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ELECTROCHEMISTRY

INTRODUCTION

Electrochemistry deals with the study of electrical properties of solutions of electrolytes and with the interrelation of chemical phenomenon and electrical energies. Electrical energy is carried through matter in the form of electric current with the help of suitable source and charge carriers (ions or electrons)

CONDUCTORS AND NON CONDUCTORS

Substances are divided into two classes

(a) Non conductor or insulator (b) Conductor

(a) **Non - conductor :** Substances which do not allow electric current to pass through them are called non-conductors or insulators examples - pure water, ice, glass, rubber etc.

(b) **Conductor :** Substances which allow electric current to flow through them are called conductors.
Examples - Metals, Aqueous solution of acids, bases and salts, fused salts and impure water etc.

Conductors are of two types :

(i) **Metallic conductors :** The conductors which conduct electric current by movement of electrons without undergoing any chemical change are known as metallic conductors.
Metals (Cu, Ag, Fe, Al etc), non metals (graphite) and various alloys and minerals are examples.

(ii) **Electrolytic conductors :** Those substances whose water solution conducts the electric current and which are decomposed by the passage of 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.
Substances whose aqueous solution does not conduct electric current are called non-electrolytes.
They do not conduct electricity in the fused state. Solutions of cane sugar, glycerine, glucose, urea etc. are the examples of non electrolytes.

Strong electrolyte : Electrolytes which are completely ionized in aqueous solution or in their molten state; are called strong electrolyte. Example - All salts, strong acid and strong base.

Weak electrolyte : Electrolytes which are not completely ionized in aqueous solution or in their molten state; are called weak electrolytes. **Examples:** All carbonic acids (except sulphonic acid), CH_3COOH, HCN, NH_3, amine, etc.

ELECTROLYTIC CONDUCTION

Conductance (C) : The amount of electric current can be passed through the solution is called conductance. Conductance is inverse to resistance.

$$\text{Conductances} = \frac{1}{\text{Resistance}} \quad \text{or} \quad C = \frac{1}{R}$$

Unit of Conductance is inverse to ohm it represent as mho.

Factors affecting electrolytic conduction :

(i) **Nature of the electrolyte :** The conductance of solution is depend on nature of electrolyte. Generally strong electrolytes ionize almost completely in the solution and hence conduct electricity to a large extent whereas weak electrolytes ionize to a small extent.

(ii) **Concentration of the solution :** The conductance of solution increase with increase the dilution. (because rate of dissociation increase with increase the dilution for weak electrolyte so no. of ions in solution increases and movability of ion also increase.)

(iii) **Temperature :** Conductances increase with increase the temperature because the all attraction force will be decrease.

(iv) **Degree of ionization :** Conductance of solution increase with increase the degree of ionization.

(v) **Interionic attractions:** Movability of ion decrease with increase the interionic attractions so conductance of electrolyte decrease.

(vi) **Viscosity :** Movability of ion decreases with increase the viscosity so conductance of electrolyte decrease.

(vii) **Solvation of ions :** Movability of ion decrease with increase the solvation so conductance of electrolyte decrease.

SPECIFIC CONDUCTIVITY (or simply called conductivity) :

Ohm's law is valid for electrolytic solution so that resistance of electrolyte R is directly proportional to its length (ℓ) and inversely proportional to its area of cross section (a). i.e., $R \propto \frac{\ell}{a}$ or $R = \rho\frac{\ell}{a}$

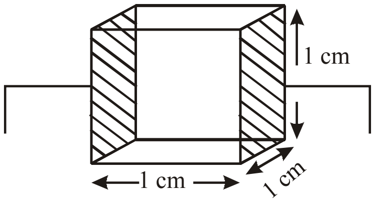
where ℓ = distance between two electrode and a = area of cross-section of electrode.

where ρ is a constant of proportionality, called Specific Resistance or Resistivity. Its value depends upon the material of the conductor.

$$\frac{1}{\text{Observed conductivity}} = \frac{1}{\text{Specific conductivity}} \times \frac{\ell}{a}$$

$$\text{or} \quad \text{Specific conductivity} = \text{conductivity} \times \frac{\ell}{a}$$

or Specific conductivity = conductivity × cell constant ratio (ℓ/a) for a cell is constant and it known as cell constant it denoted by x.
Now if $\ell = 1$ cm and a = 1 sq. cm, then
Specific conductivity = Observed conductivity



It may be defined as "conductance of one centimeter cube of the solution of the electrolyte"
If the volume of the solution is V cm^3, the specific conductivity of such a solution at this dilution V is written as K_v.

Units :

(i) Resistivity (ρ) $= R\frac{\ell}{a} = \text{ohm}\ \frac{(cm^2)}{cm} = \text{ohm cm or } \Omega \text{ cm}$

(ii) Specific conductivity (K_v) $= \frac{1}{\rho} = \frac{1}{\text{ohm cm}}$

$= \text{ohm}^{-1}\ cm^{-1} \text{ or } \Omega^{-1}\ cm^{-1} \text{ or S } cm^{-1}$

Cell constant : We know that $R = \rho\frac{\ell}{a}$; $\frac{1}{\rho} = \frac{1}{R}\frac{\ell}{a}$

$K_v = \frac{1}{R}\frac{\ell}{a}$ $\quad$ ($\frac{\ell}{a}$ = cell constant cm^{-1})

The conductivity of the solution is measured in a cell known as conductivity cell. Since in such cells the electrodes may be exactly 1 cm apart or may not have an area of 1 cm². Therefore we calculate a factor called constant (ℓ/a) For these cells.
Also, Specific conductivity = cell constant × observed conductivity or cell constant $= \frac{\text{conductivity}}{\text{conductance}}$

MOLAR CONDUCTIVITY & EQUIVALENT CONDUCTIVITY

Molar Conductivity : If one mole of an electrolyte is dissolved in a solution, then the conductivity of that solution between two parallel electrodes situated at 1 cm distance, is called molar conductivity. It is represented by λ_M. $\quad \lambda_M = K_v \times V_M$
where V_m = Volume of the solution in which 1 mole solute is dissolved. $\left(V_m = \frac{1}{C}\right)$; K_v = specific conductivity

$$\lambda_M = \frac{1000\ cm^3}{\text{M mole}} \times K_v$$

Unit of molar conductivity $= \frac{cm^3 \times \text{ohm}^{-1} cm^{-1}}{\text{mole}}$

or Unit = $cm^2\ \text{mole}^{-1}\ \text{ohm}^{-1}$

Equivalent Conductivity : If one equivalent of an electrolyte is dissolved in a solution, and conductivity of two parallel electrodes situated at 1 cm distance, is called equivalent conductivity. It is represented by λ_N.
$\lambda_N = K_V \times V$
K_v = Specific conductivity
V = Volume of the solution in which 1 gram equivalent of the solute is dissolved (V = 1/C)

$$\lambda_N = \frac{1000\ cm^3}{\text{N equivalent}} \times K_v \quad \text{or} \quad \lambda_N = \frac{1000}{N} \times K_v$$

Where N = Normality of the solution

Unit of equivalent conductivity :

$$\frac{cm^3 \times \text{ohm}^{-1} cm^{-1}}{\text{equivalent}} = cm^2\ \text{ohm}^{-1}\ \text{equivalent}^{-1}$$

Molar conductivity = Equivalent conductivity × Valency
Valency ≥ 1, $\lambda_M \geq \lambda_N$

Example 1 :
0.5 normal solution of a salt placed between two platinum electrodes 2.0 cm. apart and of area of cross section 4.0 sq. cm. has a resistance of 25 ohms. Calculate the equivalent conductivity of solution.

Sol. **1st step** – Calculate of specific conductivity.
Here $\ell = 2.0$ cm, a = 4.0 sq. cm, R = 25 ohms

$\therefore$ Conductance $C = \frac{1}{R}\frac{1}{25}\ \text{ohm}^{-1}$

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

Sp. conductivity (K) = Observed conductance × Cell const.

$= \frac{1}{25} \times \frac{1}{2} = 0.02\ \text{ohm}^{-1}\ cm^{-1}$

2nd step – Calculation of equivalent conductivity.

$$\lambda_N = K \times \frac{1000}{N}$$

Here c = 0.5 N, K = 0.02 $\text{ohm}^{-1}\ cm^{-1}$ (calculated above)

$\therefore \lambda_N = \frac{1000 \times 0.02}{0.5} = 40\ \text{ohm}^{-1}\ cm^2\ eq^{-1}$

Example 2 :
The conductivity of a solution containing 1 gram of anhydrous $BaCl_2$ in 200 cm^3 of water has been found to be 0.0058 mhocm^{-1}. What are the molar conductivity and equivalent conductivity of the solution?
(At. wt. of Ba = 137 and Cl = 35.5).

Sol. We are given, Conductivity (K) = 0.0058 mho cm^{-1}
mol. wt of $BaCl_2 = 137 + 2 \times 35.5 = 208$
As 1 gram of $BaCl_2$ is present in 200 cm^3 of the solution,

Molar concentration (c) $= \frac{1}{208} \times \frac{1}{200} \times 1000\ \text{mol } L^{-1}$
$= 0.0240\ \text{mol } L^{-1}$

∴ Molar conductivity ,

$$\lambda_m = K \times \frac{1000}{c} = 0.0058 \times \frac{1000}{0.0240}$$

$$= 241.67\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Further in case of $BaCl_2$, equivalent weight

$$= \frac{\text{Mol. Wt}}{2} = \frac{208}{2} = 104$$

∴ Concent. of the solution in gram equivalent per litre(N)

$$= \frac{1}{104} \times \frac{1}{200} \times 1000 = 0.0480$$

∴ Equivalent conductivity,

$$\lambda_N = K \times \frac{1000}{N} = 0.0058 \times \frac{1000}{0.0480}$$

$$= 120.83\ \text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

Example 3 :

Resistance of a 1.0 M solution is found to be 40 ohm. What should be the molar conductivity of the solution, if area of the electrode of a cell is 3.0 cm^2 and their distance from each other is 1.5 cm?

Sol. Specific conductivity = Observed conductivity × $\frac{\ell}{a}$

$$K_v = \left(\frac{\ell}{a}\right) \times \frac{1}{\text{Resistance}}$$

$$= \frac{1.5}{3.0} \times \frac{1}{40} \Rightarrow \frac{1}{80} = 0.012\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

$$\lambda_M = \frac{1000 \times K_v}{M} \Rightarrow \frac{1000 \times 0.012}{1.0} = 12 \text{ohm}^{-1}\ \text{cm}^2\ \text{mole}^{-1}$$

Example 4 :

If potential different of 20 volt is applied on a column of N/10 $AgNO_3$ solution, whose diameter is 4 cm and length is 12 cm, then 0.198 amp. electric current is generated. What should be the equivalent conductivities of the solution?

Sol. According to ohm's law, $V \propto I$; $V = IR$

$$R = \frac{V}{I} = \frac{20}{0.198} \text{ohm}$$

$$\text{Conductivity} = \frac{1}{\text{Resistance}} = \frac{0.198}{20}$$

Specific conductivity = Conductivity × Cell constant

$2r = 4$ or $r = 2$

$$= \frac{0.198}{20} \times \frac{12}{\pi r^2} = \frac{12}{22/7 \times 2 \times 2} \times \frac{0.198}{20} = 0.00945$$

Equivalent conductivity

$$\lambda_N = \frac{1000 \text{cm}^3 \times K_V}{N} = \frac{1000 \times 0.00945}{N/10}$$

$$= 10 \times 1000 \times 0.00945$$

$$= 94.5\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equivalent}^{-1}$$

KOHLRAUSCH'S LAW

It states that at infinite dilution, the conductivity of electrolytic solution is equal to addition of conductivity of both ion. (which are given in electrolyte)

$$\lambda_{eq}^{\infty} = \lambda_c^{\infty} + \lambda_a^{\infty}$$

Here $\lambda^{\infty}{}_{eq}$ = Equivalent conductivity at infinite dilution

$\lambda^{\infty}{}_c$ = Conductivity of Cation

$\lambda^{\infty}{}_a$ = Conductivity of Anion

According to Kohlrausch's law conductivity of ions is constant at infinite dilution and it does not depend on nature of co-ion.

For Ax.By type electrolyte, $xA^{+y} + yB^{-x}$

$$\lambda_{eq}^{\infty} = \frac{1}{z^+}\lambda_c^{\infty} + \frac{1}{z^-}\lambda_A^{\infty}$$

Here z^+ and z^- charge present on cation and anion.

$$\lambda_m^{\infty} = m\lambda_c^{\infty} + n\lambda_a^{\infty}$$

Here m and n number of moles of cation and anion.

Uses of Kohlrausch's Law :

1. **Calculation of molar conductivity at infinite dilution for weak electrolytes :**

As already mentioned, the molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally, firstly because the conductance of such a solution is low and secondly because the dissociation of such an electrolyte is not complete even at very high dilutions. The molar conductivity of such an electrolyte at infinite dilution can be calculated using Kohlrausch's law. **Ex.** $\lambda^{\circ}(CH_3COOH) = ? = \lambda^{\circ}{}_{CH_3COO^-} + \lambda^{\circ}{}_{H^+}$

Strong electrolyte

$$\lambda^{\circ}(CH_3COOK) = \lambda^{\circ}{}_{CH_3COO^-} + \lambda^{\circ}{}_{K^+} \qquad .....(1)$$

$$\lambda^{\circ}(HCl) = \lambda^{\circ}{}_{H^+} + \lambda^{\circ}{}_{Cl^-} \qquad .....(2)$$

$$\lambda^{\circ}(KCl) = \lambda^{\circ}{}_{K^+} + \lambda^{\circ}{}_{Cl^-} \qquad .....(3)$$

$$eq^n(1) + eq^n\ (2) - eq^n\ (3) = eq^n \qquad .....(4)$$

$$\lambda^{\infty}_{(CH_3COOK)} + \lambda^{\infty}_{(HCl)} - \lambda^{\infty}_{(KCl)} = \lambda^{\infty}_{(CH_3COOH)}$$

2. **Calculation of the Degree of Dissociation :**

According to Arrhenius theory of electrolytic dissociation, the increase in the molar conductivity with dilution is entirely due to the increase in the dissociation of the electrolyte ; the molar conductivity at infinite dilution being maximum because the dissociation is almost complete. Thus if $\lambda^C{}_m$ is the molar conductivity of a solution at any concentration c and $\lambda^{\circ}{}_m$ the molar conductivity at infinite dilution (i.e., zero concentration), we will have.

$$\alpha = \frac{\text{no. of dissociated ion}}{\text{no. of total ion present}}$$

$$\text{Degree of dissociation } (\alpha) = \frac{\lambda_m^c}{\lambda_m^0}$$

However, this relationship is found to hold good only for weak electrolytes. The value of λ^o_m for the weak electrolytes can be calculated, using Kohlrausch's law, as discussed already in the first application.

3. **Calculation of dissociation constant of a weak electrolyte:** Knowing the degree of dissociation, α (as calculated above) the dissociation constant (K) of the weak electrolyte at concentration C of the solution can be calculated using the formula $K_c = \dfrac{C\alpha^2}{1-\alpha}$

4. **Calculation of solubility of a sparingly soluble :** Salts such as AgCl, $BaSO_4$, $PbSO_4$ etc. which dissolve to a very small extent in water are called sparingly soluble salts. As they dissolve very little, their solutions are considered as infinitely dilute. Further as their solutions are saturated, their concentration is equal to their solubility. Thus by determining the specific conductivity (K) and the molar conductivity of such solution, we have

$$\lambda^0_m = K \times \frac{1000}{\text{Molarity}} = K \times \frac{1000}{\text{Solubility}}$$

$$\text{or} \quad \text{Solubility} = \frac{K \times 1000}{\lambda^0_m}$$

λ^0_m can be calculated by applying Kohlraush law

(e.g. for AgCl $\lambda^0{}_m = \lambda^o{}_{Ag^+} + \lambda^o{}_{Cl^-}$)

Example 5 :

From the following molar conductivities at infinite dilution,

λ^0_m for $Ba(OH)_2 = 457.6\ \Omega^{-1}\ cm^2\ mol^{-1}$

λ^0_m for $BaCl_2 = 240.6\ \Omega^{-1}\ cm^2\ mol^{-1}$

λ^0_m for $NH_4Cl = 129.8\ \Omega^{-1}\ cm^2\ mol^{-1}$

calculate λ^0_m for NH_4OH

Sol. $\lambda^o{}_m(Ba(OH)_2) = \lambda^o{}_{Ba^{2+}} + 2\lambda^o{}_{OH^-}$ ...(i)

$\lambda^o{}_m(BaCl_2) = \lambda^o{}_{Ba^{2+}} + 2\lambda^o{}_{Cl^-}$ ...(ii)

$\lambda^o{}_m(NH_4OH) = \lambda^o{}_{NH_4^+} + \lambda^o{}_{Cl^-}$ ...(iii)

$\lambda^o{}_m(NH_4OH) = \lambda^o{}_{NH_4^+} + \lambda^o{}_{OH^-}$

$= \dfrac{1}{2}\ eq^n.\ (i) + eq^n.\ (iii) - \dfrac{1}{2}\ eq^n.\ (ii)$

$= \dfrac{1}{2} \times 457.6 + 129.8 - \dfrac{1}{2} \times 240.6 = 238.3\ \Omega^{-1}\ cm^2\ mol^{-1}$

Example 6 :

The conductivity of a saturated solution of AgCl at 288 K is found to be $1.382 \times 10^{-6}\ ohm^{-1}\ cm^{-1}$. Find its solubility. Given ionic conductances of Ag^+ and Cl^- at infinite dilution are $61.9\ ohm^{-1}\ cm^2\ mol^{-1}$ and $76.3\ ohm^{-1}\ cm^2\ mol^{-1}$ respectively.

Sol. $\lambda^o{}_m(AgCl) = \lambda^o{}_{Ag^+} + \lambda^o{}_{Cl^-}$

$= 61.9 + 76.3 = 138.2\ ohm^{-1}\ cm^2\ mol^{-1}$

$$\text{Solubility} = \frac{K \times 1000}{\lambda^o{}_m} = \frac{1.382 \times 10^{-6} \times 1000}{138.2}$$

$= 10^{-5}\ mol\ L^{-1} = 10^{-5} \times 143.5\ g\ L^{-1}$

$= 1.435 \times 10^{-3}\ g\ L^{-1}$

TRY IT YOURSELF - 1

Q.1 The molar conductance of 0.025 M CH_3COOH is $46.15\ S\ cm^2\ mol^{-1}$. Calculate its degree of dissociation and dissociation constant.

Given : $\lambda^0_{(H^+)} = 349.6\ S\ cm^2\ mol^{-1}$ and

$\lambda^0_{CH_3COO^-} = 54.6\ S\ cm^2\ mol^{-1}$

Q.2 0.05 M NaOH solution offered a resistance of 31.6 ohm in a conductivity cell at 298K. If the cell constant is $0.367 cm^{-1}$, calculate its molar conductance.

Q.3 The conductance of 0.1 M acetic acid at 298 K is 5.1 and that of 0.001 M acetic acid is 48.5. The ionic conductance at infinite dilution of acetate and hydrogen ions are 41.0 and 348.9 $ohm^{-1}\ cm^2\ mol^{-1}$ respectively. Calculate percentage ionisation at these two concentrations.

Q.4 The conductivity of a solution containing 1.0g of anhydrous $BaCl_2$ in 200 cm^3 of solution has been found to be $0.0058\ S\ cm^{-1}$. Calculate its molar and equivalent conductance.

Q.5 The molar conductance at infinite dilution of NH_4Cl, NaOH and NaCl are 120.8, 210.4 & 110 $ohm^{-1} cm^2\ mol^{-1}$ respectively. Calculate molar conductance of NH_4OH at infinite dilution.

Q.6 Calculate the molar conductance of 1M sulphuric acid solution whose conductivity is $26 \times 10^{-2}\ ohm^{-1}\ cm^{-1}$.

Q.7 The conductivity of 0.20M solution of KCl at 298K is $0.0248\ S\ cm^{-1}$. Calculate its molar conductivity.

ANSWERS

(1) 0.1140, $3.67 \times 10^{-4} mol^{-1} L$ **(2)** 232.27 $ohm^{-1} cm^2 mol^{-1}$
(3) 1.3%, 12.43%
(4) (a) 241.66 $ohm^{-1}\ cm^2\ mol^{-1}$ (b) 120.83 $S\ cm^2 eq^{-1}$
(5) 221.2 $ohm^{-1}\ cm^2\ mol^{-1}$ **(6)** 260 $ohm^{-1}\ cm^{-2}\ mol^{-1}$
(7) 124 $S\ cm^2\ mol^{-1}$.

ELECTROLYSIS

On passing an electric current through electrolyte chemical change take place is called electrolysis.

Product of electrolysis depend upon following factors :

(i) Nature of electrolyte
(ii) Nature of electrode
(iii) Concentration of ion in solution
(iv) Value of flowing current

Electrodes are two types :

(i) Inert electrode or non-attached electrode :

They does not react with electrolyte.

Ex. : Graphite electrode.

(ii) Active electrode or attached electrode :

They react with electrolyte.

Ex. : Electrolysis of fused NaCl at Pt electrode.

$NaCl \longrightarrow Na^+ + Cl^-$

Cathode : $2Na^+ + 2e^- \longrightarrow 2Na$

Anode : $2Cl^- \longrightarrow Cl_2\uparrow + 2e^-$

Discharge potential : For discharging any ion at electrode are certain energy is required.

At a potential any ion discharge called discharge potential.

For Cation : $\dfrac{Li^+, K^+, Ca^{2+}, Mg^+, Al^{+3}, Zn^{+2}, Fe^{+2} ......H^+, Cu^{+2}, Hg^{+2}, Ag^+}{\text{decreasing discharge potential} \rightarrow}$

For Anion : $\dfrac{SO_4^{-2}, NO_3^-, OH^-, Cl^-, Br^-, I^-}{\text{decreasing discharge potential} \rightarrow}$

Example of Electrolysis :

(A) Electrolysis of aq. NaCl solution at Pt electrode.

$NaCl \longrightarrow Na^+ + Cl^-;\ H_2O \longrightarrow H^+ + OH^-$

At Cathode : $2H^+ + 2e^- \longrightarrow H_2\uparrow$

At Anode : $2Cl^- \longrightarrow Cl_2\uparrow + 2e^-$

(B) Electrolysis of aq. solution of concentrate H_2SO_4 at Pt electrode.

At Cathode : $2H^+ + 2e^- \longrightarrow H_2\uparrow$

At Anode : $SO_4^{-2} \xrightarrow{2e^-} SO_4^{\bullet} + H_2O \longrightarrow H_2SO_4 + OH^-$

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

Note : Electrolysis of aq. $CuSO_4$ solution at Cu Electrode.

At Cathode : $Cu^{+2} + 2e^- \longrightarrow Cu$

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

It is not an example of electrolysis. It is only method of copper purification.

Qualitative aspects of electrolysis

(i) Of the two cations, that cation is liberated at the cathode which has higher reduction potential. Of the two anions, that anion will be discharged at the anode which has lower reduction potential.

(ii) If electron is active at cathode, metal goes on depositing on cathode and at anode metal is dissolved.

(iii) It must be noted that it is not the SRP of a cation that decides its discharge, but its reduction potential. The SRP's should be used only when the concentration of ions are 1M. For concentrations other than 1M, the reduction potentials for each cation at the concentration is calculated and then the discharge of an an ion can be predicted.

(iv) The discharge of NO_3^-, PO_4^{3-} and SO_4^{2-} ions at anode does not commonly take place from aqueous solution.

FARADAY'S LAW

Faraday's First Law : When an electric current is passed through an electrolyte, the amount of substance deposited is proportional to the quantity of electric charge passed through the electrolyte.

It W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation. $W \propto Q$

A coulomb is the quantity of charge when a current of one ampere is passed for tone second. Thus, amount of charge in coulombs.

Q = current in amperes × time in seconds $= I \times t$

$W \propto I \times t$

$W = Z \times I \times t$

where Z is a constant, known as electro-chemical equivalent & is characteristic of the substance deposited.

When a current of one ampere is passing for one second, i.e., one coulomb ($Q = 1$), then $W = Z$

Thus, electrochemical equivalent can be defined as the mass of the substance deposited by one coulomb of charge or by one ampere of current passed for one second.

$$\text{Electro-chemical equivalent (Z)} = \frac{\text{equivalent wt. of element}}{96500}$$

NOTE

* 1 Faraday = 96500 coulomb = Charge of one mole electrons

One faraday is the charge required to liberate or deposit one gm equivalent of a substance at corresponding electrode.

* When a gas is evolved at an electrode, $V = \dfrac{I\,t\,V_e}{96500}$

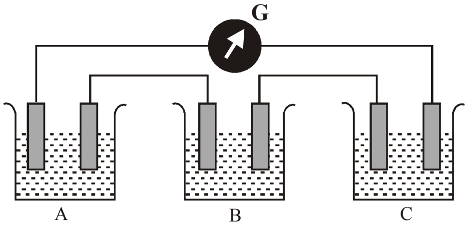
Where V = Volume of liberated gas,

V_e = equivalent volume of gas.

Equivalent volume may be defined as :

The volume of gas liberated by 96500 C at 1 atm & 0°C.

Faraday's second Law : It states that when same quantity of electricity is passed through different electrolytes then the quantity of deposit is directly proportional to its equivalent weight. (Equivalent wt. of electrolytes).



$$W \propto E \;;\; \frac{W_A}{E_A} = \frac{W_B}{E_B} = \frac{W_C}{E_C}$$

Example 7 :

Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following equation.

$$CrO_3(aq) + 6H^+(aq) + 6e^- \longrightarrow Cr(s) + 3H_2O$$

Calculate (i) how many grams of chromium will be plated out by 24,000 coulombs and (ii) how long will it take to plate out 1.5 g of chromium by using 12.5 amp current?

Sol. $CrO_3(aq) + 6H^+(aq) + 6e^- \longrightarrow Cr(s) + 3H_2O$

(i) To plate 1 mole or 52 gm of Cr 6 Faradays of electricity is used or 6 × 96500 C of electricity dissolve 52 gm of Cr

$$\therefore \quad \text{24000 coulombs will dissolve} = \frac{52}{6 \times 96500} \times 24000$$

$$= 2.1554 \text{ gm of Cr}$$

2.1554 gm of Cr are plated out by 24000 coulombs

(ii) 52 gm Cr are plated by 6 × 96500 coulombs

∴ 1.5 gm Cr will be plated by

$$6 \times \frac{96500}{52} \times 1.5 = 16701.92 \text{ coulombs}$$

$$Q = Ct \ ; \quad t = \frac{Q}{C} = \frac{16701.92}{12.5} = 1336.15 \text{ sec.}$$

Example 8 :

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 minute. It was found that after electrolysis, the absorbance of the solution was reduced to 50% of its original value. Calculate the concentration of copper sulphate in the solution to begin with.

Sol. Equivalent of Cu^{2+} lost during electrolysis

$$= \frac{i \times t}{96500} = \frac{2 \times 10^{-3} \times 16 \times 60}{96500} = 1.989 \times 10^{-5}$$

or mole of Cu^{2+} lost during electrolysis $= \dfrac{1.989 \times 10^{-5}}{2}$

This value is 50% of the initial concentration of solution

$$\text{Initial mole of } CuSO_4 = \frac{2 \times 1.989 \times 10^{-5}}{2} = 1.989 \times 10^{-5}$$

$$\text{Initial concentration of } CuSO_4 = \frac{1.989 \times 10^{-5} \times 1000}{250}$$

$[CuSO_4] = 7.95 \times 10^{-5}$ M

Example 9 :

An electric current of 100 amplere is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.

Sol. The reaction taking place at anode is

$$\begin{array}{lcl} 2Cl^- \rightarrow & Cl_2 & + \quad 2e^- \\ 71.0g & 71.0g & 2 \times 96500 \text{ coulomb} \\ & 1 \text{ mole} & \end{array}$$

$$Q = i \times t = 100 \times 5 \times 60 \times 60 \text{ coulomb}$$

The amount of chlorine liberated by passing 100 × 5 × 60 × 60 coulomb of electric charge.

$$= \frac{1}{2 \times 96500} \times 100 \times 5 \times 60 \times 60 = 9.3264 \text{ mole}$$

Volume of Cl_2 liberated at NTP = 9.3264 × 22.4 = 208.91 L

TRY IT YOURSELF - 2

Q.1 Exactly 0.2 mole electrons passed through two electrolytic cells in series containing $CuSO_4$ and $ZnSO_4$ respectively. How many grams of each metal will be deposited on the respective cathodes in the two cells?

Q.2 How much copper is deposited on the cathode if a current of 3A is passed through aqueous $CuSO_4$ solution for 15 minutes?

Q.3 If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

Q.4 Calculate the number of coulombs required to deposit 6.75g of Al when the electrode reaction is $Al^{3+} + 3e^- \rightarrow Al$.

Q.5 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20minutes. What mass of Ni is deposited at the cathode?

Q.6 A current of 2A was passed for 1.5 hours through a solution of $CuSO_4$ when 1.6g of copper was deposited. Calculate percentage current efficiency.

Q.7 How much time would be needed to deposit 0.25g of metallic nickel (Atomic mass = 58.5) on a metal object using a current of 1A during electroplating?

ANSWERS

(1) (i) 31.75g, 32.50g, (ii) 6.35g, 6.50g

(2) 0.889g **(3)** 2.246×10^{22} electrons.

(4) 72375 C **(5)** 1.825 g

(6) 45.03% **(7)** 13.74 minutes

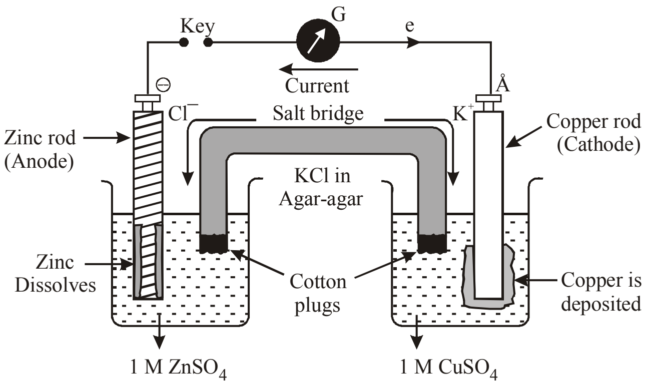
ELECTROCHEMICAL CELL

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

(a) Electrolytic cell (b) Galvanic or voltaic cell

(a) **Electrolytic cell :** It is a device in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done.

(b) **Galvanic or voltaic cell :** It is a device in which a redox reaction is used to convert chemical energy into electrical energy, i.e., electricity can be obtained with the help of oxidation and reduction reaction. The chemical reaction responsible for production of electricity takes place in two separate compartments. Each compartment consists of a suitable electrolyte solution and a metallic conductor. The metallic conductor acts as an electrode. The compartments containing the electrode and the solution of the electrolyte are called half-cells. When the two compartments are connected by a salt bridge and electrodes are joined by a wire through galvanometer the electricity begins to flow. This is the simple form of voltaic cell.



Anode : $Zn \longrightarrow Zn^{2+} + 2e^-$
(Ist half cell reaction)

Cathode : $Cu^{+2} + 2e^- \rightarrow Cu$
(IInd half cell reaction)

Total cell reaction :

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

Salt bridge :

1. It allows to flow of current by completing the circuit.
2. It maintains electrical neutrality of electrolytes in two half cells.

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 the same ionic mobility

Cell reaction

$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$$

Representation of Galvanic cell.

$$Zn/Zn^{+2} \ // \ Cu^{+2}/Cu$$

(C_1) Anode | (C_2) Cathode

salt bridge

Representation of Galvanic cell :

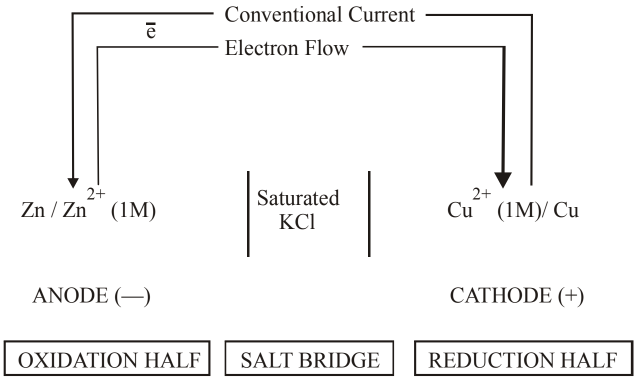
Galvanic cell is a combination of two half cells, namely, oxidation half cell and reduction half cell. If M represents the symbol of the element and Mn+ represents its cation (i.e., its oxidised state) in solution, then

Oxidation half cell is represented as $M/M^{n+}(C)$

Reduction half cell is represented as $M^{n+}(C)/M$

In both the notations C refers to the molar concentration of the ions in solution. Conventionally, a cell is represented by writing the cathode on the right hand side and anode on the left hand side. The two vertical lines are put between the two half cells which indicate salt bridge. Sometimes the formula of the electrolyte used in the salt bridge is also written below the vertical lines.

For example, zinc-copper sulphate cell is represented as follows :



Working of the cell :

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

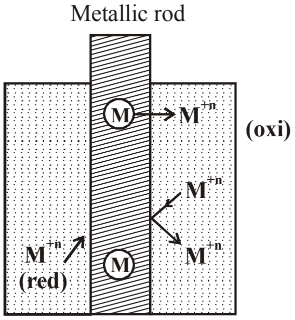
(ii) The electrons liberated during oxidation are pushed through the connecting wires to copper strip.

(iii) Copper ions move towards copper strip and pick up the electrons, and get reduced to copper atom which are deposited at the copper strip.

$$Cu^{+2}(aq) + 2e^- \rightarrow Cu(s) \text{ (reduction)}$$

ELECTRODE POTENTIAL

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 : $M \longrightarrow M^{+n} + ne^-$ (Oxidation Potential)

At cathode : $M^{+n} + ne^- \longrightarrow M$ (Reduction Potential)

The value of electrode potential depends upon :

(1) the nature of electrode

(2) the concentration of solution

(3) the temperature

Standard electrode potential (E°) :

If the concentration of ions is unity, temperature is 25°C and pressure is 1 atm (standard conditions), the potential of the electrode is called standard electrode potential.

The reference reaction is the reduction of $H^+(aq)$ ions to produce $H_2(g)$:

$$2H^+(aq, 1M) + 2e^- \longrightarrow H_2(g, 1 \text{ atm}) ; E^\circ_{red} = 0.0V$$

This is a Standard Hydrogen Electrode (SHE)

SHE consists of a platinum electrode in contact with H_2 gas and aqueous H^+ ions.

According to IUPAC the given value of electrode potential be regarded as reduction potential unless it is specifically mentioned.

Electro motive 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.

$E_{cell} = E_{red}$ (cathode) – E_{red} (anode)

or $E_{cell} = E_{oxi.}$(anode) – $E_{oxi.}$(Cathode)

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

Sign convention of EMF :

EMF of cell should be positive otherwise it will not be feasible in the given direction.

$Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$; E = +1.10 volt (Feasible)

$Cu \mid CuSO_4 \parallel ZnSO_4 \mid Zn$; E = –1.10 volt (not feasible)

Example 10 :

Standard reduction potentials for $Fe^{+2} \mid Fe$ and $Sn^{+2} \mid Sn$ are –0.44 V and – 0.14 V, respectively, then what should be the standard electromotive force for $Fe^{+2} + Sn \rightarrow Fe + Sn^{+2}$ cell reaction?

Sol. Oxidation of Sn is taking place.

Therefore, Sn acts as an anode and Fe as a cathode.

Thus, EMF = $E_{(Cathode)} - E_{(Anode)} = -0.44 - (-0.14) = -0.30$

Example 11:

Electromotive force of a cell formed by a standard copper electrode and a standard magnesium electrode couple is + 2.7 V. If standard reduction potential of the Cu electrode is + 0.34 V, then what should be the standard reduction potential of Mg?

Sol. Here $Mg \rightarrow Mg^{+2}$ is an anode and $Cu^{+2} \rightarrow Cu$ is a cathode.

Anode (R.P) = Cathode (R.P.) – EMF

= + 0.34 – (+ 2.7) = – 2.36 V

Example 12 :

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

Find out the standard EMF of the above cell if

$E^0\ Zn \longrightarrow Zn^{+2}$ = 0.76 volt

$E^0\ Co \longrightarrow Co^{+2}$ = 0.28 volt

Sol. Reduction potential of Zn = – 0.76 volt

Reduction potential of Co = – 0.28 volt

$Co^{+2} \longrightarrow Co$ Reduction

$Zn \longrightarrow Zn^{+2} + 2e^-$ Oxidation

Standard EMF of cell = $E_{(Cathode)} - E_{(Anode)} - 0.28 - (-0.76)$

= + 0.48 volt

ELECTRO CHEMICAL SERIES

The arrangement of various elements in order of increasing values of standard reduction potential is called electro chemical series.

Standard reduction potentials at 298 K

(Electrochemical Series)

Element	**Electrode Reduction Reaction**	**Standard Reduction Potential E° (in Volt)**
Li	$Li^+ + e^- \longrightarrow Li$	–3.05
K	$K^+ + e^- \longrightarrow K$	–2.93
Ba	$Ba^{2+} + 2e^- \longrightarrow Ba$	–2.90
Ca	$Ca^{2+} + 2e^- \longrightarrow Ca$	–2.87
Na	$Na^+ + e^- \longrightarrow Na$	–2.71
Mg	$Mg^{2+} + 2e^- \longrightarrow Mg$	–2.37
Al	$Al^{3+} + 3e^- \longrightarrow Al$	–1.66
Mn	$Mn^{2+} + 2e^- \longrightarrow Mn$	–1.18
Zn	$Zn^{2+} + 2e^- \longrightarrow Zn$	–0.76
Cr	$Cr^{3+} + 3e^- \longrightarrow Cr$	–0.74
Fe	$Fe^{2+} + 2e^- \longrightarrow Fe$	–0.44
Cd	$Cd^{2+} + 2e^- \longrightarrow Cd$	–0.40
Ni	$Ni^{2+} + 2e^- \longrightarrow Ni$	–0.25
Sn	$Sn^{2+} + 2e^- \longrightarrow Sn$	–0.14
Pb	$Pb^{2+} + 2e^- \longrightarrow Pb$	–0.13
H_2	$2H^+ + 2e^- \longrightarrow H_2$	0.00
Cu	$Cu^{2+} + 2e^- \longrightarrow Cu$	0.34
I_2	$I_2 + 2e^- \longrightarrow 2I^-$	0.53
Hg	$Hg_2^{+2} + 2e^- \longrightarrow 2Hg$	0.79
Ag	$Ag^+ + e^- \longrightarrow Ag$	0.80
Hg	$Hg^{+2} + 2e^- \longrightarrow Hg$	0.85
Br_2	$Br_2 + 2e^- \longrightarrow 2\,Br^-$	1.08
Cl_2	$Cl_2 + 2e^- \longrightarrow 2\,Cl^-$	1.36
Pt	$Pt^{+2} + 2e^- \longrightarrow Pt$	1.20
Au	$Au^{3+} + 3e^- \longrightarrow Au$	1.50
F_2	$F_2 + 2e^- \longrightarrow 2F^-$	2.87

Important points about this series :

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

(ii) Weakly electronegative metals in the upper part can displace more electronegative metals below them from their salts. for example, iron displaces copper from $CuSO_4$ solution, Cu displaces silver from silver salt solution, silver displaces gold from gold salt solution as in photography during gold toning process.

(iii) Hydroxides of metals in the upper part of the series are strongly basic and their salts do not undergo hydrolysis. On the other hand, hydroxides of the metals in the lower part of the series are weakly basic and their salts undergo hydrolysis.

(iv) Metals lying above hydrogen are easily rusted. Those situated below are not rusted.

(v) Metals above hydrogen displace hydrogen from dilute acids.

(vi) More weakly electropositive metals like K, Na, Ca, etc. displace hydrogen from water.

(vii) Iron and other metals above it decompose steam and liberate hydrogen.

(viii) Oxides of iron and other metals below it can be reduced easily.

(ix) Oxides of manganese and other metals above it are reduced when heated in a current of hydrogen.

(x) Oxides of mercury and other metals below it are decomposed on heating.

Applications of Electrochemical Series :

(a) **Reactivity of metals :**

(i) Alkali metals and alkaline earth metals having high –ve values of SRP which are chemically active. These react with cold water and evolve hydrogen and readily dissolve in acids.

(ii) Metals like Fe, Pb, Sn, Ni, Co, etc. do not react with cold water but react with steam to evolve hydrogen.

(iii) Metals Li, Be, Cu, Ag, and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

(b) Electropositive character of metals : Electropositive character of metals decreases from top to bottom.

(c) Displacement reactions : To predict whether a given metal will displace another, from its salt solution.
The metal having low SRP will displace the metal from its salt's solution which has higher value of SRP.

(d) Reducing power of metals : Reducing nature decreases from top to bottom in the electrochemical series.

(e) Oxidizing nature of non-metals : Oxidizing nature increases from top to bottom in the electrochemical series.

(f) Thermal stability of metallic oxides : The thermal stability of the metal oxide decreases from top to bottom.

(g) Products of electrolysis : The ion which is stronger oxidizing agent is discharged first at cathode.

(h) Corrosion of metals : Corrosion is defined as the deterioration of a substance because of its reaction with its environment. The corrosion tendency increases from top to bottom.

NERNST EQUATION

The electrode potential and the emf of the cell depend upon the nature of the electrode, temperature and the activities (concentrations) of the ions in solution. The variation of electrode and cell potentials with concentration of ions in solution. The variation of electrode and cell potentials with concentration of ions in solution can be obtained from thermodynamic considerations. For a general reaction such as

$$m_1A + m_2B + \dots \rightleftharpoons n_1X + n_2Y + \dots \quad \text{.....(i)}$$

occurring in the cell, the Gibbs free energy change is given by the equation,

$$\Delta G = \Delta G^\circ + 2.303\ RT\log_{10}\frac{a_x^{n_1}\times a_y^{n_2}}{a_A^{m_1}\times a_B^{m_2}} \quad \text{...(ii)}$$

where 'a' represents the activities of reactants and products under a given set of conditions and ΔG° refers to free energy change for the reaction when the various reactants and products are present at standard conditions. The free energy change of a cell reaction when the various reactants and products are present at standard conditions. The free energy change of a cell reaction it related to the electrical work that can be obtained from the cell, i.e.,

$\Delta G = -nFE_{cell}$ and $\Delta G^\circ = -FE^\circ$.

On substituting these values in Eq. (ii), we get

$$-nFE_{cell} = -nF\,E^0_{cell} + 2.303RT\log_{10}\frac{a_x^{n_1}\times a_y^{n_2}\dots}{a_A^{m_1}\times a_B^{m_2}\dots} \quad \text{...(iii)}$$

$$\text{or}\quad E_{cell} = E^0_{cell} - \frac{2.303RT}{nF}\log_{10}\frac{a_x^{n_1}\times a_y^{n_2}\dots}{a_A^{m_1}\times a_B^{m_2}\dots} \quad \text{.....(iv)}$$

$$E = E^0 - \frac{2.303RT}{nF}\log_{10}\frac{[\text{Products}]}{[\text{Reactants}]} \quad \text{......(v)}$$

This equation is known as Nernst equation.
Putting the values of $R = 8.314\ JK^{-1}\ mol^{-1}$, $T = 298$ K and $F = 96500$ C, Eq.(iv) reduces to

$$E = E^o - \frac{0.0591}{n}\log_{10}\frac{[\text{Products}]}{[\text{Reactants}]} \quad \text{...(vi)}$$

$$E = E^o - \frac{0.0591}{n}\log_{10}\frac{[P]}{[R]}$$

NOTE

* EMF should be +ve for a cell process to be feasible or spontaneous.

* When ΔG = positive, E = negative and the cell process will be non-spontaneous.

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

Potential of single electrode (Anode) :

Consider the general oxidation reaction,

$$M \longrightarrow M^{n+} + ne^-$$

Applying Nernst equation,

$$E_{ox} = E^0_{ox} - \frac{0.0591}{n}\log_{10}\frac{[M^{n+}]}{[M]}$$

where E_{ox} is the oxidation potential of the electrode (anode),

E^0_{ox} is the standard oxidation potential of the electrode.

The concentration of pure solids and liquids are taken as unity. $E_{ox} = E^0_{ox} - \frac{0.0591}{n}\log_{10}[M^{n+}]$

Potential of single electrode (Cathode) :

Consider the general reduction reaction.

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

$$M^{n+} + ne^- \rightarrow M$$

Applied Nernst equation,

$$E_{Reduction} = E^0{}_{Reduction} - \frac{0.0591}{n}\log_{10}\frac{[M]}{[M^{n+}]}$$

$$= E^0{}_{Reduction} + \frac{0.0591}{n}\log_{10}[M^{n+}]$$

Emf of the cell : Cell potential depend upon potential of cathode and anode.

$$E_{cell} = E_{anode} + E_{cathode}$$

$$E_{cell} = E_{ox} + E_{red} = (E^0_{ox} + E^0_{red})$$

$$-\frac{0.0591}{n}\log_{10}\left[\frac{\text{concentration of Anode}}{\text{concentration of Cathode}}\right]$$

Let us consider an example, in which the values of n for the two ions in the two half-cells are not same.

For example, in the cell $Cu \mid Cu^{2+} \parallel Ag^{+} \mid Ag$

The cell reaction is $Cu(s) + 2Ag^{+} \longrightarrow Cu^{2+} + 2Ag$

The two half-cell reactions are: $Cu \longrightarrow Cu^{2+} + 2e^{-}$

$Ag^{+} + e^{-} \longrightarrow Ag$

The second equation is multiplied by 2 to balance the number of electrons.

$2Ag^{+} + 2e^{-} \longrightarrow 2Ag$

$$E_{ox} = E^{0}_{ox} - \frac{0.0591}{2}\log_{10}[Cu^{2+}]$$

$$E_{red} = E^{0}_{red} \quad \frac{0.0591}{2}\log_{10}[Ag^{+}]^{2}$$

$$E_{cell} = E_{ox} + E_{red} = E^{0}_{ox} + E^{0}_{red} - \frac{0.0591}{2}\log_{10}\frac{[Cu^{2+}]}{[Ag^{+}]^{2}}$$

$$= E^{0}_{cell} - \frac{0.0591}{2}\log_{10}\frac{[Cu^{2+}]}{[Ag^{+}]^{2}}$$

Applications of EMF measurements :

(i) Prediction and feasibility of spontaneity of a cell reaction:

Let us see whether the cell (Daniel) is feasible or not i.e., whether Zinc will displace copper or not.

$Zn \mid (s) \mid ZnSO_4\,(1M) \parallel CuSO4\,(1M) \mid Cu\,(s)$

$$E^{0}_{Zn^{2+}/Zn} = -0.76 \text{ volt}, \; E^{0}_{Cu^{2+}/Cu} = +0.34 \text{ volt}$$

$$E^{0}_{Cell} = E^{0}_{Cu^{2+}/Cu} - E^{0}_{Zn^{2+}/Zn}$$

$$= 0.34 - (-0.76) = +1.10 \text{ volt}$$

Since $E° = +ve$, hence the cell will be feasible and zinc will displace copper from its salt solution. In the other words, zinc will reduce copper.

(ii) Determination of equilibrium constant :

We know that, $E = E° - \frac{0.0591}{n}\log Q$ .... (1)

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. $E = 0$

∴ From eq. (1), we have

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

Free energy :

$$E^{0}_{cell} = \frac{RT}{nF}\log_e K_{eq}\;;\; \Delta G^{0} = -\,nF\,E^{0}_{cell}$$

$$\Delta G^{0} = -\,nF\left(\frac{RT}{nF}\log_e K_{eq}\right) = -\,2.303\,RT\log_{10}K_{eq}$$

(iii) Solubility product : The solubility product of a sparingly doubles salt is a kind of equilibrium constant.

$MX\,(s) \rightleftharpoons M^{+}\,(aq) + X^{-}\,(aq)\;;\; K_{sp} = [M^{+}]\,[X^{-}]$

At anode : $M\,(s) \rightleftharpoons M^{+}\,(aq) + e^{-}$

At cathode : $e^{-} + MX\,(s) \rightleftharpoons M\,(s) + X^{-}\,(aq)$

Overall reaction : $MX\,(s) \rightleftharpoons M^{+}\,(aq) + X^{-}\,(aq)$

Cell representation :

$M \mid M^{+}M^{-}$ (satd. sol.) $\parallel NaA \mid MX\,(s) \mid M\,(s)$

$E°_{cell} = E°_{red} - E°_{ox}$

From thermodynamic $\Delta G° = nFE°$

$\Delta G° = -\,2.303\,RT\log K_{sp}$

Combining both equations $-\,2.303\,RT\log Ksp = -\,nFE°$

$$\text{or} \quad E° = \frac{2.303\,RT}{nF}\log K_{sp}$$

$$E° = \frac{0.0591}{n}\log K_{sp} \text{ at } 25°C$$

(iv) Determination of pH of a solution :

We can calculate of the pH of a unknown solution by using suitable reference half cell.

$Pt\,(H_2)\,(1\text{ atm}) \mid H^{+}\,(pH = ?) \parallel Cl^{-}\,(1M) \mid Hg_2Cl_2, Hg$

(calomel electrode)

At anode : $H_2\,(g) \rightarrow 2H^{+}\,(aq) + 2e\;;\; E° = 0$

At cathode : $Hg_2Cl_2\,(s) + 2e \rightarrow 2Hg\,(l) + 2Cl^{-}\;;\; E°_{red} = 0.2676$

$H_2\,(g) + Hg_2Cl_2\,(s) \rightarrow 2H^{+}\,(aq) + 2Hg\,(l) + 2Cl^{-}\,(aq)\;;$

$E°_{cell} = 0.2675$ V

$Q = [H^{+}]^{2}\,[Cl^{-1}]^{2} = [H^{+}]^{2},\, [Cl^{-}] = 1M$

$$E_{cell} = E^{0}_{cell} - \frac{0.059}{2}\log\,[H^{+}]^{2}$$

$$\Rightarrow \quad E_{cell} = E^{0}_{cell} + 0.0591\,pH \;\therefore\; pH = \frac{E_{cell} - E^{0}_{cell}}{0.0591}$$

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 cell. For such cell, $E°_{cell} = 0$.

(i) Electrode gas concentration cell :

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

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

Cell process :

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

$$H^{+}\,(c) + e^{-} \rightarrow \frac{1}{2}H_2(p_2) \quad \text{(cathode process)}$$

$$\frac{1}{2}H_2(p_1) \rightleftharpoons \frac{1}{2}H_2(p_2) \quad \text{(Net reactions)}$$

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

or At 25°C, $E = \frac{0.0591}{2} \log \left[\frac{p_1}{p_2}\right]$

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

(ii) Electrolyte concentration cell :

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

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

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

$$Zn^{2+}\,(C_2) + 2e \rightarrow Zn\,(s) \quad \text{(Cathodic process)}$$

$$Zn^{2+}\,(C_2) \rightleftharpoons Zn^{2+}\,(C_1) \quad \text{(Overall process)}$$

∴ From Nernst equation, we have

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

For spontanity of such cell reaction, $C_2 > C_1$.

Example 13 :

(a) Calculate the electrode potential at a copper electrode dipped in a 0.1 M solution of copper sulphate at 298K; assuming $CuSO_4$ to be completely dissociated. The standard electrode potential of $Cu^{2+} \mid Cu$ system is + 0.34 volts at 298K.

(b) At what concentration of copper ions will this electrode have a potential of zero volt?

Sol. (a) The reduction electrode reaction is

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

Thus here, $n = 2$; $E° = + 0.34$ volts,

$[Products] = 1$, $[Cu^{2+}] = 0.1$ M

Substituting these values in the Nernst equation,

$$E = E° - \frac{0.059}{2} \log \frac{[Products]}{[Reactants]} = 0.34 - \frac{0.059}{2} \log \frac{1}{0.1}$$

$$= 0.34 - 0.0295 \log 10 = 0.3105 \text{ volt}$$

(b) Here, $E = 0$ Volt, $[Cu^{2+}] = ?$

Applying again Nernst equation

$$E = E° - \frac{0.059}{n} \log \frac{[Cu]}{[Cu^{2+}]}$$

$$0 = 0.34 - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]} \; ; \; \log [Cu^{2+}] = - \frac{0.34}{0.0295}$$

On solving, we get $[Cu^{2+}] = 2.95 \times 10^{-12}$ M

Example 14 :

Calculate E° & E for the cell $Sn \mid Sn^{2+}\,(1M) \parallel Pb^{2+}\,(10^{-3}M) \mid Pb$, $E° = (Sn^{2+} \mid Sn) = -0.14V$, $E°\,(Pb^{2+} \mid Pb) = -0.13V$. Is cell reaction is feasible ?

Sol. No, $E_{cell} = -0.078$ V

$$E_{cell} = -E^0_{Sn^{2+}/Sn} + E^0_{Pb^{2+}/Pb} - \frac{0.059}{2} \log \frac{[Sn^{2+}]}{[Pb^{2+}]}$$

$$= +0.14 - 0.13 - \frac{0.059}{2} \log 10^3 = -0.078 \text{ V}$$

Cell will not work.

Example 15 :

The standard reduction potential of Cu^{2+}/Cu and Ag^+/Ag electrode are 0.337 and 0.799 volt respectively. Construct a galvanic cell using these electrodes so that its standard e.m.f. is positive. For what concentration of Ag^+ will the e.m.f. of the cell, at 25ºC, be zero if the concentration of Cu^{2+} is 0.01M?

Sol. $E^0_{Cu^{2+}/Cu} = 0.337$ and $E^0_{Ag^+/Ag} = 0.799$

$$E^0_{Ag^+/Ag} + E^0_{Cu/Cu^{2+}} = 0.799 - 0.337 = 0.462$$

$$\therefore \quad Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag \; ; \; \Delta E^0 = 0.462$$

Hence the galvanic cell in question will consist of anode of copper and cathode of silver.

$$E^0 = E_{cell} - \frac{0.059}{n} \log \frac{[Products]}{[Reactants]}$$

$$E_{cell} = \frac{0.059}{n} \log \frac{[Products]}{[Reactants]} \qquad [\because E^0 = 0]$$

$$0.462 = \frac{0.059}{2} \log \frac{0.01}{[Ag^+]^2}$$

$$\frac{462 \times 2}{59} = \log (10^{-2}) - \log [Ag^+]^2 \; ; \; \frac{924}{59} = -2 - \log [Ag^+]$$

On usual calculations, $[Ag^+] = 1.48 \times 10^{-9}$ M

Example 16 :

Calculate pH of the following half-cell. $Pt\ H_2 \mid H_2SO_4$. The oxidation electrode potential is + 0.3 V.

Sol. The half-cell reaction is

$$H_2 \longrightarrow 2H^+ + 2e^- \quad \text{or} \quad \frac{1}{2} H_2 \longrightarrow H^+ + e^-$$

Applying Nernst potential equation,

$$E = E^0 - \frac{0.059}{n} \log \frac{[Products]}{[Reactants]}$$

Since reactant is a gas (H_2) and its pressure (concentration) is not mentioned, it must be considered as 1.

$$\text{Hence } E = 0 - \frac{0.059}{n} \log \frac{[H^+]}{1} \qquad [\because \text{SHE} = 0 \text{ volt}]$$

Now since $pH = -\log [H^+]$

$$E = +0.059\,pH \text{ or } pH = + \frac{E}{0.059} = + \frac{0.3}{0.059} = 5.08$$

Example 17 :

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]

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

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

$$E° = 1.44 - 0.68 = 0.76 \text{ V} = \frac{0.06}{1} \log K_C \; ; \; K_C = 4.64 \times 10^{12}$$

TRY IT YOURSELF - 3

Q.1 Write redox reaction for the following electrochemical cell $A_{(s)} \mid A^{3+}_{(1M)} \parallel B^{2+}_{(1M)} \mid B_{(s)}$

Q.2 Calculate the emf of given cell

$$\underset{0.001\,M}{Ag \mid AgNO_3} \parallel \underset{0.1\,M}{AgNO_3 \mid Ag} \; ; \; E^0_{Ag^+|Ag} = 0.80\ V$$

Q.3 Write the cell reaction that occurs when the following half cells are combined

$I_2 + 2e^- \rightarrow 2I^-$; $E° = +0.54\ V$

$Br_2 + 2e^- \rightarrow 2Br^-$; $E° = +1.08\ V$

Q.4 Metal rod A is dipped in 0.1 M solution of ASO_4. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential. $(E^0_{A^{2+}/A} = -0.76\ V)$

Q.5 Find out given cell is spontaneous or non-spontaneous.

$$H_2 \underset{P_1}{/} H^+ \parallel H^+ \underset{P_2}{/} H_2 \text{ . If } P_1 > P_2$$

Q.6 Find out work done for the given cell
$Cr \mid Cr^{+3} \mid\mid Fe^{+2} \mid Fe$

$E^0_{Cr/Cr^{3+}} = 0.74\ V,\ E^0_{Fe^{2+}/Fe} = -0.44\ V$

Q.7 Predict whether the reaction between the following is feasible : (a) Fe^{3+} (aq) and I^- (aq) (b) Ag^+ (aq) and Cu (s)

Given : $E^0_{Fe^{3+}/Fe^{2+}} = +0.77V,\ E^0_{Ag^+/Ag} = +0.80V$

$E^0_{I_2/I^-} = 0.54V,\ E^0_{Cu^{2+}/Cu} = +0.34V$

Q.8 Calculate the electrode potential of given electrode
Pt, Cl_2 (1.5 bar) | $2Cl^-$ (0.01 M)

$E^0_{Cl_2|2Cl^-} = 1.36V$

Q.9 Calculate the equilibrium constant for the cell reaction
$4Br^- + O_2 + 4H^+ \rightarrow 2Br_2 + 2H_2O$; $E°_{cell} = 0.16V$

Q.10 Calculate $\Delta G°$ for the given reaction occuring in fuel cell.
(i) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$; $E° = 1.229$ volt
(ii) $2H_2 \rightarrow 4H^+ + 4e^-$; $E° = 0$ volt

Q.11 Calculate the emf of the cell in which the following reaction takes place
$Ni\ (s) + 2Ag^+_{(0.002\ M)} \rightarrow Ni^{2+}_{(0.160\ M)} + 2Ag\ (s)$
Given $E°_{cell} = 1.05$ V

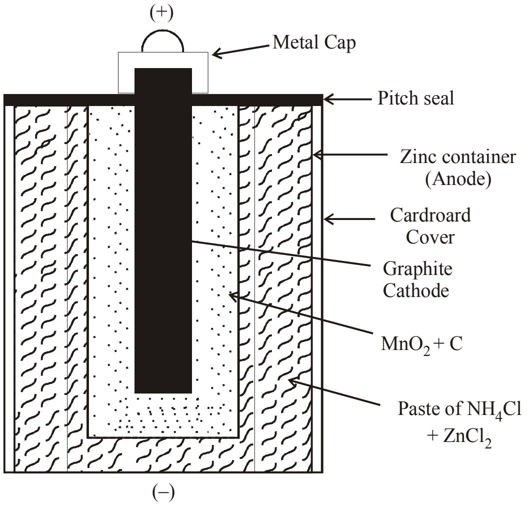
ANSWERS

(1) $2A\ (s) + 3B^{2+} \rightarrow 2A^{3+} + 3B\ (s)$
(2) 0.118 volt
(3) $2I^- + Br_2 \rightarrow I_2 + 2Br^-$; 0.54 V
(4) –0.79021 V
(5) spontaneous.
(6) 173.7 kJ
(7) (a) yes, (b) yes
(8) 1.483 V
(9) 6.31×10^{10}
(10) 474.4 kJ
(11) 0.9142 V

SOME COMMERCIAL CELLS

PRIMARY CELLS

The most familiar type of battery is the dry cell which is a compact of Leclanche cell known after its discover Leclanche



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

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. Dry cells do not have an indefinite life as acidic NH_4Cl corrodes the zinc container even when not in use. Dry cells have a potential of approximately 1.25 to 1.5V. A new type of dry cell which has found use in small electrical circuits (such as hearing aids, watches and camera) is the mercury cell. Here zinc-mercury amalgam is the anode; a paste of HgO and carbon is the cathode. The electrolyte is a paste of KOH and ZnO. Reaction of the cell is as follows:

Anode $Zn(amalgam) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

Cathode $HgO(s) + H_2O + 2e^- \longrightarrow Hg(I) + 2OH^-$

Overall reaction : $Zn(amalgam) + HgO(s) \longrightarrow ZnO(s) + Hg(I)$

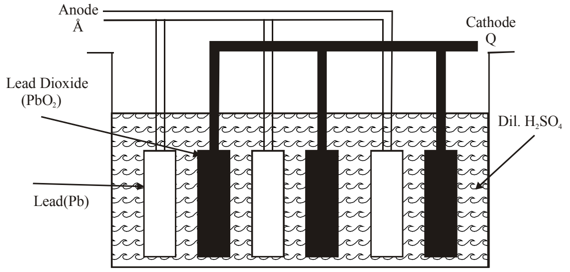
Since the overall cell reaction does not involve any ion in solution whose concentration can change, the cell shows a constancy in potential throughout its life. The cell potential is approximately 1.35V.

SECONDARY CELL

In these cells, electrode reactions can be reversed by an external electric energy source, i.e. these cells can be recharged by passing electric current. Common examples are lead storage battery and nickel–cadmium storage cell.

LEAD STORAGE BATTERY

It consists of a lead anode and a grid of lead packed with lead dissociate as cathode. A solution of sulphuric acid (38 percent by mass or having density 1.30 gm cm^{-3} is used as an electrolyte. When the cell discharges, it operates as a voltaic cell. The lead is oxidised to Pb^{+2} ion and lead plates acquire a negative charge.



Lead storage battery of 6 volts

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

At Cathode : $PbO_2(s) + SO_4^{-2}$ (aq.) $+ 4H^+ + 2e^-$

$$\longrightarrow PbSO_4^{-2}(s) + 2H_2O(\ell)$$

Overall cell reaction :

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq.) \longrightarrow 2PbSO_4(s) + 2H_2O \qquad E_{cell} \text{ is 2.041 volt.}$$

A 12 V lead storage battery is generally used which consist of 6 cells each producing 2 volt. When a potential slightly greater than the potential of battery is applied, the battery can be reacherged. During recharging the cell is operated like an electrolytic cell i.e. now electrical energy is supplied to it from an external source. The electrodes reactions are reverse of those that occur during discharge :

$$2PbSO_4 + 2H_2O \longrightarrow Pb + PbO_2 + 2H_2SO_4$$

It is clear that H_2SO_4 is used up during the discharge & produced during recharging reaction of cell. Another secondary cell is the nickel-cadmium storage cell which has a longer life than the lead storage cell.

FUEL CELL

It is an electrochemical device for continuous conversion of the portion of free energy change into electrical energy. Such cell converts 60-70% of chemical energy into electrical energy. The fuel used is in the gaseous state, $H_2 - O_2$ fuel cell is a common example.

In the cell hydrogen and oxygen are bubbled through a porous carbon electrode into concentrated aqueous sodium hydroxide. Catalysts are incorporated in the electrode. The electrode reactions are:

Anode : $2[H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(\ell) + 2e^-]$

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

Overall reaction : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(\ell)$

Nickel-cadmium storage cell :

It consists of cadmium anode and a metal grid containing NiO_2 acting as cathode. The electrolyte in this cell is KOH. Following reactions take place during discharging.

$$Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$$

$$NiO_2(s) + 2H_2O(\ell) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$$

$$Cd(s) + NiO_2(s) + 2H_2O(\ell) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

As after discharging products formed are solid. Hence, the reaction can be reversed during charging. Further, as no gases are produced during charging or discharging the cell can be sealed. It produces a potential of 1.4 V. The cell has a longer life than lead storage cell and is used in cordless appliances (Phones, pagers, mobile phones, electric shavers etc.)

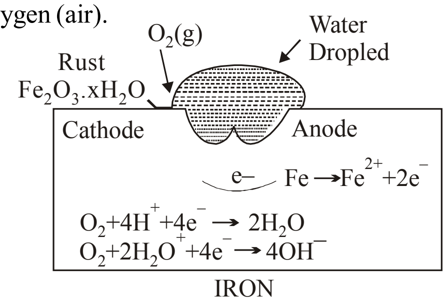
Advantages of fuel cells over ordinary batteries :

The fuel cells convert the energy of the fuel directly into electricity, while the conventional method of generating electricity by burning hydrogen, carbon fuels first convert fuels in to thermal energy and then in to electrical energy although theoretically. Fuel cells are expected to have an efficiency of 100% practically only 60–70% efficiency has been attained. Efficiency of the conventional method is only about 40%.

CORROSION

Corrosion is basically an electrochemical phenomenon. The rusting of iron, the tarnishing of silver, development of a green coating on copper and bronze are some of the examples of corrosion.

In corrosion, a metal is oxidised by loss of electrons to oxygen and forms metal oxide. Corrosion of iron (which is commonly known as rusting) occurs in presence of water and oxygen (air).



Electrochemical Theory of rusting : According to this theory follow of electric current between separate anode and cathode bar as reason because of this corrosion is held. In the anodic reason metal is destroyed by the formation of their ion or combined state (ex. oxide) in the oxidation reaction. So corrosion is always held in the anodic part.

Factors which promote corrosion :

(i) **Reactivity of the metal:** More active metals are readily corroded.

(ii) **Presence of impurities :** Presence of impurities in metals enhances the chances of corrosion. Pure metals do not corrode e.g. pure iron does not rust.

(iii) **Presence of air and moisture :** Air and moisture accelerate corrosion. Presence of gases like SO_2 and CO_2 in air catalyse the process of corrosion. Iron when placed in vacuum does not rust.

(iv) **Strains in metals :** Corrosion (e.g. rusting of iron) takes place rapidly at bends, scratches, nicks & cuts in the metal.

(v) **Presence of electrolytes :** Electrolytes, if present, also increase the rate of corrosion. For example, iron rusts faster in saline water than in pure water.

Rusting of iron : According to electrochemical theory of rusting can be represent as.

At anode Fe atom change into Fe^{+2}

Oxidation at Anode : $Fe \rightarrow F^{2+} + 2e^- ; E^0_{oxi} = 0.44V$

Reduction at Cathode : $CO_2 + H_2O \rightarrow H^+ + HCO_3^-$

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

$2H + ½ O_2 \rightarrow H_2O$

$2H^+ + ½ O_2 + 2e^- \rightarrow H_2O ; E^0_{red} = 1.23V$

Overall reaction of corrosion cell :

$Fe + 2H^+ + ½ O_2 \rightarrow Fe^{2+} + H_2O ; E^0_{cell} = 1.67V$

The ferrous ions so formed move through water and come at the surface of iron object where these are further oxidised to ferric state by atmospheric oxygen and constitute rust which is hydrated iron (III) oxide.

$2Fe^{2+} + ½ O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^+$

$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3 . xH_2O$

Prevention of corrosion :

Corrosion can be prevented by a number of ways.

Barrier Protection : The metal surface is not allowed to come in contact with moisture, oxygen and carbon dioxide. This can be achieved by the following methods :

(a) The metal surface is coated with paint which keeps it out of contact with air, moisture etc. till the paint layer develops cracks.

(b) By applying film of oil and grease on the surface of the iron tools and machinery, the rusting of iron can be prevented since it keeps the iron surface away from moisture, oxygen and carbon dioxide.

(c) The iron surface is coated with non-corroding metals such as nickel, chromium, aluminium, etc. (by electroplating) or tin, zinc, etc. (by dipping the iron article in the molten metal). This again shuts out the supply of oxygen and water to iron surface.

(d) The iron surface is coated with phosphate or other chemicals which give a tough adherent insoluble film which does not allow air and moisture to come in contact with iron surface.

USEFUL TIPS

* If E°_{red}(cathode) > E°_{red}(anode) then the electron flow from anode to cathode is spontaneous.

* E° will be positive for the case where the reaction is spontaneous.

* E° will be zero for a redox reaction at equilibrium.

* Sn can displace lead from aqueous lead bromide solution because standard reduction potential of Sn is less than that of Pb.

* When Zn piece is kept in $CuSO_4$ solution, copper gets precipitated because standard reduction potential of zinc is less than copper.

* The metal having maximum positive value of standard reduction potential is deposited in maximum amount on the cathode.

ADDITIONAL EXAMPLES

Example 1 :

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

Sol. **For NaCl (aq) :** Anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

Cathode : $2H^+ + 2e^- \longrightarrow H_2$

For $NaNO_3$ (aq) : Anode : $2OH^- \longrightarrow H_2O + ½ O_2 + 2e^-$

Cathode : $2H^+ + 2e \longrightarrow H_2$

Example 2 :

On electrolysing $CuSO_4$ solution in presence of Pt, the solution becomes colourless, blue colour of solution disappears. Why ?

Sol. At cathode : $Cu^{2+} + 2e \rightarrow Cu$

At anode : $2OH^- \rightarrow H_2O + ½ O_2 + 2e$

Cu^{2+} ions are reduced and blue colour is due to Cu^{2+}.

Example 3 :

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

Sol. Given for 0.01 N solution

$$R = 210, \frac{\ell}{a} = 0.88\ cm^{-1} ; \text{Specific conductance } \kappa = \frac{1}{R} \times \frac{\ell}{a}$$

$$\kappa = \frac{1}{210} \times 0.08 = 4.19 \times 10^{-3} \text{ mho cm}^{-1}$$

$$\Lambda_{eq} = \frac{K \times 1000}{N} = \frac{4.19 \times 10^{-3} \times 1000}{0.01}$$

$$\Lambda_{eq} = 419 \text{ mho cm}^2 \text{eq}^{-1}$$

Example 4 :

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

(b) From Ohm's law, V/i = R

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

Example 5 :

The specific conductivity of a solution containing 1.0g of anhydrous $BaCl_2$ in 200 cm^3 of the solution has been found to be 0.0058 S cm^{-1}. Calculate the molar and equivalent conductivity of the solution. Molecular wt. of $BaCl_2 = 208$.

Sol. Molarity of $BaCl_2 = \dfrac{1 \times 1000}{208 \times 200} = 0.024$ M

Also, Normality of $BaCl_2 = 0.024 \times 2 = 0.048$ N

$(\because N = M \times V.f)$

$$\mu = K \times \frac{1000}{C_M} = \frac{0.0058 \times 1000}{0.024} = 241.67 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda = K \times \frac{1000}{C_M} = \frac{0.0058 \times 1000}{0.048} = 120.83 \text{ S cm}^2 \text{ equ}^{-1}$$

Example 6 :

The resistance of a solution A is 50 ohm and that of solution B is 100 ohm, both solution being taken in the same conductivity cell. If equal volumes of solutions A and B are mixed, what will be the resistance of the mixture using the same cell? (Assuming that there is no increase in the degree of dissociation of A and B on mixing)

Sol. Let K_1 and K_2 be the specific conductance of the solution A and B respectively and the cell constant of the cell be X.

For solution A : Specific conductance

= Conductance × Cell constant

$$K_1 = \frac{1}{50} \times X \qquad \text{........... (i)}$$

For solution B : Specific conductance ,

$$K_2 = \frac{1}{100} \times X \qquad \text{........... (ii)}$$

When equal volumes of A and B are mixed, both the solutions get double diluted, hence their individual contribution towards the sp. conductance of the mixture will be $K_1/2$ and $K_2/2$ respectively and the sp. conductance of the mixture will be $\dfrac{1}{2}(K_1 + K_2)$

For the mixture $\dfrac{1}{2}(K_1 + K_2) = \dfrac{1}{R} \times X$

(R is the resistance of mixture)

From eq. (i), (ii) and (iii), R = 66.67 ohm.

Example 7 :

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

$= 129.8 + 248.1 - 126.4$

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

Example 8 :

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

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

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

$\mu^\infty_{NH_4Cl} = \lambda^\infty_{NH_4} + \lambda^\infty_{OH^-} = ?$

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

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

$$= \frac{502.88}{2} = 251.44 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Example 9 :

The equivalent conductivities of acetic acid at 298 K at the concentrations of 0.1 M and 0.001M 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 $\alpha = \dfrac{\lambda^c}{\lambda^\infty}$

(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

$$\alpha = \frac{\lambda^c}{\lambda^\infty} = \frac{5.20}{390.7} = 0.013 \text{ i.e. } 1.3\% \text{ or } \alpha = 1.3\%$$

At C = 0.001 M,

$$\alpha = \frac{\lambda^c}{\lambda^\infty} = \frac{49.2}{390.7} = 0.125 \text{ i.e. } 12.5\%$$

Example 10 :

E° of some oxidants are given as :

$I_2 + 2e^- \rightarrow 2I^-$; $E° = +0.54V$

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

$Fe^{3+} + e^- \rightarrow Fe^{2+}$; $E° = +0.77$ V

$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$; $E° = +0.1$ 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

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

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

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

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

Sol. (a) More the $E°_{OP}$ more in the tendency for oxidation.

Therefore, since maximum $E°_{OP}$ stands for :

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

$\therefore$ Strongest reductant Sn^{2+}

and weakest oxidant : Sn^{4+}

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

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

$E°_{RP} = +1.52$ V

$\therefore$ strongest oxidant: MnO_4^- & weakest reductant Mn^{2+}

Note : Stronger is oxidant, weaker is its conjugate reductant and vice versa

(c) For (i)

$$E^\circ_{cell} = E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} + E^\circ_{RP_{Sn^{4+}/Sn^{2+}}} = -0.77 + 0.1$$

Fe^{2+} oxidises, and Sn^{4+} reduces in change

$\therefore$ $E^\circ_{cell} = -0.67$ V ; E°_{cell} is negative.

$\therefore$ (i) is non-spontaneous change.

For (ii) $E^\circ_{cell} = E^\circ_{OP_{Fe^{2+}/Fe^{3+}}} + E^\circ_{RP_{I_2/I^-}}$

$$= -0.77 + 0.54 = -0.23\text{V}$$

$\therefore$ (ii) is non-spontaneous change.

For (iii),

$$E^\circ_{cell} = E^\circ_{OP_{I^-/I_2}} + E^\circ_{RP_{Sn^{4+}/Sn^{2+}}} = -0.54 + 0.1 = -0.44\text{V}$$

$\therefore$ (iii) is non-spontaneous change.

For (iv),

$$E^\circ_{cell} = E^\circ_{OP_{Sn^{2+}/Sn^{4+}}} + E^\circ_{RP_{I_2/I^-}} = -0.1 + 0.54 = +0.44\text{V}$$

(iv) is spontaneous change.

Example 11 :

Given the standard electrode potential :

$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V, $Hg^{2+}/Hg = 0.79$V, $Mg^{2+}/Mg = -2.37$V, $Cr^{3+}/Cr = -0.74$ V. Arrange these metals in their increasing order of reducing power.

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

Example 12 :

A cell is prepared by dipping a copper rod in 1M $CuSO_4$ 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 (– 0.25V) will work as anode while copper electrode with more E° value (+ 0.34 V) will work as cathode.

(ii) The cell reaction may be written as :

At anode % $Ni\,(s) \longrightarrow Ni^{2+}(aq) + 2e^-$

At cathode % $Cu^{2+}(aq) + 2e^- \longrightarrow Cu\,(s)$

Cell reaction % $Ni\,(s) + Cu^{2+}\,(aq) \longrightarrow Ni^{2+}\,(aq) + Cu\,(s)$

(iii) The cell may be represented as :

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

(iv) EMF of cell = $E^\circ_{cathode} - E^\circ_{anode}$

$= (+0.34) - (-0.25) = 0.59\text{V}$

Example 13 :

$Pt\,|\,Cl_2\,(g, P_2)\,|\,Cl^-\,(aq, C)\,\|\,Cl^-\,(aq, C)\,|\,Cl_2\,(g, P_1)\,|\,Pt$

EMF of cell positive if

(A) $P_1 > P_2$ (B) $P_2 > P_1$

(C) $P_1 = P_2$ (D) We cannot predict

Sol. **(A).** Anode half cell : $Pb\,|\,Cl_2\,(g, P_2)\,|\,Cl^-\,(aq, C)$

$$E_{ox} = E^-_{ox} - \frac{0.0591}{2}\log\frac{P_2}{C} \qquad \text{......... (1)}$$

Cathode half cell,

$Cl^-\,(aq, C)\,|\,Cl_2\,(g, P_1)\,|\,Pt$

$$E_{red} = E^0_{red} - \frac{0.0591}{2}\log\frac{C}{P_1} \qquad \text{......... (2)}$$

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

$$= E^0_{ox} + E^0_{red} - \frac{0.0591}{2}\log\frac{P_2}{C}\cdot\frac{C}{P_1}$$

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

For spontaneous reaciton, $P_1 > P_2$

Example 14 :

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

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

Sol. Given% $E^\circ_{Sn^{4+}/Sn^{2+}} = +0.15,\; E^\circ_{Br_2/Br^-} = 1.06\text{V}$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.06 - 0.15 = 0.91\text{ V}$$

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

Example 15 :

The measured emf at 25°C for the cell reaction,

$Zn\,(s) + Cu^{2+}\,(1.0M) \longrightarrow Cu\,(s) + Zn^{2+}\,(0.1M)$ is 1.3 volt.

Calculate E° for the cell reaction.

Sol. Using Nernst equation (at 298 K),

$$E_{cell} = E^\circ_{cell} - \frac{0.0591\text{V}}{2}\log\frac{[Zn^{2+}(aq)]}{[Cu^{2+}(aq)]}$$

Here, $E_{cell} = 1.3$V, $[Cu^{2+}\,(aq)] = 1.0$ M,

$[Zn^{2+}\,(aq)] = 0.1$ M, $E^\circ_{cell} = ?$

Substituting the values,

$$1.3\text{V} = E^\circ_{cell} - \frac{0.0591\text{V}}{2}\log\frac{0.1}{1.0}$$

$$1.3\text{V} = E^\circ_{cell} - 0.02955 \log 10^{-1}$$

$$1.3\text{V} = E^\circ_{cell} + 0.02955 \text{ V} \log 10$$

$$E^\circ_{cell} = 1.3\text{V} - 0.02955 \text{ V} = 1.27\text{V}$$

Example 16 :

Calculate ΔG° for the reaction :

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

Given that : $E^\circ\ Cu^{2+}/Cu = +0.34$ V, $E^\circ_{Fe^{2+}/Fe} = -0.44$ V

Sol. The cell reactions are :

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

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

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

$$E^\circ_{cell} = [E^\circ_{(Cu^{2+}/Cu)} - E^\circ_{(Fe^{2+}/Fe)}]$$

$$= (+0.34 \text{ V}) - (-0.44 \text{ V}) = +0.78 \text{ V}$$

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

$$\therefore\ \Delta G^\circ = -nF\, E^\circ_{cell} = -(2\text{ mol})\times(96500\text{ C mol}^{-1})\times(+0.78\text{ V})$$

$$= -150540 \text{ CV} = -150540 \text{ J} \quad (\because 1 \text{ CV} = 1 \text{ J})$$

Example 17 :

Calculate the equilibrium constant for the reaction at 298K.

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

Given : $E^\circ_{Zn^{2+}/Zn} = -0.76$ V and $E^\circ_{Cu^{2+}/Cu} = +0.34$V

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

$$E^\circ_{cell} = [E^\circ_{cathode} - E^\circ_{anode}]$$

$$= [(+0.34\text{ V}) - (-0.76\text{V})] = 1.10\text{ V}, n = 2,$$

$$\therefore\ \log K_C = \frac{2\times(1.10\text{V})}{(0.0591\text{ V})} = 37.29$$

$$K_C = \text{Antilog } 37.29 = 1.95\times10^{37}$$

Example 18 :

Calculate the cell emf and ΔG for the cell reaction at 298 K for the cell. $Zn(s)\,|\,Zn^{2+}(0.0004\text{ M})\,||\,Cd^{2+}(0.2\text{ M})\,|\,Cd(s)$

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 :** Calculate the cell emf.

According to be Nernst equation

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

$$E^\circ_{cell} = E^\circ_{(Cd^{2+}/Cd)} - E^\circ_{(Zn^{2+}/Zn)}$$

$$= (-0.403) - (-0.763) = 0.36 \text{ V}$$

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

$$E = (0.36) - \frac{(0.0591)}{n}\log\frac{0.0004}{0.2}$$

$$= 0.36 - \frac{(0.0591\text{V})}{n}\times(-2.69990)$$

$$= 0.36\text{V} + 0.08\text{ V} = 0.44\text{ V}$$

Step II : $\Delta G = -nFE_{cell}$

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

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

$$= -84920 \text{ CV} = -84920 \text{ J}$$

Example 19 :

How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in +1 oxidation state for a period of 8 hours at a current of 8.46 amperes. What is the area of the tray if the thickness of the silver plating is 0.00254 cm?

The density of silver is 10.5 g/cm^3.

Sol. $m = \dfrac{It}{F}\cdot\dfrac{M}{z} = \dfrac{(8.46)(8\times60\times60)(107.8)}{(96500\text{ C mol}^{-1})} = 272.18$g

Volume of silver plated out

$$V = \frac{m}{\rho} = \frac{272.18}{10.5} = 25.92 \text{ cm}^3$$

Area of tray plated = $\dfrac{25.92}{0.00254} = 10204.7$ cm^2

Example 20 :

Calculate the standard emf of the reaction

$Fe^{3+} + 3e^- \to Fe(s)$; $E^0_3 = ?$

Given : $Fe^{3+} + e^- \to Fe^{2+}$; $E^0_1 = 0.771$ V

$Fe^{2+} + 2e^- \to Fe(s)$; $E^0_2 = -0.44$ V

Sol. With the help of calculation of free energy

$$\Delta G^0_1 = -nFE^\circ = -(1)(F)(0.771\text{V}) = -0.771 \text{ V}$$

$$\Delta G^0_2 = -(2)(F)(0.44) = 0.88 \text{ FV}$$

$$\Delta G^0_3 = -(3)(F)(E^\circ) = -3FE^\circ V$$

The free energy change for the unknown process can be obtained as :

$$\Delta G^0_3 = \Delta G^0_1 + \Delta G^0_2$$

$$-3FE^\circ = -0.771\text{ F} + 0.88\text{ F} = 0.109\text{ F}$$

or $$E^\circ = -\frac{0.109}{3} = -0.036 \text{ V}$$

QUESTION BANK

CHAPTER 3 : ELECTROCHEMISTRY

EXERCISE - 1 [LEVEL-1]

Choose one correct response for each question.

PART - 1 : ELECTROCHEMICAL CELLS

Q.1 In a Daniell cell

(A) The chemical energy liberated during the redox reaction is converted to electrical energy

(B) The electrical energy of the cell is converted to chemical energy

(C) The energy of the cell is utilised in conduction of the redox reaction

(D) The potential energy of the cell is converted into electrical energy

Q.3 A cell from the following which converts electrical energy into chemical energy

(A) Dry cell
(B) Electrochemical cell
(C) Electrolytic cell
(D) None of these

Q.3 Which of the following statement is true for the electrochemical Daniel cell

(A) Electrons flow from copper electrode to zinc electrode.

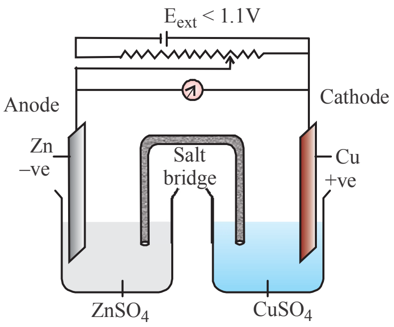
(B) Current flows from zinc electrode to copper electrode.

(C) Cations move toward copper electrode which is cathode.

(D) Cations move toward zinc electrode.

For Q.4-Q.5

Answer the following questions on the basis of the following figure given below.



Q.4 Current will flow from –

(A) Zn rod to Cu rod
(B) Cu rod to Zn rod
(C) no current will flow
(D) salt bridge

Q.5 Which of the following statement(s) is/are true?

(A) Zn dissolves at cathode and copper deposits at anode.

(B) Zn dissolves at anode and copper deposits at cathode.

(C) Zn deposits at anode and copper dissolves at anode.

(D) All of the above

PART - 2 : GALVANIC CELLS

Q.6 Salt bridge contains:

(A) calomel
(B) corrosive sublimate
(C) H_2O
(D) agar–agar paste

Q.7 Fluorine is the best oxidising agent because it has

(A) Highest electron affinity
(B) Highest reduction potential
(C) Highest oxidation potential
(D) Lowest electron affinity

Q.8 A standard hydrogen electrode has a zero potential because

(A) Hydrogen can be most easily oxidised
(B) Hydrogen has only one electron
(C) The electrode potential is assumed to be zero
(D) Hydrogen is the lightest element

Q.9 A galvanic cell with electrode potential of A = +2.23V and B = –1.43V. The value of $E°_{cell}$ is –

(A) 3.66 V
(B) 0.80 V
(C) – 0.80 V
(D) – 3.66 V

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

(A) The spoon will get coated with Al
(B) An alloy of Cu and Al is formed
(C) The solution becomes blue
(D) There is no reaction

Q.11 The charge over anode in a galvanic cell is

(A) Negative
(B) Positive
(C) No charge
(D) Sometimes negative and sometimes positive

Q.12 What does the vertical line (i) and double vertical line (ii) represent in the galvanic cell?

(A) (i) Between two electrolytes connected by salt bridge; (ii) between two electrolytes

(B) (i) Between two electrolytes; (ii) between two electrolytes connected by salt bridge

(C) (i) Between two electrolyte connected by salt bridge; (ii) between metal and electrolyte solution

(D) (i) Between the metal and electrolyte solution; (ii) between two electrolyte connected by salt bridge

Q.13 Which of the following is the correct cell representation for the given cell reaction ?

$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$

(A) $Zn \mid Zn^{2+} \parallel H^+ \mid H_2$
(B) $Zn \mid Zn^{2+} \parallel H^+, H_2 \mid Pt$
(C) $Zn \mid ZnSO_4 \parallel H_2SO_4 \mid Zn$
(D) $Zn \mid H_2SO_4 \parallel ZnSO_4 \mid H_2$

Q.14 Which of the following is the correct order in which metals displace each other from the salt solution of their salts ?

(A) Zn, Al, Mg, Fe, Cu
(B) Cu, Fe, Mg, Al, Zn
(C) Mg, Al, Zn, Fe, Cu
(D) Al, Mg, Fe, Cu, Zn

Q.15 The standard potentials at 25°C for the following half reactions are given against them

$Zn^{2+} + 2e^- \rightarrow Zn, E° = -0.762$ V

$Mg^{2+} + 2e^- \rightarrow Mg, E° = 2.37$ V

When zinc dust is added to a solution of magnesium chloride

(A) No reaction will take place
(B) Zinc chloride is formed
(C) Zinc dissolve in solution
(D) Magnesium is precipitated

Q.16 In the cell, $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$, the negative terminal is

(A) Cu
(B) Cu^{2+}
(C) Zn
(D) Zn^{2+}

Q.17 An electrochemical cell can behave like an electrolytic cell when

(A) $E_{cell} = 0$
(B) $E_{cell} > E_{ext}$
(C) $E_{ext} > E_{cell}$
(D) $E_{cell} = E_{ext}$

Q.18 Consider the Galvanic cell

$Zn^- \mid ZnSO_4 \parallel CuSO_4 + Cu^{\oplus}$

the reaction at cathode is

(A) $Cu^{2+} + 2e^- \rightarrow Cu$
(B) $Zn^{2+} + 2e^- \rightarrow Zn$
(C) $Cu^{2+} + 2e^- \rightarrow Cu + Zn^{2+}$
(D) $Zn^{2+} + Cu \rightarrow Zn + Cu^{2+}$

Q.19 Following reactions are taking place in a Galvanic cell,

$Zn \rightarrow Zn^{2+} + 2e^-; Ag^+ + e^- \rightarrow Ag$

Which of the given representations is the correct method of depicting the cell ?

(A) $Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Ag^+_{(aq)} \mid Ag_{(s)}$
(B) $Zn^{2+} \mid Zn \parallel Ag \mid Ag^+$
(C) $Zn_{(aq)} \mid Zn^{2+}_{(s)} \parallel Ag^+_{(s)} \mid Ag_{(aq)}$
(D) $Zn_{(s)} \mid Ag^+_{(aq)} \parallel Zn^{2+}_{(aq)} \mid Ag_{(s)}$

Q.20 Electrode potential data of few cells are :

$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)};$ $E° = +0.77$ V
$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)};$ $E° = -1.66$ V
$Br_{2(aq)} + 2e^- \rightarrow 2Br^-_{(aq)};$ $E° = +1.09$ V

Arrange the ions in increasing order of their reducing power.

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

Q.21 $Pt (s) \mid H_2(g, 1bar) \mid H^+ (aq, 1 M) \parallel Cu^{2+}(aq, 1M) \mid Cu$

The measured emf of the cell is 0.34 V means

(A) Cu^{2+} ions get reduced easily than H^+ ion.
(B) Hydrogen ions cannot oxidise Cu.
(C) Copper does not dissolve in HCl.
(D) All of the above

Q.22 Which of the following statements is not correct about an inert electrode in a cell ?

(A) It does not participate in the cell reaction.
(B) It provides surface either for oxidation or for reduction reaction.
(C) It provides surface for conduction of electrons.
(D) It provides surface for redox reaction.

Q.23 Which of the following statement is correct?

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

Q.24 What will be standard cell potential of galvanic cell with the following reaction ?

$2Cr_{(s)} + 3Cd^{2+}_{(aq)} \rightarrow 2Cr^{3+}_{(aq)} + 3Cd_{(s)}$

[Given $E°_{Cr^{3+}/Cr} = -0.74$ V and $E°_{Cd^{2+}/Cd} = -0.40$ V]

(A) 0.74 V
(B) 1.14 V
(C) 0.34 V
(D) –0.34 V

Q.25 Which cell will measure standard electrode potential of copper electrode ?

(A) $Pt_{(s)} \mid H_2(g, 0.1 bar) \mid H^+(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu$
(B) $Pt_{(s)} \mid H_2(g, 1bar) \mid H^+(aq., 1M) \parallel Cu^{2+}(aq., 2M) \mid Cu$
(C) $Pt_{(s)} \mid H_2(g, 1bar) \mid H^+(aq., 1M) \parallel Cu^{2+}(aq., 1M) \mid Cu$
(D) $Pt_{(s)} \mid H_2(g, 1bar) \mid H^+(aq., 0.1M) \parallel Cu^{2+}(aq., 1M) \mid Cu$

Q.26 The cell reaction of the galvanic cell;

$Cu_{(s)} \mid Cu^{2+}(aq) \parallel Hg^{2+}_{(aq)} \mid Hg\ (l)$ is

(A) $Hg + Cu^{2+} \rightarrow Hg^{2+} + Cu$
(B) $Hg + Cu^{2+} \rightarrow Cu^+ + Hg^+$
(C) $Cu + Hg \rightarrow CuHg$
(D) $Cu + Hg^{2+} \rightarrow Cu^{2+} + Hg$

PART - 3 : NERNST EQUATION

Q.27 Select the most appropriate relationship between equilibrium constant and standard potential of the cell.

(A) $E°_{cell} = \frac{nF}{2.303RT} \log K_c$
(B) $E°_{cell} = \frac{2.303\,R}{F} \log K_c$
(C) $E°_{cell} = \frac{2.303\,nF}{RT} \log K_c$
(D) $E°_{cell} = \frac{2.303\,RT}{nF} \log K_c$

Q.28 Equilibrium constant K is related to $E°_{cell}$ and not E_{cell} because :

(A) $E°_{cell}$ is easier to measure than E_{cell}
(B) E_{cell} becomes zero at equilibrium point but $E°_{cell}$ remains constant under all conditions.
(C) At a given temperature, E_{cell} changes hence value of K can't be measured.
(D) Any of the terms E_{cell} or $E°_{cell}$ can be used.

Q.29 The relationship between standard reduction potential of cell and equilibrium constant is shown

(A) $E^0_{cell} = \frac{n}{0.059} \log K_c$
(B) $E^0_{cell} = \frac{0.059}{n} \log K_c$
(C) $E^0_{cell} = 0.059\, n \log K_c$
(D) $E^0_{cell} = \frac{\log K_c}{n}$

Q.30 If the Zn^{2+}/Zn electrode is diluted to 100 times then the change in e.m.f.

(A) Increase of 59mV
(B) Decrease of 59mV
(C) Increase of 29.5 mV
(D) Decrease of 29.5 mV

Q.31 Which one of the following will increase the voltage of the cell? (T = 298 K)
$Sn + 2Ag^+ \rightarrow Sn^{2+} + 2Ag$
(A) increase in the size of silver rod
(B) increase in the concentration of Sn^{+2} ions
(C) increase in the concentration of Ag^+ ions
(D) none of the above

Q.32 Cell reaction is spontaneous, when
(A) E^o_{red} is negative (B) ΔG^o is negative
(C) E^o_{oxid} is positive (D) ΔG^o is positive

Q.33 Mark the correct Nernst equation for the given cell.
$Fe_{(s)}|Fe^{2+}(0.001M)\,||\,H^+(1M)|H_{2(g)}\,(1bar)|Pt_{(s)}$

(A) $E_{cell} = E^o_{cell} - \dfrac{0.591}{2}\log\dfrac{[Fe^{2+}]\,[H^+]^2}{[Fe]\,[H_2]}$

(B) $E_{cell} = E^o_{cell} - \dfrac{0.591}{2}\log\dfrac{[Fe]\,[H^+]^2}{[Fe^{2+}]\,[H_2]}$

(C) $E_{cell} = E^o_{cell} - \dfrac{0.0591}{2}\log\dfrac{[Fe^{2+}]\,[H_2]}{[Fe]\,[H^+]^2}$

(D) $E_{cell} = E^o_{cell} - \dfrac{0.0591}{2}\log\dfrac{[Fe]\,[H_2]}{[Fe^{2+}]\,[H^+]^2}$

Q.34 E° value of Ni^{2+}/Ni is –0.25 V and Ag^+/Ag is +0.80 V. If a cell is made by taking the two electrodes what is the feasibility of the reaction ?
(A) Since E° value for the cell will be positive, redox reaction is feasible.
(B) Since E° value for the cell will be positive, redox reaction is feasible.
(C) Ni cannot reduce Ag^+ to Ag hence reaction is not feasible.
(D) Ag can reduce Ni^{2+} to Ni hence reaction is feasible.

PART - 4 : CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

Q.35 Which of the following statement is true for molar conductivity ?
(A) It differ due to charge and size of ions in which they dissociate.
(B) $\Lambda_m\,(S\,cm^2\,mol^{-1})$

$$= \frac{\kappa\,(S\,cm^{-1})}{1000\,Lm^{-3} \times \text{molarity}\,(mol\,L^{-1})}$$

(C) $\Lambda_m\,(S\,cm^2\,mol^{-1})$

$$= \frac{\kappa\,(S\,cm^{-1}) \times 1000\,(cm^3/L)}{\text{Molarity}\,(mol\,L^{-1})}$$

(D) All of the above

Q.36 Which of the statements about solutions of electrolytes is not correct ?
(A) Conductivity depends upon viscosity of solution
(B) Conductivity of solution increases with temperature.
(C) Conductivity does not depend upon solvation of ions present in solution.
(D) None of these

Q.37 Mark the incorrect statement
(A) The limiting equivalent conductance for weak electrolytes can be computed with the help of Kohlrausch's law.
(B) EMF of a cell is the difference in the reduction potentials of cathode and anode.
(C) For cell reaction to occur spontaneously, the EMF of the cell should be negative.
(D) Fluorine is the strongest oxidising agent as its reducing potential is very high.

Q.38 The specific conductivity of N/10 KCl solution at 20°C is 0.0212 $ohm^{-1}\,cm^{-1}$ and the resistance of cell containing this solution at 20°C is 55 ohm. The cell constant is
(A) 1.166 cm^{-1} (B) 2.173 cm^{-1}
(C) 3.324 cm^{-1} (D) 4.616 cm^{-1}

Q.39 Conductivity of a strong electrolyte –
(A) Increases on dilution
(B) Does not change considerably on dilution
(C) Decreases on dilution
(D) Depends on density

Q.40 The molar conductivity is maximum for the solution of concentration –
(A) 0.001 M (B) 0.005 M
(C) 0.002 M (D) 0.004 M

Q.41 If the half cell reaction $A + e^- \rightarrow A^-$ has a large negative reduction potential, it follows that –
(A) A is readily reduced
(B) A is readily oxidised
(C) A^- is readily reduced
(D) A^- is readily oxidised

Q.42 In aqueous solution, strong electrolytes
(A) Are partially ionized
(B) Do not ionise
(C) Ionise almost completely
(D) Form polymers

Q.43 If X is the specific resistance of the solution and M is the molarity of the solution, the molar conductivity of the solution is given by
(A) $\dfrac{1000X}{M}$ (B) $\dfrac{1000}{MX}$
(C) $\dfrac{1000M}{X}$ (D) $\dfrac{MX}{1000}$

Q.44 The electrolytic conductance is a direct measure of
(A) Resistance (B) Potential
(C) Concentration (D) Dissociation

Q.45 Which of the following is not a non electrolyte
(A) Acetic acid (B) Glucose
(C) Ethanol (D) Urea

Q.46 The factor which is not affecting the conductivity of any solution is
(A) Dilution (B) Nature of electrolyte
(C) Temperature (D) None of these

Q.47 The limiting molar conductivities $\wedge^\circ$ for NaCl, KBr and KCl are 126, 152 and 150Scm^{2}mol^{-1} respectively. The $\wedge^\circ$ for NaBr is

(A) 128 S cm^2 mol^{-1} (B) 176 S cm^2 mol^{-1}

(C) 278 S cm^2 mol^{-1} (D) 302 S cm^2 mol^{-1}

Q.48 The conductance of electrolytic solution kept between the electrodes of conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution. This is called

(A) limiting molar conductivity

(B) molar conductivity

(C) conductivity

(D) All of the above

Q.49 Molar conductivity of 0.15 M solution of KCl at 298 K, if its conductivity is 0.0152 S cm^{-1} will be :

(A) 124 Ω^{-1} cm^2 mol^{-1} (B) 204 Ω^{-1} cm^2 mol^{-1}

(C) 101 Ω^{-1} cm^2 mol^{-1} (D) 300 Ω^{-1} cm^2 mol^{-1}

Q.50 Limiting molar conductivity of NaBr is

(A) $\Lambda^o_m \text{NaBr} = \Lambda^o_m \text{NaCl} + \Lambda^o_m \text{KBr}$

(B) $\Lambda^o_m \text{NaBr} = \Lambda^o_m \text{NaCl} + \Lambda^o_m \text{KBr} - \Lambda^o_m \text{KCl}$

(C) $\Lambda^o_m \text{NaBr} = \Lambda^o_m \text{NaOH} + \Lambda^o_m \text{NaBr} - \Lambda^o_m \text{NaCl}$

(D) $\Lambda^o_m \text{NaBr} = \Lambda^o_m \text{NaCl} - \Lambda^o_m \text{NaBr}$

Q.51 "Limiting molar conductivity of an electrolyte can be represented as sum of the individual contributions of anion and cation of the electrolyte".

Which law states the above statement?

(A) Independent migration of ions

(B) Kohlrausch law

(C) Kohlrausch law of independent migration of ions

(D) All of the above

Q.52 The cell constant of a conductivity cell ....

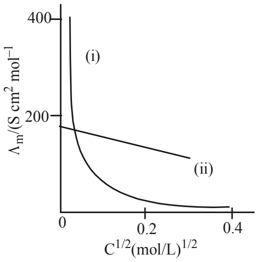
(A) Changes with change of electrolyte

(B) Changes with change of concentration of electrolyte

(C) Changes with temperature of electrolyte

(D) Remains constant for a cell

Q.53 The graph of molar conductivity versus $C^{1/2}$ is plotted. Which type of electrolyte are used in (i) and (ii) ?



(A) (i)-weak electrolyte, (ii)-strong electrolyte

(B) (i)-strong electrolyte, (ii)-weak electrolyte

(C) (i)-weak electrolyte, (ii)-weak electrolyte

(D) (i)-strong electrolyte, (ii)-strong electrolyte

Q.54 The molar conductivity is maximum for the solution of concentration

(A) 0.004 M (B) 0.002 M

(C) 0.005 M (D) 0.001 M

Q.55 Which of the following formula is applicable for weak electrolyte ?

(A) $\alpha = \dfrac{\Lambda_m}{\Lambda^\circ_m}$ (B) $K_a = \dfrac{C\alpha^2}{1-\alpha}$

(C) $K_a = \dfrac{C\Lambda^2_m}{\overset{\circ}{\Lambda}_m(\overset{\circ}{\Lambda}_m - \Lambda_m)}$ (D) All of the above

Q.56 $\Lambda^o_{m(NH_4OH)}$ is equal to

(A) $\Lambda^o_{m(NH_4OH)} + \Lambda^o_{m(NH_4Cl)} - \Lambda^o_{m(HCl)}$

(B) $\Lambda^o_{m(NH_4Cl)} + \Lambda^o_{m(NaOH)} - \Lambda^o_{m(NaCl)}$

(C) $\Lambda^o_{m(NH_4Cl)} + \Lambda^o_{m(NaCl)} - \Lambda^o_{m(NaOH)}$

(D) $\Lambda^o_{m(NaOH)} + \Lambda^o_{m(NaCl)} - \Lambda^o_{m(NH_4Cl)}$

Q.57 Electrical conductance through metals is called metallic or electronic conductance and is due to the movement of electrons. The electronic conductance depends on :

(A) The nature and structure of the metal

(B) The number of valence electrons per atom

(C) Change in temperature

(D) All of these

Q.58 Specific conductance of 0.1 M NaCl solution is 1.01×10^{-2} ohm^{-1} cm^{-1}. Its molar conductance in ohm^{-1} cm^2 mol^{-1} is :

(A) 1.01×10^2 (B) 1.01×10^3

(C) 1.01×10^4 (D) 1.01

PART - 5 : ELECTROLYTIC CELLS AND ELECTROLYSIS

Q.59 Which of the following statements is true ?

(A) When an aqueous solution of NaCl is electrolysed, sodium metal is deposited at cathode,

(B) There is no difference between specific conductivity and molar conductivity.

(C) Silver nitrate solution can be stored in a copper container.

(D) The addition of liquid bromine to iodide solution turns it violet.

Q.60 On electrolysing a solution of dilute H_2SO_4 between platinum electrodes, the gas evolved at the anode is –

(A) SO_2 (B) SO_3

(C) O_2 (D) H_2

Q.61 Electrolysis of molten anhydrous calcium chloride produces –

(A) Calcium (B) Phosphorus

(C) Sulphur (D) Sodium

Q.62 The platinum electrodes were immersed in a solution of cupric sulphate and electric current passed through the solution. After some time it was found that colour of copper sulphate disappeared with evolution of gas at the electrode. The colourless solution contains

(A) Platinum sulphate (B) Copper hydroxide

(C) Copper sulphate (D) Sulphuric acid

Q.63 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) O_2, SO_2

Q.64 How many Faradays are required to generate one gram atom of magnesium from $MgCl_2$

(A) 1 (B) 2

(C) 3 (D) 4

Q.65 Refining of impure copper with zinc impurity is to be done by electrolysis using electrods as –

Cathode	Anode
(A) Pure copper	Pure zinc
(B) Pure zinc	Pure copper
(C) Pure copper	Impure copper
(D) Pure zinc	Impure zinc

Q.66 When during electrolysis of a solution of $AgNO_3$ 9650 coulombs of charge pass thorugh the electroplating bath, the mass of silver deposited on the cathode will be –

(A) 21.6 g (B) 108 g

(C) 1.08 g (D) 10.8 g

Q.67 During the electrolysis of dilute sulphuric acid, the following process is possible at anode

(A) $2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$

(B) $2SO_4^{2-}{}_{(aq)} \rightarrow S_2O_8^{2-}{}_{(aq)} + 2e^-$

(C) $H_2O_{(l)} \rightarrow H^+_{(aq)} + OH^-_{(aq)}$

(D) $H_2O_{(l)} + e^- \rightarrow \frac{1}{2} H_{2(g)} + OH^-_{(aq)}$

Q.68 The charge required for reducing 1 mole of MnO_4^- to Mn^{2+} is

(A) 1.93×10^5 C (B) 2.895×10^5 C

(C) 4.28×10^5 C (D) 4.825×10^5 C

Q.69 If a current of 1.5 ampere flows through a metallic wire for 3 hours, then how many electrons would flow through the wire ?

(A) 2.25×10^{22} e^- (B) 1.13×10^{23} e^-

(C) 1.01×10^{23} e^- (D) 4.5×10^{23} e^-

Q.70 When an aqueous solution of $AgNO_3$ is electrolysed between platinum electrodes, the substances liberated at anode and cathode are

(A) Silver is deposited at cathode and O_2 is liberated at anode.

(B) Silver is deposited at cathode and H_2 is liberated at anode.

(C) Hydrogen is liberated at cathode and O_2 is liberated at anode.

(D) Silver is deposited at cathode and Pt is dissolved in electrolyte.

PART - 6 : BATTERIES

Q.71 Which of the following would occur when lead storage cell is charged?

(A) sulphuric acid is consumed

(B) sulphuric acid is formed

(C) lead sulphate is formed

(D) lead is consumed

Q.72 Which colourless gas evolves, when NH_4Cl reacts with zinc in a dry cell battery

(A) NH_4 (B) N_2

(C) H_2 (D) Cl_2

Q.73 The acid used in lead storage battery is

(A) H_2SO_4 (B) H_3PO_4

(C) HCl (D) HNO_3

Q.74 During discharge of a lead storage cell the density sulphuric acid in the cell:

(A) Increases

(B) Decreases

(C) remains unchanged

(D) initially increases but decrease subsequently

Q.75 When a lead storage battery is discharged,

(A) Lead sulphate is consumed

(B) Oxygen gas is evolved

(C) Lead sulphate is formed

(D) Lead sulphide is formed

Q.76 While charging the lead storage battery ......

(A) $PbSO_4$ anode is reduced to Pb

(B) $PbSO_4$ cathode is reduced to Pb

(C) $PbSO_4$ cathode is oxidised to Pb

(D) $PbSO_4$ anode is oxidised to PbO_2

Q.77 Some of the batteries are rechargeable:

I. Fuel cell , II. Dry cell, III.Lead-storage,
IV Nickel-Cadmium, V. Lithium

Select the batteries which can be recharged

(A) I, II and III (B) III, IV and V

(C) III, IV and V (D) None of above

PART - 7 : FUEL CELLS

Q.78 Which of the following statements is true for fuel cells?

(A) They are more efficient

(B) They are free from pollution

(C) They run till reactants are active

(D) All of these

Q.79 The overall reaction of a hydrogen-oxygen fuel cell is

(A) $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

(B) $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$

(C) $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

(D) $4OH^-_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$

PART - 8 : CORROSION

Q.80 When iron is rusted, it is:

(A) reduced (B) oxidised

(C) evaporated (D) decomposed

Q.81 Aluminium is more reactive than Fe. But Al is less easily corroded than iron because

(A) Al is noble metal

(B) Iron forms both mono and divalent ions

(C) Oxygen forms a protective oxide layer

(D) Fe undergoes reaction easily with H_2O

Q.82 The formation of rust on the surface of iron occurs through the reaction(s)

(A) $Fe^{2+}(aq) + O_2(g) + 4H_2O(\ell) \rightarrow 2Fe_2O_3(s) + 8H^+$

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

(C) $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(\ell)$ (at cathode)

(D) all of these

EXERCISE - 2 [LEVEL-2]

Choose one correct response for each question.

Q.1 Which one of the following metals could not be obtained on electrolysis of aqueous solution of its salts –
(A) Ag (B) Mg
(C) Cu (D) Cr

Q.2 The atomic weight of Al is 27. When a current of 5 Faradays is passed through a solution of Al^{3+} ions, the weight of Al deposited is
(A) 27 gm (B) 36 gm
(C) 45 gm (D) 39 gm

Q.3 On passing 3 ampere of electricity for 50 minutes, 1.8 gram metal deposits. The equivalent mass of metal is
(A) 20.5 (B) 25.8
(C) 19.3 (D) 30.7

Q.4 Charge required to liberate 11.5 g sodium is
(A) 0.5 F (B) 0.1 F
(C) 1.5 F (D) 96500 C

Q.5 Given $\ell / a = 0.5 cm^{-1}, R = 50 ohm, N = 1.0$.
The equivalent conductance of the electrolytic cell is
(A) $10\ ohm^{-1}cm^{2}gm\,eq^{-1}$ (B) $20\ ohm^{-1}cm^{2}gm\,eq^{-1}$
(C) $300\ ohm^{-1}cm^{2}gmeq^{-1}$ (D) $100 ohm^{-1}cm^{2}\ gmeq^{-1}$

Q.6 The standard EMF for the given cell reaction
$Zn + Cu^{2+} = Cu + Zn^{2+}$ is 1.10V at 25°C. The EMF for the cell reaction, when 0.1M Cu^{2+} and 0.1M Zn^{2+} solutions are used, at 25°C is –
(A) 1.10V (B) 0.110V
(C) –1.10V (D) – 0.110V

Q.7 A gas X at 1 atm is bubbled through a solution containing a mixture of 1 MY^{-} and 1 MZ^{-} at 25°C. If the reduction potential of Z > Y > X,
(A) Y will oxidize X and not Z
(B) Y will oxidize Z and not X
(C) Y will oxidize both X and Z
(D) Y will reduce both X and Z

Q.8 When 9.65 coulombs of electricity is passed through a solution of silver nitrate (atomic weight of Ag = 107.87 taking as 108) the amount of silver deposited is
(A) 10.8 mg (B) 5.4 mg
(C) 16.2 mg (D) 21.2 mg

Q.9 A certain current liberated 0.504 gm of hydrogen in 2 hours. How many grams of copper can be liberated by the same current flowing for the same time in a copper sulphate solution
(A) 12.7 gm (B) 15.9 gm
(C) 31.8 gm (D) 63.5 gm

Q.10 In an electroplating experiment mg of silver is deposited, when 4 amperes of current flows for 2 minutes. The amount (in gms) of silver deposited by 6 amperes of current flowing for 40 seconds will be
(A) 4m (B) m/2
(C) m/4 (D) 2m

Q.11 The hydrogen electrode is dipped in a solution of pH = 3 at 25°C. The potential of the cell would be (the value of 2.303RT/F is 0.059 V)
(A) 0.177 V (B) – 0.177 V
(C) 0.087 V (D) 0.059 V

Q.12 EMF of a cell whose half cells are given below is

$$Mg^{2+} + 2e^{-} \rightarrow Mg(s);\ E = -2.37\,V$$

$$Cu^{2+} + 2e^{-} \rightarrow Cu(s);\ E = +0.33\,V$$

(A) – 2.03 V (B) 1.36 V
(C) 2.7 V (D) 2.03 V

Q.13 Calculate standard free energy change for the reaction

$$\frac{1}{2}Cu(s) + \frac{1}{2}Cl_2(g) \rightleftharpoons \frac{1}{2}Cu^{2+} + Cl^{-}$$ taking place

at 25°C in a cell whose standard e.m.f. is 1.02 volts –
(A) – 98430 J (B) 98430 J
(C) 96500 J (D) – 49215 J

Q.14 The E° for half cells Fe/Fe^{2+} and Cu/Cu^{2+} are – 0.44 V and + 0.32 V respectively. Then
(A) Cu^{2+} oxidises Fe (B) Cu^{2+}oxidises Fe^{2+}
(C) Cu oxidises Fe^{2+} (D) Cu reduces Fe^{2+}

Q.15 An electrochemical cell is set up as follows
$Pt(H_2, 1 atm) / 0.1 M\ HCl\ \|\ 0.1 M$ acetic acid /
(H_2, 1 atm) Pt
E.M.F. of this cell will not be zero because
(A) The pH of 0.1 M HCl and 0.1 M acetic acid is not the same.
(B) Acids used in two compartments are different.
(C) E.M.F. of a cell depends on the molarities of acids used.
(D) The temperature is constant.

Q.16 If the ΔG of a cell reaction : $AgCl + e^{-} \rightarrow Ag + Cl^{-}$ is –21.20 KJ; the standard e.m.f., of cell is
(A) 0.229 V (B) 0.220 V
(C) – 0.220 V (D) – 0.110 V

Q.17 A current 2.0 A is passed for 5 hours through a molten metal salt deposits 22 g of metal (At. wt. =177). The oxidation state of the metal in the metal salt is
(A) + 1 (B) + 2
(C) + 3 (D) + 4

Q.18 The quantity of electricity needed to liberate 0.5gram equivalent of an element is
(A) 48250 Faradays (B) 48250 Coulombs
(C) 193000 Faradays (D) 193000 Coulombs

Q.19 The value of electrode potential
(10^{-4} M) H^{+}/H_2 (1 atm)/Pt at 298 K would be
(A) – 0.236 V (B) + 0.404 V
(C) + 0.236 V (D) – 0.476 V

Q.20 The standard emf of a galvanic cell involving 3moles of electrons in its redox reaction is 0.59V. The equilibrium constant for the reaction of the cell is
(A) 10^{20} (B) 10^{25} (C) 10^{30} (D) 10^{15}

Q.21 E_1, E_2 and E_3 are the emfs of the following three galvanic cells respectively:

(i) $Zn(s) \mid Zn^{2+}(0.1\ M) \parallel Cu^{2+}(1M) \mid Cu(s)$

(ii) $Zn(s) \mid Zn^{2+}(1\ M) \parallel Cu^{2+}(1M) \mid Cu(s)$

(iii) $Zn(s) \mid Zn^{2+}(1\ M) \parallel Cu^{2+}(0.1M) \mid Cu(s)$

Which one of the following is true?

(A) $E_1 > E_2 > E_3$
(B) $E_2 > E_1 > E_3$
(C) $E_3 > E_2 > E_1$
(D) $E_3 > E_1 > E_2$

Q.22 How much metal will be deposited when a current of 12 ampere with 75% efficiency is passed through the cell for 3 h ? (Given : $Z = 4 \times 10^{-4}$)

(A) 32.4 g
(B) 38.8 g
(C) 36.0 g
(D) 22.4 g

Q.23 9.65 coulombs of electric current is passed through fused anhydrous $MgCl_2$. The magnesium metal thus obtained is completely converted into a Grignard reagent. The number of moles of Grignard reagent obtained is

(A) 1×10^{-4}
(B) 5×10^{-4}
(C) 1×10^{-6}
(D) 5×10^{-5}

Q.24 The approximate time duration in hours to electroplate 30 g of calcium from molten calcium chlriode using a current of 5 amp is – [At. Mass of Ca = 40]

(A) 8
(B) 80
(C) 10
(D) 16

Q.25 The equilibrium constant of the reaction:

$A(s) + 2B^+(aq) \rightleftharpoons A^{2+}(aq) + 2B(s)$,

$E^\circ_{cell} = 0.0295\ V$ is $\left[\dfrac{2.303RT}{F} = 0.059\right]$

(A) 10
(B) 2×10^2
(C) 3×10^2
(D) 2×10^5

Q.26 Which one of the following has a potential more than zero?

(A) Pt, $\frac{1}{2}H_2\ (1\ atm) \mid HCl\ (1\ M)$

(B) Pt, $\frac{1}{2}H_2\ (1\ atm) \mid HCl\ (2\ M)$

(C) Pt, $\frac{1}{2}H_2\ (1\ atm) \mid HCl\ (0.1\ M)$

(D) Pt, $\frac{1}{2}H_2\ (1\ atm) \mid HCl\ (0.5\ M)$

Q.27 The emf of a galvanic cell constituted with the electrodes $Zn^{2+} \mid Zn\ (-0.76\ V)$ and $Fe^{2+} \mid Fe\ (-0.41V)$ is

(A) –0.35 V
(B) +1.17 V
(C) +0.35 V
(D) –1.17 V

Q.28 For $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O$; $E^o = 1.33\ V$. At $[Cr_2O_7^{2-}] = 4.5$ millimole, $[Cr^{+3}] = 15$ millimole, E is 1.067V. The pH of the solution is nearly equal to

(A) 2
(B) 3
(C) 5
(D) 4

Q.29 Impure copper containing Fe, Au, Ag as impurities is electrolytically refined. A current of 140 A for 482.5 s decreased the mass of the anode by 22.26 g and increased the mass of cathode by 22.011 g. Percentage of iron in impure copper is (Given molar mass Fe = 55.5 g mol^{-1}, molar mass Cu = 63.54 g mol^{-1})

(A) 0.95
(B) 0.85
(C) 0.97
(D) 0.90

Q.30 For hydrogen – oxygen fuel cell at one atm and 298 K

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O\ (\ell)\ ;\ \Delta G^\circ = -240\ kJ$$

E° for the cell is approximately, (Given F = 96,500 C)

(A) 2.48 V
(B) 1.24 V
(C) 2.5 V
(D) 1.26 V

Q.31 Conductivity of a saturated solution of a sparingly soluble salt AB at 298 K is $1.85 \times 10^{-5}\ S\ m^{-1}$. Solubility product of the salt AB at 298 K is

Given $\pi^\circ_m\ (AB) = 140 \times 10^{-4}\ S\ m^2\ mol^{-1}$

(A) 5.7×10^{-12}
(B) 1.32×10^{-12}
(C) 7.5×10^{-12}
(D) 1.69×10^{-12}

Q.32 While charging the lead storage battery,

(A) $PbSO_4$ on anode is reduced to Pb
(B) $PbSO_4$ on cathode is reduced to Pb
(C) $PbSO_4$ on cathode is oxidized to Pb
(D) $PbSO_4$ on anode is oxidized to PbO

Q.33 How many Coulombs of electricity are required for the oxidation of one mol of water to dioxygen?

(A) 9.65×10^4 C
(B) 1.93×10^4 C
(C) 1.93×10^5 C
(D) 19.3×10^5 C

Q.34 A secondary cell is one

(A) can not be recharged.
(B) can be recharged by passing current through it in the opposite direction.
(C) can be recharged by passing current through it in the same direction.
(D) can be recharged.

Q.35 Which of the following is incorrect in a galvanic cell ?

(A) The electrode at which electrons are lost is called cathode.
(B) The electrode at which electrons are gained is called cathode.
(C) Reduction occurs at cathode.
(D) Oxidation occurs at anode.

Q.36 The amount of current in Faraday is required for the reduction of 1 mol of $Cr_2O_7^{--}$ ions to Cr^{3+} is

(A) 4 F
(B) 6 F
(C) 2 F
(D) 1 F

Q.37 For the galvanic cell, $Cu \mid Cu^{2+} \parallel Ag^+ \mid Ag$. Which of the following observation is not correct ?

(A) Cu acts as anode and Ag acts as cathode
(B) Ag electrode loses mass and Cu electrode gains mass.
(C) Reaction at anode, $Cu \rightarrow Cu^{2+} + 2e^-$
(D) Copper is more reactive than silver.

Q.38 Zn gives hydrogen with H_2SO_4 and HCl but not with HNO_3 because

(A) Zn acts as oxidising agent when reacts with HNO_3
(B) HNO_3 is weaker acid than H_2SO_4 and HCl
(C) Zn is above the hydrogen in electrochemical series
(D) NO_3^- is reduced in preference to H^+ ion.

Q.39 For a certain redox reaction, E° is positive. This means that :
(A) ΔG° is positive, K is greater than 1
(B) ΔG° is positive, K is less than 1
(C) ΔG° is negative, K is greater than 1
(D) ΔG° is negative, K is less than 1

Q.40 How much electricity in terms of Faraday is required to produce 100g of Ca from molten $CaCl_2$?
(A) 1 F (B) 2 F
(C) 3 F (D) 5 F

Q.41 What would be the equivalent conductivity of a cell in which 0.5 N salt solution offers a resistance of 40 ohm whose electrodes are 2 cm apart and 5 cm^2 in area ?
(A) 10 ohm^{-1} cm^2 eq^{-1} (B) 20 ohm^{-1} cm^2 eq^{-1}
(C) 30 ohm^{-1} cm^2 eq^{-1} (D) 25 ohm^{-1} cm^2 eq^{-1}

Q.42 The amount of chlorine evolved by passing 2 A of current in an aqueous solution of NaCl for 30 minutes is :
(A) 2.64 g (B) 1.32 g
(C) 3.62 g (D) 4.22 g

Q.43 In a cell reaction, $Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$, $E^o_{cell} = +\ 0.46$ V. If the concentration of Cu^{2+} ions is doubled then E^o_{cell} will be
(A) Doubled (B) Halved
(C) Increased by four times (D) Unchanged

Q.44 If 54 g of silver is deposited during an electrolysis reaction, how much aluminium will be deposited by the same amount of electric current ?
(A) 2.7 g (B) 4.5 g
(C) 27 g (D) 5.4 g

Q.45 Standard reduction electrode potentials of three metals A, Band C are +0.5 V, –3.0 V, & –1.2 V respectively. The reducing power of these metals are:
(A) B > C > A (B) A > B > C
(C) C > B > A (D) A > C > B

Q.46 The standard reduction potential for the half cell reaction, $Cl_2 + 2e^- \rightarrow 2Cl^-$ will be
($Pt^{2+} + 2Cl^- \rightarrow Pt + Cl_2$, $E^\circ_{cell} = -0.15$ V;
$Pt^{2+} + 2e^- \rightarrow Pt$, $E^\circ = 1.20$ V)
(A) –1.35 V (B) +1.35V
(C) –1.05 V (D) +1.05 V

Q.47 A galvanic cell has electrical potential of 1.1 V. If an opposing potential of 1.1 V is applied to this cell, what will happen to the cell reaction and current flowing through the cell ?
(A) The reaction stops and no current flows through the cell.
(B) The reaction continuous but current flows in opposite direction.
(C) The concentration of reactants becomes unity and current flows from cathode to anode.
(D) The cell does not function as a galvanic cell and zinc is deposited on zinc plate.

Q.48 The $E^\circ_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are 0.41, + 1.57, +0.77 and + 1.97 V respectively. For which one of these metals the change in oxidation state from +2 to +3 is easiest:
(A) Co (B) Mn
(C) Fe (D) Cr

Q.49 How much time is required to deposit 1×10^{-3} cm thick layer of silver (density is 1.05 g cm^{-3}) on a surface of area 100 cm^2 by passing a current of 5 A through $AgNO_3$ solution ?
(A) 125 s (B) 115 s
(C) 18.7 s (D) 27.25 s

Q.50 E°_{cell} for the reaction, $2H_2O \rightarrow H_3O^+ + OH^-$ at 25°C is –0.8277 V. The equilibrium constant for the reaction is
(A) 10^{-14} (B) 10^{-23}
(C) 10^{-7} (D) 10^{-21}

Q.51 How many moles of Pt may be deposited on the cathode when 0.80 F of electricity is passed through a 1.0 M solution of Pt^{4+} ?
(A) 0.1 mol (B) 0.2 mol
(C) 0.4 mol (D) 0.6 mol

Q.52 E°_{cell} of the reaction is
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$;
[If $E^\circ_{Zn^{2+}|Zn} = -0.76$, $E^\circ_{Cu^{2+}|Cu} = 0.34$ V]
(A) 0.34 V (B) – 0.76 V
(C) 1.10 V (D) – 1.10V

Q.53 Limiting molar conductivity for some ions is given below (in S cm^2 mol^{-1}) : Na^+ - 50.1, Cl^- - 76.3, H^+ - 349.6, CH_3COO^- 40.9, Ca^{2+} - 119.0.
What will be the limiting molar conductivities (Λ°_m) of $CaCl_2$, CH_3COONa and NaCl respectively ?
(A) 97.65, 111.0 and 242.8 S cm^2 mol^{-1}
(B) 195.3, 182.0 and 26.2 S cm^2 mol^{-1}
(C) 271.6, 91.0 and 126.4 S cm^2 mol^{-1}
(D) 119.0, 1024.5 and 9.2 S cm^2 mol^{-1}

Q.54 Which of the following is the cell reaction that occurs when the following half-cells are combined?
$I_2 + 2e^- \rightarrow 2I^-$ (1 M); $E^\circ = +0.54$ V
$Br_2 + 2e^- \rightarrow 2Br^-$ (1 M); $E^\circ = +1.09$ V
(A) $2Br^- + I_2 \rightarrow Br_2 + 2I^-$ (B) $I_2 + Br_2 \rightarrow 2I^- + 2Br^-$
(C) $2I^- + Br_2 \rightarrow I_2 + 2Br^-$ (D) $2I^- + 2Br^- \rightarrow I_2 + Br_2$

Q.55 A weak monobasic acid is 5% dissociated in 0.01 mol dm^{-3} solution. Limiting molar conductivity of acid at infinite dilution is 4×10^{-2} ohm^{-1} m^2 mol^{-1}. What will be the conductivity of 0.05 mol dm^{-3} solution of the acid ?
(A) 8.94×10^{-6} ohm^{-1} cm^2 mol^{-1}
(B) 8.94×10^{-4} ohm^{-1} cm^2 mol^{-1}
(C) 4.46×10^{-6} ohm^{-1} cm^2 mol^{-1}
(D) 2.23×10^{-5} ohm^{-1} cm^2 mol^{-1}

Q.56 During electrolysis of a solution of $AgNO_3$, 9650 coulombs of charge is passed through the solution. What will be the mass of silver deposited on the cathode?
(A) 108 g (B) 10.8 g
(C) 1.08 g (D) 216 g

Q.57 For a cell reaction : $M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$, the Nernst equation for electrode potential at any concentration measured with respect to standard hydrogen electrode is represented as :

(A) $E_{(M^{n+}/M)} = E^o_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$

(B) $E_{(M/M^{n+})} = E^o_{(M/M^{n+})} - \frac{RT}{nF} \ln \frac{[M^{n+}]}{[M]}$

(C) $E_{(M^{n+}/M)} = E^o_{(M^{n+}/M)} - \frac{RT}{nF} \log \frac{1}{[M]}$

(D) $E_{(M^{n+}/M)} = E^o_{(M^{n+}/M)} - \frac{RT}{nF} \ln [M^{n+}]$

Q.58 I. The potential of individual half-cell can be measured.
II. Difference between the two half–cell potentials can only be measured.
III. Half-cell is called standard hydrogen electrode.
Select the correct statement(s) and choose the appropriate option.
(A) I and II
(B) II and III
(C) III and I
(D) I, II and III

Q.59 What will be the molar conductivity of Al^{3+} ions at infinite dilution if molar conductivity of $Al_2(SO_4)_3$ is 858 S cm^2 mol^{-1} and ionic conductance of SO_4^{2-} is 160 S cm^2 mol^{-1} at infinite dilution ?
(A) 189 S cm^2 mol^{-1}
(B) 698 S cm^2 mol^{-1}
(C) 1018 S cm^2 mol^{-1}
(D) 429 S cm^2 mol^{-1}

For Q.60-Q.64

$$E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33V \; ; \; E^o_{Cl_2/Cl^-} = 1.36V$$

$$E^o_{MnO_4^-/Mn^{2+}} = 1.51V \; ; \; E^o_{Cr^{3+}/Cr} = -0.74V$$

Q.60 Find out the strongest reducing agent.
(A) Cl^-
(B) Cr
(C) Cr^{3+}
(D) Mn^{2+}

Q.61 Find out which of the following is the strongest oxidising agent.
(A) Cl^-
(B) Mn^{2+}
(C) MnO_4^-
(D) Cr^{3+}

Q.62 Find out in which option the order of reducing power is correct.
(A) $Cr^{3+} < Cl^- < Mn^{2+} < Cr$
(B) $Mn^{2+} < Cl^- < Cr^{3+} < Cr$
(C) $Cr^{3+} < Cl^- < Cr_2O_7^{2-} < MnO_4^-$
(D) $Mn^{2+} < Cr^{3+} < Cl^- < Cr$

Q.63 Find out the most stable ion in its reduced form.
(A) Cl^-
(B) Cr^{3+}
(C) Cr
(D) Mn^{2+}

Q.64 Find out the most stable oxidised species.
(A) Cr^{3+}
(B) MnO_4^-
(C) $Cr_2O_7^{2-}$
(D) Mn^{2+}

EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)

NOTE : The answer to each question is a NUMERICAL VALUE.

Q.1 Calculate the volume of Cl_2 (in nearest integer in litre) at NTP produced during electrolysis of $MgCl_2$ which produces 6.50 g Mg. At. wt. of Mg = 24.3

Q.2 A current of 3 ampere has to be passed for $\frac{375.127}{x}$ sec. in a solution of $AgNO_3$ to coat a metal surface of 80 cm^2 with 0.005 mm thick layer. Density of Ag is 10.5 g/cm^3. Find the value of x.

Q.3 If 3 Faradays of electricity are passed through a solution of ferrous bromide, how many grams of iron will be deposited if its atomic weight is 56 ?

Q.4 The equilibrium constant for the reaction at 25ºC.
$Fe + CuSO_4 \rightleftharpoons FeSO_4 + Cu$ is 2.18×10^x. Find the value of x.

[Given $E^o_{OP_{Fe}} = 0.44$ V; $E^o_{OP_{Cu}} = 0.337$ V]

Q.5 An electric current is passed through three cells connected in series containing $ZnSO_4$, acidulated water and $CuSO_4$ respectively. What amount of Zn (in nearest integer in gm.) produced when 6.25 g of Cu is deposited ? Eq. wt. of Cu and Zn are 31.70 and 32.6 respectively.

Q.6 All the energy released from the reaction $X \rightarrow Y$, $\Delta_r G^o = -193$ kJ mol^{-1} is used for oxidizing M^+ as
$M^+ \rightarrow M^{3+} + 2e^-$, $E^o = -0.25V$.
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}]

Q.7 The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\lambda^0_{X^-} \approx \lambda^0_{Y^-}$, the difference in their pK_a values, pK_a (HX) – pK_a (HY), is (Consider degree of ionization of both acids to be <<1)

Q.8 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 1cm^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 ($\Lambda^0{}_m$) of this weak monobasic acid in aqueous solution is $Z \times 10^2 Scm^{-1}mol^{-1}$ The value of Z is _________.

Q.9 The standard oxidation potential of Ni/Ni^{+2} electrode is 0.236 V. If this is combined with a hydrogen electrode in acid solution, at what pH of the solution will the measured emf be zero at 25ºC. Assume $[Ni^{+2}] = 1M$.

Q.10 A certain metal salt solutions is electrolysed in series with a silver coulometer. The weights of silver and the metal deposited are 0.5094 g and 0.2653 g. The valency of the metal if its atomic weight is nearly that of silver is

EXERCISE - 4 [PREVIOUS YEARS JEE MAIN QUESTIONS]

Q.1 For the following cell with hydrogen electrodes at two different pressure p_1 and p_2

$Pt(H_2) \mid H^+(aq.) \mid Pt(H_2)$ emf is given by – **[AIEEE-2002]**

$\quad p_1 \qquad\qquad p_2$

(A) $\frac{RT}{F}\log_e\frac{p_1}{p_2}$

(B) $\frac{RT}{2F}\log_e\frac{p_1}{p_2}$

(C) $\frac{RT}{F}\log_e\frac{p_2}{p_1}$

(D) $\frac{RT}{2F}\log_e\frac{p_2}{p_1}$

Q.2 Which of the following reaction is possible at anode ?

(A) $F_2 + 2e^- \longrightarrow 2F^-$ **[AIEEE-2002]**

(B) $2H^+ + \frac{1}{2}O_2 + 2e^- \longrightarrow H_2O$

(C) $2Cr^{3+} + 7H_2O \longrightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$

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

Q.3 Refining of impure copper with zinc impurity is to be done by electrolysis using electrods as – **[AIEEE-2002]**

Cathode	Anode
(A) Pure copper	Pure zinc
(B) Pure zinc	Pure copper
(C) Pure copper	Impure copper
(D) Pure zinc	Impure zinc

Q.4 For a cell given below

$Ag \mid Ag^+ \parallel Cu^{2+} \mid Cu$

$\quad - \qquad\qquad +$

$Ag^+ + e^- \longrightarrow Ag,\ E^o = x$

$Cu^{2+} + 2e^- \longrightarrow Cu,\ E^o = y$

E° cell is – **[AIEEE-2002]**

(A) $x + 2y$

(B) $2x + y$

(C) $y - x$

(D) $y - 2x$

Q.5 For a cell reaction involving a two-electron change the standard e.m.f. of the cell is found to be 0.295 V 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}

Q.6 Standard reduction electrode potentials of three metals A, B and C are respectively +0.5 V, – 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

Q.7 For the redox reaction :

$Zn(s) + Cu^{2+}(0.1M) \rightarrow Zn^2 + (1M) + Cu(s)$

taking place in a cell, E^o_{cell} is 1.10 volt. Ecell for the cell will be $\left(2.303\frac{RT}{F} = 0.0591\right)$ **[AIEEE-2003]**

(A) 1.07 volt

(B) 0.82 volt

(C) 2.14 volt

(D) 1.8 volt

Q.8 When during electrolysis of a solution of $AgNO_3$ 9650 coulombs of charge pass thorugh the electroplating bath, the mass of silver deposited on the cathode will be –

(A) 21.6 g

(B) 108 g **[AIEEE-2003]**

(C) 1.08 g

(D) 10.8 g

Q.9 Consider the following E° values **[AIEEE-2004]**

$$E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77\text{ V}\ ;\ E^\circ_{Sn^{2+}/Sn} = -0.14\text{ V}$$

Under standard conditions the potential for the reaction $Sn_{(s)} + 2Fe^{3+}{}_{(aq)} \rightarrow 2\,Fe^{2+}{}_{(aq)} + Sn^{2+}{}_{(aq)}$ is

(A) 1.68 V

(B) 1.40 V

(C) 0.91 V

(D) 0.63 V

Q.10 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 ($F = 96500\ C\ mol^{-1}$; $R = 8.314\ JK^{-1}\ mol^{-1}$) **[AIEEE-2004]**

(A) 1.0×10^1

(B) 1.0×10^5

(C) 1.0×10^{10}

(D) 1.0×10^{30}

Q.11 The limiting molar conductivities $\wedge^\circ$ for NaCl, KBr and KCl are 126, 152 and 150 S cm² mol⁻¹ respectively. The $\wedge^\circ$ for NaBr is **[AIEEE-2004]**

(A) $128\ S\ cm^2\ mol^{-1}$

(B) $176\ S\ cm^2\ mol^{-1}$

(C) $278\ S\ cm^2\ mol^{-1}$

(D) $302\ S\ cm^2\ mol^{-1}$

Q.12 In a cell that utilises the reaction

$Zn_{(s)} + 2H^+{}_{(aq)} \rightleftarrows Zn^{2+}{}_{(aq)} + H_{2(g)}$ addition of H_2SO_4 to cathode compartment, will - **[AIEEE-2004]**

(A) lower the E and shift equilibrium to the left

(B) lower the E and shift equilibrium right

(C) increase the E and shift equilibrium to the right

(D) increase the E and shift equilibrium to the left

Q.13 Aluminium oxide may be electrolysed at 1000°C to furnish aluminium metal (At. Mass = 27 amu ; 1 Faraday = 96,500 Coulombs). The cathode reaction is $Al^{3+} + 3e^- \longrightarrow Al^o$

To prepare 5.12 kg of aluminium metal by this method would require - **[AIEEE-2005]**

(A) 1.83×10^7 C of electricity

(B) 5.49×10^7 C of electricity

(C) 5.49×10^1 C of electricity

(D) 5.49×10^4 C of electricity

Q.14

Electrolyte	KCl	KNO_3	HCl	NaOAc	NaCl
$\Lambda^\infty(S\,cm^2mol^{-1})$:	149.9	145.0	426.2	91.0	126.5

Calculate $\wedge^\infty_{HOAc}$ using appropriate molar conductance of the electrolytes listed above at infinite dilution in H_2O at 25°C **[AIEEE-2005]**

(A) 552.7

(B) 517.2

(C) 217.5

(D) 390.7

Q.15 Given the data at 25°C,

$Ag + I^- \rightarrow AgI + e^- \qquad E^o = 0.152\ V$

$Ag \rightarrow Ag^+ + e^- \qquad E^o = -0.800\ V$

What is the value of log K_{sp} for AgI?

(2.303 RT/F = 0.059V) **[AIEEE 2006]**

(A) +8.612

(B) –37.83

(C) –16.13

(D) –8.12

Q.16 The cell, Zn $|Zn^{2}$ (1M)| | Cu^{2+} (1M) | Cu (E^{o}_{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) Antilog (24.08) (B) 37.3
(C) $10^{37.3}$ (D) 9.65×10^{4}

Q.17 The equivalent conductances of two strong electrolytes at infinite dilution in H_2O (where ions move freely through a solution) at 25ºC are given below **[AIEEE 2007]**

$\Lambda^{o}_{CH_3COONa}$ = 91.0 S cm^2/equiv.

Λ^{o}_{HCl} = 426.2 S cm^2/equiv.

What additional information/quantity one needs to calculate Λº of an aqueous solution of acetic acid ?

(A) Λº of NaCl
(B) Λº of CH_3COOH
(C) The limiting equivalent conductance of $H^{+}(\lambda^{o}_{H^{+}})$
(D) Λº of chloroacetic acid ($ClCH_2COOH$)

Q.18 Given $E^{0}_{Cr^{3+}/Cr}$ = – 0.72 V, $E^{0}_{Fe^{2+}/Fe}$ = – 0.42 V. The potential for the cell Cr $|Cr^{3+}$ (0.1 M)| $|Fe^{2+}$ (0.01 M) | Fe is - **[AIEEE 2008]**

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

Q.19 Given : $E^{0}_{Fe^{3+}/Fe}$ = – 0.036V, $E^{0}_{Fe^{2+}/Fe}$ = – 0.439 V.

The value of standard electrode potential for the change, Fe^{3+} (aq) + e^{-} → Fe^{2+} (aq) will be – **[AIEEE 2009]**

(A) – 0.270 V (B) – 0.072 V
(C) 0.385 V (D) 0.770 V

Q.20 The Gibbs energy for the decomposition of Al_2O_3 at 500°C is as follows :

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

The potential difference needed for electrolytic reduction of Al_2O_3 at 500°C is at least – **[AIEEE 2010]**

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

Q.21 The reduction potential of hydrogen half-cell will be negative if – **[AIEEE 2011]**

(A) p (H_2) = 1 atm and $[H^{+}]$ = 2.0 M
(B) p (H_2) = 1 atm and $[H^{+}]$ = 1.0 M
(C) p (H_2) = 2 atm and $[H^{+}]$ = 1.0 M
(D) p (H_2) = 2 atm and $[H^{+}]$ = 2.0 M

Q.22 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+} → X^{2+} + Y will be spontaneous when **[AIEEE 2012]**

(A) X = Ni, Y = Fe (B) X = Ni, Y = Zn
(C) X = Fe, Y = Zn (D) X = Zn, Y = Ni

Q.23 Given : $E^{0}_{Cr^{3+}/Cr}$ = –0.74 ; $E^{0}_{MnO_4^{-}/Mn^{2+}}$ = 1.51V

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

Based on the data given above, strongest oxidising agent will be – **[JEE MAIN 2013]**

(A) Cl (B) Cr^{3+}
(C) Mn^{2+} (D) MnO_4^{-}

Q.24 Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^{0}_{M^{3+}/M^{2+}}$ value? **[JEE MAIN 2013]**

(A) Cr (Z = 24) (B) Mn (Z = 25)
(C) Fe (Z = 26) (D) Co (Z = 27)

Q.25 Resistance of 0.2 M solution of an electrolyte is 50Ω. The specific conductance of the solution is 1.4 S m^{-1}. The resistance of 0.5 M solution of the same electrolyte is 280Ω. The molar conductivity of 0.5 M solution of the electrolyte in S m^2 mol^{-1} is – **[JEE MAIN 2014]**

(A) 5×10^{3} (B) 5×10^{2}
(C) 5×10^{-4} (D) 5×10^{-3}

Q.26 The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞ respectively. The correct relationship between λ_C and λ_∞ is given as: (where the constant B is positive) **[JEE MAIN 2014]**

(A) $\lambda_C = \lambda_\infty - (B)\sqrt{C}$ (B) $\lambda_C = \lambda_\infty + (B)\sqrt{C}$
(C) $\lambda_C = \lambda_\infty + (B)\,C$ (D) $\lambda_C = \lambda_\infty - (B)\,C$

Q.27 Given below are the half-cell reactions:

$Mn^{2+} + 2e^{-} \rightarrow Mn$; E° = –1.18 V
$2\,(Mn^{3+} + e^{-} \rightarrow Mn^{2+})$; E° = +1.51 V

The E° for $3Mn^{2+} \rightarrow Mn + 2Mn^{3+}$ will be –

(A) –0.33 V; the reaction will not occur **[JEE MAIN 2014]**
(B) –0.33 V; the reaction will occur
(C) –2.69 V; the reaction will not occur
(D) –2.69 V; the reaction will occur

Q.28 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 MAIN 2015]**

(A) 63.5 g (B) 2 g
(C) 127 g (D) 0 g

Q.29 Galvanization is applying a coating of: **[JEE MAIN 2016]**

(A) Cr (B) Cu
(C) Zn (D) Pb

Q.30 Given : $E^{o}_{Cl_2/Cl^{-}}$ = 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:

(A) Cl^{-} (B) Cr **[JEE MAIN 2017]**
(C) Mn^{2+} (D) Cr^{3+}

Q.31 How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66g of diborane (Atomic weight of B = 10.8u) **[JEE MAIN 2018]**

(A) 3.2 hours (B) 1.6 hours

(C) 6.4 hours (D) 0.8 hours

Q.32 If the standard electrode potential for a cell is 2V at 300 K, the equilibrium constant (K) for the reaction

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

at 300 K is approximately. **[JEE MAIN 2019 (Jan)]**

($R = 8\ JK^{-1}\ mol^{-1}$, $F = 96000\ C\ mol^{-1}$)

(A) e^{160} (B) e^{320}

(C) e^{-160} (D) e^{-80}

Q.33 Given that : $E^0_{O_2/H_2O} = +1.23\ V$, $E^0_{S_2O_8^{2-}/SO_4^{2-}} = +2.05\ V$,

$E^0_{Br_2/Br^-} = +1.09\ V$, $E^0_{Au^{3+}/Au} = +1.4\ V$

The strongest oxidizing agent is **[JEE MAIN 2019 (April)]**

(A) O_2 (B) Br_2

(C) $S_2O_8{}^{2-}$ (D) Au^{3+}

Q.34 Calculate the standard cell potential in (V) of the cell in which following reaction takes place :

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

Given that

$E^0_{Ag^+/Ag} = x\ V$, $E^0_{Fe^{2+}/Fe} = y\ V$; $E^0_{Fe^{3+}/Fe} = z\ V$

[JEE MAIN 2019 (APRIL)]

(A) $x + 2y - 3z$ (B) $x - z$

(C) $x - y$ (D) $x + y - z$

Q.35 A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using 0.1 Faraday electricity. How many mole of Ni will be deposited at the cathode? **[JEE MAIN 2019 (APRIL)]**

(A) 0.20 (B) 0.05

(C) 0.10 (D) 0.15

Q.36 Given that the standard potentials (E°) of Cu^{2+}/Cu and Cu^{+}/Cu are 0.34 V and 0.522 V respectively, the E° of Cu^{2+}/Cu^{+} is : **[JEE MAIN 2020 (JAN)]**

(A) 0.158V (B) –0.158 V

(C) 0.182 V (D) –0.182 V

Q.37 Which of the following is incorrect? **[JEE MAIN 2020 (JAN)]**

(A) $\Lambda^{\circ}_m NaCl - \Lambda^{\circ}_m NaBr = \Lambda^{\circ}_m KCl - \Lambda^{\circ}_m KBr$

(B) $\Lambda^{\circ}_m H_2O = \Lambda^{\circ}_m HCl + \Lambda^{\circ}_m NaOH - \Lambda^{\circ}_m NaCl$

(C) $\Lambda^{\circ}_m NaBr - \Lambda^{\circ}_m NaI = \Lambda^{\circ}_m KBr - \Lambda^{\circ}_m NaBr$

(D) $\Lambda^{\circ}_m NaCl - \Lambda^{\circ}_m KCl = \Lambda^{\circ}_m NaBr - \Lambda^{\circ}_m KBr$

Q.38 What would be the electrode potential for the given half cell reaction at pH = 5 ?______

$2H_2O \rightarrow O_2 + 4H^{\oplus} + 4e^{-}$; $E^0_{red} = 1.23\ V$

($R = 8.314\ J\ mol^{-1}\ K^{-1}$; Temp = 298 K; oxygen under std. atm. pressure of 1 bar) **[JEE MAIN 2020 (JAN)]**

Q.39 For an electrochemical cell

$Sn\ (s)\ |\ Sn^{2+}\ (aq, 1M)\ ||\ Pb^{2+}\ (aq, 1M)\ |\ Pb\ (s)$

Determine $\dfrac{[Sn^{2+}]}{[Pb^{2+}]}$ at equilibrium

Given : $E^{\circ}_{Sn^{2+}/Sn} = -0.14\ V$,

$E^{\circ}_{Pb^{2+}/Pb} = -0.13\ V$; $\dfrac{2.303\ RT}{F} = 0.06\ V$

[JEE MAIN 2020 (JAN)]

EXERCISE - 5 [PREVIOUS YEARS AIPMT / NEET QUESTIONS]

Q.1 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 **[AIPMT 2005]**

(A) 44.8 L (B) 22.4 L

(C) 11.2 L (D) 5.6 L

Q.2 If $E^\circ_{Fe^{2+}/Fe} = -0.441V$ and $E^\circ_{Fe^{3+}/Fe^{2+}} = +771V$, the standard EMF of the reaction $Fe + 2Fe^{3+} \to 3Fe^{2+}$ will be

(A) 1.653V (B) 1.212 V **[AIPMT 2006]**

(C) 0.111V (D) 0.330V

Q.3 A hypothetical electrochemical cell is shown :

$\overset{\Theta}{A} \,|\, A^+(xM) \,||\, B^+(yM) \,\overset{\oplus}{B}$. The emf measured is +0.20V.

The cell reaction is **[AIPMT 2006]**

(A) $A^+ + e^- \to A$; $B^+ + e^- \to B$

(B) The cell reaction cannot be predicted

(C) $A + B^+ \to A^+ + B$

(D) $A^+ + B \to A + B^+$

Q.4 The efficiency of a fuel cell is given by – **[AIPMT 2007]**

(A) $\frac{\Delta G}{\Delta S}$ (B) $\frac{\Delta G}{\Delta H}$ (C) $\frac{\Delta S}{\Delta G}$ (D) $\frac{\Delta H}{\Delta G}$

Q.5 The equilibrium constant of the reaction :

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

E° = 0.46V at 298 K is – **[AIPMT 2007]**

(A) 2.0×10^{10} (B) 4.0×10^{10}

(C) 4.0×10^{15} (D) 2.4×10^{10}

Q.6 Kohlrausch's law states that at: **[AIPMT 2008]**

(A) Infinite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.

(B) finite dilution, each ion makes definite contribution to equivalent conductance of an electrolyte, whatever be the nature of the other ion of the electrolyte.

(C) Infinite dilution each icon makes definite contribution to equivalent conductance of an electrolyte depending on the nature of the other ion of the electrolyte.

(D) Infinite dilution, each ion makes definite contribution to conductance of an electrolyte whatever be the nature of the other ion of the electrolyte.

Q.7 Standard free energies of formation (in kJ/mol) at 298 K are –237.2, –394.4 and –8.2 for $H_2O(\ell)$, $CO_2(g)$ and pentane(g), respectively. The value of E°cell for the pentane-oxygen fuel cell is: **[AIPMT 2008]**

(A) 0.0968V (B) 1.968V

(C) 2.0968V (D) 1.0968V

Q.8 On the basis of the following E° values, the strongest oxidizing agent is: $[Fe(CN)_6]^{4-} \to [Fe(CN)_6]^{3-} + e^{-1}$; E° = – 0.35 V

$Fe^{2+} \to Fe^{3+} + e^{-1}$; E° = – 0.77 V **[AIPMT 2008]**

(A) $[Fe(CN)_6]^{3-}$ (B) $[Fe(CN)_6]^{4-}$

(C) Fe^{2+} (D) Fe^{3+}

Q.9 Given:

(i) $Cu^{2+} + 2e^- \to Cu$, E° = 0.337 V

(ii) $Cu^{2+} + e^- \to Cu^+$, E° = 0.153 V

Electrode potential, E° for the reaction,

$Cu^+ + e^- \longrightarrow Cu$, will be: **[AIPMT 2009]**

(A) 0.90 V (B) 0.30 V

(C) 0.38 V (D) 0.52 V

Q.10 Al_2O_3 is reduced by electrolysis at low potentials and high currents. If 4.0×10^4 amperes of current is passed through molten Al_2O_3 for 6 hours, what mass of aluminium is produced? (Assume 100% current efficiency. At. mass of Al = 27 g mol^{-1}) **[AIPMT 2009]**

(A) 8.1×10^4 g (B) 2.4×10^5 g

(C) 1.3×10^4 g (D) 9.0×10^3 g

Q.11 The equivalent conductance of M/32 solution of a weak monobasic acid is 8.0 mhos cm^2 and at infinite dilution is 400 mhos cm^2. The dissociation constant of this acid is: **[AIPMT 2009]**

(A) 1.25×10^{-6} (B) 6.25×10^{-4}

(C) 1.25×10^{-4} (D) 1.25×10^{-5}

Q.12 For the reduction of silver ions with copper metal, the standard cell potential was found to be + 0.46V at 25°C. The value of standard Gibbs energy ΔG° will be

(F = 96500 C mol^{-1}) **[AIPMT (PRE) 2010]**

(A) – 89.0 kJ (B) – 89.0 J

(C) – 44.5 kJ (D) – 98.0 kJ

Q.13 An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to:

[AIPMT (PRE) 2010]

(A) increase in ionic mobility of ions.

(B) 100% ionisation of electrolyte at normal dilution.

(C) increase in both i.e. number of ions and ionic mobility of ions.

(D) increase in number of ions.

Q.14 Which of the following expressions correctly represents the equivalent conductance at infinite dilution of $Al_2(SO_4)_3$. Given that $\Lambda_{Al^{3+}}$ & $\Lambda_{SO_4^{2-}}$ are the equivalent conductances at infinite dilution of the respective ions?

[AIPMT (MAINS) 2010]

(A) $2\Lambda_{Al^{3+}} + 3\Lambda_{SO_4^{2-}}$ (B) $\Lambda_{Al^{3+}} + \Lambda_{SO_4^{2-}}$

(C) $(\Lambda_{Al^{3+}} + 3\Lambda_{SO_4^{2-}}) \times 6$ (D) $\frac{1}{3}\Lambda_{Al^{3+}} + \frac{1}{2}\Lambda_{SO_4^{2-}}$

Q.15 Consider the following relations for emf of an electrochemical cell : **[AIPMT (MAINS) 2010]**

(i) EMF of cell = (Oxidation potential of anode) – (Reduction potential of cathode)

(ii) EMF of cell = (Oxidation potential of anode) + (Reduction potential of cathode)

(iii) EMF of cell = (Reduction potential of anode) + (Reduction potential of cathode)

(iv) EMF of cell = (Oxidation potential of anode) – (Oxidation potential of cathode)

Which of the above relations are correct

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

Q.16 The electrode potentials for Cu^{2+} (aq) + $e^- \rightarrow Cu^+$(aq) and Cu^+ (aq) + $e^- \rightarrow$ Cu (s) are +0.15 V and + 0.50 V respectively. The value of $E^0_{Cu^{2+}/Cu}$ will be **[AIPMT (PRE) 2011]**

(A) 0.150 V (B) 0.500 V
(C) 0.325 V (D) 0.650 V

Q.17 Standard electrode potential for Sn^{4+} / Sn^{2+} couple is +0.15 V and that for the Cr^{3+}/ Cr couple is – 0.74 V. These two couples in their standard state are connected to make a cell. The cell potential will be **[AIPMT (PRE) 2011]**

(A) +1.83 V (B) +1.19 V
(C) +0.89 V (D) +0.18 V

Q.18 If the E°_{cell} for a given reaction has a negative value, then which of the following gives the correct relationships for the values of ΔG° and K_{eq} ? **[AIPMT (PRE) 2011]**

(A) $\Delta G^\circ > 0; K_{eq} < 1$ (B) $\Delta G^\circ > 0; K_{eq} > 1$
(C) $\Delta G^\circ < 0; K_{eq} > 1$ (D) $\Delta G^\circ < 0; K_{eq} < 1$

Q.19 Standard electrode potential of three metals X, Y and Z are –1.2 V, + 0.5 V and –3.0 V respectively. The reducing power of these metals will be **[AIPMT (PRE) 2011]**

(A) X > Y > Z (B) Y > Z > X
(C) Y > X > Z (D) Z > X > Y

Q.20 A solution contains Fe^{2+}, Fe^{3+} and I^- ions. This solution was treated with iodine at 35°C. E° for Fe^{3+}/Fe^{2+} is + 0.77 V & E° for $I_2/2I^-$ = 0.536V. The favourable redox reaction is: **[AIPMT (MAINS) 2011]**

(A) I_2 will be reduced to I.
(B) There will be no redox reaction
(C) I^- will be oxidised to I_2
(D) Fe^{2+} will be oxidised to Fe^{3+}

Q.21 Limiting molar conductivity of NH_4OH (i.e., $\Lambda^0_m(NH_4OH)$ is equal to – **[AIPMT (PRE) 2012]**

(A) $\Lambda^0_m(NH_4Cl) + \Lambda^0_m(NaCl) - \Lambda^0_m(NaOH)$

(B) $\Lambda^0_m(NaOH) + \Lambda^0_m(NaCl) - \Lambda^0_m(NH_4Cl)$

(C) $\Lambda^0_m(NH_4OH) + \Lambda^0_m(NH_4Cl) - \Lambda^0_m(HCl)$

(D) $\Lambda^0_m(NH_4Cl) + \Lambda^0_m(NaOH) - \Lambda^0_m(NaCl)$

Q.22 Standard reduction potentials of the half reactions are

$F_2(g) + 2e^- \rightarrow 2F^-$ (aq) ; E° = + 2.85 V
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$ (aq) ; E° = + 1.36 V
$Br_2(\ell) + 2e^- \rightarrow 2Br^-$ (aq) ; E° = + 1.06 V
$I_2(s) + 2e^- \rightarrow 2I^-$ (aq) ; E° = + 0.53 V

The strongest oxidising and reducing agents respectively are **[AIPMT (MAINS) 2012]**

(A) F_2 and I^- (B) Br_2 and Cl^-
(C) Cl_2 and Br^- (D) Cl_2 and I_2

Q.23 Molar conductivities (Λ°_m) at infinite dilution of NaCl, HCl and CH_3COONa are 126.4, 425.9 & 91.0 Scm^2mol^{-1} respectively. Λ°_m for CH_3COOH will be **[AIPMT (MAINS) 2012]**

(A) 425.5 S cm^2 mol^{-1} (B) 180.5 S cm^2 mol^{-1}
(C) 290.8 S cm^2 mol^{-1} (D) 390.5 S cm^2mol^{-1}

Q.24 Four successive members of the first series of the transition metals are listed below. For which one of them the standard potential ($E^0_{M^{2+}/M}$) value has a positive sign **[AIPMT (MAINS) 2012]**

(A) Co (Z = 27) (B) Ni (Z = 28)
(C) Cu (Z = 29) (D) Fe (Z = 26)

Q.25 The Gibbs' energy for the decomposition of Al_2O_3 at 500°C : $\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2; \Delta_rG = +960 \text{ kJ mol}^{-1}$

The potential difference needed for the electrolytic reduction of aluminium oxide (Al_2O_3) at 500°C is at least **[AIPMT (MAINS) 2012]**

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

Q.26 At 25°C molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is 9.54 ohm^{-1} cm^2 mol^{-1} and at infinite dilution its molar conductance is 238 ohm^{-1} cm^2 mol^{-1}. The degree of ionisation of ammonium hydroxide at the same concentration and temperature is –

(A) 40.800% (B) 2.080% **[NEET 2013]**
(C) 20.800% (D) 4.008%

Q.27 A hydrogen gas electrode is made by dipping platinum wire in a solution of HCl of pH = 10 and by passing hydrogen gas around the platinum wire at one atm pressure. The oxidation potential of electrode would be?

(A) 1.81 V (B) 0.059 V **[NEET 2013]**
(C) 0.59 V (D) 0.118 V

Q.28 A button cell used in watches function as following

$$Zn (s) + Ag_2O (s) + H_2O(\ell) \rightleftharpoons 2Ag (s) + Zn^{2+}(aq) + 2OH^-(aq)$$

If half cell potentials are

$Zn^{2+}(aq) + 2e^- \rightarrow Zn (s)$; E° = – 0.76 V
$Ag_2O(s) + H_2O(\ell) + 2e^- \rightarrow 2Ag (s) + 2OH^-(aq)$; E° = 0.34 V

The cell potential will be – **[NEET 2013]**

(A) 1.34 V (B) 1.10 V
(C) 0.42 V (D) 0.84 V

Q.29 When 0.1 mol MnO_4^{2-} is oxidised the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is **[AIPMT 2014]**

(A) 96500 C (B) 2 × 96500 C
(C) 9650 C (D) 96.50 C

Q.30 The wt. of silver (at. wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of O_2 at STP will be **[AIPMT 2014]**

(A) 5.4 g (B) 10.8 g

(C) 54.0 g (D) 108.0 g

Q.31 A device that converts energy of combustion of fuels like hydrogen and methane, directly into electrical energy is known as : **[AIPMT 2015]**

(A) Electrolytic cell (B) Dynamo

(C) Ni-Cd cell (D) Fuel Cell

Q.32 Aqueous solution of which of the following compounds is the best conductor of electric current? **[RE-AIPMT 2015]**

(A) Ammonia, NH_3 (B) Fructose, $C_6H_{12}O_6$

(C) Acetic acid, $C_2H_4O_2$ (D) Hydrochloric acid, HCl

Q.33 The pressure of H_2 required to make the potential of H_2 electrode zero in pure water at 298 K is **[NEET 2016 PHASE 1]**

(A) 10^{-14} atm (B) 10^{-12} atm

(C) 10^{-10} atm (D) 10^{-4} atm

Q.34 The molar conductivity of a 0.5 mol/dm^3 solution of $AgNO_3$ with electrolytic conductivity of 5.76×10^{-3} S cm^{-1} at 298 K **[NEET 2016 PHASE 2]**

(A) 2.88 S cm^2/mol (B) 11.52 S cm^2/mol

(C) 0.086 S cm^2/mol (D) 28.8 S cm^2/mol

Q.35 During the electrolysis of molten sodium chloride, the time required to produce 0.10 mol of chlorine gas using a current of 3 amperes is **[NEET 2016 PHASE 2]**

(A) 55 minutes (B) 110 minutes

(C) 220 minutes (D) 330 minutes

Q.36 If the E°_{cell} for a given reaction has a negative value, which of the following gives the correct relationships for the values of ΔG° and K_{eq} ? **[NEET 2016 PHASE 2]**

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

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

Q.37 The number of electrons delivered at the cathode during electrolysis by a current of 1 ampere in 60 seconds is (Charge on electron = 1.60×10^{-19} C) **[NEET 2016 PHASE 2]**

(A) 6×10^{23} (B) 6×10^{20}

(C) 3.75×10^{20} (D) 7.48×10^{23}

Q.38 Zinc can be coated on iron to produce galvanized iron but the reverse is not possible. It is because **[NEET 2016 PHASE 2]**

(A) Zinc is lighter than iron.

(B) Zinc has lower melting point than iron.

(C) Zinc has lower negative electrode potential than iron.

(D) Zinc has higher negative electrode potential than iron.

Q.39 In the electrochemical cell :

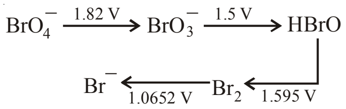
$Zn | ZnSO_4 (0.01M) || CuSO_4 (1.0\ M) | Cu$, the emf of this Daniel cell is E_1. When the concentration of $ZnSO_4$ is changed to 1.0M and that of $CuSO_4$ changed to 0.01M, the emf changes to E_2. From the followings, which one is the relationship between E_1 and E_2?

(Given, $\frac{RT}{F} = 0.059$) **[NEET 2017]**

(A) $E_1 < E_2$ (B) $E_1 > E_2$

(C) $E_2 = 0 \neq E_1$ (D) $E_1 = E_2$

Q.40 Consider the change in oxidation state of Bromine corresponding to different emf values as shown in the diagram below :



Then the species undergoing disproportionation is **[NEET 2018]**

(A) Br_2 (B) BrO_4^-

(C) BrO_3^- (D) HBrO

Q.41 Which of the following reactions are disproportionation reaction? **[NEET 2019]**

(a) $2Cu^+ \rightarrow Cu^{2+} + Cu^0$

(b) $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$

(c) $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2$

(d) $2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+$

Select the correct option from the following

(A) (a) and (b) only (B) (a), (b) and (c)

(C) (a), (c) and (d) (D) (a) and (d) only

Q.42 For a cell involving one electron $E^\circ_{cell} = 0.59$ V at 298 K, the equilibrium constant for the cell reaction is :

[Given that $\frac{2.303\ RT}{F} = 0.059$V at T = 298K] **[NEET 2019]**

(A) 1.0×10^2 (B) 1.0×10^5

(C) 1.0×10^{10} (D) 1.0×10^{30}

ANSWER KEY

EXERCISE - 1

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
A	A	C	C	B	B	D	B	C	A	D	A	D	B	C	A	C	C	A	A	A	D	D	C	C	C	D	D	B	B	A
Q	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
A	C	B	C	A	D	C	C	A	B	A	D	C	B	D	A	D	A	B	C	B	C	D	A	D	D	B	D	A	D	C
Q	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82								
A	A	D	A	B	C	D	A	D	C	A	B	C	A	B	C	A	B	D	A	B	C	D								

EXERCISE - 2

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	B	C	C	A	A	A	A	A	B	B	B	C	A	A	A	B	C	B	A	C	A	B	D	A	A
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	B	C	A	D	B	D	A	C	B	A	B	B	D	C	D	B	B	D	B	A	B	A	D	C	A
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64											
A	B	C	C	C	B	B	A	B	A	B	C	B	D	A											

EXERCISE - 3

Q	1	2	3	4	5	6	7	8	9	10
A	6	3	84	26	6	4	3	6	4	2

EXERCISE - 4

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	B	CD	C	C	B	C	A	D	C	C	A	C	B	D	C	C	A	D	D	C	C	D	D	D	C
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39											
A	A	C	A	C	B	A	A	C	A	B	A	C	1.52	2.15											

EXERCISE - 5

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	D	B	C	B	C	D	D	D	D	A	D	A	A	B	D	C	C	A	D	C	D	A	D	C	C
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42								
A	D	C	B	C	D	D	D	A	B	B	A	C	D	B	D	A	C								

ELECTROCHEMISTRY
TRY IT YOURSELF - 1

(1) **Step 1 :** Calculation of α :

$$\Lambda_m^c = 46.15\ S\ cm^2 mol^{-1}$$

$$\Lambda^0_{m(CH_3COOH)} = \Lambda^0_{m(CH_3COO^-)} + \Lambda^0_{m(H^+)}$$

$$= 54.6 + 349.6 = 404.2\ S\ cm^2\ mol^{-1}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{46.15\ S\ cm^2 mol^{-1}}{404.2\ S\ cm^2 mol^{-1}} = 0.1140$$

Step 2 : Calculation of K_a

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.025 mol^{-1}L \times (0.1140)^2}{(1-0.1140)}$$

$$= \frac{3.249 \times 10^{-4}\ mol^{-1}L}{0.1186} = 3.67 \times 10^{-4}\ mol^{-1}\ L$$

(2) Resistance of solution = 31.6 ohm
Cell constant = $0.367\ cm^{-1}$.

$$\text{Specific conductance} = \frac{\text{Cell constant}}{\text{Observed resistance}}$$

$$\kappa = \frac{0.367}{31.6} = 0.0116\ ohm^{-1}\ cm^{-1}$$

Molar conductance = Specific conductance × 1000/C

$$\Lambda_m = 0.0116 \times \frac{1000}{0.05} = 232.27\ ohm^{-1}\ cm^2\ mol^{-1}$$

(3) $$\text{Degree of dissociation} = \frac{\Lambda_m^c}{\Lambda_m^\infty}$$

$$\Lambda^\infty_{m(CH_3COOH)} = \Lambda^\infty_{m(CH_3COO^-)} + \Lambda^\infty_{(H^+)}$$

$$\Lambda^\infty_{m(CH_3COOH)} = (41.0 + 348.9) = 389.9\ ohm^{-1}\ cm^2\ mol^{-1}$$

$$\alpha\ (\text{for } 0.1\ M, \text{ acetic acid}) = \frac{5.1}{389.9} = 0.013$$

% ionisation = 0.013 × 100 = 1.3%

$$\alpha\ (\text{for } 0.001\ M, \text{ acetic acid}) = \frac{48.5}{389.9} = 0.1243$$

% ionisation = 0.1243 × 100 = 12.43%

(4) (a) Molar concentration of the solution

$$= \frac{1 \times 1000}{200 \times 208} = 0.024\ M$$

$$\text{Molar conductance} = \kappa \times \frac{1000}{C}$$

$$\Lambda_m = 0.058 \times \frac{1000}{0.024} = 241.66\ ohm^{-1}\ cm^2\ mol^{-1}$$

(b) Concentration w.r.t. number of gram equivalent i.e.,

$$\text{normality } N = \frac{1 \times 1000}{200 \times 104} = 0.048\ N$$

$$\text{Equivalent conductance} = \kappa \times \frac{1000}{N}$$

$$\Lambda_{eq} = 0.058 \times \frac{1000}{0.048} = 120.83\ ohm^{-1}\ cm^2\ (g\text{-}eq)^{-1}$$

Alternatively, $\Lambda_{eq} = \Lambda_{eq} \div n \text{ factor}$

$$= \frac{241.66}{2} = 120.83\ S\ cm^2 eq^{-1}$$

(5) $$\Lambda^\infty_{m(NH_4OH)} = \Lambda^\infty_{m(NH_4Cl)} + \Lambda^\infty_{m(NaOH)} - \Lambda^\infty_{m(NaCl)}$$

$$\Lambda^\infty_{m(NH_4OH)} = 120.8 + 210.4 - 110.0 = 221.2$$

Molar conductance of NH_4OH at infinite dilution is $221.2\ ohm^{-1}\ cm^2\ mol^{-1}$

(6) $\Lambda_m = \kappa \times \frac{1000}{C}$, where C is molar concentration.

$$\Lambda_m = 26 \times 10^{-2} \times \frac{1000}{1} = 260\ ohm^{-1}\ cm^{-2}\ mol^{-1}$$

(7) $$\lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{0.0248\ S\ cm^{-1} \times 1000\ cm^3 L^{-1}}{0.20\ mol\ L^{-1}}$$

$$= 124\ S\ cm^2\ mol^{-1}.$$

TRY IT YOURSELF - 2

(1) $$\text{Gram equivalent mass of copper} = \frac{63.5}{2} = 31.75g$$

$$\text{Gram equivalent mass of zinc} = \frac{65.0}{2} = 32.50g$$

Now, 1.0 mole of electrons deposit copper = 31.75g

$$\text{0.2 mole of electrons deposit copper} = \frac{31.75 \times 0.2}{1.0} = 6.35g$$

Similarly, 1.0 mole of electrons deposit zinc = 32.50g

$$\text{0.2 mole of electrons deposit zinc} = \frac{32.5 \times 0.2}{1.0} = 6.50g$$

(2) Quantity of electricity passed
= Current in amperes × time in seconds

Q = 3 × 15 × 60 = 2700 C

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

Two mole electrons or 2F charge can deposit 1 mole copper

$$\text{i.e., 63.5g and so 2700 C will deposit } \frac{2700 \times 63.5}{2 \times 96500} = 0.889g$$

(3) Q(coulomb) = 1 (ampere) × t (sec)
= 0.5 ampere × 2 × 60 × 60 = 3600 C

A flow of 1 F, i.e. 96500C is equivalent to flow of 1 mole of electrons i.e., 6.023×10^{23} electrons.

3600 C is equivalent to flow of electrons

$$= \frac{6.02\times10^{23}}{96500}\times 3600 = 2.246\times10^{22} \text{ electrons.}$$

(4) 1 mole Al (27g) requires 3 mole electrons or 3F charge.
27g Al require 3 × 96500 C charge

$$6.75\text{g require} = \frac{3\times96500\times6.75}{27} = 72375 \text{ C}$$

(5) Quantity of electricity passed = 5A × 20 × 60s = 6000C

$$Ni^{2+} + 2e^- \longrightarrow Ni$$

Thus, 2F, i.e. 2 × 96500C deposit Ni = 1 mole i.e. 58.7 g
(At. mass of Ni = 58.7)
Thus, 2F, i.e. 2 × 96500C deposit Ni = 1 mole

$$6000\text{C will deposit Ni} = \frac{58.7}{2\times96500}\times 6000\text{g} = 1.825 \text{ g}$$

(6) Amount of current required to deposit 1 mole Cu (63.5g) = 2 × 96500 C
Current required to deposit 1.6g of copper

$$= \frac{2\times96500\times1.6}{63.5} = 4862.99 \text{ C}$$

Current actually passed through = 2 × 1.5 × 60 × 60 = 10800

$$\text{Current efficiency} = \frac{4862.99}{10800}\times100 = 45.03\%$$

(7) $Ni^{++} + 2e^- \rightarrow Ni$
2F or 2 × 96500 C of electricity is required to deposit 58.5g of Ni.
58.5g of Ni requires 2 × 96500 C

$$0.25\text{g of Ni requires} = \frac{2\times96500\times0.25}{58.5} = 824.8 \text{ C}$$

Amount of electricity = Current in amperes × time in sec.

$$\text{Time in seconds} = \frac{\text{Amount of electricity}}{\text{Current in amperes}} = \frac{824.8}{1}$$

$$= 824.8 \text{ sec} = 13.74 \text{ minutes.}$$

TRY IT YOURSELF - 3

(1) Oxidation hall cell reaction : $A(s) \rightarrow A^{3+} + 3e^-] \times 2$
Reduction half cell reaction : $B^{2+} + 2e^- \rightarrow B(s)] \times 3$

Net redox reaction : $2A(s) + 3B^{2+} \rightarrow 2A^{3+} + 3B(s)$

(2) The given cell is concentration cell. Hence $E°_{cell} = 0$

$$E_{cell} = E°_{cell} - \frac{0.0591}{n}\log\frac{[\text{Product}]}{[\text{Reactant}]}$$

$$E_{cell} = 0 - \frac{0.0591}{1}\log\frac{10^{-3}}{10^{-1}} = 0.118 \text{ volt}$$

(3) The half cell reaction with lesser value of E° takes place at the anode while the other takes place at cathode. Thus,

At anode : $2I^- \rightarrow I_2 + 2e^-$
At cathode : $Br_2 + 2e^- \rightarrow 2Br^-$

Cell reaction : $2I^- + Br_2 \rightarrow I_2 + 2Br^-$
$EMF_{cell} = E°_c - E°_a = 1.08 - 0.54 = 0.54$ V

(4) Salt is 95% ionised

$$[A^{2+}] = \frac{95}{100}\times 0.1 = 0.095$$

The electrode reaction is : $A^{2+} + 2e^- \rightarrow A(s)$

$$E_{A^{2+}/A} = E^0_{A^{2+}/A} - \frac{0.0591}{n}\log\frac{1}{[A^{2+}]}$$

$$= -0.76V - \frac{0.0591}{n}\log\frac{1}{0.095}$$

$$= -0.76V - 0.0295\log\frac{1000}{95}$$

$$= -0.76\text{ V} - 0.0295\,[\log 1000 - \log 95]$$
$$= -0.76\text{ V} - 0.029\,[3 - 1.977] = -0.79021 \text{ V}$$

(5) Cell reaction,

At anode : $\underset{P_1}{H_2} \rightarrow 2H^+ + 2e^-$

At anode : $2H^+ + 2e^- \rightarrow \underset{P_2}{H_2}$

$$\text{Hence, } E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\frac{P_2}{P_1}$$

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

[both electrodes are identical therefore, $E°_{cell} = 0$]
If $P_1 > P_2$ then E_{Cell} will have positive value therefore it will be spontaneous.

(6) $E^0_{cell} = E^0_{cathode} - E^0_{anode} = -0.44\text{ V} + 0.74\text{ V} = 0.30$ V

[Since cell reaction $2Cr + 3Fe^{2+} \rightarrow 2Cr^{3+} + 3Fe$]
$W = -nFE° = -6 \times 96500 \times 0.30 = 173700$ J
W = 173.7 kJ

(7) (a) If the reaction will take place between Fe^{3+} (aq) and I^- (aq), Fe^{2+} and I_2 should be formed. Because $E^0_{I_2/I^-}$ has lower value than that of $E^0_{Fe^{3+}/Fe^{2+}}$, it can be oxidiesed ($2I^- \rightarrow I_2$) and Fe^{3+} can be reduced to Fe^{2+}, therefore, it can be oxidised ($2I^- \rightarrow I_2$).
(b) The possible reaction between Ag^+ (aq) & Cu(s) will be : $2Ag^+(aq) + Cu(s) \longrightarrow 2Ag(s) + Cu^{2+}$
Because the value of E^0 for Cu^{2+}/Cu is lower than of Ag^+/Ag hence, the oxidation of Cu and reduction of Ag^+, according to above equation is possible.

(8) The reaction of electrode is $\underset{1.5\text{ bar}}{Cl_2(g)} + 2e^- \rightarrow \underset{0.01\text{ M}}{2Cl^-}$

$$E = E^0 - \frac{0.0591}{n}\log\frac{[Cl^-]^2}{P_{Cl_2}}$$

$$= 1.36 - \frac{0.0591}{n}\log\frac{(0.01)^2}{1.5} = 1.483\text{ V}$$

(9) $\log K_c = \frac{nE^0_{cell}}{0.0591}$; $E^\circ_{cell} = 0.16\text{V}, n = 4$

$$\log K_c = \frac{4 \times 0.16}{0.0591} = 10.8$$

$K_c = \text{antilog } 10.8 = 6.31 \times 10^{10}$

(10) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.229 - 0. = 1.229\text{V}$

$\Delta G^\circ = -nFE^\circ = -4 \times 96500 \times 1.229 = 474.4\text{ kJ}$

(11) At anode : $Ni(s) \rightarrow Ni^{2+} + 2e^-$

At cathode : $2Ag^+ + 2e^- \rightarrow 2Ag$

The net reactions : $Ni(s) + 2Ag^+ \rightarrow Ni^{2+} + 2Ag(s)$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log\frac{[\text{Anode}]}{[\text{Cathode}]}$$

$$E_{cell} = 1.05 - \frac{0.0591}{2}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$= 1.05 - \frac{0.0591}{2}\log\frac{0.16}{(0.002)^2} = 0.9142\text{ V}$$

CHAPTER-3 : ELECTROCHEMISTRY
EXERCISE-1

(1) **(A).** Daniell cell converts the chemical energy liberated during the redox reaction to electrical energy and has an electrode potential of 1.1V.
$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

(2) **(C).** In the electrolytic cell electrical energy change into chemical energy.

(3) **(C).** In daniel cell copper rod acts as cathode so there cations move towards copper electrode and reduction take place on copper rod.

(4) **(B).** If external opposite potential is applied in galvanic cell, then current will flow from copper rod to zinc rod.

(5) **(B).** Zinc dissolves at anode and copper deposits at cathode.

(6) **(D).** Agar-Agar is a gelatin, it is used in salt bridge along with KCl electrolyte.

(7) **(B).** Higher the reduction potential, stronger is the oxidising agent.

(8) **(C).** According to convention, the standard hydrogen electrode is assigned a zero potential at all temperatures.

(9) **(A).** $E_A = 2.23V > E_B = 1.43V$
So A will act as cathode in galvanic cell. Hence

$$E^0_{Cell} = E_{Cathode} - E_{Anode} = E_A - E_B = (2.23) - (-1.43)$$

(10) **(D).** The metal placed below in electrochemical series does not react with that metal salt solution which metal is placed above in series.

(11) **(A).** In galvanic cell anode always made up of negative electrode.

(12) **(D).** Vertical line between metal and electrolyte solution and double vertical line is between two electrolytes connected by salt bridge.

(13) **(B).** $Zn \,|\, Zn^{2+} \,\|\, H^+, H_2 \,|\, Pt$ or $Zn \,|\, ZnSO_4 \,\|\, H_2SO_4 \,|\, H_2, Pt$

(14) **(C).** In reactivity series, $Mg > Al > Zn > Fe > Cu$

$$\xrightarrow{\text{Reactivity decreases}}$$

Hence, Mg can displace Al, Al can displace Zn and so on.

(15) **(A).** $Zn + MgCl_2 \rightarrow ZnCl_2 + Mg$

$$E^\circ_{cell} = E^\circ_{Zn/Zn^{+2}} + E^\circ_{Mg^{+2}/Mg}$$

$$= 0.762 - 2.37 = -1.608 \text{ V}$$

Here, E°_{cell} is negative so no reaction will take place.

(16) **(C).** In an electrochemical cell, anode (Zn) is a negative terminal.

(17) **(C).** An electrochemical cell can behave like an electrolytic cell when $E_{ext} > E_{cell}$.

(18) **(A).** $\underbrace{Cu^{2+} + 2e^- \rightarrow Cu}_{\text{Reduction}}$

(19) **(A).** $Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$ can be represented as
$Zn_{(s} \,|\, Zn^{2+}_{(aq)} \,\|\, Ag^+_{(aq)} \,|\, Ag_{(s)}$

(20) **(A).** Lower the reduction potential, more is the reducing power. $Br^- < Fe^{2+} < Al$

(21) **(D).** Cu^{2+} ion get reduced easily than H^+ ions. Hydrogen ions cannot oxidises Cu. Cu does not dissolve in HCl. In nitric acid it is oxidised by nitrate ion and not by hydrogen ion.

(22) **(D).** Inert electrode does not participate in the chemical reaction and acts only as source or sink for electrons and provides surface either for oxidation or for reduction reaction.

(23) **(C).** Only anode or cathode can't work alone so absolute value of reduction potential can't be determined.

(24) **(C).** $E^o_{cell} = E^o_{cathode} - E^o_{anode}$
$E^o_{cell} = E^o_{Cd^{2+}/Cd} - E^o_{Cr^{3+}/Cr} = -0.40 - (-0.74) = +0.34V$

(25) **(C).** $Pt_{(s)} \,|\, H_2(g, 1bar) \,|\, H^+(aq., 1M) \,\|\, Cu^{2+}(aq., 1M) \,|\, Cu$
will measure standard electrode potential of copper electrode.

To calculate the standard electrode potential of the given cell it is coupled with the standard hydrogen electrode in which pressure of hydrogen gas is one bar and the conc. of H^+ ion in the solution is one molar and also the concentrations of the oxidised and the reduced forms of the species in the right hand half-cell are unity.

(26) **(D).** Cell reaction : $Cu + Hg^{2+} \rightarrow Cu^{2+} + Hg$

(27) **(D).** $E^\circ_{cell} = \dfrac{2.303\,RT}{nF} \log K_c$

This gives relationship between equilibrium constant of the reaction and standard potential of cell.

(28) **(B).** At equilibrium, E_{cell} becomes zero which means no current is generated by the cell at this point, E^o_{cell} remains constant hence equilibrium constant is related to E^o_{cell}.

(29) **(B).** $E^o_{cell} = \dfrac{2.303\,RT}{nF} \log K = \dfrac{0.0591}{n} \log K_c$ at 298K

(30) **(A).** $E_{cell} = \dfrac{0.059}{n} \log \dfrac{1}{C} = -\dfrac{0.059}{2} \log \dfrac{1}{100}$

$$= -\frac{0.059}{2}(-2) = 0.059V = 59mV. \quad \text{(increase)}$$

(31) **(C).** $E_{cell} = E^\circ_{cell} - \dfrac{0.059}{2} \log \dfrac{[Sn^{2+}]}{[Ag^+]^2}$

Ag^+ increases, E_{cell} increases.

(32) **(B).** $\Delta G^o = -nFE^o_{cell}$

(33) **(C).** At anode : $Fe \rightarrow Fe^{2+}\,(0.001\text{ M}) + 2e^-$
At cathode : $2H^+(1M) + 2e^- \rightarrow H_2\,(1atm)$

Net reaction : $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$

Nernst equation for the given cell,

$$E_{cell} = E^o_{cell} - \frac{0.0591}{2} \log \frac{[Fe^{2+}][H_2]}{[Fe]\,[H^+]^2}$$

(34) **(A).** The cell reaction will be
$Ni_{(s)} + 2Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$
$E^o_{cell} = E_{cathode} - E_{anode} = 0.80 - (-0.25) = +1.05$ V
$\Delta G^o = -nFE^o_{cell}$. As $E^o_{cell} = +ve$,
$\Delta G^o = -ve$, hence reaction is feasible.

(35) **(D).** The conductivity of solutions of different electrolytes in the same solvent and at a given temperatures differ due to charge and size of ions in which they dissociate, the concentration of ions or ease with which ions move under a potential gradient. It is called molar conductivity denoted by Λ_m.

$$\Lambda_m\ (\text{S cm}^2\ \text{mol}^{-1}) = \frac{\kappa\ (\text{S cm}^{-1})}{1000\ \text{Lm}^{-3} \times \text{molarity (mol L}^{-1})}$$

$$\Lambda_m\ (\text{S cm}^2\ \text{mol}^{-1}) = \frac{\kappa\ (\text{S cm}^{-1}) \times 1000\ (\text{cm}^3/\text{L})}{\text{Molarity (mol L}^{-1})}$$

$1\text{S m}^2\ \text{mol}^{-1} = 10^4\ \text{S cm}^2\ \text{mol}^{-1}$

(36) **(C).** Conductivity depends upon solvation of ions present in solution. Greater the solvation of ions, lesser is the conductivity.

(37) **(C).** E^o_{cell} should be positive for a spontaneous reaction as $\Delta G^o = -nFE^o_{cell}$.

(38) **(A).** $K = \frac{1}{R} \times \text{cell constant}$

$= K \times R = 0.0212 \times 55 = 1.166\ \text{cm}^{-1}$.

(39) **(B).** Strong electrolyte ionize completely at all dilutions and the number of ions does not increase on dilution. A small increase in Λ_m volume with dilution is due to the weakening of electrostatic attraction between the ions on dilution.

(40) **(A).** Since molar conductance $\propto \frac{1}{\text{Molarity}}$.

(41) **(D).** Since E^o_{A/A^-} has large negative value, the tendency of A to be reduced to A^- is very small. In other words tendency of A^- to be oxidized to A is very large.

(42) **(C).** Strong electrolytes are almost completely ionised in polar solvent.

(43) **(B).** Molar conductivity $= \frac{1000}{MX}$.

(44) **(D).** Because conductance is increase when the dissociation is more.

(45) **(A).** The substances whose aqueous solutions allow the passage of electric current and are chemically decomposed, are termed electrolytes. Electrolytic substances are classified as strong or weak according to how readily they dissociate into conducting ions. Acetic acid is a weak electrolyte. Glucose, ethanol and urea are non-electrolytes.

(46) **(D).** Dilution, temperature and nature of electrolyte affect the conductivity of solution.

(47) **(A).** $\wedge^0_{\text{NaBr}} = \wedge^0_{\text{NaCl}} + \wedge^0_{\text{KBr}} - \wedge^0_{\text{KCl}}$

$= 126 + 152 - 150 = 128\ \text{S cm}^2\ \text{mol}^{-1}$

(48) **(B).** The conductance of an electrolytic solution kept between the electrodes of conductivity cell at unit distance but having area of cross section large enough to accommodate sufficient volume of solution is called molar conductivity.

(49) **(C).** $\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.52 \times 10^{-2} \times 1000}{0.15}$

$= 101\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

(50) **(B).** $\Lambda^o_m\text{NaBr} = \Lambda^o_m\text{NaCl} + \Lambda^o_m\text{KBr} - \Lambda^o_m\text{KCl}$

(51) **(C).** Kohlrausch law of independent migration of ions. This law states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

(52) **(D).**

(53) **(A).** When concentration approaches zero, the molar conductivity is called limiting molar conductivity. The variation in Λ_m with concentration is different

i → weak electrolyte ; ii → strong electrolyte

(54) **(D).** Molar conductivity is inversely proportional to molarity.

(55) **(D).** α is the degree of dissociation which is ratio of molar conductivity at the concentration C to the limiting molar conductivity,

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m}\ ;\ K_a = \frac{C\alpha^2}{1-\alpha} = \frac{C\Lambda_m^2}{\Lambda_m^{\circ 2}\left(1 - \frac{\Lambda_m}{\Lambda^\circ_m}\right)} = \frac{C\Lambda_m^2}{\overset{\circ}{\Lambda}_m(\overset{\circ}{\Lambda}_m - \Lambda_m)}$$

(56) **(B).** $\Lambda^o_{m(NH_4Cl)} + \Lambda^o_{m(NaOH)} - \Lambda^o_{m(NaCl)}$

$$\Lambda^o_{m(NH_4^+)} + \Lambda^o_{m(Cl^-)} + \Lambda^o_{m(Na^+)}$$

$$+\Lambda^o_{m(OH^-)} - \Lambda^o_{m(Na^+)} - \Lambda^o_{m(Cl^-)}$$

$$= \Lambda^o_{m(NH_4^+)} + \Lambda^o_{m(OH^-)} = \Lambda^o_{m(NH_4OH)}$$

(57) **(D).** The electronic conductance depends on all these factors.

(58) **(A).** $\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.01 \times 10^{-2} \times 1000}{0.1}$

$= 1.01 \times 10^2\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

(59) **(D).** When an aqueous solution of NaCl is electrolysed, hydrogen is liberated at cathode. Specific conductivity and molar conductivity are different terms. Silver nitrate solution cannot be stored in a copper container as silver will get precipitated because of high reactivity of Cu than Ag.

The addition of liquid bromine to iodide solution turns it violet.

$$\underset{\text{Reddish-brown}}{Br_{2(l)}} + 2I^-_{(aq)} \rightarrow 2Br^-_{(aq)} + \underset{\text{Violet}}{I_{2(l)}}$$

(60) **(C).** In between dilute H_2SO_4 and platinum electrode O_2 gas evolve at anode.

(61) **(A).** Calcium is produces when molten anhydrous calcium chloride is electrolysed.

(62) **(D).** During electrolysis of $CuSO_4$. Cu^{2+} gets discharged at cathode and OH^- at anode. Thus solution becomes acidic due to excess of H^+ and SO_4^{2-} or H_2SO_4.

(63) **(A).** At cathode: $2H^+ + 2e \rightarrow H_2$,

At anode : $2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e$

(64) **(B).** 1 mole of electrons = 1 faraday

$Mg^{++} + 2e^- \rightarrow Mg$;

2 moles of electrons = 2 faraday

(65) **(C).** Refining of impure copper with zinc impurity is to be done by electrolysis using following electrode
Cathode → Pure copper
anode → Impure copper
Therefore pure metal ion (M^+) are deposited on cathode.

(66) **(D).** Charge passed = 9650 coulomb = 1/10 Faraday.
So, mole of Ag deposited = 1/10

Mass of Ag deposited = $\frac{1}{10} \times 108 = 10.8$ gm.

(67) **(A).** During the electrolysis of dilute sulphuric acid, the following process is possible at anode.
$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$(dil. H_2SO_4)

(68) **(D).** $\underset{1\text{ mole}}{MnO_4^-} + \underset{5\text{ moles}}{5e^-} \rightarrow \underset{1\text{ mole}}{Mn^{2+}}$

5 moles of electrons are needed for reduction of 1 mole of MnO_4^- to Mn^{2+}
5 moles of electrons = 5 Faradays
Quantity of charge required = 5 × 96500
= 4.825×10^5 Coulombs

(69) **(C).** $Q = I \times t = 1.5 \times 3 \times 60 \times 60 = 16200$ C
Charge on 1 electron = 1.602×10^{-19} C
16200 C charge is on

$\frac{1 \times 16200}{1.602 \times 10^{-19}}$ electrons = 1.01×10^{23} electrons

(70) **(A).** At cathode : $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

At anode: $2OH^-_{(aq)} \rightarrow \frac{1}{2}O_{2(g)} + H_2O_{(l)} + 2e^-$

(71) **(B).** The charging reaction in the lead storage battery is
$2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

(72) **(C).** $2NH_4Cl + Zn \rightarrow 2NH_3 + ZnCl_2 + H_2 \uparrow$.

(73) **(A).** Dil. H_2SO_4 is used in lead in lead storage battery as electrolyte.

(74) **(B).** Discharging reaction
$Pb(s) + PbO_2(s) + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

(75) **(C).** $Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

(76) **(A).** On charging the battery the reaction is reversed and $PbSO_{4(s)}$ is converted into Pb at anode and PbO_2 at cathode.

(77) **(B).** III. Lead-storage, IV. nickel-cadmium and
V. lithium batteries are rechargeable

(78) **(D).** Fuel cells are more efficient, free from pollution and they run till reactants are active.

(79) **(A).** At anode : $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$
At cathode : $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH_{(aq)}$

Overall reaction : $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

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(80) **(B).** Rusting reaction of Fe is

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

(81) **(C).** Aluminium forms a protective oxide layer but iron does not.

(82) **(D).** Fe is active metal and is oxidised to Fe^{2+};
Fe^{2+} is dissolved in O_2 in acidic medium (or alkaline medium) forming $Fe_2O_3(s)$ – rust.

EXERCISE-2

(1) **(B).** The reduction potential of Mg is less than that of water (E° = – 0.83V). Hence their ions in the aqueous solution cannot be reduced instead water will be reduced $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

(2) **(C).** $Al^{3+} + 3e^- \rightarrow Al$; $E_{Al} = \frac{27}{3} = 9$

$W_{Al} = E_{Al} \times \text{No. of faradays} = 9 \times 5 = 45\text{gm.}$

(3) **(C).** $W_{metal} = \frac{E \times I \times t}{96500} = \frac{E \times 3 \times 50 \times 60}{96500}$

$E = \frac{96500 \times w}{3 \times 50 \times 60} = \frac{96500 \times 1.8}{3 \times 50 \times 60} = 19.3$.

(4) **(A).** $Na^+ + e^- \rightarrow Na$
Charge (in F) = moles of e^- used

= moles of Na deposited = $\frac{11.5}{23}$ gm = 0.5 Faraday.

(5) **(A).** $\ell / a = 0.5\,cm^{-1}, R = 50\,ohm$

$\rho = \frac{Ra}{\ell} = \frac{50}{0.5} = 100$

$\Lambda = k \times \frac{1000}{N} = \frac{1}{p} \times \frac{1000}{N} = \frac{1}{100} \times \frac{1000}{1}$

$= 10\,ohm^{-1}cm^2 gm\,eq^{-1}$

(6) **(A).** $E_{cell} = E^o_{cell} - \frac{0.059}{2}\log\frac{(Zn^{++})}{(Cu^{++})}$

$= 1.10 - \frac{0.059}{2}\log\frac{0.1}{0.1} = 1.10$ V .

(7) **(A).** The tendency to gain electron is in the order
Z > Y > X

Thus $Y + e \rightarrow Y^-$; $X \rightarrow X^+ + e$

(8) **(A).** $W_{Ag} = \frac{E_{Ag} \times Q}{96500} = \frac{108 \times 9.65}{96500}$

$= 1.08 \times 10^{-2}$ gm = 10.8 mg

(9) **(B).** $\frac{\text{Weight of Cu}}{\text{Weight of } H_2} = \frac{\text{Eq. weight of Cu}}{\text{Eq. weight. of H}}$

$$\frac{\text{Weight of Cu}}{0.50} = \frac{63.6/2}{1}$$

$$\text{Weight of Cu} = 15.9 \text{ gm} .$$

(10) **(B).** $m = Z \times 4 \times 120$; $M = Z \times 6 \times 40$

$$\frac{M}{m} = \frac{6 \times 40}{4 \times 120} = \frac{1}{2}; \quad M = m/2 .$$

(11) **(B).** Reduction potential of hydrogen electrode,

$$E_H = \frac{-2.303\,RT}{F} \log \frac{1}{[H^+]}$$

$$= -0.059\,pH = -0.059 \times 3 = -0.177\,V .$$

(12) **(C).** $E^o_{cell} = E^o_{cathode} - E_{anode}$;

$$E^o_{cell} = 0.34 - (-2.37) = 2.71\,V$$

(13) **(A).** $\Delta G = -nFE^o$

$$\Delta G = -1 \times 96500 \times 1.02 = -98430$$

(14) **(A).** Fe is more electropositive than copper.
Hence Cu^{2+} can oxidise Fe.

(15) **(A).** The pH of 0.1 M HCl and 0.1 M acetic acid is not the same, because HCl is a strong acid so its pH is less and CH_3COOH is a weak acid, so its pH is more.

(16) **(B).** Given: $\Delta G = -21.20$ kJ = 21200J

$$\because \ \Delta G = -nFE$$

$$E = \frac{21200}{1 \times 96500} = 0.2196\ V = 0.22\ V.$$

(17) **(C).** $E_{metal} = \frac{\text{Weight of metal} \times 96500}{\text{Number of coulombs}}$

$$= \frac{22.2 \times 96500}{2 \times 5 \times 60 \times 60} = 59.5$$

Oxidation no. of the metal $= \frac{177}{59.5} = +3$

(18) **(B).** Electricity required
= No. of gm equivalent × 96500 coulombs
$= 0.5 \times 96500 = 48250$ C.

(19) **(A).** $E = E° - \frac{0.059}{n} \log \frac{1}{[H^+]}$

$$= 0 - \frac{0.059}{1} \log \frac{1}{10^{-4}} = -0.236V$$

(20) **(C).** $\Delta G° = -nFE° = -2.303\ RT \log K_p$
$n = 3, F = 1, E° = 0.59\ V$
1 Faraday ≡ 1 mole of electrons

$$\log k_p = \frac{3 \times 0.59}{0.059} = 30 \qquad \therefore k_p = 10^{30}$$

(21) **(A).** $E = E° + \frac{0.059}{2} \log \frac{[Cu^{2+}]}{[Zn^{2+}]} \quad \therefore E_1 > E_2 > E_3$

(22) **(B).** $W = Z \times I \times T = 4 \times 10^{-4} \times 12 \times \frac{75}{100} \times 3 \times 3600 = 38.8g$

(23) **(D).** 96500 coulombs of electric current deposits 12g of magnesium 9.65 coulombs of electric current deposits $\frac{9.65 \times 12}{96500} = 1.2 \times 10^{-3}$ g of magnesium

∴ The number of moles of Grignard reagent obtained is $\frac{1.2 \times 10^{-3}}{24} = 0.05 \times 10^{-4} = 5 \times 10^{-5}$

(24) **(A).** $W = Z\,It$

$$t = \frac{W}{ZI} \ ; \ t = \frac{W}{E} \times \frac{96500}{I} = \frac{30}{20} \times \frac{96500}{5}$$

$$t = \frac{28950}{60 \times 60} = 8$$

(25) **(A).** $2.303\ RT \log K_p = nFE^0$

$$\log k_p = \frac{E^0 \times nF}{2.303RT} = \frac{0.0295 \times 2}{0.0591} = 1$$

$$\log k_p = 1 \ ; \ k_p = 10$$

(26) **(B).** Pt, $\frac{1}{2}H_2\,(1atm)\,|\,HCl\,(2M)$

(27) **(C).** $E_{cell} = E_{R.H.E} - E_{L.H.E}$
$E_{cell} = -0.41 - (-0.76) = +0.35\ V$

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

$$E = E° - \frac{2.303\ RT}{nF} \log \frac{[Cr^{+3}]^2[H_2O]^7}{[Cr_2O_7^{2-}][H^+]^{14}}$$

$$1.067 = 1.33 - \frac{0.059}{6} \log \frac{(15 \times 10^{-3})^2 (1)^7}{(4.5 \times 10^{-3})[H^+]^{14}}$$

$$-0.263 = -\frac{0.059}{6} \log \frac{225 \times 10^{-6}}{(4.5 \times 10^{-3})[H^+]^{14}}$$

$$-0.263 = -0.0098\,[\log 50 - \log (H^+)^{14}]$$

$$\frac{-0.263}{-0.0098} = 1.6990 + 14\,pH$$

$\Rightarrow$ pH = 1.7955

(29) **(D).** The amount of impurity = 22.26 – 22.011 = 0.249 g
Amount of Cu should have been deposited by a current of 140 a & 482.5 s current
$= 140 \times 482.5 = 67{,}550\ C \rightarrow ?\ Cku$
$96{,}500\ C \rightarrow 31.77$ g of Cu
∴ $67{,}550\ C \rightarrow 22.239$ g pure Cu
But only 22.011 of cathode mass has increased
∴ 22.239 – 22.011 = 0.228 g
Instead of 0.228 g of Cu the amount of Fe oxidised
0.228 – 31.77
? - 27.75

$$\frac{0.228 \times 27.75}{31.77} = 0.199\text{ g}$$

$$\therefore \quad \%\text{ of Fe} = \frac{0.199}{22.26} \times 100 = 0.89 \approx 0.90$$

(30) **(B).** $\Delta G^\circ = -nFE^\circ$

$-240\text{ kJ} = -2 \times 96500 \times E^o$

$$E^\circ = \frac{-240000}{193000} = 1.24\text{ V}$$

(31) **(D).** $S = \frac{\lambda}{\lambda_0} = \frac{k}{1000\lambda_m} = \frac{1.85 \times 10^{-5}}{1000 \times 140 \times 10^{-4}}$

$S = 1.3 \times 10^{-6}$

$K_{sp} = S^2 = (1.3 \times 10^{-6})^2 = 1.69 \times 10^{-12}$

(32) **(A).** During charging lead storage battery.

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

(33) **(C).** $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

$O^{2-} \rightarrow O_2^{0}$

$2e^- \quad 2F$

$2 \times 96500 = 1.93 \times 10^5\text{ C}$

(34) **(B).** A secondary cell is one can be recharged by passing current through it in the opposite direction.

(35) **(A).** Electron gain → cathode

(36) **(B).** The amount of current in Faraday is required for the reduction of 1 mol of $Cr_2O_7^{--}$ ions to Cr^{3+} is 6 F.

(37) **(B).** Cu electrode loses mass and Ag electrode gains mass.

(38) **(D).** Due to reduction of NO_3^- in preference to H^+ ion. H^+ ion is not reduced to give H_2 gas.

(39) **(C).** $\Delta G^o = -nFE^o$ ..... (i)

$\Delta G^o = -2.303\ RT \log K$ .....(ii)

From equation (i) if E^o is positive then ΔG^o is negative.

In equation (ii), ΔG^o is negative so, $\log K > 0 \Rightarrow K > 1$

(40) **(D).** $CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$

$$Ca^{2+} + \underset{\text{2 moles}}{2e^-} \rightarrow \underset{\text{1 mole (40g)}}{Ca}$$

40 g of Ca ≡ 2F ; 100 g ≡ 5F

(41) **(B).** $\kappa = \frac{1}{R} \times \frac{l}{A} = \frac{1}{40} \times \frac{2}{5}$

$$\Lambda_m = \kappa \times \frac{1000}{N} = \frac{1}{40} \times \frac{2}{5} \times \frac{1000}{0.5} = 20\text{ohm}^{-1}\text{ cm}^2\text{ eq}^{-1}$$

(42) **(B).** $NaCl \rightarrow Na^+ + Cl^-$

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

$Q = I \times t = 2 \times 30 \times 60 = 3600$ Coulombs

2×96500 Coulombs produce= 71g of Cl_2

3600 Coulombs will produce

$$= \frac{71}{2 \times 96500} \times 3600 = 1.32\text{g of } Cl_2$$

(43) **(D).** $E^o_{cell} = E^o_{cathode} - E^o_{anode}$

It will remain unchanged.

(44) **(B).** 1 F deposits 108 g of Ag ($Ag^+ + e^- \rightarrow Ag$)

54g of Ag will be deposited by

$$\frac{1}{108} \times 54 = \frac{1}{2}F$$

3 F deposit 27g of Al ($Al^{3+} + 3e^- \rightarrow Al$)

$$\frac{1}{2}F \text{ will deposit } \frac{27}{3} \times \frac{1}{2} = 4.5\text{g of Al}$$

(45) **(A).** More is E°_{RP}, more is oxidizing power or lesser is reducing power.

(46) **(B).** $Pt + Cl_2 \rightarrow Pt^{2+} + 2Cl^-;\ E^\circ_{cell} = 0.15V$

$Pt^{2+} + 2e^- \rightarrow Pt;\ E^o = 1.20\text{ V}$

$Cl_2 + 2e^- \rightarrow 2Cl^-;\ E^o = 1.35V$

(47) **(A).** If an external potential of 1.1 V is applied to the cell, the reaction stops and no current flows through the cell. Any further increase in external potential again starts the reaction but in opposite direction and the cell functions as an electrolytic cell.

(48) **(D).** More is E°_{RP}, more is the tendency to get reduced or lesser is tendency to get oxidised.

$E^\circ_{RpCr^{3+}/Cr^{2+}}$ is maximum among all.

(49) **(C).** Mass of Ag in coated layer = V × d

$= 1 \times 10^{-3} \times 100 \times 1.05 = 0.105\text{ g}$

$$W = \frac{I \times t \times \text{Eq. wt.}}{96500}$$

$$t = \frac{W \times 96500}{I \times \text{Eq. wt.}} = \frac{0.105 \times 96500}{5 \times 108} = 18.7\text{ s}$$

(50) **(A).** $2H_2O \rightarrow H_3O^+ + OH^-$

$$E^o_{cell} = \frac{0.0591}{n}\log K$$

$$\log K = \frac{E^o_{cell} \times n}{0.0591} = \frac{-0.8277 \times 1}{0.0591} = -14\ ;\ K = 10^{-14}$$

(51) **(B).** $Pt^{4+} + 4e^- \rightarrow Pt$

4 moles of electricity or 4 F of electricity is required to deposit 1 mole of Pt.

$$0.80\text{ F of electricity will deposit } \frac{1}{4} \times 0.80 = 0.20\text{ mol}$$

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

$E^\circ_{cell} = E^\circ_R - E^\circ_L = 0.34\text{ V} - (-0.76)\text{ V} = 1.10\text{ V}$

(53) **(C).** $\Lambda^o_{m\,CaCl_2} = \lambda^o_{Ca^{2+}} + 2\lambda^o_{Cl^-}$

$= 119.0 + 2 \times 76.3 = 271.6\text{ S cm}^2\text{ mol}^{-1}$

$$\Lambda^o_{m\,CH_3COONa} = \lambda^o_{CH_3COO^-} + \lambda^o_{Na^+}$$

$= 40.9 + 50.1 = 91\text{ S cm}^2\text{ mol}^{-1}$

$$\Lambda^o_{m\,NaCl} = \lambda^o_{Na^+} + \lambda^o_{Cl^-}$$

$= 50.1 + 76.3 = 126.4\text{ S cm}^2\text{ mol}^{-1}$

(54) **(C).** $2I^- \rightarrow I_2 + 2e^-$ (Oxidation)

$Br_2 + 2e^- \rightarrow 2Br^-$ (Reduction)

$2I^- + Br_2 \rightarrow I_2 + 2Br^-$ is net cell reaction

(55) **(B).** $K_a = C\alpha^2 = 0.01 \times (0.05)^2 = 2.5 \times 10^{-5}$

$K_a = C\alpha^2$

$2.5 \times 10^{-5} = 0.05 \times \alpha^2$; $\alpha = 0.0223.$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty} \; ; \; \Lambda_m^c = 0.0223 \times 4 \times 10^{-2}$$

$= 8.94 \times 10^{-4}\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

(56) **(B).** $\underset{1F}{Ag^+ + e^-} \rightarrow \underset{108g}{Ag}$

Amount of Ag deposited by 9650 C

$$= \frac{108}{96500} \times 9650 = 10.8\ g$$

(57) **(A).** $$E_{(M^{n+}/M)} = E^o_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

Since concentration of solid is taken as unity

$$E_{(M^{n+}/M)} = E^o_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

(58) **(B).** The potential of individual half-cell cannot be measured. The difference between two half-cell potentials give the emf of cell. Half-cell is called standard hydrogen electrode.

(59) **(A).** $\Lambda^o_{Al_2(SO_4)_3} = 2\Lambda^o_{Al^{3+}} + 3\Lambda^o_{SO_4^{2-}}$

$$\Lambda^o_{Al^{3+}} = \frac{\Lambda^o_{Al_2(SO_4)_3} - 3\Lambda^o_{SO_4^{2-}}}{2} = \frac{858 - (3 \times 160)}{2}$$

$= 189\ S\ cm^2\ mol^{-1}$

(60) **(B).** Lower the value of reduction potential, stronger is the reducing agent i.e., undergoes oxidation most easily.

$Cr \rightarrow Cr^{3+} + 3e^-$ (oxidation)

Hence, Cr is the strongest reducing agent.

(61) **(C).** Higher the reduction potential value, greater is the tendency to undergo reduction i.e., stronger will be the oxidising agent. Thus, MnO_4^- is the strongest oxidising agent.

(62) **(B).** Lower the reduction potential, higher is the reducing power. $Mn^{2+} < Cl^- < Cr^{3+} < Cr$

(63) **(D).** $E^o_{MnO_4^- | Mn^{2+}}$ has highest reduction potential hence, Mn^{2+} is the most stable reduced species.

(64) **(A).** $E^o_{Cr^{3+}/Cr}$ has lowest reduction potential hence, Cr^{3+} is the most stable oxidised species.

EXERCISE-3

(1) **6.** At cathode : $Mg^{2+} + 2e \rightarrow Mg$

At anode : $2Cl^- \rightarrow Cl_2 + 2e$

$\because$ Equivalent of Mg formed at cathode = Equivalent of Cl_2 formed at anode

$$\therefore \frac{6.5}{25.3/2} = \frac{w_{Cl_2}}{35.5} \quad \therefore \quad w_{Cl_2} = 18.99\ g$$

At NTP $PV = \frac{w}{m} RT$ or $1 \times V = \frac{18.99}{71} \times 0.0821 \times 273$

Volume of $Cl_2 = 5.99$ litre

(2) **3.** Weight of Ag deposited = Surface area × Thickness × Density = 80 × 0.0005 × 10.5 = 0.42 g

$$\text{moles of Ag deposited} = \frac{0.42}{108} = 3.89 \times 10^{-3}\ \text{mol}$$

moles of electricity required $= 3.89 \times 10^{-3} \times 96500 = 375.27$ moles

$$\text{time required} = \frac{375.127\ \text{amp. sec}}{3\ \text{amp.}} = 125.09\ \text{sec.}$$

(3) **84.** Since 2e are involved in the deposition of Fe ($Fe^{2+} + 2e \rightarrow Fe$), the g. eq. wt. of Fe in $Fe^{2+} = 28g$.

or 1F of electricity deposits 28g of Fe

$\therefore$ 3F of electricity will deposit = 84 g of Fe.

(4) **26.** In the change Fe is oxidised and Cu^{2+} is reduced

$$\therefore E^o_{cell} = E^o_{OP_{Fe/Fe^{2+}}} + E_{RP_{Cu^{2+}/Cu}}$$

$$E_{cell} = E^o_{cell} + \frac{0.059}{2} \log \frac{[Cu^{2+}]}{[Fe^{2+}]}$$

(For $Fe + CuSO_4 \rightleftharpoons FeSO_4 = Cu$)

$K_C = \frac{[Fe^{2+}]}{[Cu^{2+}]}$ and at equilibrium $E_{cell} = 0$

$$\therefore \text{By Eq. (1)}\ 0 = 0.44 + 0.337 + \frac{0.059}{2} \log \frac{1}{K_C}$$

or $\frac{1}{K_C} = 5.076 \times 10^{-27}$ or $K_c = 2.18 \times 10^{26}$

(5) **6.** $\because$ Eq. of Cu = Eq. of Zn = Eq. of H_2

$$\frac{6.25}{31.70} = \frac{w_{Zn}}{32.6} = \frac{w_{H_2}}{1} \quad \therefore w_{Zn} = 6.43\ g$$

(6) **4.** $M^+ \rightarrow M^{3+} + 2e^-$

$\Delta_r G^o = -nFE^o$ for 1 mole of M^+

$\Delta G^o = -2 \times 96500 \times (-0.25)\ J = +48250\ J/mole$

$= 48.25\ KJ/mole$

Energy released by conversion of 1 mole of $X \rightarrow Y$; $\Delta G = -193\ KJ$

$$\text{Hence mole of } M^+ \text{ convert} = \frac{193}{48.25} = 4$$

(7) **3.** $\lambda^0_{X^-} \approx \lambda^0_{Y^-}$

$\Rightarrow \lambda^0_{H^+} + \lambda^0_{X^-} \approx \lambda^0_{H^+} + \lambda^0_{Y^-} \Rightarrow \lambda^0_{HX} \approx \lambda^0_{HY}$ .... (1)

Also, $\frac{\lambda_m}{\lambda^0_m} = \alpha$, so $\lambda_m(HX) = \lambda^0_m\alpha_1$

and $\lambda_m(HY) = \lambda^0_m\alpha_2$

(Where α_1 and α_2 are degrees of dissociation of HX and HY respectively.)

Now, Given that $\lambda_m(HY) = 10\,\lambda_m(HX)$

$\Rightarrow \lambda^0_m\alpha_2 = 10\times\lambda^0_m\alpha_1$; $\alpha_2 = 10\,\alpha_1$ .... (2)

$K_a = \frac{C\alpha^2}{1-\alpha}$ but $\alpha << 1$, therefore, $K_a = C\alpha^2$.

$$\frac{K_a(HX)}{K_a(HY)} = \frac{0.01\,\alpha_1^2}{0.1\,\alpha_2^2} = \frac{0.01}{0.1}\times\left(\frac{1}{10}\right)^2 = \frac{1}{1000}$$

$\log(K_a(HX)) - \log(K_a(HY)) = -3$
$pK_a(HX) - pK_a(HY) = 3$

(8) **6.** $\Lambda^c_m = \left(\frac{1000\ K}{M}\right)$

$HA \rightarrow H^+ + A^-$
$c\,\alpha = 0.0015 \times \alpha = 10^{-4}$

$\alpha = \left(\frac{1}{15}\right)$ $\quad\because\ R = \rho\left(\frac{\ell}{A}\right)$

$\frac{1}{\rho} = \left(\frac{1}{R}\right)\left(\frac{\ell}{A}\right)$; $K = 5\times10^{-7}\left(\frac{120}{1}\right)$
$K = 6.0\times10^{-5}$

$$\Lambda^c_m = \frac{1000\times6.0\times10^{-5}}{1.5\times10^{-3}} = 40$$

$\alpha = \frac{\Lambda^c_m}{\Lambda^0_m}$; $\Lambda^0{}_m = 40\times15 = 6.0\times10^2 = z\times10^2$

So, $z = 6.0$

(9) **4.** $Ni \rightarrow Ni^{+2} + 2e; E^o = 0.236\ V$
$2H^+ + 2e \rightarrow H_2; E^o = 0.0\ V$
$\therefore E^o{}_{cell} = 0.236$

$\therefore E_{cell} = E^o{}_{cell} + \frac{0.059}{2}\log\frac{[H^+]^2}{[Ni^{+2}]}$

or $0 = 0.236 + \frac{0.059}{2}\log[H^+]^2$

or $-\log H^+ = 1\times10^{-4}$ $\quad\therefore$ pH = 4.

(10) **2.** Evidently $\frac{0.5094}{0.2653}$

$= \frac{\text{Equivalent weight of Ag}}{\text{Equivalent weight of metal}} \approx 0.2.$

$\therefore$ valency ratio $= \frac{\text{Valency of metal}}{\text{Valency of Ag}} = 2$

EXERCISE-4

(1) **(B).** $Pt(H_2)\,|\,H+(aq.)\,|\,Pt(H_2)$
$\quad p_1 \qquad\qquad p_2$
The emf of the above cell is given by Nernst equation. The concentration expressed hence in terms of partial pressure, $\frac{RT}{2F}\log_e\frac{p_1}{p_2}$

(2) **(CD).** We know that electron are lost at anode i.e. reaction in which O.N. increases should occurs at anode.
(i) $Fe^{+2} \longrightarrow Fe^{+3} + e^-$
(ii) $2Cr^{+3} + 7H_2O \longrightarrow Cr_2O_7{}^{2-} + 14H^+ + 6e^-$

(3) **(C).** Refining of impure copper with zinc impurity is to be done by electrolysis using following electrode
Cathode → Pure copper
anode → Impure copper
Therefore pure metal ion (M^+) are deposited on cathode.

(4) **(C).** $Ag^+ + e^- \longrightarrow Ag,\ E^o = x$
$Cu^{2+} + 2e^- \longrightarrow Cu,\ E^o = y$, so, $E_{cell} = y - x$

(5) **(B).** $E^\circ_{cell} = \frac{0.0591}{n}\log k_c \quad (n = 2)$

or $\quad 0.295 = 0.0295\log k_c$

$\log k_c = \frac{0.295}{0.0295} = 10$

$k_c = \text{Antilog } 10 = 1\times10^{10}$

(6) **(C).** Lesser the value of reduction potential more is the tendency to loose electron or greater is the reducing power. $\qquad B > C > A$

(7) **(A).** $E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{Zn^{2+}}{Cu^{2+}}$

$= 1.1 - 0.0295\log\frac{1}{0.1} = 1.1 - 0.0295 = 1.0705$ volt

(8) **(D).** Charge passed = 9650 coulomb = $\frac{1}{10}$ Faraday.
So, mole of Ag deposited = 1/10

Mass of Ag deposited = $\frac{1}{10}\times108 = 10.8$ gm.

(9) $Fe^{+3} + e^- \longrightarrow Fe^{+2}$; $\Delta G° = -1 \times F \times 0.77$

$Sn^{+2} + 2e^- \longrightarrow Sn\,(s)$; $\Delta G° = -2 \times F \times (-0.14)$

For the reaction,

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

$\Delta G = -[-2F \times (-0.14) + 2\,(-1 \times F \times 0.77)] = -1.82\,F$

Hence the standard potential of reduction is

$$= -\frac{1.82F}{-2 \times F} = 0.91V$$

$[Sn^{+2} + 2e^- \longrightarrow Sn\,(s)\,;\ \Delta G° = -2 \times F \times (-0.14)]$

(10) **(C).** $E° = \frac{0.0591}{1} \log k = 0.0591 \times 10 \Rightarrow \log k = 10,$

$k = 10^{10} = 1 \times 10^{10}$

(11) **(A).** $\overset{0}{\wedge}_{NaBr} = \overset{0}{\wedge}_{NaCl} + \overset{0}{\wedge}_{KBr} - \overset{0}{\wedge}_{KCl}$

$= 126 + 152 - 150 = 128\ S\ cm^2\ mol^{-1}$

(12) **(C).** $Zn(s) + 2H^+\,(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

On addition of H_2SO_4

As conc. of $H^+ \uparrow$

reaction will move in forward direction or in right side.

(13) **(B).** n_{Al} to be deposited $= \frac{5.12 \times 10^3}{27} = 189.63$

$\therefore$ Current required $= 3 \times 189.63 \times 96500 = 5.49 \times 10^7\ C$

(14) **(D).** $\overset{0}{\wedge}_{HOAc} = \overset{0}{\wedge}_{HCl} + \overset{0}{\wedge}_{NaOAc} - \overset{0}{\wedge}_{NaCl}$

$= 426.2 + 91.0 - 126.5 = 390.7\ S\ cm^2\ mole^{-1}$

(15) **(C).** $E_{cell} = E°_{cell} + \frac{0.0591}{n} \log \frac{[Cathode]}{[Anode]}$

For the reaction, $Ag^+ + I^- \longrightarrow AgI$

$$k = \frac{[AgI]}{[Ag^+][I^-]}$$

Hence, $E_{cell} = 0 = E°_{cathode} - E°_{anode}$

$$\Rightarrow\ 0 = 0.800 - (-0.152) + \frac{0.0591}{n} \log k_{sp}$$

$$= 0.952 + \frac{0.0591}{1} \log k_{sp}$$

or $\log k_{sp} = -\frac{0.0952}{0.059} = -16.13$

(16) **(C).** $E°_{cell} = \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$

$$\Rightarrow\ 1.1 = \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\Rightarrow\ 37.23 = \log \frac{[Zn^{2+}]}{[Cu^{2+}]} \Rightarrow \frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{37.23}$$

(17) **(A).** $\overset{0}{\wedge}_{CH_3COOH} = \overset{0}{\wedge}_{CH_3COONa} + \overset{0}{\wedge}_{HCl} - \overset{0}{\wedge}_{NaCl}$

(18) **(D).** $E_{cell} = E°_{cell} - \frac{0.0591}{6} \log \frac{[0.1]^2}{[0.01]^3}$

$$= 30 - \frac{0.0591}{6} \log 10^4 = 0.26V$$

(19) **(D).**

$Fe^{3+} + 3e^- \rightarrow Fe$; $E_1° = -0.036V$; $\Delta G_1° = +0.108F$

$Fe \rightarrow Fe^{2+} + 2e^-$; $E_2° = +0.439V$; $\Delta G_2° = -0.878F$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$; $\Delta G_3° = -0.77F$

$\because\ \Delta G° = -nF\,E°$ $\quad\therefore\quad E_3° = \frac{0.77F}{F} = 0.770V$

(20) **(C).** $\Delta G = -nFE \Rightarrow E = \frac{-\Delta G}{nF}$

$$E = -\frac{966 \times 10^{13}}{4 \times 96500} = -2.5\ V$$

$\therefore$ Potential difference needed for the reduction =2.5V

(21) **(C).** $2H^+(aq) + 2e^- \longrightarrow H_2\,(g)$

$$E_{red} = E°_{red} - \frac{0.0591}{n} \log \frac{P_{H_2}}{(H^+)^2}$$

$$E_{red} = 0 - \frac{0.0591}{2} \log \frac{2}{(1)^2}\ ;\ \ E_{red} = -\frac{0.0591}{2} \log 2$$

E_{red} is forund to be negative for (C) option.

(22) **(D).** $X + Y^{2+} \rightarrow X^{2+} + Y$

For reaction to be spontaneous E° must be positive.

$E°_{Zn/Zn^{+2}} + E°_{Ni^{2+}/Ni} = 0.76 + (-0.23) = +0.53$ (positive)

(23) **(D).** Higher the SRP, better is oxidising agent.

Hence MnO_4^- is strongest oxidising agent.

(24) **(D).** $E^0_{Cr^{3+}/Cr^{2+}} = -0.41V$, $E^0_{Mn^{3+}/Mn^{2+}} = +1.57V$,

$E^0_{Fe^{3+}/Fe^{2+}} = +0.77V$, $E^0_{Co^{3+}/Co^{2+}} = +1.97V$

SRP value normaly increases from left to right in the period of d-block elements. Some SRP value are exceptionally higher due to stability of product ion. For e.g.

$E^0_{Mn^{3+}/Mn^{2+}} = +1.57V$, $E^0_{Co^{3+}/Co^{2+}} = +1.97V$

(25) **(C).** $50 = \frac{1}{K} \times \frac{\ell}{A}$; $50 = \frac{1}{1.4} \times \frac{\ell}{A}$; $\frac{\ell}{A} = 70m^{-1}$

$$280 = \frac{1}{K} \times 70 \Rightarrow K = \frac{1}{4} Sm^{-1}$$

$$\Lambda_m = \frac{1}{4} \times \left(\frac{1000}{M}\right) (10^{-2}m)^3$$

$$= \frac{1}{4} \times \frac{1000}{0.5} \times 10^{-6} = 500 \times 10^{-6}$$

$= 5 \times 10^{-4}\ Sm^2\ mol^{-1}.$

(26) **(A).** According to Debye Huckel's Theory for a strong electrolyte, $\lambda_C = \lambda_\infty - (B)\sqrt{C}$

(27) **(C).** $Mn^{2+} + 2e^- \rightarrow Mn$; $E° = -1.18$ V

$2\,(Mn^{3+} + e^- \rightarrow Mn^{2+})$; $E° = +1.51$ V

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

$E° = SOP + SRP = -1.18 + (-1.51) = -2.69V$

Negative EMF reflects non-spontaneous cell reaction.

(28) **(A).** $Cu^{+2} + 2e^- \rightarrow Cu$. So, 2 F charge deposite 1 mol of Cu. Mass deposited = 63.5 g.

(29) **(C).** Galvanization means applying a coating of zinc metal to prevent corrosion.

(30) **(B).** $E°_{Red} \propto \dfrac{1}{\text{Reducing strength}}$

(31) **(A).** $B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$

$nB_2H_6 = \dfrac{27.66}{27.66} = 1$ $\qquad n_{O_2}$ required $= 3$

$2H_2O \rightarrow 2H_2 + O_2$ $\qquad$ n-factor for $O_2 = 4$

$\therefore$ Number of equivalent $= 3 \times 4 = 12F = 12 \times 96500C$

$i \times t = 12 \times 96500$

$$t = \frac{12 \times 96500}{100}\,s = \frac{12 \times 96500}{100 \times 3600}\,h = 3.2\ hr$$

(32) **(A).** $\Delta G° = -RT\ln k = -nFE°_{cell}$

$$\ln k = \frac{n \times F \times E°}{R \times T} = \frac{2 \times 96000 \times 2}{8 \times 300} = 160\ ;\quad k = e^{160}$$

(33) **(C).** For strongest oxidising agent, standard reduction potential should be highest.

(34) **(A).** $Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag\,(s)$

Cell reaction :

Anode : $Fe^{+2}(aq) \rightarrow Fe^{+3}(aq) + e^-$; $E^0_{Fe^{+2}/Fe^{+3}} = m\ V$

Cathode : $Ag^+\,(aq) + e^- \rightarrow Ag(s)$; $E^0_{Ag^+/Ag} = x\ V$

Cell standard potential $= (m + x)$ V

To find 'm';

$Fe^{+2} + 2e^- \rightarrow Fe$; $E°_1 = yV \Rightarrow \Delta°_1G = -(2F_y)$

$Fe^{+3} + 3e^- \rightarrow Fe$; $E_2° = zV \Rightarrow \Delta_2°G = -(3F_z)$

$Fe^{+2}\,(aq) \rightarrow Fe^{+3}\,(aq) + e^-$;

$E_3° = mV \Rightarrow \Delta_3°G = -(1Fm)$

$\Delta_3°G = \Delta G_1° - \Delta G_2° = (-2F_y + 3F_z) = -F_m$

$m = (2y - 3z)$

$E°_{cell} = (x + 2y - 3z)$ V

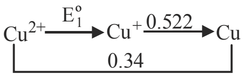
(35) **(B).** 0.1 eq. of Ni^{+2} will be discharged.

No. of eq = (No. of moles) × (n-factor)

0.1 = (No. of moles) × 2

No. of moles of Ni $= \dfrac{0.1}{2} = 0.05$

(36) **(A).**



$2 \times 0.34 = E_1° + 1 \times 0.522$

$E_1° = 0.68 - 0.522 = 0.158$

(37) **(C).** According to Kohlrausch's law correct expression is

$$(\Lambda_m^0)_{NaBr} - (\Lambda_m^0)_{NaI} = (\Lambda_m^0)_{KBr} - (\Lambda_m^0)_{KI}$$

(38) **1.52**

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

From nernst equation

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln Q \ \text{ at 1 bar \& 298 K}$$

$$\frac{2.303\,RT}{F} = 0.059\ ;\ pH = 5 \Rightarrow [H^+] = 10^{-5}\,M$$

$$E_{cell} = 1.23 - \frac{0.059}{4}\log[H^+]^4$$

$$E_{cell} = 1.23 - \frac{0.059}{4}\log(10^{-5})^4 = 1.23 + 0.295 = 1.525\ V$$

(39) **02.15**

At Equilibrium state, $E_{cell} = 0$; $E°_{cell} = 0.01V$

$Sn + Pb^{2+} \rightarrow Sn^{2+} + Pb$

$$0 = 0.01 - \frac{0.06}{2}\log\left\{\frac{[Sn^{2+}]}{[Pb^{2+}]}\right\}$$

$$0.01 = \frac{0.06}{2}\log\left\{\frac{[Sn^{2+}]}{[Pb^{2+}]}\right\}$$

$$\frac{1}{3} = \log\left\{\frac{[Sn^{2+}]}{[Pb^{2+}]}\right\} \Rightarrow \frac{[Sn^{2+}]}{[Pb^{2+}]} = 10^{1/3} = 2.1544$$

EXERCISE-5

(1) **(D).** No. of gram equivalent of H^+

$= \text{No. of gm eq. of } Al^{3+} = \dfrac{4.5}{9} = 0.5$

Eq. wt. of $Al^{3+} = \dfrac{27}{3} = 9$

No. of gm eq. of H^+ = no. of mole of H^+

Hence mass of $H^+ = 0.5 \times 1g = 0.5g$

We know that, 2g H_2 at STP = 22.4 L

$\therefore$ 0.5g H_2 at STP $= \dfrac{22.4}{2} \times 0.5 = 5.6$ L

(2) **(B).** $Fe \longrightarrow Fe^{2+} + 2e$ $\qquad$ [Anode] ; $E = -0.441$ V

$[Fe^{3+} + e \longrightarrow Fe^{2+}] \times 2$ $\qquad$ [Cathode] ; $E = +0.771$ V

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

$E°_{cell} = E°_{cathode} - E°_{Anode}$

$= 0.771 - (-0.441) = 0.771 + 0.441 = 1.212$ V

(3) **(C).** The cell reaction is as follows :

$A \rightarrow A^+ + e$

$B^+ + e^- \rightarrow B$

Addiing $A + B^+ \rightarrow A^+ + B$

(4) **(B).** Efficiency of a fuel cell $(\eta) = \dfrac{\Delta G}{\Delta H}$

(5) **(C).** As $E^{\circ}_{cell} = \dfrac{0.0591}{n} \log K_c$

$\therefore\ 0.46 = \dfrac{0.0591}{n} \log K_c \ \therefore\ \log K_c = \dfrac{2 \times 0.46}{0.0591} = 15.57$

or $K_c = \text{Antilog } 15.57 = 3.7 \times 10^{15} \approx 4.0 \times 10^{15}$

(6) **(D).** According to Kohlransch law, at infinite dilution, each ion makes definite contribution to conductance of an electrolyte whatever be the nature of the other ion of the electrolyte.

(7) **(D).** $C_5H_{12} + 8O_2(g) \longrightarrow 5CO_2(g) + 6H_2O(\ell)$

(1) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O(\ell),\ \Delta G_1 = -237.2 \text{ kJ/mol}$

(2) $C + O_2(g) \longrightarrow CO_2(g), \Delta G_2 = -394.4 \text{ kJ/mol}$

(3) $5C + 6H_2(g) \longrightarrow C_5H_{12}(g), \Delta G_3 = -8.2 \text{ kJ/mol}$

$\Delta G_4 = 6 \times \Delta G_1 + 5 \times \Delta G_2 + (-\Delta G_3)$

$= 6 \times (-237.12) + 5 \times (-394.4) + (-8.2)$

$= -1423.2 - 1972 + 8.2 = -3387 \text{ kJ/mol}$

$-nFE^{\circ} = -3387 \times 1000$

$$E^{\circ} = \frac{3387 \times 1000}{96500 \times 32} = 1.0968 V$$

(8) **(D).** Fe^{+3} has highest SRP & thus behaves as strongest oxidising agent.

(9) **(D).** $Cu^{2+} + 2e^- \rightarrow Cu,$

$\Delta G^o = -nE^oF = -2 \times F \times 0.337 = -0.674 F$

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

$\Delta G^o = -nE^oF = 1 \times F \times -1.153 = 0.153 F$

$Cu^+ + e^- \rightarrow Cu,\ \ \Delta G^o = -0.521F = -nE^oF$

$n = 1, E^o = +0.52V$

(10) **(A).** Total current $= 4.0 \times 10^4 \times 6 \times 60 \times 60$ C

96500 C liberates 9g of Al (1 g. eq)

$(4 \times 10^4 \times 6 \times 60 \times 60)$ C liberates 8.1×10^4 g of Al

(11) **(D).** $\alpha = \dfrac{\Lambda}{\Lambda_D} = \dfrac{8.0}{400} = 2 \times 10^{-2}$

$$K_{\alpha} = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2 = \frac{1}{32} \times (2 \times 10^{-2})^2 = 1.25 \times 10^{-5}$$

(12) **(A).** We know that,

Standard Gibbs energy, $\Delta G^{\circ} = -nEF^{\circ}_{cell}$

For the cell reaction,

$2Ag^+ + Cu \longrightarrow Cu^{2+} + 2Ag$

$\Delta G^{\circ} = -2 \times 96500 \times 0.46$

$= -88780 \text{ J} = -88.7 \text{ kJ} \approx -89.0 \text{ kJ}$

(13) **(A).** $\lambda_{eq} = \kappa \times V = \dfrac{\kappa \times 1000}{\text{normality}}$

On dilution, the number of current carrying particles per cm^3 decreases but the volume of solution increases.

Consequently, the ionic mobility increases, which in turn increases the equivalent conductance of strong electrolyte.

(14) **(B).** At infinite dilution, when dissociation is complete, each ion makes a definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated.

Hence, $\Lambda_{Al_2(SO_4)_3} = \Lambda_{Al^{3+}} + \Lambda_{SO_4{}^{2-}}$

(15) **(D).** EMF of a cell = Reduction potential of cathode – Reduction potential of anode

= Reduction potential of cathode + Oxidation potential of anode

= Oxidation potential of anode – Oxidation potential of cathode.

(16) **(C).** $\Delta G_3 = \Delta G_1 + \Delta G_2$

$\Rightarrow\ -2FE^{\circ} = -1F \times 0.15 + (-1F \times 0.50)$

$\Rightarrow\ -2FE^{\circ} = -0.15F - 0.50F \Rightarrow -2FE^{\circ} = -F(0.15 + 0.50)$

$\therefore\ E^{\circ} = \dfrac{0.65}{2} = 0.325$ volt

(17) **(C).** $E^{\circ}_{cell} = E^{\circ}_{cathode(RP)} - E^{\circ}_{anode(RP)}$

$= 0.15 - (-0.74) = +0.89$ V

(18) **(A).** $\Delta G^{\circ} = -nFE^{\circ}$ & $\Delta G^{\circ} = -RT \log_e K_{eq}$.

(19) **(D).** Z > X > Y; higher the reduction potential lesser the reducing power.

(20) **(C).** $2\,(e^- + Fe^{+3} \longrightarrow Fe^{+2})\ \ E^o = 0.77$ V

$2I^- \longrightarrow I_2 + 2e^- \qquad E^o = 0.536$ V

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

$E^o = E^o_{ox} + E^o_{red} = 0.77 - 0.536 = 0.164$ V

So, Reaction will take place.

(21) **(D).** $\Lambda^0_m(NH_4Cl) + \Lambda^0_m(NaOH) - \Lambda^0_m(NaCl)$

(22) **(A).** E^o more positive, reducing agent will be greater.

(23) **(D).** $\Lambda^0_m = \Lambda^0_{CH_3COONa} + \Lambda^0_{HCl} - \Lambda^0_{NaCl}$

$= 91 + 425.9 - 126.4 = 390.5$

(24) **(C).** $E^0_{Cu^{2+}/Cu} = 0.34$ volt, other has –ve E^0_{RP}

(25) **(C).** $\Delta G = -nFE^{\circ}\ \ ;\ n = \dfrac{2}{3} \times 2 \times 3$

$960 \times 10^3 = -4 \times 96.500 \times E^{\circ} = 4$ for reaction

$E^{\circ} = -2.5$ volt. So, it needed 2.5 volt for reduction.

(26) **(D).** $\%\,\alpha = \dfrac{\lambda^c}{\lambda^{\infty}} \times 100 = \dfrac{9.54}{238} \times 100 = 4.008\%$

(27) **(C).** $\frac{1}{2}H_2(g) \longrightarrow H^+ + e^-$

$$E_{O.P.} = E^{\circ}_{O.P.} - \frac{0.059}{n} \log \frac{[H^+]}{(P_{H_2})^{1/2}}$$

$$E_{O.P.} = 0 - \frac{0.059}{1} \log \frac{10^{-10}}{(1)^{1/2}}\ [pH = 10, [H^+] = 10^{-10} M]$$

$E_{O.P.} = 0.59$ V

(28) **(B).** $Zn^{2+}(aq) + 2e^- \rightarrow Zn\,(s);\ E° = -0.76\ V$

$Ag_2O(s) + H_2O(\ell) + 2e^- \rightarrow 2Ag\,(s) + 2OH^-(aq);$

$E° = 0.34\ V$

$Zn\,(s) + Ag_2O(s) + H_2O$

$\rightarrow 2Ag\,(s) + Zn^{+2}\,(aq) + 2OH^-(aq);\ E_{cell} = ?$

$E°_{cell} = (E°_{R.P.})_{cathode} - (E°_{R.P.})_{anode}$

$E°_{cell} = 0.34 - (-0.76) = 1.10\ V;\ E_{cell} = E°_{cell} = 1.10V$

(29) **(C).** $\underset{1\ mole}{\overset{+7}{Mn}O_4^{2-}} \xrightarrow{1F} \overset{+6}{Mn}O_4^{2-}$

∴ For 0.1 mole 0.1 F is required.

(30) **(D).** $W_{O_2} = \frac{5600}{22400} \times 32 = 8g = 1$ equivalents

$= 1$ equivalent of $Ag = 108$ g

(31) **(D).** Fuel cell convert chemical energy of fuel like H_2, CH_4 into electrical energy.

(32) **(D).** Aqueous solution of HCl is the best conductor of electric current because HCl is strong acid, so it dissociates completely into ions.

(33) **(A).** $2H^+\ 2e^- \rightarrow H_2\,(g)$

$$E = E° - \frac{0.0591}{2} \times \log \frac{P_{H_2}}{[H^+]^2} = 0 - \frac{0.0591}{2} \times \log \frac{P_{H_2}}{(10^{-7})^2}$$

∴ For potential of H_2 electrode to be zero, P_{H_2} should be 10^{-14} i.e., $\log \frac{10^{-14}}{10^{-14}} = 0$

(34) **(B).** $\Lambda_m = \frac{\kappa \times 100}{M} = \frac{5.76 \times 10^{-3} \times 1000}{0.5} = 11.52\ S\ cm^2/mol$

(35) **(B).** For 1 mole Cl_2, 2F electricity is required

∴ For 0.1 mole Cl_2, 0.2 F electricity will be required

∴ $Q = I \times t$

or $t = \frac{Q}{I} = \frac{0.2 \times 96500}{3 \times 60} \approx 110$ min.

(36) **(A).** $E°_{cell} = -$ ve

∴ $\Delta G° = +ve\ \&\ K_{eq} = -ve$ i.e., $\Delta G° > 0\ \&\ K_{eq} < 1$

(37) **(C).** $Q = I \times t = 1\ A \times 60\ s = 60\ C$

∴ No. of electrons $= \frac{60}{1.602 \times 10^{-19}} = 3.75 \times 10^{20}$

(38) **(D).** $E°_{Zn^{2(+)}/Zn} = -0.76V;\quad E°_{Fe^{2(+)}/Fe} = -0.44V$

(39) **(B).** For cell

$Zn\,|\,ZnSO_4\,(0.01M)\,||\,CuSO_4\,(1M)\,|\,Cu$

Cell reaction : $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$

$$E_1 = E° - \frac{0.059}{2} \log \frac{Zn^{+2}}{Cu^{+2}}$$

$$E_1 = E° - \frac{0.059}{2} \log \frac{0.01}{1} = E° - \frac{0.059}{2} \log \frac{1}{100} \quad .... (1)$$

For cell : $Zn\,|\,ZnSO_4\,(1M)\,||\,CuSO_4\,(0.01\ M)\,|\,Cu$

$$E_2 = E° - \frac{0.059}{2} \log \frac{1}{0.01} = E° - \frac{0.059}{2} \log 100\ ...\ (2)$$

$[E_1 > E_2]$

(40) **(D).** $\overset{+1}{HBrO} \rightarrow \overset{0}{Br_2},\ E°_{HBrO/Br_2} = 1.595\ V$

$\overset{+1}{HBrO} \rightarrow \overset{+5}{BrO_3^-},\ E°_{BrO_3^-/HBrO} = 1.5\ V$

$E°_{cell}$ for the disproportionation of HBrO,

$E°_{cell} = E°_{HBrO/Br_2} - E°_{BrO_3^-/HBrO}$

$= 1.595 - 1.5 = 0.095\ V = +$ ve

(41) **(A).**

(a) $2\overset{+1}{Cu^+} \rightarrow \overset{+2}{Cu^{2+}} + \overset{0}{Cu^0}$ }Disproportionation

(b) $3\overset{+6}{MnO_4^{2-}} + 4H^+ \rightarrow 2\overset{+7}{MnO_4^-} + \overset{+4}{MnO_2} + 2H_2O$

}Disproportionation

(c) $2\overset{+7}{KMnO_4} \xrightarrow{\Delta} \overset{+6}{K_2MnO_4} + \overset{+4}{MnO_2} + \overset{0}{O_2}$

}Not a Disproportionation

(d) $2\overset{+7}{MnO_4^-} + 3\overset{+2}{Mn^{2+}} + 2H_2O \rightarrow 5\overset{+4}{MnO_2} + 4H^+$

}Not a Disproportionation

(42) **(C).** $E_{cell} = E°_{cell} - \frac{0.059}{n} \log Q \qquad ...(i)$

(At equilibrium, $Q = K_{eq}$ and $E_{cell} = 0$)

$0 = E°_{cell} - \frac{0.059}{1} \log K_{eq}$ (from equation (i))

$$\log K_{eq} = \frac{E°_{cell}}{0.059} = \frac{0.59}{0.059} = 10$$

$K_{eq} = 10^{10} = 1 \times 10^{10}$