.006 volts
(B) (0.771 – 0.5 × 0.536) = 0.503 volts
(C) 0.771 – 0.536 = 0.235 volts
(D) 0.536 – 0.771 = –0.235 volts

42. For the redox reaction :
$Zn(s) + Cu^{2+}\ (0.1M) \rightarrow Zn^{2+}\ (1M) + Cu(s)$ taking place in a cell,
E°_{Cell} is 1.10 volt. E_{Cell} for the cell will be $\left(2.303\dfrac{RT}{F} = 0.0591\right)$ **[AIEEE 2003]**
(A) 1.07 volt (B) 0.82 volt (C) 2.14 volt (D) 1.80 volt

43. For a cell reaction involving a two-electron change, the standard e.m.f. of the cell is found to be 0.295V at 25° C. The equilibrium constant of the reaction at 25°C will be : **[AIEEE 2003]**
(A) 10 (B) 1×10^{10} (C) 1×10^{-10} (D) 29.5×10^{-2}

44. In a cell that utilises the reaction, **[AIEEE 2004]**
$Zn(s) + 2H^{+}(A) \longrightarrow Zn^{2+}(aq) + H_2(g)$ addition of H_2SO_4 to cathode compartment, will :
(A) increase the E_{cell} and shift equilibrium to the right
(B) lower the E_{cell} and shift equilibrium to the right
(C) lower the E_{cell} and shift equilibrium to the left
(D) increase the E_{cell} and shift equilibrium to the left

45. The standard e.m.f. of a cell, involving one electron change is found to be 0.591 V at 25°C. The equilibrium constant of the reaction is (F = 96,500C mol^{-1} ; R = 8.314 JK^{-1} mol^{-1}) **[AIEEE 2004]**

(A) 1.0×10^{10} (B) 1.0×10^{5} (C) 1.0×10^{1} (D) 1.0×10^{30}

46. Given : $E^0_{Cr^{3+}/Cr} = -0.72$ V, $E^0_{Fe^{2+}/Fe} = -0.42$V. The potential for the cell **[AIEEE 2008]**

$Cr_{(s)} \mid Cr^{3+}_{(aq)}$ (0.1 M) $\|$ $Fe^{2+}_{(aq)}$ (0.01 M)$|Fe_{(s)}$ is

(A) 0.26 V (B) 0.339 V (C) – 0.339 V (D) – 0.26 V

47. The cell $Zn \mid Zn^{+2}_{(aq)}(1M) \| Cu^{+2}_{(aq)}{}^{(1M)} \mid Cu$ ($E°_{cell}$ = 1.10 V) was allowed to be completely discharged at 298 K. The relative concentration of Zn^{+2} to Cu^{+2}, $\left\{\frac{[Zn^{+2}]}{[Cu^{+2}]}\right\}$ is : **[AIEEE 2007]**

(A) 9.65×10^4 (B) Antilog (24.08) (C) 37.3 (D) $10^{37.3}$

48. 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)

$\left(2.303\frac{RT}{F} = 0.059V\right)$ **[AIEEE 2006]**

(A) –8.12 (B) +8.612 (C) –37.83 (D) –16.13

5. 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.)

5.1 Primary Batteries

5.1.1 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.

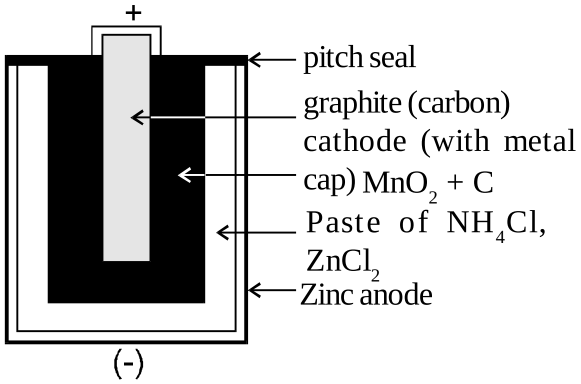


Fig. : A dry cell

- **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.

5.1.2 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:

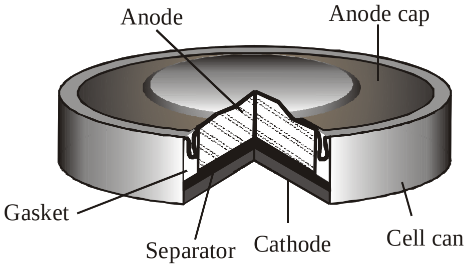
Anode : $Zn(Hg) + 2OH- \rightarrow ZnO(s) + H_2O + 2e-$

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

The overall reaction is represented by

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

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.

5.2 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.

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

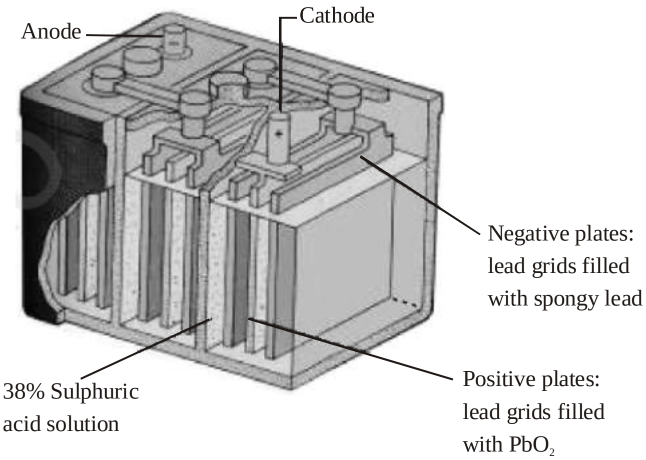
Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(\ell)$

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

.

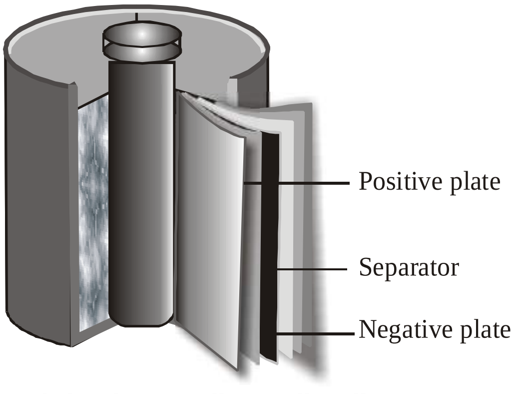


The Lead storage battery

5.2.2 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

5.3 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:

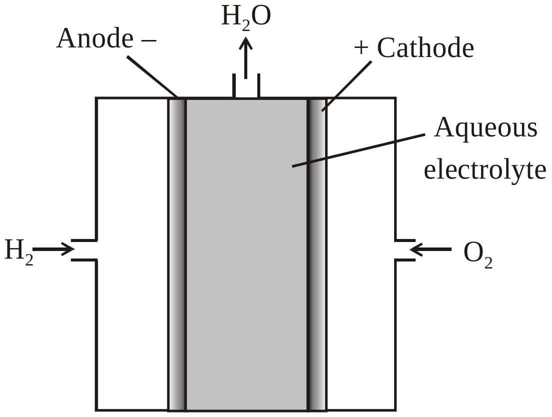
Cathode: $O_2(g) + 2H_2O(I) + 4e^- \rightarrow 4OH^-(aq)$

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

Overall reaction being:

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

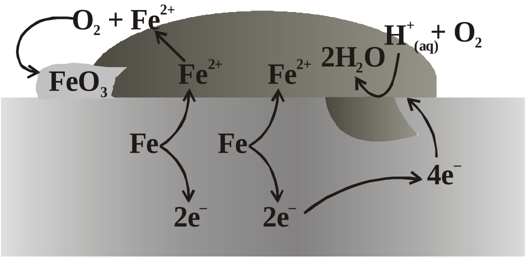
The cell runs continuously as long as the reactions are supplied Fuel cells produce electricity with an efficiency of about 70% compared to thermal plants whose efficiency is about 40%. There has been tremendous progress in the development of new electrode materials, better catalysts and electrolytes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

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

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(I)$

Atmospheric

Corrosion of iron in atmosphere

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.

Ex.1 ***E° of some oxidants are given as :***

$$I_2 + 2e^- \longrightarrow 2I^-, \qquad E° = +0.54\ V$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O, \qquad E° = +1.52\ V$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+}, \qquad E° = +0.77\ V$$

$$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}, \qquad E° = +0.1\ V$$

(a) Select the strongest reductant and oxidant in these.

(b) Select the weakest reductant and oxidant in these.

(c) Select the spontaneous reaction from the changes given below.

(i) $Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$

(ii) $2Fe^{2+} + I_2 \longrightarrow 2Fe^{3+} + 2I^-$

(iii) $Sn^{4+} + 2I^- \longrightarrow Sn^{2+} + I_2$

(iv) $Sn^{2+} + I_2 \longrightarrow Sn^{4+} + 2I^-$

Sol. (a) More the $E°_{OP}$, more is the tendency for oxidation. Therefore, since maximum $E°_{OP}$ stands for :

$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$ $\quad E°_{OP} = -0.1V$

∴ *Strongest reductant* : Sn^{2+}

and weakest oxidant : Sn^{4+}

(b) More +ve is $E°_{RP}$, more is the tendency for reduction. Therefore, since maximum $E°_{RP}$ stands for :

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ $\quad E°_{RP} = +1.52\ V$

∴ *Strongest oxidant* : MnO_4^-

and *weakest reductant* : Mn^{2+}

Note :- *Stronger is oxidant, weaker is its conjugate reducant and vice-versa.*

(c) For (i) $E°_{Cell} = E°_{OP_{Fe^{2+}/Fe^{3+}}} + E°_{RP_{Sn^{4+}/Sn^{2+}}} = -0.77 + 0.1$

Fe^{2+} oxidizes and Sn^{4+} reduces in change.

∴ $E°_{Cell} = E°_{OP_{Fe^{2+}/Fe^{3+}}} + E°_{RP_{Sn^{4+}/Sn^{2+}}} = -0.77 + 0.1 = -0.67\ V$

$E°_{Cell}$ is negative.

∴ (i) Is non-spontaneous change.

For (ii) $E°_{Cell} = E°_{OP_{Fe^{2+}/Fe^{3+}}} + E°_{RP_{I_2/I^-}} = -0.77 + 0.54 = -0.23\ V$

∴ (ii) reaction is non-spontaneous change.

For (iii) $E°_{Cell} = E°_{OP_{I^-/I_2}} + E°_{RP_{Sn^{4+}/Sn^{2+}}} = -0.54 + 0.1 = -0.44\ V$

∴ (iii) Reaction is non-spontaneous change.

For (iv) $E°_{Cell} = E°_{OP_{Sn^{2+}/Sn^{4+}}} + E°_{RP_{I_2/I^-}} = -0.1 + 0.54 = +0.44\ V$

(iv) Reaction is spontaneous change.

Ex.1 ***Given the standard electrode potentials ;***

$K^+|K = -2.93$ V, $Ag^+|Ag = 0.80$ V, $Hg^{2+}|Hg = 0.79$ V, $Mg^{2+}|Mg = -2.37$ V, $Cr^{3+}|Cr = -0.74$V.

Arrange these metals in their incresing order of reducing power.

Sol. More is $E°_{RP}$, more is the tendency to get reduced or more is the oxidising power or lesser is reducing power. Ag < Hg < Cr < Mg < K

Ex.2 ***A cell is prepared by dipping a copper rod in 1 M $CuSO_4$ solution and a nickel rod in 1M $NiSO_4$. The standard reduction potentials of copper and nickel electrodes are + 0.34 V and –0.25 V respectively.***

(i) Which electrode will work as anode and which as cathode ?

(ii) What will be the cell reaction ?

(iii) How is the cell represented ?

(iv) Calculate the EMF of the cell.

Sol. (i) The nickel electrode with smaller E° value (–0.25 V) will work as anode while copper electrode with more E° value (+0.34V) will work as cathode.

(ii) The cell reaction may be written as :

At anode : $Ni\,(s) \xrightarrow{\quad} Ni^{2+}\,(aq.) + 2e^-$

At cathode : $Cu^{2+}\,(aq) + 2e^- \xrightarrow{\quad} Cu\,(s)$

Cell reaction : $Ni\,(s) + Cu^{2+}\,(aq) \xrightarrow{\quad} Ni^{2+}\,(aq) + Cu\,(s)$

(iii) The cell may be represented as :

$Ni(s)|Ni^{2+}\,(aq)\,||\,Cu^{2+}\,(aq)|Cu\,(s)$

(iv) EMF of cell = $E°_{cathode} - E°_{anode} = (+0.34) - (-0.25) = 0.59$ V

Ex.4 ***Predict whether the following reaction can occur under standard conditions or not.***

$$Sn^{2+}\,(aq) + Br_2\,(\ell) \xrightarrow{\quad} Sn^{4+}\,(aq) + 2Br^-(aq)$$

Given : $E°_{Sn^{4+}|Sn^{2+}} = +0.15$; $E°_{Br^{2}|Br-} = 1.06$V.

Sol.

$$E°_{cell} = E°_{cathode} - E°_{anode} = 1.06 - 0.15 = 0.91\text{V}.$$

Since, $E°_{cell}$ comes out be positive, this means that the reaction can occur.

Ex.5 ***Given that, $Co^{3+} + e^- \xrightarrow{\quad} Co^{2+}$ E° = + 1.82V***

$$2H_2O \xrightarrow{\quad} O_2 + 4H^+ + 4e^- ;\ E° = -1.23\text{V}.$$

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

Sol. The $E°_{cell}$ can be calculated as follows :

$$4 \times [Co^{3+} + e^- \xrightarrow{\quad} Co^{2+}] ;\ E° = +1.82\text{V}$$

$$1 \times [2H_2O \xrightarrow{\quad} O_2 + 4H^+ + 4e^-] ;\ E° = -1.23\text{ V}.$$

Add : $4Co^{3+} + 2H_2O \xrightarrow{\quad} 4Co^{2+} + 4H^+ + O_2$; E° = 1.82 – 1.23 = + 0.59V.

Since, $E°_{cell}$ is positive, the cell reaction is spontaneous. This means that Co^{3+} ions will take part in the reaction. Therefore, Co^{3+} is not stable.

Ex.6 ***The 0.1 M copper sulphate solution in which copper electrode is dipped at 25°C. Calculate the electrode reduction potential of copper electrode.***

[Given : $E^0_{Cu^{2+}|Cu} = 0.34V$ **]**

Sol : $Cu^{+2} + 2e^{-} \rightarrow Cu$

$$E_{red} = E_{red}{}^{0} - \frac{0.059}{n}\log Q = E^0_{Cu^{2+}|Cu} - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]}$$

$$\text{So } E = 0.34 - \frac{0.0591}{2}\log 10$$

$$= 0.34 - 0.03 = 0.31 \text{ volts}$$

Ex.7 ***Calculate the EMF of the cell : Cr|Cr^{+3} (0.1M) || Fe^{+2} (0.01M)|Fe***
(Given : $E°_{Cr^{+3}|Cr} = -0.75$ V , $E°_{Fe^{+2}|Fe} = -0.45$ V)

Sol. Half cell reactions are :

- **At anode :** $[Cr \rightarrow Cr^{+3} + 3e^{-}] \times 2$
- **At cathode :** $[Fe^{+2} + 2e^{-} \rightarrow Fe] \times 3$

Over all reaction : $2Cr(s) + 3Fe^{+2}(aq.) \rightarrow 2Cr^{+3}(aq.) + 3Fe(s.)$

$$E°_{cell} = E°_{Cr|Cr^{+3}} + E°_{Fe^{+3}|Fe} = 0.75 + (-0.45) = 0.30 \text{ V}$$

$$E_{cell} = E^0 - \frac{0.0591}{n}\log Q = 0.30 - \frac{0.0591}{6}\log\frac{\left[Cr^{+3}\right]^2}{\left[Fe^{+2}\right]^3} = 0.30 - \frac{0.0591}{6}\log\frac{[0.1]^2}{[0.01]^3} = 0.26 \text{ V}$$

Ex.8 ***The measured e.m.f. at 25°C for the cell reaction,***
$Zn(s) + Cu^{2+}_{(aq)}(1.0M) \longrightarrow Cu(s) + Zn^{2+}_{(aq)}(0.1\ M)$ is 1.3 volt, Calculate E° for the cell reaction.

Sol. Using Nernst equation (at 298 K), $E_{cell} = E^{\circ}_{cell} - \frac{0.059}{2}\log\frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$

Here, $E_{cell} = 1.3$ V, $[Cu^{2+}(aq)] = 1.0$ M, $[Zn^{2+}(aq)] = 0.1$ M, $E^{\circ}_{cell} = ?$

Substituting the values , $E^0_{cell} = 1.27$ V

Ex.9 ***The emf of a cell corresponding to the reaction***
$Zn + 2H^{+}(aq) \longrightarrow Zn^{2+}(0.1M) + H_2(g)$ 1 atm
is 0.28 volt at 25°C. Calculate the pH of the solution at the hydrogen electrode.

$E^{\circ}_{Zn^{2+}|Zn} = -0.76$ ***volt and*** $E^{\circ}_{H^{+}|H_2} = 0$

Sol. $E^{\circ}_{cell} = 0.76 \text{volt}$

Applying Nernst equation, $E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]P_{H_2}}{[H^{+}]^2}$

$$0.28 = 0.76 - \frac{0.0591}{2}\log\frac{(0.1)\times 1}{[H^{+}]^2}\ ,\ \text{pH} = 8.62$$

Ex.10 The half cell oxidation potential of a half-cell $A^{x+}, A^{(x+n)+}$ | Pt were found to be as follows :

% of reduced form	24.4	48.8
Cell potential |V	0.101	0.115

Determine the value of n.

[take $\frac{2.303RT}{F} = 0.06$, $\log_{10} 24.4 = 1.387$, $\log_{10} 75.6 = 1.878$, $\log_{10} 48.8 = 1.688$, $\log_{10} 51.2 = 1.709$]

Sol. The half-cell reaction is -

$A^{x+} \rightarrow A^{(x+n)+} + ne^-$

Its Nernst equation is -

$$E = E^\circ - 2.303\frac{RT}{nF}\log\frac{[A^{(x+n)+}]}{[A^{x+}]} = E^\circ - \left(\frac{0.06V}{n}\right)\log\left(\frac{\text{oxidized form}}{\text{reduced form}}\right)$$

Substituting the given values, we get

$$0.101\text{ V} = E^\circ - \left(\frac{0.06V}{n}\right)\log\frac{75.6}{24.4} = E^\circ - \left(\frac{0.06\,V}{n}\right)(0.491)\ ....(i)$$

$$0.115\text{ V} = E^\circ - \left(\frac{0.06V}{n}\right)\log\frac{51.2}{48.8} = E^\circ - \left(\frac{0.06\,V}{n}\right)(0.021)\ ....(ii)$$

eq. (ii) – (i) , n = 2

Ex.11 ***What is the standard electrode potential for the electrode MnO_4^- | MnO_2 in solution***

$E^\circ_{MnO_4^-|Mn^{2+}}$ ***= 1.51 volt,*** $E^\circ_{MnO_2|Mn^{2+}}$ ***=1.23 volt***

Sol. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4\,H_2O$; E° = 1.51 volt

$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2\,H_2O$; E° = 1.23 volt

---

$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2\,H_2O$;E° = ?

$$E^\circ = \frac{5\times1.51 - 2\times1.23}{3} = \frac{7.55-2.45}{3} = \frac{5.09}{3} = 1.70\text{ volt}$$

Ex.12 ***Calculate ΔG° for the reaction : Cu^{2+} (aq) + Fe (s) ⇌ Fe^{2+} (aq) + Cu (s) .***

Given that $E^\circ_{Cu^{2+}|Cu}$ = + 0.34 V, $E^\circ_{Fe^{+2}/Fe}$ ***= – 0.44 V***

Sol. The cell reactions are :

$Fe (s) \longrightarrow Fe^{2+} (aq) + 2e^-$ .... at (anode)

$Cu^{2+} (aq) + 2e^- \longrightarrow Cu (s)$ .... at (cathode)

We know that : $\Delta G^\circ = -nF\,E^0_{cell}$; n = 2

$E^\circ_{cell} = \left[E^\circ_{(Cu^{2+}/Cu)} - E^\circ_{(Fe^{2+}/Fe)}\right]$ = (+ 0.34 V) – (–0.44 V) = + 0.78 V and F = 96500 C

$\therefore$ $\Delta G^\circ = -\,nF\,E^\circ_{cell}$ = –(B) × (96500 C) × (+0.78 V) = – 150540 CV = –150540 J

Ex.13 At 298 K the standard free energy of formation of $H_2O(l)$ is– 256.5 kJ|mol & OH^- is 80 kJ|mol. What will be emf at 298 K of the cell H_2(g, 1 bar) | H^+(1M) | | OH^-(1M) | O_2 (g, 1 bar)

$$H_2 + H_2O + \frac{1}{2}O_2 \longrightarrow 2H^+ + 2OH^-$$

$\Delta G° = -256.5 + 2 \times 80 = -96.5$ kJ

$-\Delta G° = nFE°$

$+ 96.5 \times 1000 = 2 \times 96500 \times E°$

$E° = 0.5$ Volt

Ex.14 ***Calculate the equilibrium constant for the reaction at 298 K.***

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

Given , $E^{\circ}_{Zn^{2+}|Zn} = -0.76\ V$ ***and*** $E^{\circ}_{Cu^{2+}|Cu} = +0.34\ V$

Sol. We know that, $\log K_c = \dfrac{nE^0_{cell}}{0.0591}$

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

$\therefore \quad \log K_C = \dfrac{2 \times (1.10\ V)}{(0.0591\ V)} = 37.29$, K_c = Antilog 37.29 = 1.95×10^{37}

Ex.15 ***Calculate the cell e.m.f. and ΔG for the cell reaction at 298 K for the cell.***

Zn (s) | Zn^{2+} (0.0004M) | | Cd^{2+} (0.2M) | Cd(s)

Given, $E^{\circ}_{Zn^{2+}|Zn} = -\ 0.763\ V$ ***;*** $E^{\circ}_{Cd^{2+}|Cd} = -\ 0.403\ V$ ***at 298 K.***

$F = 96500\ C\ mol^{-1}$.

Sol. **Step I.** Calculation of cell e.m.f. :

According to Nernst equation,

$$E = E° - \frac{0.0591}{n}\log\frac{[Zn^{2+}(aq)]}{[Cd^{2+}(aq)]}$$

$$E^{\circ}_{cell} = E^{\circ}_{(Cd^{2+}/Cd)} - E^{\circ}_{(Zn^{2+}/Zn)} = (-\ 0.403) - (-\ 0.763) = 0.36\ V$$

$[Zn^+(aq)] = 0.0004$ M, $[Cd^{2+}\ (aq)] = 0.2$ M, n = 2

$$E\ = (0.36) - \frac{(0.059V)}{2}\log\frac{0.0004}{0.2}\ =\ 0.36 - \frac{(0.059\ V)}{2} \times (-2.69990)\ = 0.36\ V + 0.08 =\ 0.44\ V$$

Step II. Calculation of ΔG :

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

$E_{cell} = 0.44$ V, n = 2 mol , F = 96500 c mol^{-1}

$\therefore \quad \Delta G = -\ (2\ mol) \times\ (96500\ C\ mol^{-1}) \times\ (0.44\ V)$

$= -\ 84920\ CV = -\ 84920\ J$

Ex.16 ***The cell Pt | H_2(g) (1 atm) | H^+ ; pH = x | | Normal calomal electrode has EMF of 0.64 volt at 25°C. The standard reduction potential of normal calomal electrode is 0.28 V. What is the pH of solution in anodic compartment. Take $\frac{2.303RT}{F} = 0.06$ at 298 K.***

Sol. $E_{H^+/H_2} = -0.06\log\frac{1}{[H^+]} = -0.06pH$

$\Rightarrow \quad 0.64 = E_{cathode} - E_{Anode} = 0.28 - (-0.06\ pH)$

$\Rightarrow \quad pH = \frac{0.64 - 0.28}{0.06} = \frac{0.36}{0.06} = 6$

Ex.17 ***Consider a Galvenic cell,***

Zn(s) | Zn^{2+}(0.1 M) | | Cu^{2+}(0.1 M) | Cu(s)

by what factor, the electrolyte in anodic half cell should be diluted to increase the emf by 9 milli volt at 298 K.

Ans. $E = E^\circ_{cell} - \frac{0.06}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$

$E_1 = E^\circ_{cell} - 0.03\ \log\frac{(0.1)}{(0.1)}$

$E_2 = E^\circ_{cell} - 0.03\ \log\frac{(0.1/x)}{(0.1)}$ {x is the factor by which electrolyte is diluted.}

$E_2 - E_1 = 9 \times 10^{-3} = 0 - 0.03\ \log\left(\frac{1}{x}\right)$

$0.009 = 0.03\ \log X$

$\frac{9\times10^{-3}}{3\times10^{-2}} = 0.3 = \log X$

$X = 2$

Ex.18 ***A disposable galvanic cell Zn$|Zn^{2+}\|Sn^{2+}|$Sn is produced using 1.0 mL of 0.5 M $Zn(NO_3)_2$ and 1.0 mL of 0.50 M $Sn(NO_3)_2$. It is needed to power a pace-maker that draws a constant current of 10^{-6} Amp to run it and requires atleast 0.50 V to function. Calculate the value of [Zn^{2+}] when cell reaches 0.5 V at 298 K.***

(Given : E° (Zn^{2+}|Zn) = – 0.76V; E° (Sn^{2+}|Sn) = – 0.14 V).

Ans. **1**

$E = 0.5\ V = 0.62 - \frac{0.059}{2}\log\frac{0.5+x}{0.5-x}$

$\because \quad Zn + \underset{0.5-x}{Sn^{2+}} \rightleftharpoons Sn + \underset{0.5+x}{Zn^{2+}}$

$\Rightarrow \quad \log\frac{0.5+x}{0.5-x} = \frac{0.12\times2}{0.0592} \approx 4$

$\Rightarrow \quad \frac{0.5+x}{0.5-x} = 10^4$

or $\quad x \approx 0.5\ M$

$\therefore \quad [Zn^{2+}] = 1.0\ M$

Ex.19 ***An alloy of Pb-Ag weighing 54 mg was dissolved in desired amount of HNO_3 & volume was made upto 500ml. An Ag electrode was dipped in solution and then connected to standard hydrogen electrode anode. Then calculate % of Ag in alloy.***

Given : $E_{cell} = 0.5\ V$; $E^{\circ}_{Ag^+|Ag} = 0.8V$ $\frac{2.303RT}{F} = 0.06$

Ans. $Ag^+ + 1\ e^- \longrightarrow Ag$

$$E_{cell} = 0.5 = 0.8 + \frac{0.06}{1} \log [Ag^+]$$

$$\log [Ag^+] = \frac{-0.30}{0.06} = -5$$

$[Ag^+] = 10^{-5}$ mol|L

$$\text{moles of } Ag^+ \text{ in 500 ml} = \frac{10^{-5}}{2}$$

$$\text{Mass of Ag} = \frac{10^{-5}}{2} \times 108$$

$$\%\ Ag = \frac{\frac{10^{-5}}{2} \times 108}{54 \times 10^{-3}} \times 100 = 1$$

Ex.20. ***A solution contains A^+ and B^+ in such a concentration that both deposit simultaneously. If current of 9.65 amp was passed through 100 ml solution for 55 seconds then find the final concentration of A^+ ions if initial concentration of B^+ is 0.1M.***

Given : $A^+ + e^- \longrightarrow A$ $E^{\circ} = -0.5$ ***volt***

$B^+ + e^- \longrightarrow B$ $E^{\circ} = -0.56$ ***volt***

$$\frac{2.303RT}{F} = 0.06$$

Sol. $$-0.5 - \frac{0.06}{1}\log\frac{1}{[A^+]} = -0.56 - \frac{0.06}{1}\log\frac{1}{[B^+]}$$

$$0.06 = \frac{0.06}{1}\log\frac{[B^+]}{[A^+]}$$

$$\frac{[B^+]}{[A^+]} = 10$$

$[A^+]_{initial} = 0.01M$

Ex.21 ***While the discharging of a lead storage battery following reaction take place.***

$PbO_2 + Pb + 4H^+ + 2SO_4^{-2} \rightarrow 2PbSO_4 + 2H_2O$; $E^{\circ} = 2.01$

Calculate the energy (in kJ) obtained from a lead storage battery in which 0.014 mol of lead is consumed. Assume a constant concentration of 10.M H_2SO_4 (log2 = 0.3)

Ans. $$E = E^{\circ} - \frac{0.059}{n}\log\frac{1}{[H^+]^4[SO_4^{-2}]^2} = 2.01 - \frac{0.059}{2}\log\frac{1}{[20]^4[10]^2} = 2.22\ V$$

Energy = qE

= 2 × 0.014 × 96500 × 2.22

= 6000 J = 6 kJ

Ex.22 Consider the following standard reduction potentials :-

$Fe^{2+} + 2e^- \rightleftharpoons Fe$; $E^\circ = -0.41\ V$

$Ag^+ + e^- \rightleftharpoons Ag$; $E^\circ = 0.80\ V$

$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$; $E^\circ = 0.40\ V$

What would happen if a block of silver metal is connected to a buried iron pipe via a wire:-

(A) The silver metal would corrode, a current would be produced in the wire, and O_2 would be reduced on the surface of the iron pipe.

(B) The silver metal would corrode, a current would be produced in the wire, and Fe^{2+} would be reduced on the surface of the iron pipe.

(C) The iron pipe would corrode, a current would be produced in the wire , and Ag^+ would be reduced on the surface of the silver metal.

(D) The iron pipe would corrode, no current would be produced in the wire, and O_2 would be reduced on the surface of the iron pipe.

Sol. (D)

7. 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. $\mathbf{2H_2O(\ell) + 2e^- \longrightarrow H_2(g) - + 2OH^-(aq)}$
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 $\because$ highly conducting , unreactive.
     highly malleable and ductile.

❖ **Examples of Electrolysis :**

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

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

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

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

  $E_{ext} > 1.206\ V$

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

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

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

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

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

$\therefore$ Cu discharged at cathode and O_2 at anode.

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

  Cathode : $Na^+ + e^- \rightarrow Na$ $\quad E^0 = -2.71\ V$

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

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

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

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. Electrode potential values do not take into account such effects as : Activation energy of process or non-uniform ionic concentration in solution.

(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

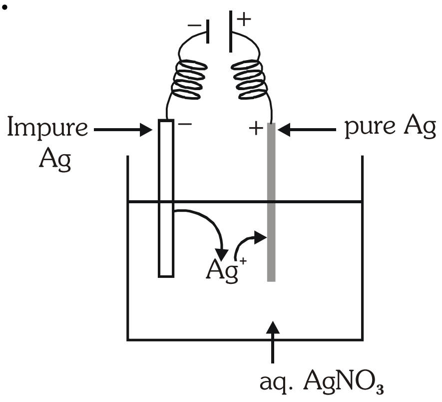
Cathode (reduction) : $Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = +0.34$ V

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

∴ 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 → Anode ;

Pure Metal → Cathode ;

Metal salt solution → Electrolyte

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

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

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

(impure)

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

∴ 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	O_2	Cu
(vii)	Dilute HCl	Pt or Graphite	Cl_2	H_2
(viii)	Dilute H_2SO_4	Pt or Graphite	O_2	H_2
(ix)	Aqueous $AgNO_3$	Pt of Graphite	O_2	Ag
(x)	Aqueous CH_3COONa	Pt of Graphite	$CH_3–CH_3 + CO_2$	H_2

8. *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

$$\mathbf{W \propto Q \propto i \times t}$$

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

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 ≅ 96500 C

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

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.

(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)

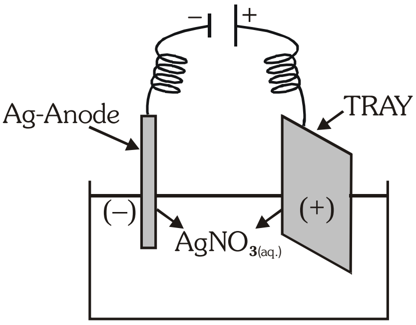
If W_1 and W_2 be the amounts of two different substances deposited at electrodes and E_1 and E_2 be the equivalent weights respectively then -

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

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

EXERCISE # III

49. 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

50. 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.

51. 0.5 mole of electron is passed through two electrolytic cells in series. One contains silver ions, and the other zinc ions. Assume that only cathode reaction in each cell is the reduction of the ion to the metal. How many gm of each metals will be deposited.

52. If 0.224 litre of H_2 gas is formed at the cathode, how much O_2 gas is formed at the anode under identical conditions?

53. Chromium metal can be plated out from an acidic solution containing CrO_3 according to following equation:
$CrO_3(aq) + 6H^+(aq) + 6e^- \rightarrow Cr(s) + 3H_2O$
Calculate :
(i) How many grams of chromium will be plated out by 24125 coulombs and
(ii) How long will it take to plate out 1.5 gm of chromium by using 12.5 ampere current

54. Which of the substances Na, Hg, S, Pt and graphite can be used as electrodes in electrolytic cells having aqueous solution ?
(A) Hg and Pt
(B) Hg, Pt and graphite
(C) Na, S
(D) Na, Hg, S

55. 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

56. A solution of sodium sulphate in water is electrolysed using inert electrodes. The products at the cathode and anode are respectively.

(A) H_2, O_2 (B) O_2, H_2 (C) O_2, Na (D) none

57. When an aqueous solution of lithium chloride is electrolysed using graphite electrodes

(A) Cl_2 is liberated at the anode.

(B) Li is deposited at the cathode

(C) as the current flows, pH of the solution remains constant

(D) as the current flows, pH of the solution decreases.

58. The amount of an ion discharged during electrolysis is not directly proportional to :

(A) resistance (B) time

(C) current strength (D) electrochemical equivalent of the element

59. 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}

60. When one coulomb of electricity is passed through an electrolytic solution the mass deposited on the electrode is equal to :

(A) equivalent weight (B) molecular weight

(C) electrochemical equivalent (D) one gram

61. Electro chemical equivalent of a substance is 0.0006; its e wt. is :

(A) 57.9 (B) 28.95

(C) 115.8 (D) cannot be calculated

62. W g of copper deposited in a copper voltameter when an electric current of 2 ampere is passed for 2 hours. If one ampere of electric current is passed for 4 hours in the same voltameter, copper doposited will be :

(A) W (B) W|2 (C) W|4 (D) 2W

63. When the same electric current is passed through the solution of different electrolytes in series the amounts of elements deposited on the electrodes are in the ratio of their:

(A) atomic number (B) atomic masses (C) specific gravities (D) equivalent masses

64. The amount of electricity that can deposit 108 g. of silver from silver nitrate solution is:

(A) 1 ampere (B) 1 coulomb

(C) 1 Faraday (D) 2 ampere

65. The ratio of weights of hydrogen and magnesium deposited by the same amount of electricity from aqueous H_2SO_4 and fused $MgSO_4$ are :

(A) 1 : 8 (B) 1 : 12 (C) 1 : 16 (D) None of these

66. A current of 9.65 amp. flowing for 10 minute deposits 3.0 g of a metal. The equivalent wt. of the metal is :

(A) 10 (B) 30 (C) 50 (D) 96.5

67. 1 mole of Al is deposited by X coulomb of electricity passing through aluminium nitrate solution. The number of moles of silver deposited by X coulomb of electricity from silver nitrate solution is

(A) 3 (B) 4 (C) 2 (D) 1

68. When an electric current is passed through acid diluted water, 112 ml. of hydrogen gas at STP collects at the cathode in 965 second. The current passed, in ampere is :

(A) 1.0 (B) 0.5 (C) 0.1 (D) 2.0

69. A factory produces 40 kg. of calcium in two hours by electrolysis. How much aluminium can be produced by the same current in two hours :–

(At wt. of Ca = 40, Al = 27)

(A) 22 kg. (B) 18 kg. (C) 9 kg. (D) 27 kg.

70. Calculate the volume of hydrogen at STP obtained by passing a current of 0.536 ampere through acidified water for 30 minutes.

(A) 0.135 litre (B) 0.227 litre (C) 0.057 litre (D) 0.454 litre

71. An electric current is passed through silver voltameter connected to a water voltameter in series. The cathode of the silver voltameter weighed 0.108g more at the end of the electrolysis. The volume of oxygen evolved at STP is :

(A) 56.75cm^3 (B) 567.5 cm^3 (C) 5.675 cm^3 (D) 113.5 cm^3

72. When, during electrolysis of a solution of $AgNO_3$ 9650 coulombs of charge pass through the electroplating bath, the mass of silver deposited on the cathode will be : **[AIEEE 2003]**

(A) 21.6g (B) 108g (C) 1.08g (D) 10.8g

73. Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (1 Faraday = 96500 Coulombs).The cathode reaction is **[AIEEE 2005]**

$Al^{3+} + 3e^- \longrightarrow Al$

To prepare 5.12 kg of aluminium metal by this method would require,

(A) 5.49×10^4 C of electric charge (B) 5.49×10^1 C of electric charge

(C) 5.49×10^7 C of electric charge (D) 1.83×10^7 C of electric charge

Ex.23 How much charge is present on 1 mole of Cu^{+2} ion in faraday. (1 Faraday = 96500 coulomb)

Ans. 1 mole e^- = 1 mol proton = 1F

2 Faraday

Ex.24 For an element 'X' the process of oxidation is : $X_2O_4^{-2} \longrightarrow$ product

If 965 A current when passed for 100 seconds for 0.1 mol of $X_2O_4^{-2}$, find oxidation state of X in new compound ?

Ans. **+3**

$X_2O_4^{-2} \longrightarrow 2X^{+n}$

$\because$ oxidation process 3 < n , N-factor = 2 (n – 3)

so $0.1 \times 2(n-3) = \frac{i \times t}{96500} = \frac{965 \times 100}{96500}$

2(n–3) = 10, n – 3 = 5 , n = 8

node06\B0AI-B0\Kota\JEE(Advanced)\Enthusiast\Chem\Sheet\Electrochemistry\Eng\01_Theory.p65

Ex.25 ***How many litres of chlorine at 1atm & 273K will be deposited by 100 amp. current flowing for 5 hours through molten NaCl?***

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

$$W = ZQ = \frac{E}{96500} \times 18 \times 10^5 = \frac{18E}{96500} \times 10^5 = 662.2\text{ g}, \left(E_{Cl_2} \frac{71}{2} = 35.5\right)$$

$\because$ Volume of 71 g Cl_2 at 1atm & 273K = 22.4 L

$\therefore$ Volume of 662.2 g Cl_2 at NTP $= \frac{22.4}{71} \times 662.2 = 208.9$ L

Ex.26 ***How much time is required for complete decomposition of two moles of water at anode using 4 amperes current ?***

Sol. $H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$

For $H_2 : 2 \times 2 = \frac{4 \times t}{96500} \Rightarrow t = 96500$ sec,

Ex.27 ***How much charge (in F) must flow through solution during electrolysis of aq. Na_2SO_4 at 0°C and 1 atm to produce 33.6 L of product gases at 50% current efficiency ?***

Ans. $H_2O \xrightarrow{2F} H_2 + \frac{1}{2}O_2$

V V|2 $\Rightarrow \frac{3}{2}V = 33.6L \Rightarrow V = 22.4$ L

$Q \times \frac{50}{100} = 2F \Rightarrow Q = 4F$

Ex.28 ***Calculate the time required to coat a metal surface of 80 cm^2 with 0.005 mm thick layer of silver (density = 10.5 g cm^{-3}) with the passage of 3A current through silver nitrate solution.***

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

$\therefore$ Mass = Density × volume $= 10.5 \times 0.04 = 0.42$ g

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

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

Ex.29 ***A Solution of copper (II) sulphate is electrolysed between copper electrodes by a current of 10.0 amperes passing for one hour. What changes occur at the electrodes and in the solution?***

Sol. According to Faraday's first law of electrolysis :

The reaction at cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$

63.5 2×96500 C

The quantity of charge passed = I × t = (10 amp) × (60 × 60s) = 36000 C.

2 × 96500 C of charge deposit copper - 63.5 g

36500 C of charge deposit copper $= \frac{(63.5\text{ g})}{(2\times 96500\text{ C})}\times(36000\text{ C}) = 11.84\text{ g}$

Thus, 11.84 g of copper will dissolve from the anode and the same amount from the solution will get deposited on the cathode. The concentration of the solution will remain unchanged.

Ex.30 ***An aqueous solution of Na_2SO_4 was electrolysed for 10 min. 82 ml of a gas was produced at anode and collected over water at 27°C at a total pressure of 580 torr. Determine the current that was used in amp., Given : Vapour pressure of H_2O at 27°C = 10 torr, R = 0.082 atm L|mol-K***

Ans **(1.6A)**

At anode reaction will be

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$$

Vo_2 collected = 82 ml

By PV = nRT $\frac{(580-10)}{760}\times\frac{82}{1000} = (n_{O_2})\times 0.0821\times 300$, $n_{O_2} = \frac{1}{400}$

By Faraday law $\frac{W}{E} = \frac{i\times t}{96500}$

$$\left(\frac{W}{M}\right)\times n = \frac{i\times t}{96500}, \quad \left(\frac{1}{400}\times 4\right) = \frac{i\times 10\times 60}{96500}, \text{ i = 1.6 A}$$

Ex.31 ***The same current if passed through solution of silver nitrate and cupric salt connected in series. If the weight of silver deposited is 1.08 g. calculate the weight of copper deposited.***

Sol. According to faradays second law

$$\frac{W_1}{W_2} = \frac{E_1}{E_2} \Rightarrow \frac{1.08}{W_2} = \frac{108}{31.75} \Rightarrow W_2 = 0.3175\text{ g}$$

10 ELECTROLYTIC CONDUCTANCE

10.1 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

$$\mathbf{R} \propto \ell$$

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

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

10.2 Conductance or resistivity (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).

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

10.3 Specific resistance or conductivity (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).

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

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

10.4 Specific conductance (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 $\ell = 1$ cm & $A = 1$ cm^2 then $\kappa = G$

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}

10.5 Molar conductance (λ_m or $\wedge_m$) : It is defined as the product of specific conductance (κ) and the volume (V in mL) in which contains one mole of the electrolyte.

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

- It can also be defined as conductance of 1 mole electrolyte completely dissolved between two plates separated by unit distance.

10.6 Equivalent conductance (λ_{eq}or Λ_{eq}) : It is defined as the product of specific conductance (κ) and the volume (V in mL) in which contains one equivalent of the electrolyte.

$\Lambda_m = \kappa \times v$ and $\Lambda_m = \frac{\kappa \times 1000}{M}$ $\mathbf{ohm^{-1}\ cm^{2}\ eq^{-1}}$ **[SI unit : S m^2 eq^{-1}]**

- It can also be defined as conductance of 1 equivalent electrolyte completely dissolved between two plates separated by unit distance.

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

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

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

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

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

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

11 EFFECT OF DILUTION ON THE CONDUCTIVITY OF ELECTROLYTES

(i) The degree of ionisation of weak electrolytes increases with the increase of dilution of the solution the conductivity is increases due to increasing the number of ions.

(ii) Effect of dilution on specific conductance :
Specific conductance decreases with the increase of dilution of the solution due to the presence of no. of ions in 1 cm^3 solution decreases conductance also decrease on dilution.

(iii) Effect of dilution on equivalent|molar conductivity :
The equivalent|molar conductivity increases with dilution. For strong electrolyte λ_m or λ_{eq} increases very slowly but for weak electrolytes λ_m & λ_{eq} increase sharply on dilution.

- When the whole of the electrolyte has ionised, further addition of the water brings a small change in the value of equivalent|molar conductance. This stage is called ***infinite dilution***.
- The ratio of equivalent conductivity at any dilution to equivalent conductivity at infinite dilution is called ***conductivity ratio*** or degree of dissociation of solute -

$$\boxed{\alpha = \frac{\lambda_{eq.}}{\lambda_m^{\infty}} = \frac{\lambda_m}{\lambda_m^{\infty}}}$$ [λ_m^{∞} = molar conductance at ∞ dilution.]

❖ **Variation of conductivity and molar conductivity with concentration :**

- Conductance and conductivity always decreases with the decrease in concentration both for weak and strong electrolytes.
- It is because the number of ions per unit volume that carry the current in a solution decreases on dilution decreasing I, C and K.

❖ Strong Electrolytes :

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

  $\Lambda = \Lambda° - A\, C^{1/2}$. A = constant

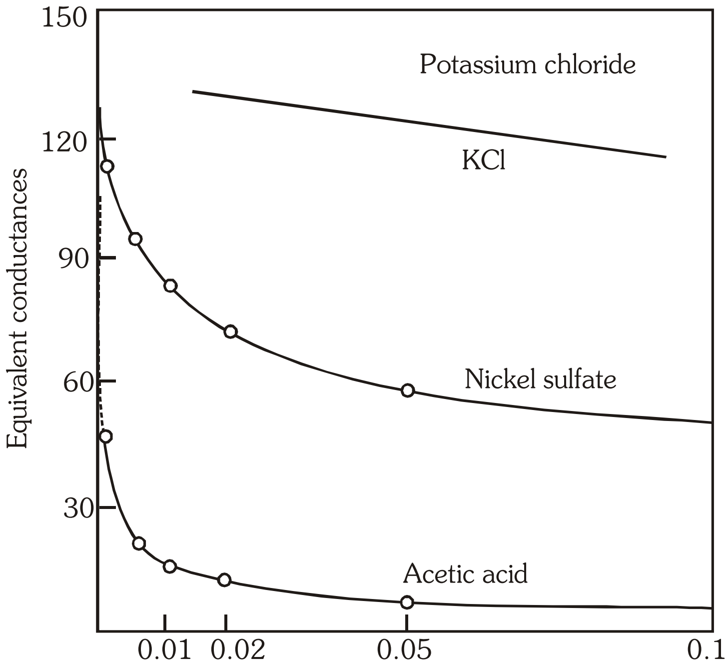
  On dilution interionic separation increases causing free movement & less hindrance. This increases Λ_m & $\Lambda_{eq.}$.

  For strong electrolytes Λ° or Λ^{∞} can be calculated graphically from y-intercept.

  It can be seen that if we plot . L_m against $c^{1/2}$, we obtain a straight line with intercept equal to $A°_m$ and slope equal to –A. The value of the constant A for a given solvent and temperature depends on the type of the electrolyte i.e., the charges on the cation and anion produced on the dissociation of the electrolyte in the solution. Thus, NaCl , $CaCl_2$, $MgSO_4$ are known as 1 – 1, 2 – 1 and 2 – 2 electrolytes respectively. All electrolytes of a particular type have the same value for A.

❖ Weak electrolytes :

- Weak electrolytes like acetic acid have lower degree of dissociation at higher concentration and hence for such electrolytes, the change in Λ with dilution is due to increase in the number of ions solution containing a given amount of electrolyte.



Conductances of electrolytes of different types

KCl → Strong

Ni_2SO_4 → Moderate

CH_3COOH → Weak electrolyte

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.

12. KOHLARAUSCH'S LAW

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

i.e., 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 : $\lambda^{\infty} = \lambda^{\circ}$

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

$$\lambda^0_{eq} = \frac{\lambda^0_m}{\text{chargeon the anion}} \qquad \lambda^0_{eq}\text{, electrolyte} = \frac{\lambda^0_m \text{ electrolyte}}{\text{total +ve charge on cations in electrolyte}}$$

or

total -ve charge on anions in electrolyte

The Independent Migration of Ions. A survey of equivalent conductances at infinite dilution of a number of electrolytes having an ion in common will bring to light certain regularities ;

COMPARISON OF EQUIVALENT CONDUCTANCES AT INFINITE DILUTION

Electrolyte	Λ_0	**Electrolyte**	Λ_0	**Difference**
KCl	130.0	NaCl	108.9	21.1
KNO_3	126.3	$NaNO_3$	105.2	21.1
K_2SO_4	133.0	Na_2SO_4	111.9	21.1

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 Kohlarausch'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

$$\begin{aligned}\Lambda^{\circ}(CH_3COOH) &= \Lambda^{\circ}(HCl) + \Lambda^{\circ}(CH_3COONa) - \Lambda^{\circ}(NaCl)\\ &= 426.16 + 91.0 - 126.45\\ &= 390.71 \text{ ohms}^{-1}\text{ cm}^2 \text{ at } 25.\end{aligned}$$

Similarly :

$$\Lambda_m^{\circ}[BaSO_4] = \Lambda_m^{\circ}[BaCl_2] + \Lambda_m^{\circ}[Na_2SO_4] - 2\Lambda_m^{\circ}[NaCl]$$

- **Degree of dissociation :**

∴ Degree of dissociation

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

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

- **Dissociation constant** of weak electrolyte :

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

- **Solubility(s) and K_{SP} of any sparingly soluble salt.**
  Sparingly soluble salt = Very small solubility
  Solubility = molarity $\cong$ $S \rightarrow 0$
  So, solution can be considered to be of zero conc or infinite dilution.

$$\Lambda_m^s \simeq \Lambda_m^s = \kappa = \frac{1000}{s}$$

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

EXERCISE # IV

74. The resistance of a conductivity cell filled with 0.01N solution of NaCl is 200 ohm at18°C.Calculate the equivalent conductivity of the solution. The cell constant of the conductivity cell is 0.88 cm^{-1}.

75. 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 ?

76. The conductivity of pure water in a conductivity cell with electrodes of cross sectional area 4 cm^2 and 2 cm apart is 8×10^{-7} S cm^{-1}.
(i) What is resistance of conductivity cell ?
(ii) What current would flow through the cell under an applied potential difference of 1 volt?

77. For 0.01N KCl, the resistivity 800 ohm cm. Calculate the conductivity and equivalent conductance.

78. Equivalent conductance of 0.01 N Na_2SO_4 solution is 120 ohm^{-1} cm^2 eq^{-1}. The equivalent conductance at infinite dilution is 150 ohm^{-1} $cm^2 eq^{-1}$. What is the degree of dissociation in 0.01 N Na_2SO_4 solution?

79. Saturated solution of AgCl at 25°C has specific conductance of 1.12×10^{-6} ohm^{-1} cm^{-1}. The λ_∞ (Ag^+) and $\lambda_\infty(Cl^-)$ are 54 and 58 ohm^{-1} cm^2 | equi. respectively. Calculate the solubility product of AgCl at 25°C.

80. 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.

81. 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.

82. 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

83. 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

84. Which of the following solutions of KCl has the lowest value of equivalent conductance ?

(A) 1 M (B) 0.1 M (C) .01 M (D) .001 M

85. 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

86. The equivalent conductivity of 0.1 N CH_3COOH at 25 °C is 80 and at infinite dilution 400. The degree of dissociation of CH_3COOH is :

(A) 1 (B) 0.2 (C) 0.1 (D) 0.5

87. The specific conductance of a 0.01 M solution of KCl is 0.0014 ohm^{-1} cm^{-1}at 25° C. Its equivalent conductance (cm^2 ohm^{-1} $equiv^{-1}$) is :–

(A) 140 (B) 14 (C) 1.4 (D) 0.14

88. The resistance of 0.01 N solution of an electrolyte was found to be 200 ohm at 298 K using a conductivity cell of cell constant 1.5 cm^{-1}. The equivalent conductance of solution is :–

(A) 750 $mhocm^2$ eq^{-1} (B) 75 mho cm^2 eq^{-1}

(C) 750 mho^{-1} cm^2 eq^{-1} (D) 75 $mho^{-1}cm^2$ eq^{-1}

89. 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

90. If 0.01 M solution of an electrolyte has a resistance of 40 ohms in a cell having a cell constant of 0.4 cm^{-1} then its molar conductance in ohm^{-1} cm^2 mol^{-1} is :

(A) 10 (B) 10^2 (C) 10^3 (D) 10^4

91. The conductivity of a saturated solution of $BaSO_4$ is 3.06×10^{-6} ohm^{-1} $cm^{-1}$and its molar conductance is 1.53 ohm^{-1} cm^2 mol^{-1}. The K_{sp} of $BaSO_4$ will be :

(A) 2×10^{-4} (B) 4×10^{-4} (C) 4×10^{-3} (D) 4×10^{-6}

92. The limiting molar conductivities Λ^0 for NaCl, KBr and KCl are 126,152 and 150Scm^2 mol^{-1} respectively. The Λ^0_m for NaBr is : **[AIEEE 2004]**

(A) 278 S cm^2 mol^{-1} (B) 176 S cm^2 mol^{-1} (C) 128 S cm^2 mol^{-1} (D) 302 S cm^2 mol^{-1}

93.

Electrolyte	Λ^∞ (S cm^2 mol^{-1})
KCl	149.9
KNO_3	145.0
HCl	426.2
NaOAC	91.0
NaCl	126.5

Calculate Λ^∞_{HOAc} using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25°C **[AIEEE 2005]**

(A) 390.7 (B) 217.5 (C) 517.2 (D) 552.7

94. The highest electrical conducitivity of the following aqueous solution is of **[AIEEE 2005]**

(A) 0.1 M fluoroacetic acid (B) 0.1 M difluoroacetic acid

(C) 0.1 M acetic acid (D) 0.1 M chloroacetic acid

95. The molar conductivities, Λ^0_{NaOAc} and Λ^0_{HCl} at infinite dilution in water at 25°C are 91.0 and 426.2 S cm^2|mol respectively. To calculate Λ^0_{HOAc} the additional value required is :

(A) KCl (B) NaOH (C) NaCl (D) H_2O**[AIEEE 2006]**

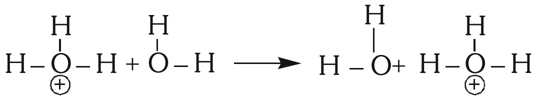
96. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1M is 100Ω. The conductivity of this solution is 1.29 Sm^{-1}. Resistance of the same cell when filled with 0.02M of the same solution is 520Ω. The molar conductivity of 0.02M solution of the electrolyte will be.

(A) 124×10^{-4} $Sm^2\ mol^{-1}$ (B) 1240×10^{-4} $Sm^2\ mol^{-1}$ **[AIEEE 2006]**

(C) 1.24×10^{4} $Sm^2\ mol^{-1}$ (D) 12.4×10^{-4} $Sm^2\ mol^{-1}$

❖ **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



$$\mathrm{H-\underset{\oplus}{\overset{H}{O}}-H + \overset{H}{O}-H \longrightarrow H-\overset{H}{O}+\; H-\underset{\oplus}{\overset{H}{O}}-H}$$

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.

13. CONDUCTOMETRIC TITRATION :

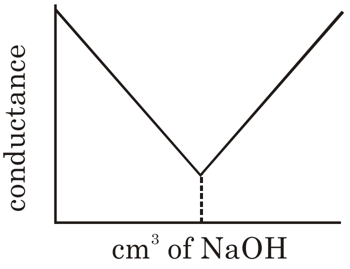
The principle of conductometric titration is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that conductivity of the solution varies during the course of titration. The equivalence point 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 conductometric 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 obtuse, a small error in the conductance data can cause a large deviation. The following approximate rules will be found

- The smaller the conductivity of the ion which replaces 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 ions 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 give good results, since the conductivity increases continuously from the commencement. 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 indicator method can be used for the neutralization titration of phenol ($K_a \times 10^{-10}$) a conductometric endpoint can be successfully applied.

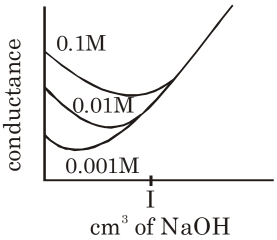
Cation	H_3O^+	NH_4^+	K^+	Na^+	Ag^+	Ca^{2+}	Mg^{2+}
$\lambda^{\infty}_{m}/(\Omega^{-1}cm^2mol^{-1})$	350.0	73.5	73.5	50.1	62.1	118.0	106.1
Anion	OH^-	Br	Cl^-	NO_3^-	CH_3COO^-	SO_4^{2-}	
$\lambda^{\infty}_{m}/(\Omega^{-1}cm^2mol^{-1})$	199.2	78.1	76.5	71.4	40.0	159.6	

Some Typical Conductometric Titration Curves are :

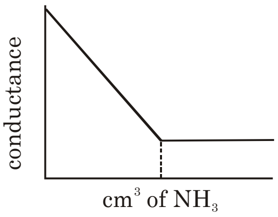
13.1 Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as H^+ ions react with OH - ions to form undissociated water. This decrease in the conducta 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.



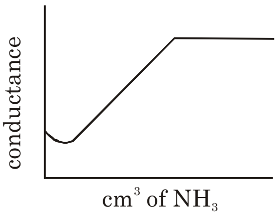
13.2 **Weak Acid with a Strong Base, e.g. acetic acid with NaOH:** Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid 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.



13.3 **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.

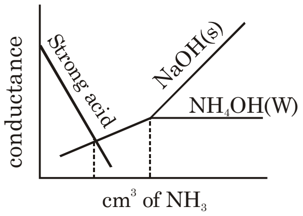


13.4. Weak Acid with a Weak Base : The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base. After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not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

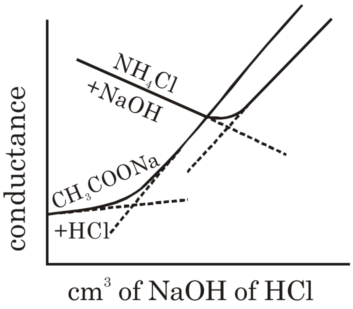


Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base : In this curve there are two break points. The first break point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance

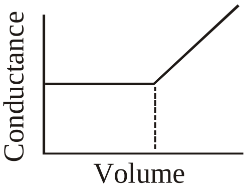
increases due to the excess of OH - ions in case of a strong base as the titrant. However, when the titrant is a weak base, it remains almost constant after the end point similar to



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 obtained, 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 replacement 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 titration of 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.



13.5 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

14. IONIC MOBILITY :

It is the speed of ion under unit potential gradient applied through solution.

$$u = \frac{\text{speed of ion (s)}}{\text{Potential gradient}\left(\frac{dV}{dx}\right)} = \frac{cm^2}{\text{volt} - \text{sec.}} = \frac{\Lambda}{ZF}$$

$u/10^{-8}\ m^2\text{-}s^{-1}\text{-}v^{-1}$ in H_2O at 298 K

Li^+	4.01 4.65	Ca^{+2}	6.17	Rb^+	7.92	CH_3COO^-	7.92	CO_3^{--}	7.91	SO_4^{--}	8.29	OH^-	20.64
Na^+	5.19	Ag^+	6.24	H^+	7.92	F^-	7.92	Cl^-	7.96	$[Fe(CN)_6]^{3-}$	7.96		
Cu^{+2}	5.47 5.56	NH_4^+	7.43	H^+	36.23	NO_3^-	7.40	I^-	7.91	$[Fe(CN)_6]^{4-}$	11.4		

Ex.32 The resistance of a 1 N solution of salt is 50 Ω. Calculate the equivalent conductance of the solution, if the two platinum electrodes in solution are 2.1 cm apart and each having an area of 4.2 cm^2.

Sol : $\kappa = \frac{1}{\rho} = \frac{1}{R}\left(\frac{\ell}{A}\right) = \frac{1}{50} \times \frac{2.1}{4.2} = \frac{1}{100}$ and $\lambda_{eq.} = \frac{\kappa \times 1000}{N} = \frac{1}{100} \times \frac{1000}{1} = 10 = \Omega^{-1}cm^2\text{-}eq^{-1}$

Ex.33 ***Which of the following have maximum molar conductivity.***

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

(ii) 0.1 M solution and its resistivity is $50\ \Omega\,cm$.

Sol. (i) $\wedge_m = \dfrac{\kappa \times 1000}{M} = 2 \times 10^{-2} \times \dfrac{1000}{0.08} = 250\ \Omega^{-1}\ cm^2\ mol^{-1}$

(ii) $\wedge_m = \dfrac{\kappa \times 1000}{M} \qquad \because\ \kappa = \dfrac{1}{\rho} \qquad \therefore\ \Lambda_m = \dfrac{1}{50} \times \dfrac{1000}{0.1} = 200\ \Omega^{-1}\ cm^2\ mol^{-1}$

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

Ex.34 ***The equivalent conductivity of H_2SO_4 at infinite dilution is 384 $\Omega^{-1}\ cm^2\ eq^{-1}$. If 49 g H_2SO_4 per litre is present in solution and specific resistance is 18.4 Ω–cm then calculate the degree of dissociation.***

Sol : Equivalent of $H_2SO_4 = \dfrac{49}{49} = 1$ N

Specific conductance $= \dfrac{1}{\text{specific resistance}} = \dfrac{1}{18.4}$

$\Rightarrow \lambda_{eq.} = \dfrac{1000 \times \kappa}{N} = \dfrac{1000 \times 1}{18.4} = 55$

Degree of dissociation $(\alpha) = \dfrac{\lambda^{C}_{eq.}}{\lambda^{\infty}_{eq.}} = \dfrac{55}{384}$

$= 0.14 \Rightarrow \alpha\ \% = 14\%$

Ex.35 Explain following ionic conductance data of 25°C for various fatty acid anions.

Anion	**Formula**	**λ^0_- AT 25°C (in ohm^{-1}cm^{2}eq^{-1})**
Formate	HCO_2^-	–52
Acetate	$CH_3CO_2^-$	40.9
Propionate	$CH_3CH_2CO_2^-$	35.8
Butyrate	$CH_3(CH_2)_2CO_2^-$	32.6
Valerianate	$CH_3(CH_2)_2CO_2^-$	~29
Caproate	$CH_3(CH_2)_4CO_2^-$	~28

Sol. With increasing chain length bulk increases decreasing ionic mobility and thus equivalent conductance decreases.

$\because$ Charge is identical λ_m also decreases.

Ex.36 ***The resistance of a 0.01 N solution of an electolyte was found to 210 ohm at 298 K using a conductivity cell with a cell constant of 0.88 cm^{-1}. Calculate specific conductance and equivalent conductance of solution.***

Sol. Given, for 0.01 N solution.

$R = 210$ ohm , $\dfrac{\ell}{a} = 0.88\ cm^{-1}$

Specific conductance,

$$\therefore \quad \kappa = \frac{1}{R} \times \frac{\ell}{a} \Rightarrow \kappa = \frac{1}{210} \times 0.88 = 4.19 \times 10^{-3} \text{ mho cm}^{-1}$$

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} = \frac{4.19 \times 10^{-3} \times 1000}{0.01} = 419 \text{ mho cm}^2 \text{ eq}^{-1}.$$

Ex.37 ***The conductivity of pure water in a conductivity cell with electrodes of cross-sectional area 4 cm^2 placed at a distance 2 cm apart is 8 × 10^{-7} S cm^{-1}. Calculate;***

(a) The resistance of water.

(b) The current that would flow through the cell under the applied potential difference of 1 volt.

Sol. Cell constant = $\frac{\ell}{a} = \frac{2}{4} = \frac{1}{2}$ cm^{-1}

(a) Also, $\kappa = \frac{1}{R} \times \frac{\ell}{a}$

$$R = \frac{1}{\kappa} \times \frac{\ell}{a} = \frac{1}{8 \times 10^{-7}} \times \frac{1}{2} = 6.25 \times 10^5 \text{ ohm}$$

(b) From Ohm's law, $\frac{V}{i} = R$

$$\therefore \quad i = \frac{1}{6.25 \times 10^5} = 1.6 \times 10^{-6} \text{ ampere}$$

Ex.38 Molar conductance of 1 M solution of weak acid HA is 20 ohm^{-1} cm^2 mol^{-1}. Find % dissocaition of HA :

$$\begin{pmatrix} \overset{\circ}{\Lambda}_m(H^+) = 350 \text{ S cm}^2 \text{ mol}^{-1} \\ \overset{\circ}{\Lambda}_m(A^-) = 50 \text{ S cm}^2 \text{ mol}^{-1} \end{pmatrix}$$

Ans. $\overset{\circ}{\Lambda}_m(HA) = 350 + 50 = 400$

$$\alpha = \frac{\Lambda_m^C}{\overset{\circ}{\Lambda}_m} \times 100 = \frac{20}{400} \times 100 = 5\ \%$$

Ex.39 ***Conductivity of an aqueous solution of 0.1 M HX (a weak mono-protic acid) is 5 × 10^{-4} Sm^{-1}. Find pK$_a$[HX. Given :*** $\Lambda_m^{\infty}[H^+] = 0.04 \text{ Sm}^2\text{mol}^{-1}$ ***;*** $\Lambda_m^{\infty}[X^-] = 0.01 \text{ Sm}^2\text{mol}^{-1}$

Ans. $HX \rightleftharpoons H^+ + X^-$

$0.1(1-\alpha) \qquad 0.1\alpha \qquad 0.1\alpha$

$$\wedge m = k \times \frac{1000}{C} \Rightarrow 5 \times 10^6 \times \frac{1000}{0.1} = 0.05\Omega^{-1}\text{cm}^2\text{-mol}^{-1}$$

$$a = \frac{\Lambda_m}{\Lambda_m} = \frac{0.05}{50}\Omega^{-1} - \text{cm}^2\text{mol}^{-1} = 10^{-4}$$

$K_a = C\alpha^2 = 0.1 \times (10^{-4})^2 = 10^{-9}$

$pK_a = 9$

Ex.40 ***Specific conductance of 10^{-4} M n-Butyric acid aqueous solution is 1.9×10^{-9} S m^{-1}. If molar conductance of n-Butyric acid at infinite dilution is 380×10^{-4} S m^2 mol^{-1}, then K_a for n-Butyric acid is :***

Sol.

$$\Lambda_m = 1000 \times \frac{1.9\times10^{-9}}{10^{-4}} = 1.9 \times 10^{-2}$$

$$\alpha = \frac{1.9\times10^{-2}}{380\times10^{-4}} = 0.5$$

$$K_a = \frac{10^{-4}(0.5)^2}{1-0.5} = 5 \times 10^{-5}\ M$$

Ex.41 ***The specific conductance of a saturated AgCl solution is found to be 2.12×10^{-6} S cm^{-1} and that for water is 6×10^{-8} S cm^{-1}. The solubility of AgCl is :***

($l_{eq.}^{¥}$ = 103 S $equiv^{-1}$ cm^2)

Sol. So.= 241.67 S cm^2 mol^{-1}

$$S = \frac{(F_{Ag\,sol.} - F_{H_2O})\times1000}{(\Lambda^0_{eq.})_{AgCl}} = 2\times10^{-5} M$$

Ex.42 ***The value of μ^∞ for NH_4Cl, NaOH and NaCl are 129.8, 248.1 and 126.4 ohm^{-1} cm^2 mol^{-1} respectively. Calculate μ^∞ for NH_4OH solution.***

Sol.

$$\mu^\infty_{NH_4OH} = \mu^\infty_{NH_4Cl} + \mu^\infty_{NaOH} - \mu^\infty_{NaCl}$$

$$= 129.8 + 248.1 - 126.4$$

$$\mu^\infty_{NH_4OH} = 251.5\ ohm^{-1}\ cm^2\ mol^{-1}$$

Ex.43 ***Calculate molar conductance for NH_4OH, given that molar conductances for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl are 523.28, 280.0 and 129.8 ohm^{-1} cm^2 mol^{-1} respectively.***

Sol.

$$\mu^\infty_{Ba(OH)_2} = \lambda^\infty_{Ba^{2+}} + 2\lambda^\infty_{OH^-} = 523.28 \quad ....(i)$$

$$\mu^\infty_{BaCl_2} = \lambda^\infty_{Ba^{2+}} + 2\lambda^\infty_{Cl^-} = 280.00 \quad .... (ii)$$

$$\mu^\infty_{NH_4Cl} = \lambda^\infty_{NH_4^+} + \lambda^\infty_{Cl^-} = 129.80 \quad .... (iii)$$

$$\mu^\infty_{NH_4OH} = \lambda^\infty_{NH_4^+} + \lambda^\infty_{OH^-} = ?$$

$$\text{Eq.(iii)} + \frac{\text{Eq.(i)}}{2} - \frac{\text{Eq.(ii)}}{2} \text{ will gives}$$

$$\lambda^\infty_{NH_4^+} + \lambda^\infty_{OH^-} = \lambda^\infty_{NH_4OH} = \frac{502.88}{2} = 251.44\ ohm^{-1}\ cm^2\ mol^{-1}$$

Ex.44 ***The equivalent conductivities of acetic acid at 298 K at the concentrations of 0.1 M and 0.001 M are 5.20 and 49.2 S cm^2 eq.$^{-1}$ respectively. Calculate the degree of dissociation of acetic acid at these concentrations. Given that, $\lambda^\infty(H^+)$ and $\lambda^\infty(CH_3COO^-)$ are 349.8 and 40.9 ohm^{-1} cm^2 mol^{-1} respectively.***

Sol. Degree of dissociation is given by $\alpha = \frac{\lambda^c}{\lambda^\infty}$

(i) Evaluation of $\lambda^\infty_{CH_3COOH}$:

$$\lambda^\infty_{CH_3COOH} = \lambda^\infty_{CH_3COO^-} + \lambda^\infty_{H^+}$$

$$= 40.9 + 349.8 = 390.7 \text{ ohm}^{-1}\text{ cm}^2\text{ eq.}^{-1}$$

(ii) Evaluation of degree of dissociation :

At C = 0.1 M $\alpha = \frac{\lambda^c}{\lambda^\infty} = \frac{5.20}{390.7} = 0.013$

i.e. 1.3%

At C = 0.001 M $\alpha = \frac{\lambda^c}{\lambda^\infty} = \frac{49.2}{390.7} = 0.125$

i.e. 12.5%

Ex.45 ***At infinite dilution the molar conductance of Al^{+3} and SO_4^{-2} ion are 189 and 160 Ω^{-1} cm^2 mole^{-1} respectively. Calculate the equivalent and molar conductivity at infinite dilute of $Al_2(SO_4)_3$.***

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

$$= \frac{1}{3}\times 189 + \frac{1}{2}\times 160$$

$$= 143\ \Omega^{-1}\text{ cm}^2\text{ eq}^{-1}$$

Molar conductivity= $\lambda_{eq} \times$ V. F. = 143 × 6

$= 858\ \Omega^{-1}\text{cm}^2\text{ mol}^{-1}$

Ex.46 ***Find Λ_m^∞ (in Ω^{-1} cm^2 mol^{-1}) for strong electrolyte AB_2 in water at 25° from the following data.***

Conc.C(mole/L)	0.25	1
$\wedge_m$(W^{-1}cm^2/mol)	160	150

Sol. $160 = \Lambda_m^\infty - b \times \sqrt{.25}$ ....(A)

$150 = \Lambda_m^\infty - b \times \sqrt{1}$ ....(B)

b = 20 and $\Lambda_m^\infty = 170$

y = 170 – 20x
Intercept = 170
$\Lambda_m^\infty = 170\ \Omega^{-1}\,\text{cm}^2\,\text{mol}^{-1}$

Ex.47 ***For any sparingly soluble salt $[M(NH_3)_4Br_2]\ H_2PO_2$***

Given : $\lambda^0_{M(NH_3)_4Br_2^+} = 400$ ***S-m^2–mol^{-1},***

$\lambda^0_{H_2PO_2^-} = 100$ ***S-m^2–mol^{-1}***

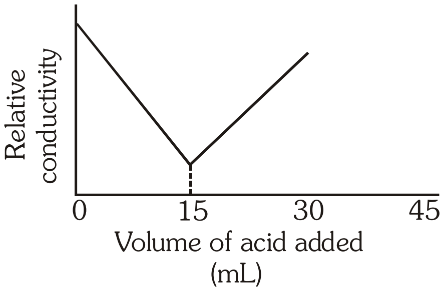
Specific resistance of saturated $[M(NH_3)_4Br_2]H_2PO_2$ solution is 200 Ω-cm.
If solubility product constant of the above salt is 10^{-x}. What will be the value of x.

Ans. $\wedge_m^\infty = \kappa \times \dfrac{1000}{m} \times 10^{-6}$

$500 = \dfrac{1}{200} \times \dfrac{1000}{5} \times 10^{-6}$

$S = 10^{-8}$ mol|L , $K_{sp} = S^2 = 10^{-16}$

Ex.48 ***20 mL of KOH solution was titrated with 0.2 M H_2SO_4 solution in a conductivity cell. The data obtained were plotted to given the graph shown below :***



the concentration of KOH solution was -

(A) 0.3 M ***(B) 0.15 M*** ***(C) 0.12 M*** ***(D) 0.075 M***

Sol. **(A)**

20 × M = 0.2 × 2 × 15 ⇒ M= 0.15

ANSWER KEY

EXERCISE # I

1. Ans. 1.61 V
2. Ans.1.35 V
3. Ans.– 0.80 V, N_0
4. Ans. – 0.0367 V
5. Ans. (C)
6. Ans.(C)
7. Ans. (C)
8. Ans.(B)
9. Ans.(C)
10. Ans.(C)
11. Ans.(A)

12 For a spontaneous reaction the ΔG, equilibrium constant (K) and E^0_{Cell} will be respectively

12 Ans.(C)
13. Ans.(A)
14 Ans.(D)
15. Ans. (B)
16. Ans.(A)
17. Ans.(C)
18. Ans.

EXERCISE # II

19. Ans. (a) $2Ag + Cu^{2+} \longrightarrow 2Ag^{+} + Cu$, (b) $MnO_4^- + 5Fe^{2+} + 8H^{+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(c) $2Cl^{-} + 2Ag^{+} \longrightarrow 2Ag + Cl_2$, (d) $H_2 + Cd^{2+} \longrightarrow Cd + 2H^{+}$

20. Ans.(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^{+} , $Cr^{3+} \mid Pt$

21. Ans. E =1.159V
22. Ans. E^0_{cell} = +0.01V, E_{cell} = –0.0785V, correct representation is $Pb|Pb^{2+}$ (10^{-3}M)||Sn^{2+}(1M)|Sn
23. Ans. $[Cu^{2+}] = 2.97 \times 10^{-12}$M for E =0
24. Ans. $K_c = 7.6 \times 10^{12}$
25. Ans. $K_c = 2.18 \times 10^{26}$
26. E^0 = 0.7826 V
27. Ans. (7)
28. Ans. 0.0295 V
29. Ans. pH = 4
30. Ans. (B)
31. Ans.(D)
32. Ans.(C)
33. Ans.(A)
34. Ans.(C)
35. Ans.(B)
36. Ans.(D)
37. Ans.(A)
38. Ans.(C)
39. Ans.(B)
40. Ans.(B)
41. Ans.(C)
42. Ans.(A)
43 Ans.(B)
44 Ans.(A)
45. Ans.(A)
46. Ans.(A)
47. Ans.(D)
48. Ans.(D)

EXERCISE # III

49. Ans. (a) 6.02×10^{22} electrons lost, (b) 1.89×10^{22} electrons gained, (c) (b) 1.80×10^{23} electrons gained

50. Ans. (a) 0.75 F, (b) 0.69 F, (c)1.1 F

51. Ans. (i) 54 gm, (ii) 16.35 gm

52. Ans.0.112 litre

53. Ans. (i) 2.17 gm ; (ii) 1336. 15 sec

54. Ans.(B

55. Ans.(C)

56. Ans.(A)

57. Ans.(A)

58. Ans.(A)

59. Ans.(C)

60. Ans.(C)

61. Ans.(A)

62. Ans.(A)

63. Ans.(D)

64. Ans.(C)

65. Ans.(B)

66. Ans.(C)

67. Ans.(A)

68. Ans.(A)

69. Ans.(B)

70. Ans.(A)

71. Ans.(C)

72. Ans.(D)

73. Ans.(C)

EXERCISE # IV

74. Ans. 442 S cm^2 equivalent^{-1}

75. Ans. 0.00040 S cm^{-1} ; 2500 ohm cm

76. Ans. (i) 6.25×10^5 ohm, (ii) 1.6×10^{-6} amp

77. Ans. 0.0125 mho g equiv^{-1} m^2, 1.25×10^{-3} mho cm^{-1}

78. Ans. 0.8

79. Ans. 10^{-10} mole^2 |litre^2

80. Ans. (i) 400 S cm^2 mol^{-1} (ii) 12 %

81. Ans. 510×10^{-4} mho cm^2 mol^{-1}

82. Ans.(B)

83. Ans.(D)

84. Ans.(A)

85. Ans.(B)

86. Ans.(B)

87. Ans.(A)

88. Ans.(A)

89. Ans.(A)

90. Ans.(C)

91. Ans.(D)

92 Ans.(C)

93 Ans.(A)

94 Ans.(B))

95 Ans.(C)

96. Ans.(A)

SOME PREVIOUS YEAR SOLVED EXAMPLE

1. Find the solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell Ag|Ag^+ (satd.Ag_2 CrO_4 soln.) || Ag $^+$(0.1 M) | Ag is 0.164 V at 298K. **[JEE 1998]**

1. Ans.(K_{sp} = 2.287 × 10^{-12})

Sol. Ag|Ag^+ sat. sol^n || Ag^+ (0.1 M)| Ag

$AgClO_4$)

$$0.164 = 0 - \frac{.059}{1}\log\frac{[Ag^+]A}{0.1}$$

$\therefore [Ag^+]_A = (1.66 \times 10^{-4}) \times (.83 \times 10^{-4})$

$= 2.287 \times 10^{-12}$

2. Calculate the equilibrium constant for the reaction, $2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$. The standard reduction potentials in acidic conditions are 0.77 and 0.54 V respectively for Fe^{3+} | Fe^{2+} and I_3^- | I^- couples. **[JEE 1998]**

2. Ans. (K_C = 6.26 × 10^7)

Sol. $2Fe^{+3} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$

$E° = 0.77 + (-.54) = 0.23$, $Keq = 10^{\frac{2\times.23}{.059}}$

$Keq = 6.26 \times 10^7$

3. A gas X at 1 atm is bubbled through a solution containing a mixture of 1 M Y and 1 M Z at 25°C. If the reduction potential of Z > Y > X, then **[JEE 1999]**

(A) Y will oxidise X and not Z
(B) Y will oxidise Z and X
(C) Y will oxidise both X and Z
(D) Y will reduce both X and Z.

3. Ans. (A)

4. The following electrochemical cell has been set up

$$Pt_{(I)} \mid Fe^{3+}, Fe^{2+}(a=1) \parallel Ce^{4+}, Ce^{3+}(a=1) \mid Pt_{(II)}$$

$$E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\text{ V and } E^\circ_{Ce^{4+}/Ce^{3+}} = 1.61\text{ V}$$

If an ammetter is connected between the two platinum electrodes. predict the direction of flow of current. Will the current increase or decrease with time? **[JEE 2000]**

4. Ans. (decrease with time)

Sol. $E°_{cell}$ is (+) ve so cell will work and current will flow from cathode to anode. Current will decrease with time

5. Copper sulphate solution (250 mL) was electrolysed using a platinum anode and a copper cathode. A constant current of 2 mA was passed for 16 mintue. It was found that after electrolysis, the absorbance (concentration) of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with. **[JEE 2000]**

5. Ans.(7.95 × 10^{-5}M)

Sol. $\left(n_{Cu^{+2}}\right)_{reduced} = \dfrac{2\times10^{-3}\times16\times60}{96500\times2} = \dfrac{.96}{96500}$

$(n_{Cu^{+2}})_{\text{originally present}} = \dfrac{1.92}{96500}$

$\therefore$ M = $\dfrac{1.92}{96500}\times\dfrac{1000}{250}$ = 7.958 × 10^{-5}

$E°_{cell}$ = – .77 + 1.61 = 0.84

6. For the electrochemical cell, M | M^+ || X^- | X, E° (M^+|M) = 0.44 V and E° (X|X^-) = 0.33V. From this data , one can deduce that **[JEE 2000]**

(A) M + X $\longrightarrow$ $M^+ + X^-$ is the spontaneous reaction

(B) $M^+ + X^-$ $\longrightarrow$ M + X is the spontaneous reaction

(C) E_{cell}= 0.77 V

(D) E_{cell}= – 0.77 V

6. Ans.(B)

Sol. $E°_{cell} = E^0_{MM^+} + E°_{M/M^+} + E°_{X^-/X} = –.44 + –.33 = –0.77$ V

so (B)

7. The standard potential of the following cell is 0.23 V at 15° C & 0.21 V at 35° C

Pt | H_2(g) | HCl (aq) | AgCl(s) | Ag(s)

(i) Write the cell reaction.

(ii) Calculate ΔH^0 ,ΔS^0 for the cell reaction by assuming that these quantities remain unchanged in the range 15°C to 35°C.

(iii) Calculate the solubility of AgCl in water at 25°C. Given standard reduction potential of the Ag^+|Ag couple is 0.80 V at 25°C. **[JEE 2001]**

7. Ans.ΔH^0 = – 49987 Jmol^{-1}, ΔS^0 =– 96.5 J mol^{-1} K^{-1}, s =1.47 ×10^{-5} M

Sol. (i) Anode : $\frac{1}{2}H_2 \longrightarrow H^+ + e^-$

Cathode : $\dfrac{AgCl + e^- \longrightarrow Ag + Cl^-}{\frac{1}{2}H_2 + AgCl \longrightarrow H^+ + Cl^- + Ag}$

(ii) $\dfrac{\partial E}{\partial T} = \dfrac{.21-.23}{308-288} = \dfrac{.02}{10} = –2 \times 10^{-3}$

$\Delta G° = –nFE°$ so $(\Delta G°)_{288K} = –22195$ $(\Delta G°)_{308K} = –20265$ J

now using $\Delta G° = \Delta H° – T\Delta S° \Rightarrow \Delta H° = –49987$ J, $\Delta S° = –96.5$ J

(iii) $E°_{25°C} = 0.22V$ $E°_{cell} = E°_{Cl^-/AgCl/Ag} = 0.22$

so –.8 + 0.22 = $\dfrac{0.59}{1}$ log Ksp

$\therefore$ Ksp = 1.47 × 10^{-10} $\Rightarrow$ S = 1.21 × 10^{-5}

8. Saturated solution of KNO_3 is used to make salt bridge because

(A) velocity of K^+ is greater than that of NO_3^-

(B) velocity of NO_3^- is greater than that of K^+

(C) velocities of both K^+ and NO_3^- are nearly the same

(D) KNO_3 is highly soluble in water **[JEE 2001]**

8. Ans.(C)

Sol. Fact

9. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl and KCl is

(A) LiCl > NaCl > KCl (B) KCl > NaCl > LiCl **[JEE 2001]**

(C) NaCl > KCl > LiCl (D) LiCl > KCl > NaCl

9. Ans.(B)

Sol. Fact

10. The reaction, **[JEE 2001]**

$3ClO^-(aq) \longrightarrow ClO_3^-(aq) + 2Cl^-(aq)$

is an example of

(A) Oxidation reaction (B) Reduction reaction

(C) Disproportionation reaction (D) Decomposition reaction

10. Ans.(C)

Sol Fact

11. Standard electrode potential data are useful for understanding the suitablilty of an oxidant in a redox titration. Some half cell reactions and their standard potentials are given below: **[JEE 2002]**

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l);\ E° = 1.51\ V$$

$$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6e^- \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l);\ E° = 1.38\ V$$

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

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq);\ E° = 1.40\ V$$

Identify the only incorrect statement regarding quantitative estimation of aqueous $Fe(NO_3)_2$

(A) MnO_4^- can be used in aqueous HCl

(B) $Cr_2O_7^{2-}$ can be used in aqueous HCl

(C) MnO_4^- can be used in aqueous H_2SO_4

(D) $Cr_2O_7^{2-}$ can be used in aqueous H_2SO_4

11. Ans.(A)

Sol. MnO_4^- will oxidise Cl^- into Cl_2 so MnO_4^- can not be used in aqueous HCl

12. Two students use same stock solution of $ZnSO_4$ and a solution of $CuSO_4$. The e.m.f of one cell is 0.03 V higher than the other. The conc. of $CuSO_4$ in the cell with higher e.m.f value is 0.5 M. Find out the conc. of $CuSO_4$ in the other cell $\left(\frac{2.303RT}{F} = 0.06\right)$. **[JEE 2003]**

12. Ans.(0.05)

Sol. $E_1 = E° - \log \frac{[Zn^{+2}]}{[Cu^{+2}]_1}$

$$E_2 = E° - \log \frac{[Zn^{+2}]}{[Cu^{+2}]_2}$$

$$E_2 - E_1 = -.03 \log \frac{[Cu^{+2}]_1}{[Cu^{+2}]_2} \Rightarrow 0.03 = -\frac{.059}{2} \log \frac{[Cu^{+2}]}{5}$$

$$\therefore 0.03 = -03 \log \frac{[Cu^{+2}]}{5} \Rightarrow [Cu^{+2}] = .05 \text{ M}$$

13. In the electrolytic cell, flow of electrons is from:

(A) Cathode to anode in solution
(B) Cathode to anode through external supply
(C) Cathode to anode through internal supply
(D) Anode to cathode through internal supply. **[JEE 2003]**

13. Ans.(C)

14. Find the equilibrium constant at 298 K for the reaction,

$$Cu^{2+}(aq) + In^{2+}(aq) \rightleftharpoons Cu^{+}(aq) + In^{3+}(aq)$$

Given that $E^{\circ}_{Cu^{2+}|Cu^{+}} = 0.15V$, $E^{\circ}_{In^{3+}|In^{+}} = -0.42V$, $E^{\circ}_{In^{2+}|In^{+}} = -0.40V$ **[JEE 2004]**

14. Ans.(K_C = 10^{10})

Sol. $E^{\circ}_{Cell} = E^{\circ}_{In^{+2}/In^{+3}} + E^{\circ}_{Cu^{+2}/Cu^{+}}$

$= .44 + .15 = .59$

$$E^{\circ}_{In^{+2}/In^{+3}} = \frac{1\alpha - 0.4 + 2\alpha 0.42}{1} = .44$$

$$K_{eq} = 10^{\frac{1 \times .59}{.059}} = 10^{10}$$

15. Zn | Zn^{2+} (a = 0.1M) || Fe^{2+} (a = 0.01M)|Fe. The emf of the above cell is 0.2905 V. Equilibrium constant for the cell reaction is

(A) $10^{0.32|0.0591}$ (B) $10^{0.32|0.0295}$ (C) $10^{0.26|0.0295}$ (D) $e^{0.32|0.295}$ **[JEE 2004]**

15. Ans.(B)

Sol. $0.2905 = E° - \frac{.059}{2} \log \frac{.1}{0.01} \Rightarrow E° = .32$

$\therefore K_{sp} = 10^{\frac{2\times.32}{0.0591}} = 10^{\frac{.32}{0.0295}} \Rightarrow B$

16. (a) Calculate ΔG_f^0 of the following reaction

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

Given : ΔG_f^0 (AgCl) = –109 kJ|mole, ΔG_f^0 (Cl^-) = –129 kJ|mole, ΔG_f^0 (Ag^+) = 77 kJ|mole

Represent the above reaction in form of a cell

Calculate E^0 of the cell. Find $\log_{10}K_{SP}$ of AgCl

(b) 6.539×10^{-2} g of metallic Zn (amu = 65.39) was added to 100 ml of saturated solution of AgCl.

Calculate $\log_{10}\frac{[Zn^{2+}]}{[Ag^+]^2}$, given that

$Ag^+ + e^- \longrightarrow Ag \quad E^0 = 0.80$ V ; $Zn^{2+} + 2e^- \longrightarrow Zn \quad E^0 = -0.76$V

Also find how many moles of Ag will be formed? **[JEE 2005]**

16. Ans.(a) E^0 = 0.59 V, $\log_{10}K_{SP}$ = –10 (b) 52.8, 10^{-6} moles

Sol. (a) $\Delta G° = (-109) - [-129 + 77] = -57$

$$E° = \frac{-57\times1000}{1\times96500} = 0.59$$

$$\Delta G° = -2.303RT \log K_{sp} \Rightarrow \log K_{sp} = \frac{-57\times1000}{-2.303\times8.314\times298}$$

$\log K_{sp} = 9.989 \cong 10$

(b) $Zn + 2Ag^+ \longrightarrow Zn^{+2} + 2Ag \quad E^{\circ}_{cell} = 1.56$

$$\therefore \log_{10}\frac{[Zn^{+2}]}{[Ag^+]^2} = \frac{1.56\times2}{.059} = 52.8$$

$[Ag^+] = \sqrt{Ksp} = \sqrt{10^{-10}} = 10^{-5}$

$\therefore n_{Ag^+} = 10^{-5} \times .1 = 10^{-6}$

17. The half cell reactions for rusting of iron are: **[JEE 2005]**

$2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O$; E^0 = + 1.23 V, $Fe^{2+} + 2e^- \longrightarrow Fe$; E^0 = –0.44 V

ΔG^0 (in kJ) for the reaction is:

(A) –76 (B) –322 (C) –122 (D) –176

17. Ans.(B)

Sol. $\Delta G° = -nFE°$

$$= \frac{-2 \times 96500 \times 1.67}{1000} - 322$$

18. 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 find conductivity (specific conductance) of this solution in terms of 10^{-7} S m^{-1} **[JEE 2006]**

Given : $\lambda^0_{(Ag^+)} = 6 \times 10^{-3}$ **S m² mol⁻¹** ; $\lambda^0_{(Br^-)} = 8 \times 10^{-3}$ **S m² mol⁻¹** ; $\lambda^0_{(NO_3^-)} = 7 \times 10^{-3}$ **S m² mol⁻¹**

18. Ans.(55 S m⁻¹)

Sol. $AgBr \rightleftharpoons \underset{s}{Ag^+} + \underset{s}{Br^-}$

$AgNO_3 \longrightarrow \underset{10^{-7}}{Ag^+} + \underset{10^{-7}}{NO_3^-}$

$\therefore (K_{sp})_{AgBr} = [Ag^+][Br^-] \Rightarrow 12 \times 10^{-14} = (s + 10^{-7})\cdot(s)$

$s^2 + 10^{-7} s - 12 \times 10^{-14} = 0 \Rightarrow s = 3 \times 10^{-7}$

$\therefore [Ag^+] = 4 \times 10^{-7}$ $[Br] = 3 \times 10^{-7}$ $[NO_3] = 10^{-7}$

now $\Lambda^\infty_M = \frac{1000\,k}{M}$

for $Ag^+ \Rightarrow 6 \times 10^{-3} \times 10^4 = \frac{1000k}{4 \times 10^{-7}} \Rightarrow k_{Ag^+} = 24$

$Br^- \Rightarrow 8 \times 10^{-3} \times 10^4 = \frac{1000k}{3 \times 10^{-7}} \Rightarrow k_{Br^-} = 24$

$NO_3^- \Rightarrow 7 \times 10^{-3} \times 10^4 = \frac{1000\,k}{10^{-7}} \Rightarrow R_{NO_3^-} = 7$

Ans. 55

Question No. 19 to 21 (3 questions)

Tollen's reagent is used for the detection of aldehyde when a solution of $AgNO_3$ is added to glucose with NH_4OH then gluconic acid is formed

$Ag^+ + e^- \longrightarrow Ag$; $E^0_{red} = 0.8$ V

$C_6H_{12}O_6 + H_2O \longrightarrow C_6H_{12}O_7$ (Gluconic acid) $+ 2H^+ + 2e^-$; $E^0_{red} = -0.05$ V

$Ag(NH_3)_2^+ + e^- \longrightarrow Ag(s) + 2NH_3$; $E^0 = -0.337$ V

[Use $2.303 \times \frac{RT}{F} = 0.0592$ and $\frac{F}{RT} = 38.92$ at 298 K] **[JEE 2006]**

19. $2Ag^+ + C_6H_{12}O_6 + H_2O \longrightarrow 2Ag(s) + C_6H_{12}O_7 + 2H^+$

Find ln K of this reaction

(A) 66.13 (B) 58.38 (C) 28.30 (D) 46.29

19. Ans.(A)

Sol. $\log K = \frac{2.303 \times n \times E°}{.059} = \frac{2.303 \times 2 \times .85}{.059} = 66.13$

20. When ammonia is added to the solution, pH is raised to 11. Which half-cell reaction is affected by pH and by how much?

(A) E_{oxd} will increase by a factor of 0.65 from E^0_{oxd}

(B) E_{oxd} will decrease by a factor of 0.65 from E^0_{oxd}

(C) E_{red} will increase by a factor of 0.65 from E^0_{red}

(D) E_{red} will decrease by a factor of 0.65 from E^0_{red}

20. Ans.(A)

Sol. Since H^+ is involved in oxidation half reaction so E_{oxd} will be affected and it will increase

$$E_{oxd} = E°_{oxd} - \frac{.059}{2}\log\frac{[C_6H_{12}O_7][H^+]^2}{[C_2H_{12}O_6]}$$

21. Ammonia is always is added in this reaction. Which of the following must be incorrect?

(A) NH_3 combines with Ag^+ to form a complex.

(B) $Ag(NH_3)_2^+$ is a weaker oxidising reagent than Ag^+.

(C) In absence of NH_3 silver salt of gluconic acid is formed.

(D) NH_3 has affected the standard reduction potential of glucose|gluconic acid electrode.

21. Ans.(D)

Sol. $E°_{Red}$ in a constant quantity

Paragraph for Question Nos. 22 to 24 (3 questions)

Chemical reactions involve interaction of atoms and molecules. A large number of atoms|molecules (approximately 6.023×10^{23}) are present in a few grams of any chemical compound varying with their atomic|molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical| electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrodes **(atomic mass : Na = 23, Hg = 200; 1 Faraday = 96500 coulombs)** **[JEE 2007]**

22. The total number of moles of chlorine gas evolved is

(A) 0.5 (B) 1.0 (C) 2.0 (D) 3.0

22. Ans.(B)

Sol. At anode $2Cl^- \longrightarrow Cl_2 + 2e^-$

$$\begin{matrix} 2 & & 1 \end{matrix}$$

23. If the cathode is a Hg electrode, the maximum weight (g) of amalgam formed from this solution is

(A) 200 (B) 225 (C) 400 (D) 446

23. Ans.(D)

Sol. At cathode $2Na^+ + 2e^- \longrightarrow 2Na(s)$

$$\begin{matrix} 2 & & 2 \end{matrix}$$

$$2Na + 2Hg \longrightarrow 2Na\text{–}Hg$$

$$2 \qquad 2 \qquad \therefore W = 446$$

24. The total charge (coulombs) required for complete electrolysis is
(A) 24125 (B) 48250 (C) 96500 (D) 193000

24. Ans.(D)

Sol. 2 moles on e^- = 2F = 193000 C

Paragraph for Question Nos. 25 & 26 (2 questions)

Redox reactions play a pivoted role in chemistry and biology. The values of standard redox potential (E°) of two half-cell reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reactions (acidic medium) along with their E° (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to Questions 14-16.

$I_2 + 2e^- \rightarrow 2I^-$ E° = 0.54
$Cl_2 + 2e^- \rightarrow 2Cl^-$ E° = 1.36
$Mn^{3+} + e^- \rightarrow Mn^{2+}$ E° = 1.50
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ E° = 0.77
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ E° = 1.23 **[JEE 2007]**

25. Among the following, identify the correct statement.
(A) Chloride ion is oxidised by O_2 (B) Fe^{2+} is oxidised by iodine
(C) Iodine ion is oxidised by chlorine (D) Mn^{2+} is oxidised by chlorine

25. Ans.(C)

Sol. as E° will be positive

26. While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because
(A) O_2 oxidises Mn^{2+} to Mn^{3+}
(B) O_2 oxidises both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}
(C) Fe^{3+} oxidises H_2O to O_2
(D) Mn^{3+} oxidises H_2O to O_2

26. Ans.(D)

Sol. as E° will be positive

28. For the reaction of NO_3^- ion in an aqueous solution, E° is +0.96 V. Values of E° for some metal ions are given below

$V^{2+}(aq) + 2e^- \rightarrow V$ E° = – 1.19 V
$Fe^{3+}(aq) + 3e^- \rightarrow Fe$ E° = – 0.04 V
$Au^{3+}(aq) + 3e^- \rightarrow Au$ E° = + 1.40 V
$Hg^{2+}(aq) + 2e^- \rightarrow Hg$ E° = + 0.86 V

The pair(s) of metal that is(are) oxidised by NO_3^- in aqueous solution is(are) **[JEE 2009]**
(A) V and Hg (B) Hg and Fe
(C) Fe and Au (D) Fe and V

28. Ans.(A,B,D)

Sol. (A,B,D) as E° will be positive

Paragraph for Questions 29 to 30

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 : **[JEE 2010]**

$M(s)|M^+(aq\ ;\ 0.05\ molar)\ ||\ M^+(aq\ ;\ 1\ molar)|M(s)$

For the above electrolytic cell the magnitude of the cell potential $|E_{cell}| = 70$ mV.

29. For the above cell :-

(A) $E_{cell} < 0\ ;\ \Delta G > 0$ (B) $E_{cell} > 0\ ;\ \Delta G < 0$

(C) $E_{cell} < 0\ ;\ \Delta G^0 > 0$ (D) $E_{cell} > 0\ ;\ \Delta G^0 < 0$

29. Ans.(B)

Sol. $E_1 = -\frac{.059}{1}\log\frac{.05}{1} = (+)\text{ve} \Rightarrow \text{so}$

30. 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 :-

(A) 35 mV (B) 70 mV (C) 140 mV (D) 700 mV

30. Ans.(C)

Sol. $E_2 = -\frac{.059}{1}\log\frac{0.0025}{1}$

$= 2 \times El = 140\text{ mV} \Rightarrow \text{so}$

EXERCISE (S-I)

ELECTRODE POTENTIAL CELL EMF.

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
$Cu^+ + e^- \longrightarrow Cu$
also predict whether Cu^+ undergoes disproportionation or not.

2. For a cell $Mg(s) \mid Mg^{2+}(aq) \parallel Ag^+(aq) \mid Ag$,
(i) Calculate the equilibrium constant at 25°C.
(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.

3. The pK_{sp} of Agl is 16.07 . If the E° value for $Ag^+|$ Ag is 0.7991 V . Find the E° for the half cell reaction $AgI(s) + e^- \longrightarrow Ag + I^-$.

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. $E^0 (Zn^{2+}| Zn) = -0.76V$.

EQUILIBRIUM CONSTANT :

5. The standard reduction potential at 25°C for the reduction of water
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ is –0.8277 volt. Calculate the equilibrium constant for the reaction
$2H_2O \rightleftharpoons H_3O^+ + OH^-$ at 25°C.

6. For the reaction, $4Al(s) + 3O_2(g) + 6H_2O + 4\,OH^- \rightleftharpoons 4\,[Al(OH)_4^-]$; $E^{\circ}_{cell} = 2.73$ V.
If $\Delta G^{\circ}_f(OH^-) = -157$ kJ mol^{-1} and $\Delta G^{\circ}_f(H_2O) = -237.2$ kJ mol^{-1}, determine $\Delta G^{\circ}_f\,[Al(OH)_4^-]$.

7. For the cell reaction :
$Hg_2Cl_2(s) + 2Ag(s) \rightarrow 2Hg(l) + 2AgCl(s)$
temperature coefficient of cell emf is found to be 0.02 VK^{-1}. Find $\Delta_rS°$ for cell reaction in kJ mole^{-1}

8. From the standard potential in acidic medium as shown in the following latimer diagram , the value of $(E_1^o + E_2^o)$, in volts, is -

$$\begin{tikzcd}
MnO_4^- \arrow[r, "0.55V"] \arrow[rr, bend left, "E_1^0"] & MnO_4^{2-} \arrow[r, "2.26\ V"] & MnO_2 \arrow[r, "0.96V"] \arrow[rr, bend right, "E_2^0"'] & Mn^{3+} \arrow[r, "1.66\ V"] & Mn^{2+}
\end{tikzcd}$$

CONCENTRATION CELLS :

9. Equinormal Solutions of two weak acids, HA ($pK_a = 3$) and HB ($pK_a = 5$) are each placed in contact with equal pressure of hydrogen electrode at 25°C. When a cell is constructed by interconnecting them through a salt bridge, find the emf of the cell.

10. In two vessels each containing 500ml water, 0.5m mol of aniline ($K_b = 10^{-9}$) and 50mmol of HCl are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately.

ELECTROLYTIC CELL :

11. The electrosynthesis of MnO_2 is carried out from a solution of $MnSO_4$ in H_2SO_4 (aq). If a current of 25.5 ampere is used with a current efficiency of 85%, how long would it take to produce 1 kg of MnO_2?
12. Calculate the quantity of electricity that would be required to reduce 12.3 g of nitrobenzene to aniline, if the current efficiency for the process is 50 percent. If the potential drop across the cell is 3.0 volts, how much energy will be consumed?
13. A constant current of 30 A is passed through an aqueous solution of NaCl for a time of 1.0 hr. How many grams of NaOH are produced? What is volume of Cl_2 gas at 1atm,273K produced (in litre) ?
14. Assume 96500 C as one unit of electricity. If cost of electricity of producing x gm Al is Rs x, what is the cost of electricity of producing x gm Mg?
15. 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 of electricity required to deposit the same mass of Cu from $CuSO_4$?
16. After electrolysis of NaCl solution with inert electrodes for a certain period of time. 600 mL of the solution was left. Which was found to be 1N in NaOH. During the same time, 31.75 g of Cu was deposited in the copper voltameter in series with the NaCl electrolytic cell. Calculate the percentage yield of NaOH obtained.
17. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 ampere for 20 mintue. What mass of Ni is deposited at the cathode?
18. 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 $Ni(NO_3)_2$ solution at the end of electrolysis?

CONDUCTANCE

19. A solution containing 2.08 g of anhydrous barium chloride is 500 CC of water has a specific conductivity 0.005 $ohm^{-1}cm^{-1}$. What are molar and equivalent conductivities of this solution.

APPLICATION OF KOHLRAUSCH'S LAW

20. Specific conductance of a saturated solution of AgBr is 8.075×10^{-7} $ohm^{-1}cm^{-1}$ at 25^0C. Specific conductance of pure water at 25°C is 0.75×10^{-7} ohm^{-1} cm^{-2}. Λ_m^{∞} for KBr , $AgNO_3$ and KNO_3 are 140 , 130 , 110 (S cm^2 mol^{-1}) respectively. Calculate the solubility of AgBr in gm|litre.
21. 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.
22. At 25°C, $\lambda_{\infty}(H^+) = 3.5 \times 10^{-2}$ S m^2 mol^{-1} and $\lambda_{\infty}(OH^-) = 2 \times 10^{-2}$ S m^2mol^{-1}.
Given: Sp. conductnace = 5.5×10^{-6} S m^{-1} for H_2O, determine pH and K_w.

EXERCISE (S-II)

1. Calculate the emf of the cell
Pt, H_2(1.0 atm) | CH_3COOH (0.1M) || NH_3(aq, 0.01M) | H_2 (1.0 atm),
Pt $K_a(CH_3COOH) = 1.8 \times 10^{-5}$, K_b $(NH_3) = 1.8 \times 10^{-5}$.

2. The Edison storage cell is represented as Fe(s) | FeO(s) | KOH(aq) | Ni_2O_3 (s) | NiO(s) The half–cell reaction are
$Ni_2O_3(s) + H_2O(i) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-$, $E^0 = + 0.40V$
$FeO(s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^-$, $E^0 = - 0.87V$

(i) What is the cell reaction?

(ii) What is the cell e.m.f.? How does it depend on the concentration of KOH?

(iii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3?

3. The standard reduction potential for Cu^{2+} | Cu is 0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $Cu(OH)_2$ is 1×10^{-19}.

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

5. Consider the cell Ag|AgBr(s)|Br^-||Cl^- | AgCl(s)| 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 ?

6. For the galvanic cell : Ag|AgCl(s)| KCl (0.2M) || K Br (0.001 M)| AgBr(s) | Ag,
Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25^{0}C.

$$[K_{sp(AgCl)} = 2.8\times10^{-10}; K_{sp(AgBr)} = 3.3\times10^{-13}]$$

7. Given, E° = –0.268 V for the Cl^- | $PbCl_2$ | Pb couple and – 0.126 V for the Pb^{2+} | Pb couple, determine K_{sp} for $PbCl_2$ at 25°C?

8. Calculate the equilibrium constant for the reaction:
$3Sn(s) + 2Cr_2O_7^{2-} + 28H^+ \longrightarrow 3Sn^{4+} + 4Cr^{3+} + 14H_2O$
E^0 for Sn|Sn^{2+} =0.136 V E^0 for Sn^{2+}|Sn^{4+} = – 0.154 V
E^0 for $Cr_2O_7^{2-}$|Cr^{3+} = 1.33 V

9. One of the methods of preparation of per disulphuric acid, $H_2S_2O_8$, involve electrolytic oxidation of H_2SO_4 at anode ($2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^-$) with oxygen and hydrogen as by–products. In such an electrolysis, 9.722 L of H_2 and 2.35 L of O_2 were generated at STP. What is the weight of $H_2S_2O_8$ formed?

10. A current of 3 amp was passed for 2 hour through a solution of $CuSO_4$,3 g of Cu^{2+} ions were deposited as Cu at cathode. Calculate percentage current efficiency of the process.

11. Dal lake has water 8.2×10^{12} litre approximately. A power reactor produces electricity at the rate of 1.5×10^6coulomb per second at an appropriate voltage.How many years would it take to electrolyse the lake?

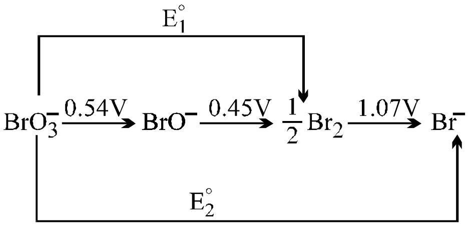
12. The equivalent conductance of 0.10 N solution of $MgCl_2$ is 97.1 mho cm^2 $equi^{-1}$ at 25°C. a cell with electrode that are 1.5 cm^2 in surface area and 0.5 cm apart is filled with 0.1 N $MgCl_2$ solution. How much current will flow when potential difference between the electrodes is 5 volt.

13. When a solution of specific conductance 1.342 ohm^{-1} $metre^{-1}$ was placed in a conductivity cell with parallel electrodes, the resistance was found to be 170.5 ohm. Area of electrodes is 1.86×10^{-4} m^2. Calculate separation of electrodes.

14. The specific conductance at 25°C of a saturated solution of $SrSO_4$ is 1.482×10^{-4} ohm^{-1} cm^{-1}while that of water used is 1.5×10^{-6} mho cm^{-1}. Determine at 25°C the solubility in gm per litre of $SrSO_4$ in water. Molar ionic conductance of Sr^{2+} and SO_4^{2-} ions at infinite dilution are 59.46 and 79.8 ohm^{-1} cm^2 $mole^{-1}$ respectively. [Sr = 87.6 , S = 32 , O = 16]

15. The EMF of the cell M | M^{n+} (0.02M) || H^+ (1M) | H_2(g) (1 atm), Pt at 25°C is 0.81V. Calculate the valency of the metal if the standard oxidation of the metal is 0.76V.

16. From the standard potentials shown in the following diagram, calculate the potentials E_1° and E_2°.



17. Calculate the EMF of the cell,

$$Zn - Hg(c_1M) \mid Zn^{2+}\,(aq) \mid Hg - Zn(c_2M)$$

at 25°C, if the concentrations of the zinc amalgam are: c_1 = 10g per 100g of mercury and c_2 = 1g per100 g of mercury.

18. 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 5μm thick layer? Density of silver = 10.8g|cm^3.

19. 10g solution of $CuSO_4$ is electrolyzed using 0.01F of electricity. Calculate:

(a)The weight of resulting solution

(b) Equivalents of acid or alkali in the solution.

20. Cadmium 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 on a cathode of 2gm Hg (Cd=112.4)

EXERCISE (O-I)

GALVANIC CELL

1. The thermodynamic efficiency of cell is given by-

(A) $\frac{\Delta H}{\Delta G}$ (B) $\frac{nFE_{cell}}{\Delta G}$ (C) $-\frac{nFE_{cell}}{\Delta H}$ (D) Zero

2. 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) and (iii) (B) (ii) and (iv) (C) (i) and (iii) (D) (i) and (iv)

3. 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

4. The standard emf for the cell reaction,

$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ 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+} solution are used at 25°C is :

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

5. 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

6. Consider the cell, $Cu|Cu^{+2}||Ag^+|Ag$. If the concentration of Cu^{+2} and Ag^+ ions becomes ten times the emf of the cell :–

(A) Becomes 10 times (B) Remains same

(C) Increase by 0.0295 V (D) Decrease by 0.0295 V

7. The standard emf of a galvanic cell involving cell reaction with n = 4 is found to be 0.295 V at 25°C. The equilibrium constant of the reaction would be,

(A) 1.0×10^{20} (B) 2.0×10^{11} (C) 4.0×10^{12} (D) 1.0×10^{2}

8. By how much times will potential of half cell $Cu^{+2}|Cu$ change if, the solution is diluted to 100 times at 298 K :–

(A) Increases by 59 mV (B) Decrease by 59 mV

(C) Increases by 29.5 mV (D) Decreases by 29.5 mV

ELECTROLYTIC CELL

9. When an electric current is passed through a cell containing an electrolyte, positive ions move towards the cathode and negative ions towards the anode. What will happen if the cathode is pulled out of the solution?

(A) The positive ions will start moving towards the anode and negative ions will stop moving.

(B) The negative ions will continue to move towards the anode and the positive ions will stop moving

(C) Both positive and negative ions will move towards the anode.

(D) None of these movements will take place.

10. Electrolysis of a $CuSO_4$ produces :–

(A) An increase in pH (B) A decrease in pH
(C) Either decrease or increase (D) None

11. The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate $[Ni(NO_3)_2]$and chromium nitrate $[Cr(NO_3)_3]$ respectively. If 0.3 g of nickel was deposited in the first cell, the amount of chromium deposited is :
(at. wt. of Ni = 59, at. wt. of Cr = 52)

(A) 0.1 g (B) 0.17 g (C) 0.3 g (D) 0.6 g

12. The electric charge for electro deposition of 1 equivalent of a substance is :

(A) one ampere per second (B) 4 faraday
(C) one ampere for one hour (D) charge on one mole of electrons

13. 3.17 g., of a substance was deposited by the flow of 0.1 mole of electrons. The equivalent weight of the substance is :

(A) 3.17 (B) 0.317 (C) 317 (D) 31.7

14. A current of 9.65 amp. passing for 16 min. 40 sec. through a molten tin salt deposits 5.95 g. of tin The oxidation state of the tin in the salt is : (at. wt of Sn = 119)

(A) +4 (B) +3 (C) +2 (D) +1

15. The time required for a current of 3 amp. to decompose electrolytically 18 g of H_2O is:

(A) 18 hour (B) 36 hour (C) 9 hour (D) 18 seconds

16. An ion is reduced to the element when it absorbs 6×10^{20} electrons. The number of gm equivalents of the ion is :

(A) 0.10 (B) 0.01 (C) 0.001 (D) 0.0001

17. How many coulombs of electric charge are required for the oxidation of 1 mole of H_2O to O_2 ?

(A) 9.65×10^4 C (B) 4.825×10^5 C (C) 1.93×10^5 C (D) 1.93×10^4 C

18. The time required to coat ameter surface of 80 cm^2 with 5×10^{-3} cm thick layer of silver (density 1.08 g cm^{-3}) with the passage of 9.65A current through a silver nitrate solution is :

(A) 10 sec. (B) 40 sec. (C) 30 sec. (D) 20 sec.

19. One gm metal M^{+2} was discharged by the passage of 1.2×10^{22} electrons. What is the atomic weight of metal?

(A) 25 (B) 50 (C) 100 (D) 75

20. One mole of electron passes through each of the solution of $AgNO_3$, $CuSO_4$ and $AlCl_3$ when Ag, Cu and Al are deposited at cathode. The molar ratio of Ag, Cu and Al deposited are

(A) 1 : 1 : 1 (B) 6 : 3 : 2 (C) 6 : 3 : 1 (D) 1 : 3 : 6

21. During electrolysis of an aqueous solution of sodium sulphate, 2.4 L of oxygen at STP was liberated at anode. The volume of hydrogen at STP, liberated at cathode would be

(A) 1.2 L (B) 2.4 L (C) 2.6 L (D) 4.8 L

22. The charge required for the oxidation of one mole Mn_3O_4 into MnO_4^{2-} in presence of alkaline medium is

(A) 5 × 96500 C (B) 96500 C (C) 10 × 96500 C (D) 2 × 96500 C

CONDUCTANCE

23. Equivalent conductances of Ba^{+2} and Cl^- ions are 127 & 76 $ohm^{-1}\,cm^2\,eq^{-1}$ respectively. Equivalent conductance of $BaCl_2$ at infinite dilution is -

(A) 379 (B) 139.5 (C) 203 (D) 330

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

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

EXERCISE (O-II)

Single correct :

1. Consider the reaction,

$Cl_{2(g)} + 2Br^{-}_{(aq)} \longrightarrow 2Cl^{-}_{(aq)} + Br_{2(g)}$

The emf of the cell when $[Cl^-]=[Br^-]=0.01M$ and Cl_2 gas at 1 atm pressure while $Br_2(g)$ at 0.01 atm 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

2. How much will the reduction potential of a hydrogen electrode change when its solution initially at pH = 0 is neutralised to pH = 7 ?

(A) increase by 0.059V (B) decrease by 0.059V

(C) increase by 0.413V (D) decrease by 0.413V

3. If the pressure of H_2 gas is increased from 1 atm to 100 atm keeping H^+ concentration constant at 1 M, the change in reduction potential of hydrogen half cell at 25°C will be

(A) 0.059 V (B) 0.59 V (C) 0.0295 V (D) 0.118 V

4. A silver wire dipped in 0.1 M HCl solution saturated with AgCl develops oxidation potential of –0.209 V. If $E^{\circ}_{Ag/Ag^{+}} = -0.799$ 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}

5. Salts of A (atomic weight = 7), B (atomic weight =27) and C (atomic weight = 48) were electrolysed under identical conditions using the same quantity of electricity. It was found that when 2.1 g of A was deposited, the weights of B and C deposited were 2.7 and 7.2 g. The valencies of A, B and C respectively are

(A) 3, 1 and 2 (B) 1, 3 and 2 (C) 3, 1 and 3 (D) 2, 3 and 2

6. During electro refining of Cu by electrolysis of an aqueous solution of $CuSO_4$ using copper electrodes, if 2.5 g of Cu is deposited at cathode, then at anode

(A) decrease of more than 2.5 g of mass takes place

(B) 450 ml of O_2 at STP is liberated

(C) 2.5 g of copper is deposited

(D) a decrease of 2.5 g of mass takes place

7. The conductivity of a saturated solution of Ag_3PO_4 is 9×10^{-6} S m^{-1} and its equivalent conductivity is 1.50×10^{-4} S m^2 equivalent^{-1}. The K_{sp} of Ag_3PO_4 is

(A) 4.32×10^{-18} (B) 1.8×10^{-9} (C) 8.64×10^{-13} (D) None of these

8. Equal volumes of 0.015 M CH_3COOH & 0.015 M NaOH are mixed together. What would be molar conductivity of mixture if conductivity of CH_3COONa is 6.3×10^{-4} S cm^{-1}

(A) 8.4 S cm^2 mol^{-1} (B) 84 S cm^2 mol^{-1} (C) 4.2 S cm^2 mol^{-1} (D) 42 S cm^2 mol^{-1}

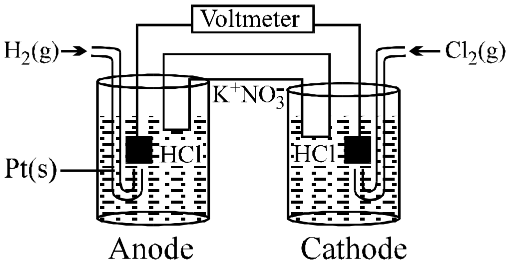
9. For the fuel cell reaction $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$; $\Delta_f H^{o}_{298}(H_2O, l) = -285.5$ kJ|mol

What is ΔS^{o}_{298} for the given fuel cell reaction?

Given: $O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$ E° = 1.23 V

(A) – 0.322 J|K (B) – 0.635 kJ|K (C) 3.51 kJ|K (D) – 0.322 kJ|K

10. Consider the following Galvanic cell.



By what value the cell voltage change when concentration of ions in anodic and cathodic compartments both increased by factor of 10 at 298 K

(A) +0.0590 (B) –0.0590 (C) –0.1180 (D) 0

11. The standard reduction potentials at 25°C for the following half reactions are :

$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s),\ E^\circ_{RP} = -0.762V$

$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s),\ E^\circ_{RP} = -0.740V$

$2H^+_{(aq)} + 2e^- \rightleftharpoons H_2(g),\ E^\circ_{RP} = 0.00\ V$

$Fe^{3+}_{(aq)} + 2e^- \rightleftharpoons Fe^{2+}_{(aq)},\ E^\circ_{RP} = 0.77V$

Which is the strongest reducing agent ?

(A) Zn (B) Cr (C) $H_2(g)$ (D) Fe^{2+} (aq)

12. Using the standard electrode potential values given below, decide which of the statements, I, II, III and IV are correct. Choose the right answer from (A), (B), (C) and (D).

$Fe^{2+}_{(aq)} + 2e^- \rightleftharpoons Fe_{(s)}\ ;\quad E^\circ = -0.44\ V$

$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}\ ;\quad E^\circ = +0.34\ V$

$Ag^{+}_{(aq)} + e^- \rightleftharpoons Ag_{(s)}\ ;\quad E^\circ = +0.80\ V$

I. Copper can displace iron from $FeSO_4$ solution.

II. Iron can displace copper from $CuSO_4$ solution.

III. Silver can displace copper 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

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

14. The cost of electricity required to deposit 1 g of Mg is Rs. 5.00. How much would it cost to deposit 9 g of Al (At wt. Al = 27, Mg = 24)

(A) Rs. 10 (B) Rs. 27 (C) Rs. 40 (D) Rs. 60

15. 4.5g of aluminium (at. mass 27 amu) is deposited at cathode from Al^{3+} solution by a certain quantity of electric charge. The volume of hydrogen produced at STP from H^+ ions in solution by the same quantity of electric charge will be –

(A) 45.4L (B) 11.35L (C) 22.7L (D) 5.675 L

16. The density of A is 10 g cm^{-3}. The quantity of electricity needed to plate an area 10 cm × 10 cm to a thickness of 10^{-2} cm using ASO_4 solution would be (Atomic mass of A = 193)

(A) 5000 C (B) 10000 C (C) 40000 C (D) 20000 C

17. The resistance of 0.5 M solution of an electrolyte in a cell was found to be 50 Ω. If the electrodes in the cell are 2.2 cm apart and have an area of 4.4 cm^2 then the molar conductivity (in S m^2 mol^{-1}) of the solution is

(A) 0.2 (B) 0.02 (C) 0.002 (D) None of these

18. Equivalent conductance of 0.1 M HA(weak acid) solution is 10 $Scm^2equivalent^{-1}$ and that at infinite dilution is 200 $Scm^2equivalent^{-1}$ Hence pH of HA solution is

(A) 1.3 (B) 1.7 (C) 2.3 (D) 3.7

19. The dissociation constant of n-butyric acid is 1.6×10^{-5} and the molar conductivity at infinite dilution is 380×10^{-4} Sm^2mol^{-1}. The specific conductance of the 0.01 M acid solution is

(A) 1.52×10^{-5} Sm^{-1} (B) 1.52×10^{-2} Sm^{-1}

(C) 1.52×10^{-3} Sm^{-1} (D) None

MULTIPLE CORRECT :

20. 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

21. 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.

22. If 270.0 g of water is electrolysed during an experiment performed by miss Abhilasha 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

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

$$Cl_2\,(a) + 2e \rightleftharpoons 2Cl^-(a) \qquad E^o_{Cl_2/Cl^-} = +1.36 \text{ volt}$$

$$Br_2\,(a) + 2e \rightleftharpoons 2Br^-(a) \qquad E^o_{Br_2/Br^-} = +1.09 \text{ volt}$$

$$I_2(s) + 2e \rightleftharpoons 2I^-\,(a) \qquad E^o_{I_2/I^-} = +0.54 \text{ volt}$$

$$S_2O_8^{2-}\,(a) + 2e \rightleftharpoons 2SO_4^{2-}\,(a) \qquad E^o_{S_2O_8^{2-}/SO_4^{2-}} = +2.00 \text{ volt}$$

(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^-

24. The EMF of the following cell is 0.22 volt.

$Ag(s) \mid AgCl(s) \mid KCl\ (1M) \mid H^+(1M) \mid H_2(g)\ (1atm)\ ;\ Pt(s)$.

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.

Assertion & Reasoning type questions :

25. Statement -1 : The voltage of mercury cell remains constant for long period of time.

Statement -2 : It is because net cell reaction does not involve active species.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

26. Statement -1 : The SRP of three metallic ions A^+,B^{2+}, C^{3+} are –0.3, –0.5, 0.8 volt respectively, so oxidising power of ions is $C^{3+} > A^+ > B^{2+}$.

Statement -2 : Higher the SRP, higher the oxidising power.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

27. Statement -1 : We can add the electrode potential in order to get electrode potential of net reaction.

Statement -2 : Electrode potential is an intensive property.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

Table type :

1 TABLE (3Q)

	Column-I		**Column-II**		**Column-III**
(P)	$Zn(s) \mid ZnSO_4(0.1M) \mid\mid Zn(NO_3)\ (0.01M)Zn(s)$	(A)	Has metal -insoluble salt - anion electrode.	(I)	$E_{cell} < 0$
(Q)	$Pt, Cl_2(0.1bar) \mid KCl(1M) \mid\mid NaCl(1M)\ Cl_2(1bar), Pt$	(B)	Electrolytic concentration cell	(II)	$E^0_{cell} = 0$
(R)	$Ag(s) \mid AgCl(s) \mid KCl\ (0.1M) \mid\mid Ag^+(0.1M) \mid Ag(s)$ $Ksp[AgCl] = 10^{-10}$.	(C)	Electrode concentration cell	(III)	$E_{cell} > 0$
(S)	$Pt, H_2(1bar) \mid H_2SO_4\ (0.05M) \mid\mid HNO_3(0.1M) \mid H_2\ (1bar), Pt$	(D)	Has gas-ion electrode	(IV)	$E_{cell} = 0$

(1) Use : $\frac{2.303RT}{F} = 0.06$

(2) Assume constant P,T condition of operation.

28. Which option is incorrectly matched ?

(A) P - B - II (B) Q - C - II (C) R - A - I (D) S - D - IV

29. For galvanic cell in option 'Q' on increasing concentration of KCl, cell potential will -

(A) Increase (B) decrease (C) remains constant (D) cannot predict

30. On increasing Ag^+ concentration in anodic compartment in option (R) cell potential will

(A) Remain same (B) increase (C) decrease (D) can't predict

Match the column

31.

	Column I		**Column II** (Electrolysis product using inert electrode)
(A)	Dilute solution of HCl	(P)	O_2 evolved at anode
(B)	Dilute solution of NaCl	(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

32.

Column-I Cell notation :		**Column-II** E_{cell}
(P) $\mathrm{Mn}\Big\vert\underset{(0.1\mathrm{M})}{\mathrm{Mn^{2+}}}\Big\Vert\underset{(0.01\mathrm{M})}{\mathrm{Cu^{2+}}}\Big\vert\mathrm{Cu}$	(1)	0.33
(Q) $\mathrm{Ag}\Big\vert\mathrm{AgBr}\Big\vert\underset{(0.1\mathrm{M})}{\mathrm{Br^{-}}}\Big\Vert\underset{(0.01\mathrm{M})}{\mathrm{Ag^{+}}}\Big\vert\mathrm{Ag}$	(2)	0.6
(R) $\mathrm{Pt,H_2(4atm)}\Big\vert\underset{(0.01\mathrm{M})}{\mathrm{H^{+}}}\Big\Vert\underset{(0.2\mathrm{M})}{\mathrm{Cl^{-}}}\Big\vert\underset{(1\mathrm{atm})}{\mathrm{Cl_2}}\Big\vert\mathrm{Pt}$	(3)	1.49
(S) $\mathrm{Pt,}\Big\vert\underset{(0.2\mathrm{M})}{\mathrm{Fe^{2+}}}\ \underset{(0.02\mathrm{M})}{\mathrm{Fe^{+3}}}\Big\Vert\underset{(0.1\mathrm{M})}{\mathrm{MnO_4^{-}}},\underset{(0.1\mathrm{M})}{\mathrm{Mn^{+2}}},\underset{\mathrm{pH=5}}{\mathrm{H^{+}}}\Big\vert\mathrm{Pt}$	(4)	1.54

Given :

$E^0_{\mathrm{Cu^{2+}/Cu}} = 0.34\mathrm{V}$

$K_{sp}(\mathrm{AgBr}) = 10^{-13}$

$E^0_{\mathrm{Mn^{2+}/Mn}} = -1.18\mathrm{V}$

$\dfrac{2.303RT}{F} = 0.06$

$E^0_{\mathrm{Ag^{+}/Ag}} = 0.8\mathrm{V}$

$E^0_{\mathrm{Fe^{3+}/Fe^{2+}}} = 0.77\mathrm{V}$

$E^0_{\mathrm{MnO_4^{-}/Mn^{2+}}} = 1.52\mathrm{V}$

$E^0_{\mathrm{Cl_2/Cl^{-}}} = 1.36\mathrm{V}$

Code:

	P	Q	R	S
(A)	4	3	4	4
(B)	2	3	1	4
(C)	3	2	4	1
(D)	4	3	2	1

EXERCISE (J-MAINS)

1. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.3 S m^{-1}. If resistance of the 0.4M solution of the same electrolyte is 260 Ω, its molar conductivity is :- **[AIEEE 2011]**

   (1) 6250 S m^2 mol^{-1} (2) 6.25×10^{-4} S m^2 mol^{-1}
   (3) 625×10^{-4} S m^2 mol^{-1} (4) 62.5 S m^2 mol^{-1}

2. The reduction potential of hydrogen half-cell will be negative if :- **[AIEEE 2011]**

   (1) $p(H_2) = 2$ atm $[H^+] = 1.0$ M (2) $p(H_2) = 2$ atm and $[H^+] = 2.0$ M
   (3) $p(H_2) = 1$ atm and $[H^+] = 2.0$ M (4) $p(H_2) = 1$ atm and $[H^+] = 1.0$ M

3. 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]

   (1) X = Zn, Y = Ni (2) X = Ni, Y = Fe (3) X = Ni, Y = Zn (4) X = Fe, Y = Zn

4. Given : **[JEE-MAINS 2013]**

   $E^0_{Cr^{3+}/Cr} = -0.74\,V$; $E^0_{MnO_4^-/Mn^{2+}} = 1.51\,V$

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

   Based on the data given above, strongest oxidising agent will be :
   (1) Cl^- (2) Cr^{3+} (3) Mn^{2+} (4) MnO_4^-

5. 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 : **[JEE-MAINS 2014]**
   (where the constant B is postive)

   (1) $\lambda_C = \lambda_\infty - (2)\sqrt{C}$ (2) $\lambda_C = \lambda_\infty + (2)\sqrt{C}$
   (3) $\lambda_C = \lambda_\infty + (2)$ C (4) $\lambda_C = \lambda_\infty - (2)C$

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-MAINS 2014]**

   (1) 5×10^3 (2) 5×10^2 (3) 5×10^{-4} (4) 5×10^{-3}

7. 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

8. 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

9. Two Faraday of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is : (at. mass of Cu = 63.5 amu) **[JEE-MAINS 2015]**

(1) 2g (2) 127 g (3) 0 g (4) 63.5 g

10. 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

11. 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

12. 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^-

13. 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

14. 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

15. 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

16 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

17. 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

EXERCISE (J-ADVANCED)

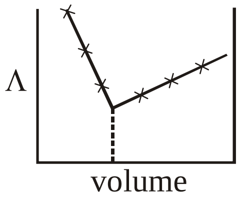
1. Consider the following cell reaction : **[JEE 2011]**

$2Fe_{(s)}+O_{2(g)}+4H^{+}_{(aq)} \rightarrow 2Fe^{2+}_{(a)}+2H_2O(\ell)$ E° = 1.67 V

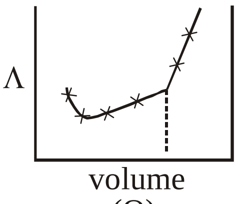
At$[Fe^{2+}] = 10^{-3}$ M, $P(O_2) = 0.1$ atm and pH = 3, the cell potential at 25°C is -

(A) 1.47 V (B) 1.77 V (C) 1.87 V (D) 1.57 V

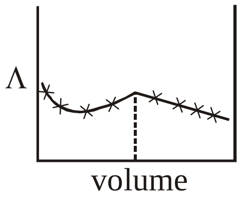
2. $AgNO_3$ (a) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. the plot of conductance (Λ) versus the volume of $AgNO_3$ is - **[JEE 2011]**



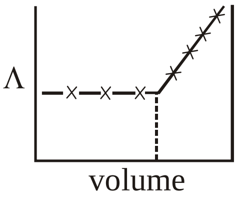
(P)



(Q)



(R)



(S)

(A) (P) (B) (Q) (C) (R) (D) (S)

Paragraph for Question 3 and 4

The electrochemical cell shown below is a concentration cell. **[JEE 2012]**

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 concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059V.

3. The value of ΔG (kJ mol^{-1}) for the given cell is (take If = 96500 C mol^{-1})

(A) –5.7 (B) 5.7 (C) 11.4 (D) –11.4.

4. The solubility product (K_{sp} ; $mol^3 dm^{-9}$) of MX_2 at 298 K based on the information available for the given concentration cell is (take 2.303 × R × 298|F = 0.059 V)

(A) 1×10^{-15} (B) 4×10^{-15} (C) 1×10^{-12} (D) 1×10^{-12}

5. The standard reduction potential data at 25°C is given below **[JEE-Adv. 2013]**

$E^o (Fe^{3+}, Fe^{2+}) = +0.77$ 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° of the redox 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)	–0.18 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

6. 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-Adv. 2013]**

	List-I		List-II
(P)	$(C_2H_5)_3N + CH_3COOH(1)$ X Y		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

7. In a galvanic cell , the salt bridge - **[JEE-Adv. 2014]**

(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 occurence of the cell reaction

(D) Ensures mixing of the two electrolytic solutions

8. 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 (0.1 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-Adv. 2015]

9. All the energy released from the reaction X → Y, $\Delta_r G^o = -193$ kJ mol^{-1} is used for the oxidizing M^+ and $M^+ \rightarrow M^{3+} + 2e^-$, $E^o = -0.25$ V. **[JEE-Adv. 2015]**

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}]

10. For the following electrochemical cell at 298K, **[JEE-Adv. 2016]**

$Pt(s) \mid H_2(g, 1bar) \mid H^+ (aq, 1M) \parallel M^{4+}(a), M^{2+}(a) \mid Pt(s)$

$E_{cell} = 0.092$ V when $\frac{[M^{2+}(aq.)]}{[M^{4+}(aq.)]} = 10^x$

Given : $E^0_{M^{4+}/M^{2+}} = 0.151V$; $2.303 \frac{RT}{F} = 0.059V$

The value of x is -

(A) –2 (B) –1 (C) 1 (D) 2

11. 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 (Λ^0_m) of this weak monobasic acid in aqueous solution is $Z \times 10^2 S\ cm^{-1} mol^{-1}$. The value of Z is.

12. For the following cell : **[JEE-Adv. 2017]**

$Zn(s) \mid ZnSO_4 (aq.) \parallel CuSO_4 (aq.) \mid Cu(s)$

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°(cell) = 1.1V]

(A) 2.303 RT + 1.1F (B) 2.303 RT – 2.2F

(C) 1.1 F (D) –2.2 F

13. Consider an electrochemical cell: $A(s) \mid A^{n+} (aq, 2M) \parallel B^{2n+} (aq, 1M) \mid B(s)$. 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.)

14. For the electrochemical cell,

$Mg(s) \mid Mg^{2+}(aq, 1M) \parallel Cu^{2+} (aq, 1M) \mid Cu(s)$

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)

ANSWER KEY

EXERCISE (S-I)

1. Ans. 0.53 V, disproportionation
2. Ans.$K_c = 2.868 \times 10^{107}$, $\Delta G^0 = -611.8$ kJ
3. Ans. $E^0 = -0.14903$V
4. Ans. $E = -0.81$ V
5. Ans.$K_w \approx 10^{-14}$
6. Ans. -1.30×10^3 kJ mol^{-1}
7. Ans 3.86
8. Ans. (3)
9. Ans.E = 0.059
10. Ans. E = 0.413 V
11. Ans. 1.023×10^5 sec
12. Ans. 115800C, 347.4 kJ
13. Ans. 1.12 mol, 12.535 litre
14. Ans. Rs. 0.75 x
15. Ans. A = 114, Q = 5926.8C
16. Ans. 60 %
17. Ans. 1.825g
18. Ans. 2M
19. Ans. (i) 250 mho cm^2 mol^{-1} , (ii) 125 mho cm^2 equivalent^{-1}
20. Ans. 9.4×10^{-4} gm|litre
21. Ans. $\alpha = 0.5$, $k = 10 \times 10^{-4}$
22. Ans. (i) 7 (ii) 1×10^{-14}

EXERCISE (S-II)

1. Ans.– 0.46 V
2. Ans.(ii). 1.27 V, (iii) 245.1 kJ
3. Ans. $E^0 = -0.22$ V
4. Ans.$K_{sp} = 1.1 \times 10^{-16}$
5. Ans. $[Br^-] : [Cl^-] = 1 : 200$
6. Ans.–0.037 V
7. Ans.1.536×10^{-5} M^3
8. Ans.$K = 10^{268}$
9. Ans. 43.456g
10. Ans.42.2 %
11. Ans.1.9×10^6 year
12. Ans.0.1456 ampere
13. 4.25×10^{-2} metre
14. Ans.0.1934 gm|litre
15. Ans.n = 2
16. Ans.0.52 V, 0.61 V
17. Ans.0.0295 V
18. Ans. t = 193 sec
19. Ans. Final weight = 9.6g, 0.01 Eq of acid
20. Ans. t = 93.65 sec.

EXERCISE (O-I)

1. Ans. C
2. Ans.A
3. Ans.C
4. Ans.A
5. Ans.C
6. Ans.C
7. Ans.A
8. Ans.B
9. Ans.D
10. Ans.B
11. Ans.B
12. Ans.D
13. Ans.D
14. Ans.C
15. Ans.A
16. Ans.C
17. Ans.C
18. Ans.B
19. Ans.C
20. Ans.B
21. Ans.D
22. Ans.C
23. Ans.C
24. Ans.C

EXERCISE (O-II)

1. Ans.B
2. Ans.D
3. Ans.A
4. Ans.B
5. Ans. B
6. Ans.A
7. Ans.A
8. Ans.B
9. Ans.D
10. Ans.C
11. Ans. A
12. Ans.C
13. Ans.(B)
14. Ans.D
15. Ans.D
16. Ans.B
17. Ans.C
18. Ans.C
19. Ans.C
20. Ans. C,D
21. Ans.B,C,D
22. Ans.A,B
23. Ans.B,C
24. Ans.A,D
25. Ans.A
26. Ans.A
27. Ans.D
28. Ans.(C)
29. Ans.(A)
30. Ans.(C)
31. Ans. (A) P, Q (B) P, Q (C) Q, R, (D) P,S
32. Ans.(C)

EXERCISE (J-MAINS)

1. Ans.(2)
2. Ans.(1)
3. Ans.(1)
4. Ans.(4)
5. Ans. (1)
6. Ans.(3)
7. Ans. (3)
8. Ans. (2)
9. Ans.(4)
10. Ans.(2)
11 Ans. (1)
12. Ans. (1)
13. Ans.(3)
14. Ans.(2)
15. Ans.(2)
16. Ans.(2)
17. Ans.(4)

EXERCISE (J-ADVANCED)

1. Ans.(D)
2. Ans.(D)
3. Ans.(D)
4. Ans.(B)
5. Ans.(D)
6. Ans.(A)
7. Ans.(A,B)
8. Ans. (3)
9. Ans. (4)
10. Ans.(D)
11. Ans.(6)
12. Ans.(B)
13. Ans.(–11.62)
14. Ans.(10)