## 1. INTRODUCTION

Electrochemistry is a branch of chemistry which deals with inter-conversion of chemical energies and electrical energy. We'll discuss electrolytic reactions (reactions that occur when electricity passes through solutions) as well as electromagnetic reaction (reactions that produce electric energy). Some examples of electrolytic reactions are electrolysis, electroplating, electro refining of metals, etc. Some examples of electro genetic reactions are reactions occurring in cells or batteries.

## 2. TERMINOLOGIES IN ELECTROCHEMISTY

Some important terms used in Electrochemistry are as follows:
(a) Electrical Conductors: Materials that allow flow of electrons are known as conductors. There are broadly two types of conductors-Electronic/Metallic and Electrolytic/Solution.

Table 17.1: Difference between Electronic Conductor and Electrolytic Conductors

|  | Electronic Conductors or Metallic Conductors | Electrolytic Conductors or Solution Conductors |
| :--- | :--- | :--- |
| 1. | Passage of current by movement of electrons in the <br> metallic lattice, e.g., Cu, Ag, etc. | Passage of current by ions in molten state or in aqueous solution <br> of electrolytes, e.g., NaCl (aq) or NaCl (fused). |
| 2. | Passage of current brings in only physical changes. | Passage of current brings in physical as well as chemical changes. |
| 3. | It generally shows no transfer of matter. | It involves transfer of matter in the form of ions. |
| 4. | It generally shows an increase in resistance during the <br> passage of current due to increase in temperature. <br> Thermal motion of metal ions hindering the flow of <br> electrons increases with increase in temperature. | It generally shows a decrease in resistance due to decrease in <br> viscosity of the medium and degree of hydration of ions with <br> increase in temperature. |
| 5. | The conducting power of metals is usually high. | The conducting power of electrolytic conductors is relatively low. |

(b) Insulators: Those materials which don't allow the passage of electrons are known as Insulators. For e.g. wood, wool, plastic, silk, etc.
(c) Electrolytes: The substance that in solution or in the molten state, conducts electric current and is simultaneously decomposed is called an electrolyte. The extent or degree of dissociation of different electrolytes in solution is different. Electrolytes can be broadly categorized into two: Strong and Weak Electrolytes.
(d) Strong Electrolytes: Substances which are largely dissociated and form a highly conducting liquid in water are strong electrolytes, e.g., All salts (except $\mathrm{CdBr}_{2^{\prime}} \mathrm{HgCl}_{2}$ ), mineral acids like $\mathrm{HCl}_{\mathbf{2}} \mathrm{H}_{2} \mathrm{SO}_{4}, \mathrm{HNO}_{3^{\prime}}$ etc. and bases like $\mathbf{N a O H}, \mathbf{K O H}$, etc. are strong electrolytes. The strong electrolytes are almost $100 \%$ ionized at normal dilution.
(e) Weak Electrolytes: Substances which dissociate only to a small extent in aqueous solution forming low conducting liquid are weak electrolytes, e.g., All organic acids (except sulphonic acids), inorganic acids like $\mathrm{HCN}, \mathrm{H}_{3} \mathrm{BO}_{3}$, etc. and bases like $\mathrm{NH}_{3}$, amines, etc. are weak electrolytes.
(f) Electrodes: In order to pass the current through an electrolytic conductor, two rods or plates are always needed which are connected with the terminals of a battery. These rods/plates are called Electrodes. The electrode where oxidation reaction takes place is anode and electrode where reduction takes place is cathode.

## 3. ELECTROLYSIS

The phenomenon in which passage of current through an electrolyte (molten or solution) brings in chemical changes involving electronation (reduction) as well as de-electronation (oxidation) of ions is known as electrolysis.

### 3.1 Preferential Discharge Theory

If an electrolytic solution consists of more than two ions and the electrolysis is done, it is observed that all the ions are not discharged from the electrodes simultaneously but certain ions are liberated from the electrodes in preference to others. This is explained by preferential discharge theory. It states that if more than one type of ions are attracted towards a particular electrode, then the one discharged is the ion which requires least energy. The potential at which the ion is discharged or deposited on the appropriate electrode is termed the discharge potential or deposition potential. The values of discharge potential are different for different ions.

Table 17.2: Examples of preferential discharge theory

| Electrolyte | Electrode | Cathodic reaction | Anodic reaction |
| :--- | :---: | :--- | :--- |
| Aqueous acidified <br> CuCl solution | Pt | $\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{Cu}$ | $2 \mathrm{Cl}^{-} \longrightarrow \mathrm{Cl}_{2}+2 \mathrm{e}^{-}$ |
| Molten $\mathrm{PbBr}_{2}$ | Pt | $\mathrm{Pb}^{2+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{Pb}$ | $2 \mathrm{Br}^{-} \longrightarrow \mathrm{Br}_{2}+2 \mathrm{e}^{-}$ |
| Sodium chloride <br> solution | Hg | $2 \mathrm{Na}^{+}+2 \mathrm{e}^{-} \longrightarrow 2 \mathrm{Na}$ | $2 \mathrm{Cl}^{-} \longrightarrow \mathrm{Cl}_{2}+2 \mathrm{e}^{-}$ |
| Silver nitrate solution | Pt | $\mathrm{Ag}^{+}+\mathrm{e}^{-} \longrightarrow \mathrm{Ag}$ | $2 \mathrm{OH}^{-} \longrightarrow \frac{1}{2} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-}$ |
| Sodium nitrate <br> solution | Pt | $2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{H}_{2}$ | $2 \mathrm{OH}^{-} \longrightarrow \frac{1}{2} \mathrm{O}_{2}+\mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-}$ |

Illustration 1: Find the charge in coulomb on 1 g -ion of $\mathrm{N}^{3-}$.
(JEE MAIN)
Sol: First determine charge on one ions of this can be calculated as product of number of electron and charge of electron. According to Avogadro's law one g of ion contains $6.02 \times 10^{23}$ ions. So, charge on one g-ion of $\mathrm{N}^{3-}$ can be calculated by multiplying charge.
Charge on one ions of $\mathrm{N}^{3-}$ into Avogadro number.
Charge on one ions of $\mathrm{N}^{3-}=3 \times 1.6 \times 10^{-19}$ coulomb One g-ion $=6.02 \times 10^{23}$ ions
Thus, charge on one g-ion of $\mathrm{N}^{3-}=3 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{23}=2.89 \times 10^{5}$ coulomb

Illustration 2: Explain the reaction: (a) $2 \mathrm{KI}+\mathrm{Cl}_{2} \longrightarrow 2 \mathrm{KCl}+\mathrm{I}_{2}$, (b) $2 \mathrm{KClO}_{3}+\mathrm{I}_{2} \longrightarrow 2 \mathrm{KIO}_{3}+\mathrm{Cl}_{2}$
Sol: Compound which undergoes oxidation acts as a reducing agent and compound which undergoes reduction acts as an oxidizing agent.
(a) $\mathrm{Cl}_{2}$ acts as oxidizing agent: $2 \mathrm{e}^{-}+\mathrm{Cl}_{2} \longrightarrow 2 \mathrm{Cl}^{-} ; \quad 2 \mathrm{I}^{-} \longrightarrow \mathrm{I}_{2}+2 \mathrm{e}^{-}$
(b) $\mathrm{I}_{2}$ acts as reducing agent: $2 \mathrm{Cl}^{5+}+10 \mathrm{e}^{-} \longrightarrow \mathrm{Cl}_{2}$;
$\mathrm{I}_{2}^{0} \longrightarrow 2 \mathrm{I}^{5+}+10 \mathrm{e}^{-}$

## PLANCESS CONCEPTS

Misconception: Electrolysis does not mean breaking up of an ionic compound into ions. An ionic compound even on dissolution in water furnishes ions.

Note: During electrolysis, oxidation-reduction occurs simultaneously. Oxidation occurs at anode whereas reduction occurs at cathode.

Nikhil Khandelwal (JEE 2009 AIR 94)

### 3.2 Faraday's Law of Electrolysis

The relationship between the quantity of electric charge passed through an electrolyte and the amount of the substance deposited at the electrodes was presented as the 'laws of electrolysis' by Faraday in 1834.

### 3.2.1 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.

If W be the mass of the substance deposited by passing Q coulomb of charge, then according to the law, we have the relation: $\mathrm{W} \propto \mathrm{Q}$
$\mathrm{Q}=$ current in amperes $\times$ time in seconds $=\mathrm{I} \times \mathrm{t}$
So, $W \propto I \times t$ or $W=Z \times I \times t$
Where $Z$ is a constant, known as electrochemical equivalent and is characteristic of the substance deposited. When a current of one ampere is passed for one second, i.e., one coulomb $(Q=1)$, then $W=Z$.

Definition of electrochemical equivalent: Mass of the substance deposited by one coulomb of charge or one ampere current for one second.

### 3.2.2 Faraday's Second Law

When the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses. Again according to first law, $W=Z \times Q$
When, $\mathrm{Q}=96500$ coulomb, W becomes gram equivalent mass ( E ).
Thus, $E=Z \times 96500$ or $Z=\frac{E}{96500} ; \frac{Z_{1}}{Z_{2}}=\frac{E_{1}}{E_{2}}$

### 3.2.3 Faraday's Law for Gaseous Electrolytic Product

For the gases, we use $\mathrm{V}=\frac{\mathrm{ItV}_{\mathrm{e}}}{96500}$
Where, $\mathrm{V}=$ Volume of gas evolved at STP at an electrode
$\mathrm{V}_{\mathrm{e}}=$ Equivalent volume $=$ Volume of gas evolved at an electrode at STP by 1 faraday charge

Example: A 40.0 amp current flowed through molten iron (III) chloride for 10.0 hours ( $36,000 \mathrm{~s}$ ). Determine the mass of iron and the volume of chlorine gas (measured at $25^{\circ} \mathrm{C}$ and 1 atm ) that is produced during this time.

## Sol:

1. Write the half-reaction that take place at the anode and at the cathode.

Anode (oxidation): $2 \mathrm{Cl}^{-} \rightarrow \mathrm{Cl}_{2}(\mathrm{~g})+2 \mathrm{e}^{-}$Cathode (reduction): $\mathrm{Fe}^{3+}+3 \mathrm{e}^{-} \rightarrow \mathrm{Fe}(\mathrm{s})$
2. Calculate the number of moles of electrons.
$40.0 \mathrm{amps} \times 36,000 \mathrm{~s}=1.44 \times 10^{6} \mathrm{C}$
$1.44 \times 10^{6} \mathrm{C} \times \frac{1 \mathrm{~F}}{96,485 \mathrm{C}}=14.9 \mathrm{~F} ; 14.9 \mathrm{~F} \times \frac{1 \mathrm{~mole} \mathrm{e}^{-}}{1 \mathrm{~F}}=14.9 \mathrm{~mole} \mathrm{e}^{-}$
3. Calculate the moles of iron and of chlorine produced using the number of moles of electrons calculated and the stoichiometry from the balanced half-reactions. According to the equations, three moles of electrons produce one mole of iron and 2 moles of electrons produce 1 mole of chlorine gas.
$14.9 \mathrm{~mole} \mathrm{e}^{-} \times \frac{1 \mathrm{~mole} \mathrm{Fe}}{3 \mathrm{~mole} \mathrm{e}^{-}}=4.97 \mathrm{~mole} \mathrm{Fe} ; 14.9 \mathrm{~mole} \mathrm{e}^{-} \times \frac{1 \mathrm{~mole} \mathrm{Cl}_{2}}{2 \mathrm{~mole} \mathrm{e}^{-}}=7.45 \mathrm{~mole} \mathrm{Cl}_{2}$
4. Calculate the mass of iron using the molar mass and calculate the volume of chlorine gas using the ideal gas law ( $\mathrm{PV}=\mathrm{nRT}$ ).
$4.97 \mathrm{~mole} \mathrm{Fe} \times \frac{55.847 \mathrm{gFe}}{1 \mathrm{~mole} \mathrm{Fe}}=278 \mathrm{gFe} ; \frac{\left(7.45 \mathrm{moleCl}_{2}\right)(0.0821 \mathrm{~atm} \mathrm{~L} / \mathrm{mole} \mathrm{K})(298 \mathrm{~K})}{1 \mathrm{~atm}}=182 \mathrm{LCl}_{2}$

## Calculating the Time required

To determine the quantity of time required to produce a known quantity of a substance given the amount of current that flowed:
(i) Find the quantity of substance produced/consumed in moles.
(ii) Write the balanced half-reaction involved.
(iii) Calculate the number of moles of electrons required.
(iv) Convert the moles of electrons into coulombs.
(v) Calculate the time required.

Example: How long must a 20.0 amp current flow through a solution of $\mathrm{ZnSO}_{4}$ in order to produce 25.00 g of Zn metal?

## Sol:

(i) Convert the mass of Zn produced into moles using the molar mass of Zn .
$25.00 \mathrm{gZn} \times \frac{1 \mathrm{~mole} \mathrm{Zn}}{65.39 \mathrm{gZn}}=0.3823 \mathrm{~mole} \mathrm{Zn}$
(ii) Write the half-reaction for the production of Zn at the cathode. $\mathrm{Zn}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Zn}(\mathrm{s})$
(iii) Calculate the moles of $\mathrm{e}^{-}$required to produce the moles of Zn using the stoichiometry of the balanced halfreaction. According to the equation, 2 moles of electrons will produce one mole of zinc.
$0.3823 \mathrm{~mole} \mathrm{Zn} \times \frac{2 \mathrm{~mole} \mathrm{e}^{-}}{1 \mathrm{~mole} \mathrm{Zn}^{2}}=0.7646 \mathrm{~mole} \mathrm{e}^{-}$
(iv) Convert the moles of electrons into coulombs of charge using Faraday's constant.
$0.76 \mathrm{~mole} \mathrm{e}^{-} \times \frac{1 \mathrm{~F}}{1 \mathrm{molee}^{-}}=0.7646 \mathrm{~F} ; 0.7646 \mathrm{~F} \times \frac{96,485 \mathrm{C}}{1 \mathrm{~F}}=73,770 \mathrm{C}$
(v) Calculate the time using the current and the coulombs of charge.

$$
20.0 \mathrm{amps} \times \mathrm{t}=73,770 \mathrm{C} ; \quad \mathrm{t}=3,688 \mathrm{~s} \text { or } 1.03 \mathrm{~h}
$$

## Calculating the Current required

To determine the amount of current necessary to produce a known quantity of substance in a given amount of time:
(i) Find the quantity of substance produced/or consumed in moles.
(ii) Write the equation for the half-reaction taking place.
(iii) Calculate the number of moles of electrons required.
(iv) Convert the moles of electrons into coulombs of charge.
(v) Calculate the current required.

Example: What amount of current is required to produce 400.0 L of hydrogen gas, measured at STP, from the electrolysis of water in 1 hour ( 3600 s )?

## Sol:

(i) Calculate the number of moles of $\mathrm{H}_{2}$. (Remember, at STP, 1 mole of any gas occupies 22.4 L ) $400.0 \mathrm{~L} \mathrm{H}_{2} \times \frac{1 \mathrm{~mole} \mathrm{H}_{2}}{22.4 \mathrm{~L} \mathrm{H}_{2}}=17.9 \mathrm{~mole} \mathrm{H}_{2}$
(ii) Write the equation for the half-reaction that takes place.

Hydrogen is produced during the reduction of water at the cathode. The equation for this half-reaction is:
$4 \mathrm{e}^{-}+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \rightarrow 2 \mathrm{H}_{2}(\mathrm{~g})+4 \mathrm{OH}^{-}(\mathrm{aq})$
(iii) Calculate the number of moles of electrons. According to the stoichiometry of the equation, 4 mole of $\mathrm{e}^{-}$are required to produce 2 moles of hydrogen gas, or 2 moles of $\mathrm{e}^{-} \mathrm{s}$ for every one mole of hydrogen gas.
$17.9 \mathrm{~mole}_{2} \times \frac{2 \mathrm{~mole} \mathrm{e}^{-}}{1 \mathrm{~mole} \mathrm{H}_{2}}=35.8 \mathrm{~mole} \mathrm{e}^{-}$
(iv) Convert the moles of electrons into coulombs of charge.
$35.8 \mathrm{~mole}^{-} \times \frac{1 \mathrm{~F}}{1 \mathrm{~mole} \mathrm{e}^{-}}=35.8 \mathrm{~F} ; 35.8 \mathrm{~F} \times \frac{96,485 \mathrm{C}}{1 \mathrm{~F}}=3.45 \times 10^{6} \mathrm{C}$
(v) Calculate the current required. $\mathrm{I} \times 3600 \mathrm{~s}=3.45 \times 10^{6} \mathrm{C}$; $\mathrm{I}=958 \mathrm{C} / \mathrm{s}=958 \mathrm{amps}$

## PLANCESS CONCEPTS

As one faraday ( 96500 coulombs) deposits one gram equivalent of the substance, hence electrochemical equivalent can be calculated from the equivalent weight,
i.e., $Z=\frac{\text { Eq.wt. of the substance }}{96500}$

Note: Knowing the weight of the substance deposited (W gram) on passing a definite quantity of electricity
(Q coulombs), the equivalent weight of the substance can be calculated, i.e., Eq. wt. $=\frac{W}{Q} \times 96500$

## PLANCESS CONCEPTS

Tip: The quantity of electricity actually passed is calculated from the current and time as follows:

## Quantity of electricity in columbs = Current amperes $\times$ time in seconds

Thus, knowing the quantity of electricity passed, the amount of substance deposited can be calculated.
Faraday's first law and second law can be combined to give a mathematical relation as follows:-
$W=Z Q=\frac{E}{F} \times Q=\frac{Q}{F} \times E=\frac{Q}{F} \times \frac{M}{Z}=\frac{C \times t}{F} \times \frac{M}{Z}$
z = Electrochemical equivalent; $\mathbf{Q}=$ Quantity of electricity passed, $\mathrm{E}=\mathrm{Eq} . \mathrm{wt}$. of the metal,
F = 1 Faraday, $\mathbf{M}=$ Atomic mass of the metal; $\mathbf{z}=$ Valency of the metal; C = Current passed,
$t=$ Time for which current is passed.
Saurabh Gupta (JEE 2010 AIR 443)

Illustration 3: Electric current of 100 ampere is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.
(JEE MAIN)
Sol: Here current and time is given so from this first calculate quantity of electricity passed (charge) and from this calculate the amount of chlorine liberated. Volume of $\mathrm{Cl}_{2}$ liberated at NTP can be determined by multiplying the amount of chlorine liberated by 22.4 L

The reaction taking place at anode is: $\underset{71.0 \mathrm{~g}}{2 \mathrm{Cl}^{-} \longrightarrow} \underset{\substack{71.0 \mathrm{~g} \\ 1 \text { mole }}}{\mathrm{Cl}_{2}}+\underset{\text { 2 } 90500 \text { coulomb }}{2 \mathrm{e}^{-}} \mathrm{Q}=\mathrm{I} \times \mathrm{t}=100 \times 5 \times 60 \times 60$ coulomb
The amount of chlorine liberated by passing $100 \times 5 \times 60 \times 60$ coulomb of electric charge
$=\frac{1}{2 \times 96500} \times 100 \times 5 \times 60 \times 60=9.3264$ mole Volume of $\mathrm{Cl}_{2}$ liberated at NTP $=9.3264 \times 22.4=201 \mathrm{~L}$

Illustration 4: How much electric charge is required to oxidize (a) 1 mole of $\mathrm{H}_{2} \mathrm{O}$ to $\mathrm{O}_{2}$ and
(b) 1 mole of FeO to $\mathrm{Fe}_{2} \mathrm{O}_{3}$ ?
(JEE MAIN)
Sol: Charge $=$ No of electrons involved in the reaction x faradays constant
So first find out the no of electron reaction involved in the reaction by writing the chemical reaction, balancing it and then calculate the charge.
(a) The oxidation reaction is: $\underset{1 \text { mole }}{\mathrm{H}_{2} \mathrm{O} \longrightarrow} \longrightarrow \frac{1}{2} \mathrm{O}_{2}+2 \mathrm{H}^{+}+\underset{2 \text { mole }}{2 \mathrm{e}^{-}} ; \mathrm{Q}=2 \times \mathrm{F}=2 \times 96500=193000$ coulomb
(b) The oxidation reaction is: $\mathrm{FeO}+\frac{1}{2} \mathrm{H}_{2} \mathrm{O} \longrightarrow \frac{1}{2} \mathrm{Fe}_{2} \mathrm{O}_{3}+\mathrm{H}^{+}+\mathrm{e}^{-} ; \mathrm{O}=\mathrm{F}=96500$ coulomb

Illustration 5: An aqueous solution of sodium chloride on electrolysis gives $\mathrm{H}_{2}(\mathrm{~g}), \mathrm{Cl}_{2}(\mathrm{~g})$ and NaOH according to the reaction. $2 \mathrm{Cl}^{-}$(aq.) $+2 \mathrm{H}_{2} \mathrm{O} \longrightarrow 2 \mathrm{OH}^{-}$(aq.) $+\mathrm{H}_{2}(\mathrm{~g})+\mathrm{Cl}_{2}$ (g).
A direct current of 25 ampere with a current efficiency $62 \%$ is passed through 20 L of NaCl solution ( $20 \%$ by mass). Write down the reactions taking place at the anode and cathode. How long will it take to produce $1 \mathrm{~kg} \mathrm{of}_{\mathrm{Cl}}^{2}$ ? What will be the molarity of the solution with respect to hydroxide ion? Assume no loss due to evaporation.
(JEE ADVANCED)

Sol: Time can be calculate by using charge and current relationship. Effective current is determined by using current efficiency. Here it is given that we have to find out the molarity of the solution with respect to hydroxide Ion. Volume is given. We have to find out the no of moles of oxygen.

This can be achieved by calculating the no of mole of $\mathrm{Cl}_{2}$ present in 1 kg .
Reactions at anode and cathode are: $2 \mathrm{Cl}^{-} \longrightarrow \mathrm{Cl}_{2}+2 \mathrm{e}^{-}$(at anode)
$2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-} \longrightarrow \mathrm{H}_{2}+2 \mathrm{OH}^{-}$(at cathode) 1 kg of $\mathrm{Cl}_{2}=\frac{1000}{71.0}=14.08$ mole
Charge to produce one mole of $\mathrm{Cl}_{2}=2 \times 96500$
Charge to produce 14.08 mole of $\mathrm{Cl}_{2}=2 \times 96500 \times 14.08$
Effective current $=\frac{62}{100} \times 25.0=15.5$ ampere
Time $=\frac{\text { Charge }}{\text { Current }}=\frac{2 \times 96500 \times 14.08}{15.5}=175318.7$ second $=48.699$ hour
$\mathrm{OH}^{-}$ions produced $=2 \times$ moles of $\mathrm{Cl}_{2}=2 \times 14.08=28.16$

Molarity $=\frac{\text { Mole }}{\text { Volume }}=\frac{28.16}{20}=1.408 \mathrm{M}$

Illustration 6: An acidic solution of $\mathrm{Cu}^{2+}$ salt containing 0.4 g of $\mathrm{Cu}^{2+}$ is electrolyzed until all the copper is deposited. The electrolysis is continued for seven more minutes with volume of solution kept at 100 mL and the current at 1.2 amp. Calculate the gases evolved at NTP during the entire electrolysis.
(JEE ADVANCED)
Sol: 0.4 g of $\mathrm{Cu}^{2+}=\frac{0.4}{31.75}=0.0126 \mathrm{~g}-$ equivalent
At the same time, the oxygen deposited at anode $=\frac{8}{32} \times 0.0126 \mathrm{~g}=0.00315 \mathrm{~g}$-mole
After the complete deposition of copper, the electrolysis will discharge hydrogen at cathode and oxygen at anode. The amount of charge passed $=1.2 \times 7 \times 60=504$ coulomb
So, Oxygen liberated $=\frac{1}{96500} \times 504=0.00523 \mathrm{~g}$ - equivalent $=\frac{8}{32} \times 0.00523=0.001307 \mathrm{~g}-$ mole
Hydrogen liberated $=0.00523 \mathrm{~g}$-equivalent $=\frac{1}{2} \times 0.00523=0.00261 \mathrm{~g}-$ mole
Total gases evolved $=(0.00315+0.001307+0.00261) \mathrm{g}-$ mole $=0.007067 \mathrm{~g}-\mathrm{mole}$
Volume of gases evolved at NTP $=22400 \times 0.007067 \mathrm{~mL}=158.3 \mathrm{~mL}$

## 4. ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

In order to explain the properties of electrolytic solutions, Arrhenius put forth a comprehensive theory. The main postulates of the theory are:
(a) An electrolyte, when dissolved in water, breaks up into two types of charged particles, one carrying a positive charge and the other a negative charge. These charged particles are called ions. Positively charged ions are termed as cations and negatively charged as anions.

$$
\mathrm{A}^{+} \mathrm{B}^{-}+\mathrm{aq} . \longrightarrow \mathrm{A}^{+}(\text {aq. })+\mathrm{B}^{-} \text {(aq.) }
$$

(b) The process of splitting of the molecules into ions of an electrolyte is called ionization. The fraction of the total number of molecules present in solution as ions is known as degree of ionizations or degree of dissociation. It is denoted by ' $\alpha$ '
(c) $\quad \alpha=\frac{\text { Number of molecules dissociated into ions }}{\text { Total number of molecules }}$
(d) Ions present in solution constantly re-unite to form neutral molecules and, thus, there is a state of dynamic equilibrium between the ionized and non-ionized molecules, i.e. $A B \rightleftharpoons A^{+}+B^{-}$
(e) Applying the law of mass action to the above equilibrium $\frac{\left[A^{+}\right]\left[B^{-}\right]}{[A B]}=K . K$ is known as ionization constant. The electrolytes having high value of $K$ are termed strong electrolytes and those having low value of $K$ as weak electrolytes.
(f) When an electric current is passed through the electrolytic solution, the positive ions (cations) move towards cathode and the negative ions (anions) move towards anode and get discharged, i.e., electrolysis occurs. The ions are discharged always in equivalent amounts, no matter what their relative speeds are.
(g) The electrolytic solution is always neutral in nature as the total charge on one set of ions is always equal to the total charge on the other set of ions. However, it is not necessary that the number of two sets of ions must be equal always.
$A B \rightleftharpoons A^{+}+B^{-} \quad$ (Both ions are equal)
$\mathrm{NaCl} \rightleftharpoons \mathrm{Na}^{+}+\mathrm{Cl}^{-} \quad$ (Both ions are equal)
$A B_{2} \rightleftharpoons A^{2+}+2 B^{-} \quad$ (Anions are double that of cations)
$\mathrm{BaCl}_{2} \rightleftharpoons \mathrm{Ba}^{2+}+2 \mathrm{Cl}^{-} \quad$ (Anions are double that of cations)
$A_{2} B \rightleftharpoons 2 A^{+}+B^{2-} \quad$ (Cations are double that of anions)
$\mathrm{Na}_{2} \mathrm{SO}_{4} \rightleftharpoons 2 \mathrm{Na}^{+}+\mathrm{SO}_{4}^{2-}$ (Cations are double that of anions)
(h) The properties of electrolytes in solution are the properties of ions present in solution. For example, acidic solution always contains $\mathrm{H}^{+}$ions while basic solution contains $\mathrm{OH}^{-}$ions and characteristic properties of solutions are those of $\mathrm{H}^{+}$ions and $\mathrm{OH}^{-}$ions respectively.

## Limitations of Arrhenius Theory

(i) You cannot apply Ostwald's dilutions law which is based on Arrhenius theory to strong electrolytes.
(ii) Strong electrolytes conduct electricity in a fused state, i.e., in the absence of water. This is in contradiction of Arrhenius theory which states that the presence of solvent is imperative for ionization.
(iii) Arrhenius theory assumes independent existence of ions but fails to account for the factors which influence the mobility of the ions.

### 4.1 Factors Affecting Degree of Ionization

(a) Nature of solute: When the ionizable parts of a molecule of a substance are held more by covalent bonding than by electrovalent bonding, less ions are furnished in solution.
(b) Nature of solvent: The main function of the solvent is to weaken the electrostatic forces of attraction between the two ions and separate them.
(c) Dilution: The extent of ionization of an electrolyte is inversely proportional to the concentration of its solution. Thus, degree of ionization increases with the increase of dilution of the solution, i.e., decreasing the concentration of the solution.
(d) Temperature: The degree of ionization increases with the increase in temperature. This is due to the fact that at higher temperatures molecular speed is greater than before which overcomes the forces of attraction between the ions.

## 5. ELECTRICAL CONDUCTANCE

The conductance is the property of the conductor (metallic as well as electrolytic) which facilitates the flow of electricity through it. It is equal to the reciprocal of resistance, i.e.

$$
\begin{equation*}
\text { Conductance }=\frac{1}{\text { Resistance }}=\frac{1}{R} \tag{i}
\end{equation*}
$$

It is expressed in the unit called reciprocal ohm (ohm ${ }^{-1}$ or mho) or Siemens.

### 5.1 Specific Conductance or Conductivity

The resistance of any conductor varies directly with its length (l) and inversely with its cross-sectional area (a),
i.e. $R \propto \frac{1}{a}$ or $R=\rho \frac{1}{a}$

Where, $\rho$ is called the specific resistance. If $I=1 \mathrm{~cm}$ and $a=1 \mathrm{~cm}^{2}$, then $R=\rho$
The specific resistance is, thus, defined as the resistance of one centimeter cube of a conductor.
The reciprocal of specific resistance is termed the specific conductance or it is the conductance of one centimeter cube of a conductor. It is denoted by the symbol $\kappa$, Thus,
$\kappa=\frac{1}{\rho}, \kappa=$ kappa - The specific conductance
Specific conductance is also called conductivity.
From eq. (ii), we have $\rho=\frac{a}{l} \cdot R$ or $\frac{1}{\rho}=\frac{1}{a} \cdot \frac{1}{R} ; \kappa=\frac{1}{a} \times C \quad\left(\frac{l}{a}=\right.$ cell constant $)$
or Specific conductance $=$ conductance $\times$ cell constant

### 5.2 Equivalent Conductance

Equivalent conductance is defined as the conductance of all the ions produced by one gram-equivalent of an electrolyte in a given solution. It is denoted by $\Lambda$.
In general $\Lambda=\kappa \times V$
Where, V is the volume in mL containing 1 g -equivalent of the electrolyte.
In case the concentration of the solution is c g-equivalent per liter, then the volume containing
1 g -equivalent of the electrolyte will be 1000/c.
So, equivalent conductance $\Lambda=\kappa \times \frac{1000}{c}$
$\Lambda=\kappa \times \frac{1000}{N}$; where, $N=$ normality. The unit of equivalent conductance is ohm ${ }^{-1} \mathrm{~cm}^{2} \mathrm{eq}^{-1}$.

### 5.3 Molar Conductance

The molar conductance is defined as the conductance of all the ions produced by ionization of $\mathbf{1} \mathbf{g}$-mole of an electrolyte when present in V ml of solution. It is denoted by $\mu$.
Molar conductance $\mu=\kappa \times V$

Where, V is the volume in mL containing 1 g -mole of the electrolyte. If c is the concentration of the solution in g -mole per liter, then $\mu=\kappa \times \frac{1000}{\mathrm{c}}$ Its unit is $\mathrm{ohm}^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$.
Equivalent conductance $=\frac{\text { Molar conductance }}{n} ;$ where, $n=\frac{\text { Molecular mass }}{\text { Equivalent mass }}$

Illustration 7: 1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and $4.2 \mathrm{sq} . \mathrm{cm}$ in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution.
(JEE MAIN)
Sol: As Equivalent conductivity $=\kappa \times \mathrm{V}$
In order to find equivalent conductivity we have to calculate specific conductance.
Specific conductance ( $\kappa$ ) is given as $\kappa=\frac{1}{a} \cdot \frac{1}{R}$
Given, $\mathrm{I}=2.1 \mathrm{~cm}, \mathrm{a}=4.2 \mathrm{sq} . \mathrm{cm}, \mathrm{R}=50 \mathrm{ohm}$. Specific conductance, $\kappa=\frac{\mathrm{l}}{\mathrm{a}} \cdot \frac{1}{\mathrm{R}}$
Or $\kappa=\frac{2.1}{4.2} \times \frac{1}{50}=0.01 \mathrm{ohm}^{-1} \mathrm{~cm}^{-1}$; Equivalent conductivity $=\kappa \times \mathrm{V}$
$\mathrm{V}=$ The volume containing 1 g -equivalent $=1000 \mathrm{~mL}$
So, Equivalent conductivity $=0.01 \times 1000=10 \mathrm{ohm}^{-1} \mathrm{~cm}^{2} \mathrm{eq}^{-1}$

Illustration 8: The specific conductivity of 0.02 M KCl solution at $25^{\circ} \mathrm{C}$ is $2.768 \times 10^{-3} \mathrm{ohm}^{-1} \mathrm{~cm}^{-1}$. The resistance of this solution at $25^{\circ} \mathrm{C}$ when measured with a particular cell was 250.2 ohm. The resistance of $0.01 \mathrm{M} \mathrm{CuSO}_{4}$ solution at $25^{\circ} \mathrm{C}$ measured with the same cell was 8331 ohm . Calculate the molar conductivity of the copper sulphate solution.
(JEE ADVANCED)
Sol: Molar conductivity is given by $=$ Sp. cond. $\times \frac{1000}{C}$ so first we have to calculate specific conductivity of the solution. Sp.conductivity is given as a product of cell constant and conductance. Now cell constant is not provided; we can calculate it from the conductance and Sp.conductivity of KCl solution.
Cell constant $=\frac{\text { Sp. cond. of } \mathrm{KCl}}{\text { Conductance of } \mathrm{KCl}}=\frac{2.768 \times 10^{-3}}{1 / 250.2}=2.768 \times 10^{-3} \times 250.2$
For $0.01 \mathrm{M} \mathrm{CuSO}_{4}$ solution
Sp. Conductivity $=$ Cell constant $\times$ Conductance $=2.768 \times 10^{-3} \times 250.2 \times \frac{1}{8331}$
Molar conductance $=$ Sp. cond. $\times \frac{1000}{C}=\frac{2.768 \times 10^{-3} \times 250.2}{8331} \times \frac{1000}{1 / 100}=8.312 \mathrm{ohm}^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$

## 6. KOHLRAUSCH'S LAW

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 ion with which it is associated and the value of molar conductions of its constituent ions, i.e., $\Lambda=\lambda_{+}+\lambda_{-} \lambda_{\mathrm{c}}$ and $\lambda_{\mathrm{a}}$ are called the ionic conductance of cation and anion at infinite dilution respectively. The ionic conductance are proportional to their ionic mobilities. Thus, at infinite dilution, $\lambda_{\mathrm{c}}=k u_{\mathrm{c}}$ and $\lambda_{\mathrm{a}}=k u_{\mathrm{a}^{\prime}}$ where, $\mathrm{u}_{\mathrm{c}}$ and $\mathrm{u}_{\mathrm{a}}$ are ionic mobilities of cation and anion respectively at infinite dilution. The value of $k$ is equal to 96500 C, i.e., one Faraday.
Thus, assuming that increase in equivalent conductance with dilution is due to increase in the degree of dissociation of the electrolyte, it is evident that the electrolyte achieves the degree of dissociation as unity when it is completely ionized at infinite dilution. Therefore, at any other dilution, the equivalent conductance is proportional to the degree of dissociation. Thus,

Degree of dissociation $\alpha=\frac{\Lambda}{\Lambda_{\infty}}=\frac{\text { Equivalent conductance at a given concentration }}{\text { Equivalent conductance at infinite dilution }}$
Ionic Mobility, $\boldsymbol{\mu}$ : It is the distance travelled by an ions per second under a potential gradient of 1 volt per meter.

1. For an, $\mu=\lambda^{\circ} / \mathrm{F}$
2. Ionic mobility of an ion depends on its charge, size, viscosity of solvent, temperature, etc.
3. For aqueous solution, greater the charge or smaller the size of gaseous ion, greater will be the size of aqueous ion. When such a big ion moves in solution, it experiences greater resistance by the size of solvent particles. This results in a decrease in its conductance as well as ionic mobility. Following are the increasing order of ionic mobilities of some ions:
$\mathrm{Li}^{+}<\mathrm{Na}^{+}<\mathrm{K}^{+}<\mathrm{Rb}^{+}<\mathrm{Cs}^{+} ; \mathrm{F}^{-}<\mathrm{Cl}^{-}<\mathrm{Br}^{-}<\mathrm{I}^{-} ; \mathrm{Al}^{3+}<\mathrm{Mg}^{2+}<\mathrm{Na}^{+}$
4. The size of gaseous $\mathrm{H}^{+}$ion is smallest among all the ions and hence its ionic mobility should be minimum but among all the ions, it is maximum. The ion with second highest ionic mobility is $\mathrm{OH}^{-}$. The very high ionic mobilities of these ions are due to interchange of hydrogen bonds and covalent bonds, by which migration of charge occurs without any large displacement in the ions (Grotthus mechanism).

## Applications of Kohlrausch's Law:

(a) Determining $\Lambda_{\mathrm{m}}^{0}$ of a weak electrolyte: In order to calculate $\Lambda_{\mathrm{m}}^{0}$ of a weak electrolyte say $\mathrm{CH}_{3} \mathrm{COOH}$, we determine experimentally $\Lambda_{\mathrm{m}}^{0}$ values of the following three strong electrolytes:
(i) A strong electrolyte containing same cation as in the test electrolyte, say HCl
(ii) A strong electrolyte containing same anion as in the test electrolyte, say $\mathrm{CH}_{3} \mathrm{COONa}$
(iii) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl .
$\Lambda_{\mathrm{m}}^{0}$ of $\mathrm{CH}_{3} \mathrm{COOH}$ is then given as: $\Lambda_{\mathrm{m}}^{0}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=\Lambda_{\mathrm{m}}^{0}(\mathrm{HCl})+\Lambda_{\mathrm{m}}^{0}\left(\mathrm{CH}_{3} \mathrm{COONa}\right)-\Lambda_{\mathrm{m}}^{0}(\mathrm{NaCl})$
Proof: $\quad \Lambda_{\mathrm{m}}^{0}(\mathrm{HCl})=\lambda_{\mathrm{H}}^{0}+\lambda_{\mathrm{Cl}^{-}}$
$\Lambda_{\mathrm{m}}^{0}\left(\mathrm{CH}_{3} \mathrm{COONa}\right)=\lambda_{\mathrm{CH}_{3} \mathrm{COO}^{-}}^{0}+\lambda_{\mathrm{Na}^{+}}$
$\Lambda_{\mathrm{m}}^{0}(\mathrm{NaCl})=\lambda_{\mathrm{Na}^{+}}^{0}+\lambda_{\mathrm{Cl}}{ }^{0}$
Adding equation (I) and equation (II) and subtracting (III) from them:
$\Lambda_{(\mathrm{HCl})}^{0}+\Lambda_{\left(\mathrm{CH}_{3} \mathrm{COONa}\right)}^{0}-\Lambda_{(\mathrm{NaCl})}^{0}=\lambda_{\left(\mathrm{H}^{+}\right)}^{0}+\lambda_{\left(\mathrm{CH}_{3} \mathrm{COO}^{-}\right)}^{0}=\Lambda_{0\left(\mathrm{CH}_{3} \mathrm{COOH}\right)}$
(b) Determination of degree of dissociation ( $\alpha$ : $: \alpha=\frac{\text { No. of molecules ionised }}{\text { Total number of molecules dissolved }}=\frac{\Lambda_{\mathrm{m}}}{\Lambda_{\mathrm{m}}^{0}}$
(c) Determination of solubility of sparingly soluble salt: $\Lambda_{\mathrm{m}}^{0}=\frac{1000 \kappa}{\mathrm{C}}$,

Where C is the molarity of solution and hence the solubility.
(d) Determination of ionic product of water: From Kohlrausch's law, we determine $\Lambda_{\mathrm{m}}^{0}$ of $\mathrm{H}_{2} \mathrm{O}$ where $\Lambda_{\mathrm{m}}^{0}$ is the molar conductance of water at infinite dilution when one mole of water is completely ionized to give one mole of $\mathrm{H}^{+}$and one mole of $\mathrm{OH}^{-}$ions i.e. $\Lambda_{\mathrm{m}}^{0}\left(\mathrm{H}_{2} \mathrm{O}\right)=\lambda_{\mathrm{H}^{+}}^{0}+\lambda_{\mathrm{OH}^{-}}^{0}$
Again using the following $\Lambda_{\mathrm{m}}=\frac{\kappa \times 1000}{\mathrm{C}}$, where $\mathrm{C}=$ molar concentration i.e. mole $\mathrm{L}^{-1}$ or mole $\mathrm{dm}^{-3}$
$\Rightarrow \quad \Lambda_{\mathrm{m}}=\frac{\kappa}{\mathrm{C}}$, where $\mathrm{C}=$ concentration in mole $\mathrm{m}^{-3}$
Assuming that $\Lambda_{\mathrm{m}}$ differs very little from $\Lambda_{\mathrm{m}}^{0} ; \Lambda_{\mathrm{m}}^{0}=\frac{\kappa}{\mathrm{C}} \Rightarrow \mathrm{C}=\frac{\kappa}{\Lambda_{\mathrm{m}}^{0}}$
Specific conductance ( $\kappa$ ) of pure water is determined experimentally. Thereafter, molar concentration of dissociated water is determined using the above equation. $\mathrm{K}_{\mathrm{w}}$ is then calculated as: $\mathrm{K}_{\mathrm{w}}=\mathrm{C}^{2}$

## 7. THEORY OF WEAK ELECTROLYTES

(i) Electrolytes that are not completely ionized when dissolved in a polar medium like water are called weak electrolytes. There exists equilibrium between ions and unionized molecules. $A B \rightleftharpoons A^{+}+B^{-}$
(ii) The Concept of chemical equilibrium and law of mass action can be applied to ionic equilibrium also.

|  | AB | $\mathrm{A}^{+}+\mathrm{B}^{-}$ |  |  |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{t}=0$ | C | 00 |  |  |
| $\mathrm{t}_{\text {eq. }}$ | C-C ${ }^{\text {a }}$ | C $\alpha$ | $C \alpha ; K=\frac{\left[\mathrm{A}^{+}\right]\left[\mathrm{B}^{-}\right]}{[\mathrm{BB}]}=\frac{\mathrm{C} \alpha \times \mathrm{C} \alpha}{\mathrm{C}(1-\alpha)}$ | $K=\frac{C \alpha^{2}}{1-\alpha}$ |

For weak electrolytes, $\alpha \ll 1 \quad \therefore \quad(1-\alpha) \approx 1$
Thus, equation (i) can be written as: $\mathrm{K}=\mathrm{C} \alpha^{2} \Rightarrow \alpha=\sqrt{\frac{\mathrm{K}}{\mathrm{C}}}$
From eq. (ii), it is clear that on dilution concentration decreases, as a result of which degree of ionization ' $\alpha$ ' increases. Both equivalent and molar conductance increase when at a high degree of ionization.
(iii) Degree of ionization can be calculated as: $\alpha=\frac{\Lambda_{\mathrm{e}}^{\mathrm{C}}}{\Lambda_{\mathrm{e}}^{\infty}}=\frac{\Lambda_{\mathrm{m}}^{\mathrm{C}}}{\Lambda_{\mathrm{m}}^{\infty}}$
$\Lambda_{\mathrm{e}}^{\mathrm{C}}, \Lambda_{\mathrm{m}}^{\mathrm{C}}=$ Equivalent and molar conductance at concentration ' $\mathrm{C}^{\prime}$
$\Lambda_{\mathrm{e}}^{\infty}, \Lambda_{\mathrm{m}}^{\infty}=$ Equivalent and molar conductance at infinite dilution.
$\Lambda_{\mathrm{e}}, \Lambda_{\mathrm{m}}=$ Equivalent and molar conductance at infinite dilution.
Substituting the values of ' $\alpha$ ' from eq. (iii) in eq. (i), we get $\mathrm{K}=\frac{\mathrm{C} \times\left(\frac{\mathrm{C}}{\Lambda_{\mathrm{e}}^{\infty}}\right)^{2}}{1-\frac{\Lambda_{\mathrm{e}}^{\mathrm{C}}}{\Lambda_{\mathrm{e}}^{\infty}}}=\frac{\mathrm{C}\left(\Lambda_{\mathrm{e}}^{\mathrm{C}}\right)^{2}}{\Lambda_{\mathrm{e}}^{\infty}\left(\Lambda_{\mathrm{e}}^{\infty}-\Lambda_{\mathrm{e}}^{\mathrm{C}}\right)}$
Similarly $\mathrm{K}=\frac{\mathrm{C}\left(\Lambda_{\mathrm{m}}^{\mathrm{C}}\right)^{2}}{\Lambda^{\infty}\left(\Lambda^{\infty}-\Lambda^{\mathrm{C}}\right)}$

Equations (iv) and (v) are called Ostwald equation.

Illustration 9: A decinormal solution of NaCl has specific conductivity equal to 0.0092 . If ionic conductance of $\mathrm{Na}^{+}$ and $\mathrm{Cl}^{-}$ions at the same temperature are 43.0 and $65.0 \mathrm{ohm}^{-1}$ respectively, calculate the degree of dissociation of NaCl solution.
(JEE MAIN)
Sol: Degree of dissociation is calculated as equivalent conductance at a particular dilution divided by equivalent conductance at infinite dilution.so first we have to calculate $\Lambda_{\infty}$
$\Lambda_{v} \cdot \Lambda_{\infty}$ is determined by summing up ionic conductance of each ion. $\Lambda_{v}$ is product of specific conductance and dilution.
Equivalent conductance of $\mathrm{N} / 10 \mathrm{NaCl}$ solution
$\Lambda_{v}=$ Sp.conductivity $\times$ dilution $=0.0092 \times 10,000=92 \mathrm{ohm}^{-1}$;
$\Lambda_{\infty}=\lambda_{\mathrm{Na}^{+}}+\lambda_{\mathrm{Cl}^{-}}=43.0+65.0=108 \mathrm{ohm}^{-1}$

Degree of dissociation, $\alpha=\frac{\Lambda_{\mathrm{v}}}{\Lambda_{\infty}}=\frac{92}{108}=0.85$

Illustration 10: At $18^{\circ} \mathrm{C}$, the conductivities at infinite dilution of $\mathrm{NH}_{4} \mathrm{Cl}, \mathrm{NaOH}$ and NaCl are 129.8, 217.4 and 108.9 mho respectively. If the equivalent conductivity of $\mathrm{N} / 100$ solution of $\mathrm{NH}_{4} \mathrm{OH}$ is 9.93 mho, calculate the degree of dissociation of $\mathrm{NH}_{4} \mathrm{OH}$ at this dilution.
(JEE ADVANCED)
Sol: Degree of dissociation is calculated as equivalent conductance at a particular dilution divided by equivalent conductance at infinite dilution. $\Lambda_{v}$ is given. $\Lambda_{\infty}$ is determined by summing up ionic conductance of each ion

$$
\begin{align*}
& \Lambda_{\infty \mathrm{NH}_{4} \mathrm{Cl}}=\lambda_{\mathrm{NH}_{4}^{+}}+\lambda_{\mathrm{Cl}^{-}}=129.8  \tag{i}\\
& \Lambda_{\infty \mathrm{NaOH}}=\lambda_{\mathrm{Na}^{+}}+\lambda_{\mathrm{OH}^{-}}=217.4 \tag{ii}
\end{align*}
$$

Adding eqs. (i) and (ii) and subtracting eq. (iii),
$\Lambda_{\mathrm{NH}_{4}^{+}}+\lambda_{\mathrm{Cl}^{-}}+\lambda_{\mathrm{Na}^{+}}+\lambda_{\mathrm{OH}^{-}}-\lambda_{\mathrm{Na}^{+}}-\lambda_{\mathrm{Cl}^{-}}=\lambda_{\mathrm{NH}_{4}^{+}}+\lambda_{\mathrm{OH}^{-}}=129.8+217.4-108.9$
$\Lambda_{\infty \mathrm{NH}_{4} \mathrm{OH}}=238.3$ mho. Degree of dissociation, $\alpha=\frac{\Lambda_{\mathrm{V}}}{\Lambda_{\infty}}=\frac{9.93}{238.3}=0.04167$ or $4.17 \%$ dissociated.

## 8. ELECTROCHEMICAL CELLS

### 8.1 Electrolytic Cells

Electrolytic cells are devices 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.

### 8.2 Galvanic Cells

This is a device where a redox reaction is used to convert chemical energy into electrical energy, i.e., electricity is 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 and the compartments containing the electrode and the electrolyte solution are called half-cells. When the two compartments are connected by a salt bridge and electrodes are joined by a wire through the galvanometer, the electricity begins to flow. This is the simple form of voltaic cell.

### 8.3 Daniel Cell



Figure 17.1: Representation of a daniel cell

Oxidation half reaction, $\mathrm{Zn}(\mathrm{s}) \longrightarrow \mathrm{Zn}^{2+}$ (aq.) $+2 \mathrm{e}^{-}$
Reduction half reaction, $\mathrm{Cu}^{2+}$ (aq.) $+2 \mathrm{e}^{-} \longrightarrow \mathrm{Cu}(\mathrm{s})$
Net reaction $\mathrm{Zn}(\mathrm{s})+\mathrm{Cu}^{2+}$ (aq.) $\longrightarrow \mathrm{Zn}^{2+}$ (aq.) $+\mathrm{Cu}($ s $)$
Salt Bridge: A Salt bridge is usually an inverted U-tube filled with a concentrated solution of inert electrolytes. An inert electrolyte is one whose ions are neither involved in any electrochemical change nor do they react chemically with the electrolytes in the two half-cells.
Significance of salt bridge: The following are the functions of the salt bridge:
(i) It connects the solutions of two half-cells and completes the cell circuit.
(ii) It prevents transference or diffusion of the solutions from one half-cell to the other.
(iii) It keeps the solutions in two half-cells electrically neutral.
(iv) It prevents liquid-liquid junction-potential, i.e., the potential difference which arises between two solutions when in contact with each other.

A broken vertical line or two parallel vertical lines in a cell reaction indicates the salt bridge.
$\mathrm{Zn}\left|\mathrm{Zn}^{2+} \| \mathrm{Cu}^{2+}\right| \mathrm{Cu}$
Electrode Potential: A metal placed in a solution of its ions obtains either a positive or negative charge with respect to the solution. On account of this, a definite potential is developed between the metal and the solution. This potential difference is called electrode potential. It depends on the nature of electrode, concentration of ions and temperature.

Oxidation Potential: It is the tendency of an electrode to get oxidized, i.e., to lose electrons.
$\mathrm{M} \longrightarrow \mathrm{Mn}^{+}+\mathrm{ne}^{-}$
Reduction potential: It is the tendency of an electrode to get reduced, i.e., to accept electrons.

$$
\mathrm{Mn}^{+}+\mathrm{ne}^{-} \longrightarrow \mathrm{M}
$$

Standard Electrode Potential: The potential difference developed between metal electrode and the solution of its ions of unit molarity $(1 \mathrm{M})$ at $25^{\circ} \mathrm{C}(278 \mathrm{~K})$ is called standard electrode potential.

## The magnitude of potential depends on the following factors:

(i) Nature of the electrode,
(ii) Concentration of the ions in solution,
(iii) Temperature.

Standard Electrode Potential: While dipping an electrode in a solution in order to compare the electrode potentials of different electrodes, it is essential to first specify the ion concentration in the solution as well as the temperature of the half cell. The potential difference developed between metal electrode and the solution of its ions of unit molarity $(1 \mathrm{M})$ at $25^{\circ} \mathrm{C}(298 \mathrm{~K})$ is called standard electrode potential. Standard oxidation potential = -Standard reduction potential

EMF of a cell: It is the difference in the potential across left and right electrodes due to which electrons flow from anode to cathode.

Standard EMF: The EMF values of an electrode under standard conditions (1 atm, 298 K ) and the unit concentrations of its ions is called as standard EMF and is denoted by $E_{\text {cell }}^{\circ}$
$E_{\text {cell }}^{\circ}=E_{\text {cathode }}^{\circ}-E_{\text {anode }}^{\circ}$ or $E_{\text {cell }}^{\circ}=E_{\text {right electrode }}^{\circ}-E_{\text {left electrode }}^{\circ}$

### 8.4 Reference Electrode (Standard Hydrogen Electrode, SHE or NHE)

The potential of an individual half-cell cannot be measured but the difference in the potential of two half-cells can be measured experimentally. It is therefore, necessary to couple the electrodes with another electrode whose potential is known. This electrode is termed as reference electrode like standard hydrogen electrode (SHE). Which is standard electrode potential considered zero.


Figure 17.2: Representation of reference electrode
The hydrogen electrode thus obtained forms one of two half-cells of a voltaic cell. A voltaic cell is created when this half-cell is connected with any other half-cell. The hydrogen electrode can act as cathode or anode with respect to other electrode.

SHE half reaction

$$
\mathrm{H}_{2} \longrightarrow 2 \mathrm{H}^{+}+2 \mathrm{e}^{-}
$$

$$
2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{H}_{2}
$$

Electrode potential
0.0 V (Anode)
0.0 V (Cathode)

### 8.5 Some other Reference Electrodes

(i) Calomel Electrode:


Figure 17.3: Representation of calomel electrode
Reaction when electrode act as cathode: $\frac{1}{2} \mathrm{Hg}_{2} \mathrm{Cl}_{2}+\mathrm{e}^{-} \rightleftarrows \mathrm{Hg}+\mathrm{Cl}$
(ii) Silver-silver chloride electrode: This is another widely used reference electrode. It is reversible and stable and can be combined with cells containing chlorides without inserting liquid junction.
Silver chloride is deposited electrolytically on a silver or platinum wire and it is then immersed in a solution containing chloride ions. Its standard electrode potential with respect to the standard hydrogen electrode is 0.2224 V at 298 K . The electrode is represented as: $\mathrm{Ag}|\mathrm{AgCl}| \mathrm{Cl}^{-}$

The electrode reaction is: $\mathrm{AgCl}+\mathrm{e}^{-} \longrightarrow \mathrm{Ag}+\mathrm{Cl}^{-}$

## PLANCESS CONCEPTS

In $\mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+}+5 \mathrm{e} \longrightarrow \mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O}$, oxidant should be taken as $\left[\mathrm{MnO}_{4}^{-}\right]\left[\mathrm{H}^{+}\right]^{8}$,ie., all ions concentration present with oxidant should be reported accordingly in Nernst half-cell potential. Similarly for reductant, all ions present with reductant should be considered.

Aman Gour (JEE 2012 AIR 230)

### 8.6 Nernst Equation

Nernst Equation: Suppose, for example, that we reduce the concentration of $\mathrm{Zn}^{2+}$ in the $\mathrm{Zn} / \mathrm{Cu}$ cell from its unitactivity value of around 0.5 M to a much smaller value:

$$
\mathrm{Zn}(\mathrm{~s}) \mid \mathrm{Zn}^{2+}(0.001 \mathrm{M})\left\|\mathrm{Cu}^{2+}\right\| \mathrm{Cu}(\mathrm{~s})
$$

This will reduce the value of Q for the cell reaction $\mathrm{Zn}(\mathrm{s})+\mathrm{Cu}^{2+} \longrightarrow \mathrm{Zn}^{2+}+\mathrm{Cu}(\mathrm{s})$
The free energy change $\Delta G$ more negative than $\Delta G^{\circ}$, so than $E$ would be more positive than $E^{\circ}$.
The relation between the actual cell potential $E$ and the standard potential $E^{\circ}$ is developed in the following way.
According to cell potential and Gibb's free energy change: $\Delta G^{0}=-n E^{\circ} F ; \Delta G=-n E F$
These expressions can then be substituted into the relation $\Delta G=\Delta G^{0}+R T \ln Q$
Which gives $-n E F=-n E^{\circ} F+R T \ln Q$. Which can be rearranged to $E=E^{\circ}-\frac{R T}{n F} \ln Q$
This is Nernst Equation, which relates the cell potential to the standard potential $E^{\circ}$. If Q is unity then at $25^{\circ} \mathrm{C}$
Nernst Equation will be $\mathrm{E}=\mathrm{E}^{\circ}-\frac{0.059}{\mathrm{n}} \log \mathrm{Q}$
And for a general electrochemical reaction of the type $a A+b B c C+d D$
Nernst equation can be written as: $E_{\text {cell }}=E_{\text {(cell) }}^{\circ}-\frac{R T}{n F} \operatorname{lnQ}=E_{\text {(cell) }}^{\circ}-\frac{R T}{n F} \ln \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$

## PLANCESS CONCEPTS

- The overall reaction and $\Delta G^{0}$ for each cell is same.
- $E_{\text {cell }}^{\circ}$ and ' $n$ ' values are different for each cell.
- $E_{\text {cell }}^{0} \times n$ is same for each cell.
- $\Delta G^{\circ}$ depends on cell reaction and $E_{\text {cell }}^{\circ}$ depends upon making up of a cell.


### 8.7 Electrochemical Series

## Characteristics of electrochemical series

(a) Negative sign of SRP (standard reduction potential) indicates that an electrode when joined with SHE acts as anode and oxidation occurs on this electrode. Similarly positive sign of SRP indicates that an electrode when joined with SHE acts as cathode and reduction occurs on this electrode.
(b) In the series, those substances that are stronger reducing agents than hydrogen are placed above it.
(c) The substances which are stronger oxidizing agents than $\mathrm{H}^{+}$ion are placed below hydrogen in the series.
(d) The activity decreases from top to bottom and the metals on top are called active metals.

## Application of electrochemical series

(i) Reactivity of metals

- Alkali metals and alkaline earth metals having high -ve values of SRP which are chemically active react with cold water, evolve hydrogen and readily dissolve in acids.
- Metals like $\mathrm{Fe}, \mathrm{Pb}, \mathrm{Sn}, \mathrm{Ni}, \mathrm{Co}$ etc. do not react with cold water but react with steam to evolve hydrogen.
- Metals Li, Be, Cu, Ag and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.
(ii) Electropositive character of metals: Electropositive character of metals decreases from top to bottom.
(iii) Displacement reactions: The metal having low SRP will displace the metal from its salt's solution which has higher value of SRP.
(iv) Reducing power of metals: Reducing nature decreases from top to bottom in the electrochemical series.
(v) Oxidizing nature of non-metals: Oxidizing nature increases from top to bottom in the electrochemical series.
(vi) Thermal stability of metallic oxides: The thermal stability of the metal oxide decreases from top to bottom.
(vii) Products of electrolysis: The ion which is a stronger oxidizing agent is discharged first at cathode. $\mathrm{K}^{+}, \mathrm{Ca}^{2+}, \mathrm{Na}^{+}, \mathrm{Mg}^{+2}, \mathrm{Al}^{+3}, \mathrm{Zn}^{+2}, \mathrm{Fe}^{+2}, \mathrm{H}^{+}, \mathrm{Cu}^{+2}, \mathrm{Ag}^{+}, \mathrm{Au}^{+3}$ increasing order of deposition.
(viii) Corrosion of metals: Corrosion is defined as the deterioration of a substance because of its reaction with its environment. The corrosion tendency decreases from top to bottom.
(ix) Extraction of metals: Ag and Au extracted by cyanide process.

Table 17.3: Reduction potential of different ions

|  | Reaction (Oxidized form + $\mathrm{ne}^{-}$) | $\rightarrow$ Reduced form |  | E\%/V |
| :---: | :---: | :---: | :---: | :---: |
| Increasing strength of oxidizing agent | $\mathrm{F}_{2}(\mathrm{~g})+2 \mathrm{e}^{-}$ |  |  | 2.87 |
|  | $\mathrm{Co}^{3+}+\mathrm{e}^{-}$ | $\rightarrow \mathrm{Co}^{2+}$ |  | 1.81 |
|  | $\mathrm{H}_{2} \mathrm{O}_{2}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-}$ | $\rightarrow 2 \mathrm{H}_{2} \mathrm{O}$ |  | 1.78 |
|  | $\mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+}+5 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O}$ |  | 1.51 |
|  | $\mathrm{Au}^{3+}+3 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Au}(\mathrm{s})$ |  | 1.40 |
|  | $\mathrm{Cl}_{2}(\mathrm{~g})+2 \mathrm{e}^{-}$ | $\rightarrow 2 \mathrm{Cl}^{-}$ |  | 1.36 |
|  | $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+14 \mathrm{H}^{+}+6 \mathrm{e}^{-}$ | $\rightarrow 2 \mathrm{Cr}^{3+}+7 \mathrm{H}_{2} \mathrm{O}$ |  | 1.33 |
|  | $\mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{+}+4 \mathrm{e}^{-}$ | $\rightarrow 2 \mathrm{H}_{2} \mathrm{O}$ |  | 1.23 |
|  | $\mathrm{MnO}_{2}(\mathrm{~s})+4 \mathrm{H}^{+}+2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Mn}^{2+}+2 \mathrm{H}_{2} \mathrm{O}$ |  | 1.23 |
|  | $\mathrm{Br}_{2}+2 \mathrm{e}^{-}$ | $\rightarrow 2 \mathrm{Br}^{-}$ |  | 1.09 |
|  | $\mathrm{NO}_{3}^{-}+4 \mathrm{H}^{+}+3 \mathrm{e}^{-}$ | $\rightarrow \mathrm{NO}(\mathrm{g})+2 \mathrm{H}_{2} \mathrm{O}$ | $\begin{aligned} & \text { ס } \\ & \text { ס } \\ & \hline \end{aligned}$ | 0.97 |
|  | $2 \mathrm{Hg}^{2+}+2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Hg}_{2}^{2+}$ | - | 0.92 |
|  | $\mathrm{Ag}^{+}+\mathrm{e}^{-}$ | $\rightarrow \mathrm{Ag}(\mathrm{s})$ | $\stackrel{\square}{0}$ | 0.80 |
|  | $\mathrm{Fe}^{3+}+\mathrm{e}^{-}$ | $\rightarrow \mathrm{Fe}^{2+}$ | 谷 | 0.77 |
|  | $\mathrm{O}_{2}(\mathrm{~g})+2 \mathrm{H}^{+} 2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{H}_{2} \mathrm{O}_{2}$ | $\begin{aligned} & \stackrel{\#}{4} \\ & \text { on } \end{aligned}$ | 0.68 |
|  | $\mathrm{I}_{2}+2 \mathrm{e}^{-}$ | $\rightarrow 2 \mathrm{I}^{-}$ | 気 | 0.54 |
|  | $\mathrm{Cu}^{+}+\mathrm{e}^{-}$ | $\rightarrow \mathrm{Cu}(\mathrm{s})$ | $\stackrel{\text { ¢ }}{\text { ¢ }}$ | 0.52 |
|  | $\mathrm{Cu}^{2+}+2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Cu}(\mathrm{s})$ |  | 0.34 |
|  | $\mathrm{AgCl}(\mathrm{s})+\mathrm{e}^{-}$ | $\rightarrow \mathrm{Ag}(\mathrm{s})+\mathrm{Cl}^{-}$ |  | 0.22 |
|  | $\mathrm{AgBr}(\mathrm{s})+\mathrm{e}^{-}$ | $\rightarrow \mathrm{Ag}(\mathrm{s})+\mathrm{Br}^{-}$ |  | 0.10 |
|  | $2 \mathrm{H}^{+}+2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{H}_{2}(\mathrm{~g})$ |  | 0.00 |
|  | $\mathrm{Pb}^{2+}+2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Pb}$ (s) |  | -0.13 |
|  | $\mathrm{Sn}^{2+}+2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Sn}$ (s) |  | -0.14 |
|  | $\mathrm{Ni}^{2+}+2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Ni}(\mathrm{s})$ |  | -0.25 |


|  | Reaction（Oxidized form＋ $\mathrm{ne}^{-}$） | $\rightarrow$ Reduced form |  | E\％／V |
| :---: | :---: | :---: | :---: | :---: |
| $\text { — Increasing strength of oxidizing agent } \longrightarrow$ | $\mathrm{Fe}^{2+}+2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Fe}(\mathrm{s})$ |  | －0．44 |
|  | $\mathrm{Cr}^{3+}+3 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Cr}(\mathrm{s})$ | $\pm$ | －0．74 |
|  | $\mathrm{Zn}^{2+}+2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Zn}(\mathrm{s})$ | － | －0．76 |
|  | $2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{H}_{2}(\mathrm{~g})+2 \mathrm{OH}^{-}(\mathrm{aq})$ | － | －0．83 |
|  | $\mathrm{Al}^{3+}+3 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Al}(\mathrm{s})$ | $\xrightarrow[4]{\text { ®. }}$ | －1．66 |
|  | $\mathrm{Mg}^{2+}+2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Mg}(\mathrm{s})$ | 告 | －2．36 |
|  | $\mathrm{Na}^{+}+\mathrm{e}^{-}$ | $\rightarrow \mathrm{Na}(\mathrm{s})$ | 告 | －2．71 |
|  | $\mathrm{Ca}^{2+}+2 \mathrm{e}^{-}$ | $\rightarrow \mathrm{Ca}$（s） | 気 | －2．87 |
|  | $\mathrm{K}^{+}+\mathrm{e}^{-}$ | $\rightarrow \mathrm{K}(\mathrm{s})$ | $\stackrel{\square}{\square}$ | －2．93 |
|  | $\mathrm{Li}^{+}+\mathrm{e}^{-}$ | $\rightarrow \mathrm{Li}(\mathrm{s})$ | $\downarrow$ | －3．05 |

Two important parameters that can be determined from a cell potential are the equilibrium constant for the cell reaction and the free energy change for the cell reaction．
1．Determining the equilibrium constant from $E_{\text {cell }}^{\circ}$
2．Determining the standard state free energy change from $E_{\text {cell }}^{\circ}$
3．Determining the non－standard free energy change

## Determining the Equilibrium Constant from $E_{\text {cell }}^{\circ}$

To calculate the equilibrium constant for an electrochemical cell we need to know：
1．The standard state potential for a cell
2．The half－reactions involved
The Nernst equation is used in calculating the equilibrium constant．$E_{\text {cell }}^{\circ}=\frac{R T}{n F} \ln Q$
At equilibrium $Q=K$ ，Substituting in $K$ for $Q$ and the values for $R, T$ and $F$ we get：
$E_{\text {cell }}^{\circ}=\frac{0.0257}{n} \operatorname{lnK}=\frac{0.0592}{n} \log K$

Example：Find the value of the equilibrium constant at $25^{\circ} \mathrm{C}$ for the cell reaction for the following electrochemical cell： $\mathrm{Cu}\left|\mathrm{Cu}^{2+}(1 \mathrm{M}) \| \mathrm{Ag}^{+}(1 \mathrm{M})\right| \mathrm{Ag}$

Sol：（i）Write the equations for the cell half－reactions，calculate the standard cell potential and determine the number of electrons transferred．

$$
\begin{array}{lr}
2 \mathrm{Ag}^{+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Ag}(\mathrm{~s}) & \mathrm{E}_{\text {reduction }}^{\circ}=+0.799 \mathrm{~V} \\
\mathrm{Cu}(\mathrm{~s}) \rightarrow \mathrm{Cu}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} & \mathrm{E}_{\text {oxidation }}^{\circ}=-0.518 \mathrm{~V} \\
2 \mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{Al}(\mathrm{~s}) \rightarrow 2 \mathrm{Ag}(\mathrm{~s})+\mathrm{Cu}^{2+}(\mathrm{aq}) & \mathrm{E}_{\text {cell }}^{\circ}=+0.281 \mathrm{~V}
\end{array}
$$

$\mathrm{n}=2$ moles of electrons
(ii) Substitute into the above equations and solve for $K$.

$$
E_{\text {cell }}^{\circ}=\frac{0.0592}{n} \log K ; 0.281=\frac{0.0592}{2} \log K ; \log K=9.49 ; K=10^{9.49}=3.1 \times 10^{9}
$$

Note: values for the equilibrium constant for electrochemical cell reactions are sometimes very large.

## Determining the Standard State Free Energy Change from $E_{\text {cell }}^{\circ}$

To determine the standard state free energy change for a cell reaction

1. Determine the $E_{\text {cell }}^{\circ}$
2. Determine the number of moles of electrons transferred in the reaction.
3. Solve for $\Delta G^{\circ}$ using the equation $\Delta G^{\circ}=-n F E_{\text {cell }}^{\circ}$
$\Delta \mathrm{G}^{\circ}=$ standard state free energy change (joules); $\mathrm{n}=$ number of moles of electrons transferred
$F=$ Faraday's constant $\left(96,485 \mathrm{C} /\right.$ mole $\left.\mathrm{e}^{-}\right) ; \mathrm{E}_{\text {cell }}^{\circ}=$ standard state cell potential (volts or joules/C)

Example: Find the value of the equilibrium constant at $25^{\circ} \mathrm{C}$ for the cell reaction for the following electrochemical cell: $\mathrm{Cu} \mid \mathrm{Cu}^{2+}(1 \mathrm{M}) \| \mathrm{Ag}^{+}(1 \mathrm{M}) \mathrm{Ag}$
(The solution for the determination of the $E_{\text {cell }}^{\circ}$ and the number of moles of electrons, $n$, are shown in the example in the previous section.)

1. Determine the $E_{\text {cell }}^{\circ}$. $E_{\text {cell }}^{\circ}=+0.281$ volts
2. Determine the number of moles of electrons transferred. $n=2$ moles of $\mathrm{e}^{-}$
3. Substitute into the equation and solve.
$\Delta G^{\circ}=-\left(2 \mathrm{~mole}^{-}\right)\left(96,485 \mathrm{C} / \mathrm{mole}^{-}\right) 0.281 \mathrm{~J} / \mathrm{C} ; \Delta \mathrm{G}^{\circ}=-54,200 \mathrm{~J}$ or -54.2 kJ

## Determining the Non-Standard State Free Energy Change

To determine the non-standard state free energy change:

1. Calculate the standard cell potential, $E_{\text {cell }}^{\circ}$
2. Determine the number of moles of electrons transferred, $n$
3. Calculate the reaction quotient, Q
4. Calculate the non-standard cell potential, $E_{\text {cell, }}$ using the Nernst equation
5. Calculate the non-standard free energy change using the equation: $\Delta \mathrm{G}=-\mathrm{nFE} \mathrm{E}_{\text {cell }}$

Example: Calculate the free energy change for the following electrochemical cell.

$$
\mathrm{Zn}(\mathrm{~s})\left|\mathrm{Zn}^{2+}(1.50 \mathrm{M}) \| \mathrm{Cu}^{2+}(0.25 \mathrm{M})\right| \mathrm{Cu}(\mathrm{~s})
$$

1. Calculate $E_{\text {cell }}^{\circ}$.

$$
\begin{array}{lr}
\mathrm{Zn}(\mathrm{~s}) \rightarrow \mathrm{Zn}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} & \mathrm{E}_{\text {oxidiation }}^{\circ}=+0.762 \text { volts } \\
\mathrm{Cu}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}(\mathrm{~s}) & \mathrm{E}_{\text {reduction }}^{\circ}=+0.339 \text { volts } \\
\mathrm{Zn}(\mathrm{~s})+\mathrm{Cu}^{2+}(\mathrm{aq}) \rightarrow \mathrm{Zn}^{2+}(\mathrm{aq})+\mathrm{Cu}(\mathrm{~s}) & \mathrm{E}_{\text {cell }}^{\circ}=+1.101 \text { volts }
\end{array}
$$

2. Determine " $n$ ". $n=2$ moles of electrons
3. Calculate $\mathrm{Q} ; \mathrm{Q}=\frac{\left[\mathrm{Zn}^{2+}\right]}{\left[\mathrm{Cu}^{2+}\right]}=\frac{1.50}{0.25}=6.0$
4. Calculate $E_{\text {cell }} ; E_{\text {cell }}=1.101$ volts $-\frac{0.0257}{2} \ln 6=1.078$ volt
5. Calculate $\Delta \mathrm{G}$.
$\Delta G=-n F E_{\text {cell }}=-\left(2 \mathrm{~mole} \mathrm{e}^{-}\right)\left(96,485 \mathrm{C} / \mathrm{mole} \mathrm{e}^{-}\right)(1.078$ volts $) ; \Delta \mathrm{G}=-208,000$ joules or -208 kJ

### 8.8 Corrosion

The weakening and deterioration of a substance because of its reaction with its environment is called as corrosion. This is also defined as the process by which metals have the tendency to go back to their combined state, i.e., reverse of extraction of metals.


Figure 17.4 : Process of corrosion
Oxidation: $\mathrm{Fe}(\mathrm{s}) \longrightarrow \mathrm{Fe}^{2+}$ (aq.) $+2 \mathrm{e}^{-}$
Reduction: $\mathrm{O}_{2}+4 \mathrm{H}^{+}$(aq.) $+4 \mathrm{e}^{-} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(l)$
Atmospheric: $4 \mathrm{Fe}^{2+}+\mathrm{O}_{2}+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \longrightarrow 2 \mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})+8 \mathrm{H}^{+}$(aq.)
Oxidation: $\mathrm{Fe}_{2} \mathrm{O}_{3}+x \mathrm{H}_{2} \mathrm{O} \longrightarrow \underset{\text { Rust }}{ } \mathrm{Fe}_{2} \mathrm{O}_{3} \cdot \mathrm{xH}_{2} \mathrm{O}$

### 8.9 Dry Cell

In this cell, once the chemicals have been consumed, further reaction is not possible. It cannot be regenerated by reversing the current flow through the cell using an external direct current source of electrical energy.
As the cell operates, the zinc is oxidized to $\mathrm{Zn}^{2+} ; \mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+}+2 \mathrm{e}^{-} \quad$ (Anode reaction)
The electrons are utilized at carbon rod (cathode) as the ammonium ions are reduced.

$$
2 \mathrm{NH}_{4}^{+}+2 \mathrm{e}^{-} \longrightarrow 2 \mathrm{NH}_{3}+\mathrm{H}_{2} \quad \text { (Cathode reaction) }
$$

The cell reaction is $\mathrm{Zn}+2 \mathrm{NH}_{4}^{+} \longrightarrow \mathrm{Zn}^{2+}+2 \mathrm{NH}_{3}+\mathrm{H}_{2}$
Hydrogen is oxidized by $\mathrm{MnO}_{2}$ in the cell. $2 \mathrm{MnO}_{2}+\mathrm{H}_{2} \longrightarrow 2 \mathrm{MnO}(\mathrm{OH})$
Ammonia produced at cathode combines with zinc ions to form complex ion.
$\mathrm{Zn}^{2+}+4 \mathrm{NH}_{3} \longrightarrow\left[\mathrm{Zn}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+} ; \mathrm{E}_{\text {cell }}$ is 1.6 volt.

## PLANCESS CONCEPTS

- These are called dry cells but are not actually dry. These contain moist paste and operate only as long as the paste in it remains wet.
- In alkaline cells, e.m.f. is independent of concentration of alkali because redox reaction does not involve $\left[\mathrm{OH}^{-}\right]$.
- Alkaline cells retards corrosion as corrosion is favored more in $\mathrm{H}^{+}$ions.
- Alkaline cells show more efficient ion transport because of alkaline electrolyte and thus give rise to more stable current and voltage.

Mredul Sharda JEE Advanced 2013 AIR

### 8.10 Fuel Cell

Fuel cells are another means to convert chemical energy to electrical energy. . The main disadvantage of a primary cell is that it can deliver current for a short period only. This is because the quantity of oxidizing agent and reducing agent is limited. But energy can be obtained indefinitely from a fuel cell as long as the outside supply of fuel is maintained. One of the examples is the hydrogen-oxygen fuel cell. The cell consists of three compartments separated by a porous electrode. Hydrogen gas is introduced into one compartment and oxygen gas is fed into another compartment. These gases then diffuse slowly through the electrodes and react with electrodes that are made of porous carbon and the electrolyte is a resin containing concentrated aqueous sodium hydroxide solution. Hydrogen is oxidized at anode and oxygen is reduced at cathode. The overall cell reaction produces water. The reactions which occur are:

Anode: $\left[\mathrm{H}_{2}(\mathrm{~g})+2 \mathrm{OH}^{-}(\mathrm{aq}.) \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+2 \mathrm{e}^{-}\right] \times 2$
Cathode: $\mathrm{O}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(l)+4 \mathrm{e}^{-} \longrightarrow 4 \mathrm{OH}^{-}$(aq.)
Overall: $2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
These type of cells are used in space-crafts. Fuel cells are efficient and pollution free.
Thermodynamic efficiency of fuel cells is the ratio of the electrical free energy to the enthalpy of the reaction.
$\eta=\frac{\Delta G}{\Delta H}$

### 8.11 Concentration Cell

(a) Electrode concentration cells: In these cells, the potential difference is developed between two like electrodes at different concentrations dipped in the same solution of the electrolyte. For example, two hydrogen electrodes at different gas pressures in the same solution of hydrogen ions constitute a cell of this type.


If $p_{1}>p_{2}$, oxidation occurs at LHS electrode and reduction occurs at RHS electrode.
$E_{\text {cell }}=\frac{0.0591}{2} \log \frac{\left(p_{1}\right)}{\left(p_{2}\right)}$ at $25^{\circ} \mathrm{C}$
In the amalgam cells, two amalgams of the same metal at two different concentrations are immersed in the same electrolytic solution. $\mathrm{M}\left(\mathrm{HgC}_{1}\right)\left|\mathrm{M}^{\mathrm{n}+}\right| \mathrm{Zn}\left(\mathrm{HgC}_{2}\right)$

The e.m.f of the cell is given by the expression $E_{\text {cell }}=\frac{0.0591}{n} \log \frac{C_{1}}{C_{2}}$ at $25^{\circ} \mathrm{C}$
(b) Electrolyte concentration cells: In these cells, electrodes are identical but these are immersed in a solution of the same electrolyte of different concentrations. The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration. With the expiry of time, the two concentrations tend to become equal. Thus, at the beginning, the e.m.f of the cell is at its maximum and it gradually falls to zero. Such a cell is represented in the following manner: ( $\mathrm{C}_{2}$ is greater than $\mathrm{C}_{1}$ ).

$$
\mathrm{M}\left|\mathrm{M}^{\mathrm{n+}}\left(\mathrm{C}_{1}\right) \| \mathrm{M}^{\mathrm{n+}}\left(\mathrm{C}_{2}\right)\right| \mathrm{M} \text { or } \frac{\mathrm{Zn} \mid \mathrm{Zn}^{2+}\left(\mathrm{C}_{1}\right)}{\text { Anode }} \| \frac{\mathrm{Zn}^{2+}\left(\mathrm{C}_{2}\right) \mid \mathrm{Zn}}{\text { Cathode }}
$$

The e.m.f of the cell is given by the following expression: $E_{\text {cell }}=\frac{0.0591}{n} \log \frac{C_{2(\text { RHS })}}{C_{1(L H S)}}$ at $25^{\circ} \mathrm{C}$
The concentration cells are used to determine the solubility of sparingly soluble salts, valency of the cation of the electrolyte and transition point of the two allotropic forms of a metal used as electrodes, etc.

Example: Find the standard cell potential for an electrochemical cell with the following cell reaction.

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

## Sol:

(i) Write the half-reactions for each process. $\mathrm{Zn}(\mathrm{s}) \rightarrow \mathrm{Zn}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} ; \mathrm{Cu}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}(\mathrm{s})$
(ii) Look up the standard potentials for the reduction half-reaction. $\mathrm{E}_{\text {reduction }}^{\circ}$ of $\mathrm{Cu}^{2+}=+0.339 \mathrm{~V}$
(iii) Look up the standard reduction potential for the reverse of the oxidation reaction and change the sign.

$$
\mathrm{E}_{\text {reduction }}^{\circ} \text { of } \mathrm{Zn}^{2+}=-0.762 \mathrm{~V}, \mathrm{E}_{\text {oxidation }}^{\circ} \text { of } \mathrm{Zn}=-(-0.762 \mathrm{~V})=+0.762 \mathrm{~V}
$$

(iv) Add the cell potentials together to get the overall standard cell potential.

Oxidation: $\mathrm{Zn}(\mathrm{s}) \rightarrow \mathrm{Zn}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \quad \mathrm{E}_{\text {oxidation }}^{\circ}=-\mathrm{E}_{\text {reduction }}^{\circ}=-(-0.762 \mathrm{~V})=+0.762 \mathrm{~V}$
Reduction: $\mathrm{Cu}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}(\mathrm{s}) \quad \mathrm{E}_{\text {reduction }}^{0}=+0.339 \mathrm{~V}$
Overall: $\mathrm{Zn}(\mathrm{s})+\mathrm{Cu}^{2+}(\mathrm{aq}) \rightarrow \mathrm{Zn}^{2+}(\mathrm{aq})+\mathrm{Cu}(\mathrm{s}) \mathrm{E}_{\text {cell }}^{\circ}=+1.101 \mathrm{~V}$

Example: Predict the cell potential for the following reaction when the pressure of the oxygen gas is 2.50 atm , the hydrogen ion concentration is 0.10 M and the bromide ion concentration is 0.25 M .

$$
\mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{+}(\mathrm{aq})+4 \mathrm{Br}^{-}(\mathrm{aq}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(l)+2 \mathrm{Br}_{2}(l)
$$

Sol: (i) Calculate the standard cell potential for the reaction, $\mathrm{E}_{\text {cell, }}^{\circ}$, using the tabled values:
Oxidation: $4 \mathrm{Br}^{-}(\mathrm{aq}) \rightarrow 2 \mathrm{Br}_{2}(l)+4 \mathrm{e}^{-} \mathrm{E}_{\text {oxidation }}^{\circ}=-\mathrm{E}_{\text {reduction }}^{0}=-(+1.077 \mathrm{~V})=-1.077 \mathrm{~V}$
Reduction: $\mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{+}(\mathrm{aq})+4 \mathrm{e}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \quad \mathrm{E}_{\text {reduction }}^{\circ}=+1.229 \mathrm{~V}$
Overall: $\mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{+}(\mathrm{aq})+4 \mathrm{Br}^{-}(\mathrm{aq}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(l)+2 \mathrm{Br}_{2}(l) \mathrm{E}_{\text {cell }}^{0}=+0.152 \mathrm{~V}$
(ii) Determine the new cell potential resulting from the changed conditions.
(iii) Calculate the value for the reaction quotient, Q. (Note: We calculate Q using molar concentrations for solutions and pressures for gases. Water and bromine are both liquids, therefore they are not included in the calculation of Q.)
$\mathrm{Q}=\frac{1}{\mathrm{P}_{\mathrm{O}_{2}}\left[\mathrm{H}^{+}\right]^{4}\left[\mathrm{Br}^{-}\right]^{4}} ; \mathrm{Q}=\frac{1}{(2.50 \mathrm{~atm})(0.10 \mathrm{M})^{4}(0.25 \mathrm{M})^{4}} ; \mathrm{Q}=1.02 \times 10^{6}$
(iv) Calculate the number of moles of electrons transferred in the balanced equation, $n$.
$\mathrm{n}=4$ moles of electrons
(v) Substitute values into the Nernst equation and solve for the non-standard cell potential, $\mathrm{E}_{\text {cell }}$.

$$
\mathrm{E}_{\text {cell }}=+0.152 \mathrm{~V}-(0.0257 / 4) \operatorname{In}\left(1.02 \times 10^{6}\right), \mathrm{E}_{\text {cell }}=0.063 \mathrm{~V}
$$

Illustration 11: Reaction $\rightarrow 2 \mathrm{Ag}+\mathrm{Cd}^{2+}$. The standard electrode potentials for $\mathrm{Ag}^{+} \rightarrow \mathrm{Ag}^{\text {and }} \mathrm{Cd}^{2+} \rightarrow \mathrm{Cd}$ couples are 0.80 volt and -0.40 volt respectively
(i) What is the standard potential $E^{\circ}$ for this reaction?
(ii) For the electrochemical cell, in which this reaction takes place which electrode is negative electrode?
(JEE MAIN)
Sol: First write down the two half-cell. Standard potential $E^{\circ}$ for the cell is given by standard potential of reducing electrode+ standard potential of oxidising electrode. The electrode having less electrode potential act as negative electrode.
(i) The half reactions are: $2 \mathrm{Ag}^{+}+\underset{\substack{\text { Reduction } \\ \text { (Cathode) }}}{2 \mathrm{e}^{-}} \longrightarrow 2 \mathrm{Ag}$
$\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}^{\circ}=0.80$ volt (Reduction potential); $\left.\mathrm{Cd} \longrightarrow \longrightarrow \begin{array}{c}\text { Xxidation } \\ \text { (Anode) }\end{array}\right)$
$\mathrm{E}_{\mathrm{Cd}^{2+} / \mathrm{Cd}}^{\circ}=-0.40$ volt $\quad$ (Reduction potential) or $\mathrm{E}_{\mathrm{Cd} / \mathrm{Cd}^{2+}}^{\circ}=+0.40$ volt
$\mathrm{E}^{\circ}=\mathrm{E}_{\mathrm{Cd} / \mathrm{Cd}^{2+}}^{\circ}+\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}^{\circ}=0.40+0.80=1.20$ volt

Illustration 12: The standard oxidation potential of zinc is 0.76 volt and of silver is -0.80 volt. Calculate the e.m.f of the cell:

$$
\underset{0.25 \mathrm{M}}{\mathrm{Zn} \mid \mathrm{Zn}\left(\mathrm{NO}_{3}\right)_{2}} \| \underset{0.1 \mathrm{M}}{\mathrm{AgNO}_{3}} \mid \mathrm{Ag} \text { At } 25^{\circ} \mathrm{C} .
$$

(JEE MAIN)

Sol: First calculate the standard potential for reaction which is calculated as

$$
E_{\text {cell }}^{\circ}=E_{\text {oxidation }}^{\circ}-E_{\text {reduction }}^{\circ}
$$

After calculating $\mathrm{E}_{\text {cell }}^{0}$ e.m.f of the cell can be easily calculated using following equation

$$
\mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\circ}-\frac{0.0591}{\mathrm{n}} \log \frac{[\text { Products }]}{[\text { Reactants }]}
$$

The cell reaction is $\mathrm{Zn}+2 \mathrm{Ag}^{+} \longrightarrow 2 \mathrm{Ag}+\mathrm{Zn}^{2+} ; \mathrm{E}_{\text {oxidation }}^{0}$ of $\mathrm{Zn}=0.76$ volt
$\mathrm{E}_{\text {reduction }}^{\circ}$ of $\mathrm{Ag}=0.80$ volt $; \mathrm{E}_{\text {cell }}^{\circ}=\mathrm{E}_{\text {oxidation }}^{\circ}$ of $\mathrm{Zn}+\mathrm{E}_{\text {reduction }}^{\circ}$ of $\mathrm{Ag}=0.76+0.80=1.56$ volt
We know that, $\mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\circ}-\frac{0.0591}{\mathrm{n}} \log \frac{[\text { Products }]}{[\text { Reactants }]}$
$=\mathrm{E}_{\text {cell }}^{\circ}-\frac{0.0591}{\mathrm{n}} \log \frac{0.25}{0.1 \times 0.1}=1.56-\frac{0.0591}{2} \times 1.3979=(1.56-0.0413)$ volt $=1.5187$ volt.

Illustration 13: Calculate the e.m.f of the cell. $\mathrm{Mg}(\mathrm{s})\left|\mathrm{Mg}^{2+}(0.2 \mathrm{M}) \| \mathrm{Ag}^{+}\left(1 \times 10^{-3}\right)\right| \mathrm{Ag}$

$$
\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}^{0}=+0.8 \mathrm{volt}^{2} \mathrm{E}_{\mathrm{Mg}^{2+} / \mathrm{Mg}}^{0}=-2.37 \mathrm{volt}
$$

What will be the effect on e.m.f if concentration of $\mathrm{Mg}^{2+}$ ion is decreased to 0.1 M ?
(JEE MAIN)
Sol: First calculate the standard potential for reaction which is calculated as

$$
\mathrm{E}_{\text {cell }}^{\circ}=\mathrm{E}_{\text {oxidation }}^{\circ}-\mathrm{E}_{\text {reduction }}^{\circ}
$$

After calculating $\mathrm{E}_{\text {cell }}^{\circ}$ e.m.f of the cell can be easily calculated using following equation

$$
\begin{aligned}
& E_{\text {cell }}=E_{\text {cell }}^{\circ}-\frac{0.0591}{n} \log \frac{[\text { Products }]}{[\text { Reactants }]} \\
& E_{\text {cell }}^{\circ}=E_{\text {Cathode }}^{\circ}-E_{\text {Anode }}^{\circ}=0.80-(-2.37)=3.17 \mathrm{volt}
\end{aligned}
$$

$$
\text { Cell reaction, } \mathrm{Mg}+2 \mathrm{Ag}^{+} \longrightarrow 2 \mathrm{Ag}+\mathrm{Mg}^{2+} ; \mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\circ}-\frac{0.0591}{\mathrm{n}} \log \frac{\mathrm{Mg}^{2+}}{\left[\mathrm{Ag}^{+}\right]^{2}}
$$

$$
=3.17-\frac{0.0591}{2} \log \frac{0.2}{\left[1 \times 10^{-3}\right]^{2}}=3.17-0.1566=3.0134 \text { volt when } \mathrm{Mg}^{2+}=0.1 \mathrm{M}
$$

$$
\mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\circ}-\frac{0.0591}{2} \log \frac{0.1}{\left(1 \times 10^{-3}\right)^{2}}=(3.17-0.1477) \text { volt }=3.0223 \text { volt. }
$$

Illustrations 14: To find the standard potential of $\mathrm{M}^{3+} / \mathrm{M}$ electrode, the following cell is constituted:
$\mathrm{Pt}|\mathrm{M}| \mathrm{M}^{3+}\left(0.0018 \mathrm{~mol}^{-1} \mathrm{~L}\right)| | \mathrm{Ag}^{+}\left(0.01 \mathrm{~mol}^{-1} \mathrm{~L}\right) \mid \mathrm{Ag}$
The e.m.f of this cell is found to be 0.42 volt. Calculate the standard potential of the half reaction
$\mathrm{M}^{3+}+3 \mathrm{e}^{-} \longrightarrow \mathrm{M} . \mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}^{0}=0.80$ volt.
(JEE MAIN)
Sol: Here e.m.f is given we have to calculate standard potential of anode. So first we have to calculate standard potential of the cell and subtract it from the provided standard potential of cathode.
Standard potential of cell can be determined using following expression, Nernst equation

$$
\mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\circ}-\frac{0.0591}{3} \log \frac{\left[\mathrm{M}^{3+}\right]}{\left[\mathrm{Ag}^{+}\right]^{3}}
$$

The cell reaction is $\mathrm{M}+3 \mathrm{Ag}^{+} \longrightarrow 3 \mathrm{Ag}+\mathrm{M}^{3+}$
Applying Nernst equation, $\mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\circ}-\frac{0.0591}{3} \log \frac{\left[\mathrm{M}^{3+}\right]}{\left[\mathrm{Ag}^{+}\right]^{3}}$

$$
\begin{aligned}
& 0.42=E_{\text {cell }}^{\circ}-\frac{0.0591}{3} \log \frac{(0.0018)}{(0.01)^{3}}=E_{\text {cell }}^{\circ}-0.064 ; E_{\text {cell }}^{\circ}=(0.42+0.064)=0.484 \mathrm{volt} \\
& E_{\text {cell }}^{\circ}=E_{\text {Cathode }}^{\circ}-E_{\text {Anode }}^{\circ} \text { or } E_{\text {Anode }}^{\circ}=E_{\text {Cathode }}^{\circ}-E_{\text {Cell }}^{\circ}=(0.80-0.484)=0.32 \mathrm{volt} .
\end{aligned}
$$

## PROBLEM-SOLVING TACTICS

(a) Related to electrolysis: Electrolysis comprises of passing an electric current through either a molten salt or an ionic solution. Thus the ions are "forced" to undergo either oxidation (at the anode) or reduction (at the cathode). Most electrolysis problems are really stoichiometry problems with the addition of some amount of electric current. The quantities of substances produced or consumed by the electrolysis process is dependent upon the following:
(i) Electric current measured in amperes or amps
(ii) Time measured in seconds
(iii) The number of electrons required to produce or consume 1 mole of the substance

## (b) To calculate amps, time, coulombs, faradays and moles of electrons:

Three equations related these quantities:
(i) Amperes $\times$ time $=$ Coulombs
(ii) 96,485 coulombs $=1$ Faraday
(iii) 1 Faraday $=1$ mole of electrons

The through process for interconverting amperes and moles of electrons is:
Amps and time $\longleftrightarrow$ Coulombs $\longleftrightarrow$ Faradays $\longleftrightarrow$ Moles of electrons
Use of these equations are illustrated in the following sections.
(c) To calculate the quantity of substance produced or consumed: To determine the quantity of substance either produced or consumed during electrolysis, given the time a known current flowed:
(i) Write the balanced half-reactions involved.
(ii) Calculate the number of moles of electrons that were transferred.
(iii) Calculate the number of moles of substance that was produced/consumed at the electrode.
(iv) Convert the moles of substance to desired units of measure.
(d) Determination of standard cell potentials: A cell's standard state potential is the potential of the cell under standard state conditions, and it is approximated with concentrations of 1 mole per liter ( 1 M ) and pressures of 1 atmosphere at $25^{\circ} \mathrm{C}$.
(i) To calculate the standard cell potential for a reaction.
(ii) Write the oxidation and reduction half-reactions for the cell.
(iii) Look up the reduction potential, $E_{\text {reduction, }}^{\circ}$ for the reduction half-reaction in a table of reduction potentials.
(iv) Look up the reduction potential for the reverse of the oxidation half-reaction and reverse the sign to obtain the oxidation potential. For the oxidation half-reaction, $E_{\text {oxidation }}^{\circ}=-E_{\text {reduction }}^{\circ}$.
(v) Add the potentials of the half-cells to get the overall standard cell potential. $E_{\text {cell }}^{\circ}=-E_{\text {reduction }}^{\circ}+E_{\text {oxidation }}^{\circ}$
(e) For determining non-standard state cell potentials: To determine the cell potential when the conditions are other than standard state (concentrations not 1 molar and/or pressures not 1 atmosphere):
(i) Determine the standard state cell potential.
(ii) Determine the new cell potential resulting from the changed conditions.
(iii) Determine Q , the reaction quotient.
(iv) Determine n , the number of electrons transferred in the reaction " n ".
(v) Determine $\mathrm{E}_{\text {cell, }}$, the cell potential at the non-standard state conditions using the Nernst equation.
$E_{\text {cell }}=E_{\text {cell }}^{0}-(R T / n F) \ln Q$
$\mathrm{E}_{\text {cell }}=$ cell potential at non-standard state conditions; $\mathrm{E}_{\text {cell }}^{\circ}=$ standard state cell potential
$\mathrm{R}=$ constant ( $8.31 \mathrm{~J} /$ mole K ); $\mathrm{T}=$ absolute temperature (Kelvin scale)
$\mathrm{F}=$ Faraday's constant $\left(96,485 \mathrm{C} /\right.$ mole $\left.\mathrm{e}^{-}\right)$
$\mathrm{n}=$ Number of moles of electrons transferred in the balanced equation for the reaction occurring in the cell;
$Q=$ Reaction quotient for the reaction. $a A+b B \rightarrow c C+d D, Q=\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$
If the temperature of the cell remains at $25^{\circ} \mathrm{C}$, the equation simplifies to:
$E_{c e l l}=E_{\text {cell }}^{\circ}-(0.0257 / n) \ln Q$ or in terms of $\log _{10} ; E_{\text {cell }}=E_{\text {cell }}^{\circ}-(0.0592 / n) \log Q$

## POINTS TO REMEMBER

| S.No. |  | Description |
| :---: | :---: | :---: |
| 1 | Electrolyte | Any substance which dissolves in water to form a solution that will conduct an electric current (ionic substances).Electrolytes may be classified as strong ( $\mathrm{NaCl}, \mathrm{HCl}, \mathrm{NaOH}$ ) or weak $\left(\mathrm{NH}_{4} \mathrm{OH}, \mathrm{CH}_{3} \mathrm{COOH}, \mathrm{HF}\right)$. Solutions that do not conduct electricity at all are called non-electrolytes. |
| 2 | Strong and Weak Electrolytes | Strong electrolyte - Solutions in which the substance dissolved (solute) is present entirely as ions. <br> Weak electrolyte - A solute that yields a relatively low concentration of ions in solution. |
| 3 | Dissociation | The separation of ions that occurs when an ionic substance dissolves: $\mathrm{CaCl}_{2}(\mathrm{~s})+\mathrm{H}_{2} \mathrm{O} \rightarrow$ $\mathrm{Ca}^{+2}(\mathrm{aq})+2 \mathrm{Cl}^{-}(\mathrm{aq})$. |
| 4 | Electrochemical Cells | A system of electrodes and electrolytes in which a spontaneous or non-spontaneous redox reaction occurs. |
| 5 | Components of Electrochemical cells | a. Electrode: An electrical conductor (metal strip) used to establish contact with a nonmetallic part of the circuit (usually an electrolyte). <br> b. Anode: The electrode at which oxidation occurs. <br> c. Cathode: The electrode at which reduction occurs. <br> d. Electrolyte: A liquid, paste, or gel that serves to conduct charge by moving ions in the cell. <br> e. Half-cell: A single electrode immersed in a solution of its ions. <br> f. Salt bridge: A device (porous disk or bridge i.e. U-tube containing inert electrolytic solution, $\mathrm{KCl}, \mathrm{NH}_{4} \mathrm{NO}_{3^{\prime}}$ etc.) placed between the cells which maintains electrical neutrality by allowing ions to migrate between the cells. <br> g. External circuit: The part of the cell where charge is conducted as a current of moving electrons. <br> h. Standard Electrode Reduction Potential E ${ }^{\circ}$ : The measurement, in volts, of the tendency for a half reaction to occur as a reduction half reaction. |


| S.No. |  | Description |
| :---: | :---: | :---: |
| 6 | Voltaic/Galvanic Cells | Redox reactions are spontaneous and chemical energy is transformed into electrical energy. The cell potential $E^{\circ}$ is positive and the anode is the negative electrode. i.e. batteries $\mathrm{Zn}(\mathrm{~s})\left\|\mathrm{Zn}^{+2}(1 \mathrm{M})\right\|\left\|\mathrm{Cu}^{+2}(1 \mathrm{M})\right\| \mathrm{Cu}(\mathrm{~s})$ <br> anode \|| cathode |
| 7 | Electrolytic Cells | Cell in which an external electric current is required to drive a non-spontaneous redox reaction. The cell potential $\left(E^{\circ}\right)$ is negative and the anode is the positive electrode. i.e. electrolysis, electroplating, etc. $\mathrm{Cu}(\mathrm{~s})\left\|\mathrm{Cu}^{+2}(1 \mathrm{M})\right\|\left\|\mathrm{Cu}^{+2}(1 \mathrm{M})\right\| \mathrm{Cu}(\mathrm{~s})$ <br> anode \|| cathode |
| 8 | Quick Comparison of Electrolytic Cells |  |
| 9 | Faraday's First law of Electrolysis | The amount of electrolyte discharged at an electrode is directly proportional to the quantity of electricity passed: $\begin{aligned} & \mathrm{W} \propto \mathrm{Q} \quad \text { where, }=\mathrm{I} . \mathrm{t} \\ & \mathrm{I}=\text { Current strength in ampere } \\ & \mathrm{T}=\text { time in seconds } \\ \Rightarrow \quad & \mathrm{W}=\mathrm{ZQ}=\mathrm{Zit} \end{aligned}$ <br> $Z$ is a constant called electrochemical equivalence (ECE) |
| 10 | Electrochemical Equivalent | It is the amount of an electrolyte discharged on passing one coulomb of electricity. |
| 11 | Faraday's Constant | It is the charge possessed by 1.0 mole of electrons and it is equal to 96500 coulombs (approx.). In terms of faraday's constant the number of gram equivalent of electrolyte discharged at an electrode is equal to the number of faraday's passed. $\Rightarrow \quad \mathrm{W}=\mathrm{E}\left(\frac{\mathrm{Q}}{96500}\right) \text { where, } \mathrm{E}=\text { Equivalent weight }$ |
| 12 | Faraday's Second Law | Second Law: If same quantity of electricity is passed through different cells connected in series, same number of gram equivalent of electrolytes are discharged at each of the electrodes: $\Rightarrow \quad \frac{W_{1}}{W_{2}}=\frac{E_{1}}{E_{2}}$ <br> Where, $W_{1}$ and $W_{2}$ are the weights of electrolytes discharged at two different electrodes in two different cells connected in series and $E_{1}$ and $E_{2}$ are their respective equivalent weights. |


| S.No. |  | Description |
| :--- | :--- | :--- |
| 13 | Nernst Equation | $\mathrm{E}_{\text {half-cell }}=\mathrm{E}^{\circ}{ }_{\text {half-cell- }} \frac{2.303 \mathrm{RT}}{\mathrm{nF}} \log \frac{[\text { Reduced form }]}{\text { [Oxidised form] }}$ |
|  |  | At 298 K , the Nernst equation can be written as, |
|  |  | $\mathrm{E}_{\text {half-cell }}=\mathrm{E}_{\text {half-cell }}^{\circ} \frac{0.0591}{\mathrm{n}} \log \frac{\text { [Reduced form] }}{\text { [Oxidised form] }}$ |

## Solved Examples

## JEE Main/Boards

Example 1: Zn and iron can replace Cu in a solution but Pt and Au cannot. Why?

Sol: Both Zn and iron have more $\mathrm{E}_{\mathrm{OP}}^{\circ}$ than Cu , whereas Pt and Au have less $\mathrm{E}_{\mathrm{OP}}^{\circ}$

Example 2: Which of the following metals cannot be obtained by the electrolysis of their aqueous salt solution and why?
$\mathrm{Al}, \mathrm{Na}, \mathrm{Cu}, \mathrm{Ag}$.
Sol: Al and Na cannot be obtained because they have higher $\mathrm{E}_{\mathrm{OP}}^{\circ}$ than H and thus, reduction of $\mathrm{Cu}^{2+}$ and $\mathrm{Ag}^{+}$ will give Cu and Ag.

Example 3: Calculate the no. of electron lost or gained during electrolysis of $2 \mathrm{~g} \mathrm{Cl}^{-}$from NaCl (aq) to give $\mathrm{Cl}_{2}$ at anode.

Sol: First calculate the equivalent of $\mathrm{Cl}^{-}$used during the reaction and on multiplying it with avogadro number will give us the no of electron lost during the reaction
$\because \quad 2 \mathrm{Cl}^{-} \rightarrow \mathrm{Cl}_{2}+2 \mathrm{e}^{-}$
Eq. of $\mathrm{Cl}^{-}$used $=2 / 35.5$
$\because 1$ eq. of an element involves 1 faraday charge or N electrons
$\therefore(2 / 35.5)$ eq. of an element involves
$=\frac{\mathrm{N} \times 2}{35.5}$ electrons $=\frac{6.023 \times 10^{23} \times 2}{35.5}$
$=3.4 \times 10^{22}$ electrons

Example 4: Evaluate the $\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}^{\circ}$ and $\mathrm{E}_{\mathrm{Zn}^{2+} / \mathrm{Zn}}^{\circ}$ from the $=9.32 \times 10^{-19}$
$\therefore$ By Eq. (i),
$\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}=0.799+(0.059 / 1) \log \left(9.32 \times 10^{-9}\right)$
$=0.799-0.474=0.32 \mathrm{~V}$
Also, $\mathrm{E}_{\mathrm{I} / \mathrm{AgI} / \mathrm{Ag}}^{\circ}=\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}^{\circ}+(0.059 / 1) \log \mathrm{K}_{\mathrm{sp}_{\mathrm{AgI}}}$
$=0.799+(0.059 / 1) \log \left[8.7 \times 10^{-17}\right]$
$=0.799-0.948=-0.149 \mathrm{~V}$

Example 6: The reduction potential diagram for Cu in acid solution is:


Calculate X . Does $\mathrm{Cu}^{+}$disproportionate in solution?

Sol: Given;

$$
\begin{align*}
& \mathrm{Cu}^{2+}+\mathrm{e}^{-} \rightarrow \mathrm{Cu}^{+} ; \quad \mathrm{E}_{1}^{\circ}=0.15 \mathrm{~V} \\
& -\Delta \mathrm{G}_{1}^{\circ}=1 \times \mathrm{E}_{1}^{\circ} \times \mathrm{F}  \tag{i}\\
& \mathrm{Cu}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Cu} ; \quad \mathrm{E}_{2}^{\circ}=0.5 \mathrm{~V} \\
& -\Delta \mathrm{G}_{2}^{\circ}=1 \times \mathrm{E}_{2}^{\circ} \times \mathrm{F}  \tag{ii}\\
& \mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu} ; \quad \mathrm{E}_{3}^{\circ}=? \\
& -\Delta \mathrm{G}_{3}^{\circ}=2 \times \mathrm{E}_{3}^{\circ} \times \mathrm{F} \tag{iii}
\end{align*}
$$

Adding Eqs. (i) and (ii)
$\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu} ;-\left(\Delta \mathrm{G}_{1}^{\circ}+\Delta \mathrm{G}_{2}^{\circ}\right)$
i.e., $-\Delta G_{3}^{\circ}=-\left(\Delta G_{1}^{\circ}+\Delta G_{2}^{\circ}\right)$
$2 \times \mathrm{E}_{3}^{\circ} \times \mathrm{F}=[1 \times 0.15 \times \mathrm{F}+1 \times 0.5 \times \mathrm{F}]$
$\therefore \quad \mathrm{E}_{3}^{\circ}=0.325 \mathrm{~V}$

Example 7: The standard oxidation potential of $\mathrm{Ni} / \mathrm{Ni}^{2+}$ 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 e.m.f. be zero at $25^{\circ} \mathrm{C}$ ?
(Assume $\left[\mathrm{Ni}^{2+}\right]=1 \mathrm{M}$ )
Sol: Here we are provided with standard oxidation potential of nickel electrode and we all know that reduction potential of hydrogen electrode is always zero so first the standard electrode potential of the cell is equal the oxidation potential of nickel electrode. Here it we are also with e.m.f of the cell (zero) so substitute the values of different term in Nernst equation and
calculate the concentration of hydrogen ion. From the concentration one can easily find out the pH as using the following expression

$$
\begin{aligned}
& \mathrm{pH}=-\log \mathrm{H}^{+} \\
& \mathrm{Ni} \rightarrow \mathrm{Ni}^{2+}+2 \mathrm{e}^{-} ; \mathrm{E}_{\mathrm{OP}}^{\circ}=0.236 \mathrm{~V} \\
& 2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2^{i}} \mathrm{E}_{\mathrm{RP}}^{\circ}=0 \\
& \therefore \mathrm{E}_{\mathrm{Cell}}^{\circ}=\mathrm{E}_{\mathrm{OP}_{\mathrm{Ni}}^{\circ}}^{\circ}+\mathrm{E}_{\mathrm{RP}_{\mathrm{H}}^{\circ}}^{\circ}=0.236+0.0=0.236 \mathrm{~V} \\
& \therefore \quad \mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\circ}+\frac{0.059}{2} \log _{10} \frac{\left[\mathrm{H}^{+}\right]^{2}}{\left[\mathrm{Ni}^{2+}\right]} \\
& 0=0.236+\frac{0.059}{2} \log _{10}\left[\mathrm{H}^{+}\right]^{2} \\
& \text { or } \quad-\log \mathrm{H}^{+}=4 \\
& \therefore \quad \mathrm{pH}=4
\end{aligned}
$$

Example 8: A current of 3 ampere was passed for 2 hour through a solution of $\mathrm{CuSO}_{4} \cdot 3 \mathrm{~g}$ of $\mathrm{Cu}^{2+}$ ions were discharged at cathode. Calculate current efficiency. (At wt. of $\mathrm{Cu}=63.5$ )

Sol: Find out current in ampere and from the calculated current passed, determine the current efficiency.

Current efficiency =
$\frac{\text { Current passed actually }}{\text { Total current passed experimentally }} \times 100$
$\because \quad \mathrm{w}_{\mathrm{Cu}}=$ E. i. $\mathrm{t} / 96500$
$\therefore 3=\frac{63.5 \times \mathrm{i} \times 2 \times 60 \times 60}{2 \times 96500}$ or $\mathrm{i}=1.266$ ampere
Current efficiency

$$
\begin{aligned}
& =\frac{\text { Current passed actually }}{\text { Total current passed experimentally }} \times 100 \\
& =(1.266 / 3) \times 100=42.2 \%
\end{aligned}
$$

Example 9: An ammeter and copper voltmeter are connected in series in an electric circuit through which a constant direct current flows. The ammeter shows 0.525 ampere. If 0.6354 g of Cu is deposited in one hour, what is percentage error of ammeter? (At. Wt. of $\mathrm{Cu}=63.54$ )

Sol: In order to find out the error first from the given Weight, time and other term calculate the actual current flow. The difference between the two will give us the error shown by the ammeter. As we are asked to calculate percentage error divide the error by actual current flow

Current flown $=0.525$ ampere as shown by ammeter Actual current flown
(I) $=\frac{w}{E \times t} \times 96500$

$$
\frac{0.6354 \times 96500}{(63.54 / 2) \times 60 \times 60} \quad(\because t=60 \times 60 \mathrm{sec})
$$

$\therefore \quad i=0.536$ ampere
Thus, error in $(\mathrm{I})=0.536-0.525=0.011$
$\therefore \%$ error in ammeter $=\frac{0.011 \times 100}{0.536}=2.05 \%$

Example 10: 3 ampere current was passed through an aqueous solution of unknown salt of Pd for 1 hour 2.977 g of $\mathrm{Pd}^{\mathrm{n+}}$ was deposited at cathode. Find n . (At. Wt. of $\mathrm{Pd}=106.4$ )

Sol: For the reduction: $\mathrm{Pd}^{\mathrm{n+}}+\mathrm{ne}^{-} \rightarrow \mathrm{Pd}$
Eq. of $\operatorname{Pd}$ or $(w / E)=(I \times t) / 96500$
or $\frac{2.977}{106.4 / n}=\frac{3 \times 1 \times 60 \times 60}{96500}$
$\therefore \quad \mathrm{n}=4$ (an integer).

## JEE Advanced/Boards

Example 1: Calculate the quantity of electricity that will be required to liberate 710 g of $\mathrm{Cl}_{2}$ gas by electrolyzing a conc. solution of NaCl . What weight of NaOH and what volume of $\mathrm{H}_{2}$ at $27^{\circ} \mathrm{C}$ and 1 atm pressure is obtained during this process?

Sol: Quantity of electricity can be calculated using
Simple relationship
$\mathrm{W}=\frac{\mathrm{E} \times \mathrm{i} \times \mathrm{t}}{96500}(\because \mathrm{Q}=\mathrm{i} \times \mathrm{t})$
Similarly calculate $\mathrm{w}_{\mathrm{NaOH}}$ and $\mathrm{w}_{\mathrm{H}_{2}}$ from the value of $\mathrm{W}_{\mathrm{H}_{2}}$ volume can be calculated using ideal gas equation.
$\because \quad 2 \mathrm{Cl}^{-} \rightarrow \mathrm{Cl}_{2}+2 \mathrm{e} ; 2 \mathrm{H}^{+}+2 \mathrm{e} \rightarrow \mathrm{H}_{2}$
$\therefore \quad$ Eq. wt. of $\mathrm{Cl}_{2}=\mathrm{M}$. Wt./2
Now $w=\frac{E \times i \times t}{96500}=\frac{E \times Q}{96500} \quad(\because Q=i \times t)$
$\therefore \quad Q=\frac{W}{E} \times 96500=\frac{710}{71 / 2} \times 96500$
$=1.93 \times 10^{6}$ coulomb
Also Eq. of NaOH formed
$=$ Eq. of $\mathrm{H}^{+}$discharged= Eq. of $\mathrm{Cl}_{2}$ formed

$$
\therefore \quad \mathrm{w}_{\text {Маон }}=\{710[71 / 2]\} \times 40=800 \mathrm{~g}
$$

And $\mathrm{w}_{\mathrm{H}_{2}}=\{710 /[71 / 2]\} \times 1=20 \mathrm{~g}$
$\therefore \quad V_{\mathrm{H}_{2}}=\mathrm{wRT} / \mathrm{mp}$
$=[20 \times 0.0821 \times 300] /[2 \times 1]=246.3$ liter

Example 2: $50 \mathrm{~mL} 0.1 \mathrm{M} \mathrm{CuSO}_{4}$ solution is electrolyzed using Pt electrodes with a current of 0.965 ampere for a period of 1 minute. Assuming that volume of solution does not change during electrolysis, calculate $\left[\mathrm{Cu}^{2+}\right]$, $\left[\mathrm{H}^{+}\right]$and $\left[\mathrm{SO}_{4}^{2-}\right]$ after electrolysis. What will be the concentration of each species, if current is passed using Cu electrodes?

Sol: Meq. Of $\mathrm{CuSO}_{4}$ in solution $=$ Meq. Of $\mathrm{Cu}^{2+}$
$=50 \times 0.1 \times 2=10(\because$ Meq. $\mathrm{Of} \mathrm{N} \times \mathrm{V}$ in mL$)$
The redox changes are:
$\mathrm{Cu}^{2+}+2 \mathrm{e} \rightarrow \mathrm{Cu} \quad$ (at cathode)
$2 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{H}^{+}+\mathrm{O}_{2}+4 \mathrm{e} \quad$ (at anode)
$\because \quad \mathrm{w} / \mathrm{E}=\mathrm{i} . \mathrm{t} / 96500$
And Eq. of $\mathrm{Cu}^{2+}$ lost $=$ Equivalent of $\mathrm{H}^{+}$formed
$=\frac{\text { i. t. }}{96500}=\frac{0.965 \times 1 \times 60}{96500}=6 \times 10^{-4}$
Or Meq. Of $\mathrm{Cu}^{2+}$ lost $=0.6$
$\therefore$ Meq. of $\mathrm{Cu}^{2+}$ or Meq. of $\mathrm{CuSO}_{4}$ left in solution
$=10-0.6=9.4$
$\therefore\left[\mathrm{Cu}^{2+}\right]=\frac{\mathrm{Nu}^{2+}}{2}=\frac{\text { Meq. of } \mathrm{Cu}^{2+}}{2 \times \text { Volume of solution (in } \mathrm{mL} \text { ) }}$
$=\frac{9.4}{2 \times 50}=0.094 \mathrm{M}$
$\left[\mathrm{H}^{+}\right]=\left(\mathrm{N}_{\mathrm{H}^{+}} / 1\right)=(0.6 / 50)=0.012 \mathrm{M}$
$\left[\mathrm{SO}_{4}^{2-}\right]=0.1 \mathrm{M}$
( $\because \mathrm{SO}_{4}^{2-}$ is not involved in redox changes)
Also, if Cu electrodes are used, $\mathrm{Cu}^{2+}$ ions are discharged at cathode and $\mathrm{Cu}^{2+}$ are formed at anode and thus no changes in molarity of $\mathrm{CuSO}_{4}$ solution. Anode $\mathrm{Cu} \rightarrow \mathrm{Cu}^{2+}+2 \mathrm{e}^{-}$
Cathode $\mathrm{Cu}^{2+}+2 \mathrm{e} \rightarrow \mathrm{Cu}$

Example 3: Two students use same stock solution $\mathrm{ZnSO}_{4}$ and a solution of $\mathrm{CuSO}_{4}$. The e.m.f., of one cell is 0.03 V higher than the other. The conc. of $\mathrm{CuSO}_{4}$ in the cell with higher e.m.f. value is 0.5 M . Find out the conc. of $\mathrm{CuSO}_{4}$ in the other cell.
$\left(\frac{2.303 R T}{F}=0.06\right)$

Sol: First write down the half-cell reaction and nernst equation for both the half cell. By comparing both the equation, value of $\mathrm{C}_{2}$ can be calculated.

Cell I: $\mathrm{Zn}\left|\mathrm{ZnSO}_{4}\right|\left|\mathrm{CuSO}_{4}\right| \mathrm{Cu}$

$$
\begin{align*}
& \left(\mathrm{C}_{2}=0.5 \mathrm{M}\right) ; \mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\circ}+\frac{0.060}{2} \log \frac{\left[\mathrm{Cu}^{2+}\right]}{\left[\mathrm{Zn}^{2+}\right]} \\
& =\mathrm{E}_{\text {cell }}^{\circ}+\frac{0.060}{2} \log \frac{\left[\mathrm{C}_{2}\right]}{\left[\mathrm{C}_{1}\right]} \tag{i}
\end{align*}
$$

Cell II: $\mathrm{Zn}\left|\underset{\mathrm{C}_{1}}{\mathrm{ZnSO}_{4}}\right| \underset{\mathrm{C}_{2}^{\prime}}{\mathrm{CuSO}_{4}} \mid \mathrm{Cu}$

$$
\begin{equation*}
\mathrm{E}_{\text {cell }}^{\prime}=\mathrm{E}_{\text {cell }}^{\circ}+\frac{0.06}{2} \log \frac{\left[\mathrm{C}_{2}^{\prime}\right]}{\left[\mathrm{C}_{1}\right]} \tag{ii}
\end{equation*}
$$

By Eqs. (i) and (ii) $E_{\text {cell }}-E_{\text {cell }}^{\prime}=\frac{0.06}{2} \log \frac{\left[C_{2}\right]}{\left[C_{2}^{\prime}\right]}$
$0.03=\frac{0.06}{2} \log \frac{0.5}{C_{2}^{\prime}}$ or $\quad C_{2}^{\prime}=0.05 \mathrm{M}$
Example 4: Two weak acid solutions $\mathrm{HA}_{1}$ and $\mathrm{HA}_{2}$ each with the same concentration and having $\mathrm{pK}_{\mathrm{a}}$ values 3 and 5 are placed in contact with hydrogen electrode ( 1 atm at $25^{\circ} \mathrm{C}$ )) and are interconnected through a salt bridge. Find e.m.f. of cell.

Sol: First write down the nernst equation for two halfcell as both solutions are acid we have to find out the concentration of hydrogen ion we can express it in the form of pH . As an acid undergoes dissociation, by substituting pH in terms of degree of dissociation and concentration in nernst equation, e.m.f of the cell can be easily determined.
Consider the cell
Pt $\mathrm{H}_{2(1 \mathrm{~atm})}\left|\mathrm{HA}_{2}\right|\left|\mathrm{HA}_{1}\right|\left(\mathrm{H}_{2}\right)_{(1 \mathrm{~atm})} \mathrm{Pt}$
At L.H.S. $\mathrm{E}_{\mathrm{H} / \mathrm{H}^{+}}=\mathrm{E}_{\mathrm{O}{ }_{\mathrm{H} / \mathrm{H}^{+}}^{\circ}}-\frac{0.059}{1} \log \left[\mathrm{H}^{+}\right]_{2}$
$\because \quad-\log \mathrm{H}^{+}=\mathrm{pH}$
$\therefore \quad \mathrm{E}_{\mathrm{H} / \mathrm{H}^{+}}=\mathrm{E}_{\mathrm{OP}}^{\mathrm{H} / \mathrm{H}^{+}}{ }^{+}+0.059(\mathrm{pH})_{2}$
At R.H.S. $E_{\mathrm{H}^{+} / H}=\mathrm{E}_{\mathrm{RP}_{\mathrm{H}^{+} / \mathrm{H}}^{\circ}}+\frac{0.059}{1} \log \left[\mathrm{H}^{+}\right]_{1}$
$\mathrm{E}_{\mathrm{H}^{+} / \mathrm{H}}=\mathrm{E}_{\mathrm{RP}_{\mathrm{H}^{+} / \mathrm{H}}^{\circ}}-0.059(\mathrm{pH})_{1}$
For acid $\mathrm{HA}_{1} \quad \mathrm{HA}_{1} \rightleftharpoons \mathrm{H}^{+}+\mathrm{A}_{1}^{-}$
$\left[\mathrm{H}^{+}\right]=\mathrm{C} \alpha=\sqrt{\mathrm{K}_{\mathrm{a}} \cdot \mathrm{C}}$
$\therefore \mathrm{pH}_{1}=\frac{1}{2} \mathrm{pK}_{\mathrm{a}_{1}}-\frac{1}{2} \log \mathrm{C}$
Similarly, $\mathrm{pH}_{2}=\frac{1}{2} \mathrm{pK}_{\mathrm{a}_{2}}-\frac{1}{2} \log \mathrm{C}$
( $\because$ C are same) By Eqs. (i) and (ii), $\mathrm{E}_{\text {cell }}$
$=\mathrm{E}_{\mathrm{OP}_{\mathrm{H} / \mathrm{H}^{+}}^{\circ}}+\mathrm{E}_{\mathrm{RP}_{\mathrm{H} / \mathrm{H}^{+}}^{\circ}}+0.059\left[\frac{1}{2} \mathrm{pK}_{\mathrm{a}_{2}}-\frac{1}{2} \mathrm{pK}_{\mathrm{a}_{1}}\right]$
$=0+0.059 \times 5[5-3] / 2=+0.059$ volt

Example 5: Calculate the minimum weight of NaOH required to added in RHS to consume all the $\mathrm{H}^{+}$present in RHS of cell of e.m.f. +0.701 V at $25^{\circ} \mathrm{C}$ before its use. Also report the e.m.f. of cell after addition of NaOH .
$\mathrm{Zn}\left|\begin{array}{l|l}\mathrm{Zn} \\ \\ 0.1 \mathrm{M}\end{array}\right| \begin{aligned} & \mathrm{HCl} \\ & 1 \\ & 1 \text { litre }\end{aligned} \left\lvert\, \begin{aligned} & \mathrm{Pt}_{\left(\mathrm{H}_{2}\right)} \mathrm{atm}\end{aligned} \mathrm{E}_{\mathrm{Zn} \mid \mathrm{Zn}^{2+}}^{\circ}=+0.760 \mathrm{~V}\right.$
Sol: For given cell $\because \mathrm{E}_{\mathrm{OP}}^{\mathrm{Zn} / \mathrm{Zn}^{2+}}{ }>\mathrm{E}_{\mathrm{OP}}^{\mathrm{H} / \mathrm{H}^{+}}{ }$
$\therefore$ Redox changes will be: $\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+}+2 \mathrm{e}$
$2 \mathrm{H}^{+}+2 \mathrm{e} \rightarrow \mathrm{H}_{2^{\prime}} \mathrm{E}_{\text {cell }}=\mathrm{E}_{\mathrm{OP}_{\mathrm{Zn} / \mathrm{Zn}}{ }^{2+}}+\mathrm{E}_{\mathrm{RP}_{\mathrm{H}+/ \mathrm{H}}}$
$=\mathrm{E}_{\mathrm{OP}}^{\mathrm{Zn} / \mathrm{Zn}}{ }^{2+}-\frac{0.059}{2} \log _{10}\left[\mathrm{Zn}^{2+}\right]$
$+\mathrm{E}_{\mathrm{RP}_{\mathrm{H}^{+} / \mathrm{H}}^{\circ}}+\frac{0.059}{2} \log _{10} \frac{\left[\mathrm{H}^{+}\right]^{2}}{\left(\mathrm{P}_{\mathrm{H}_{2}}\right)}$
$\mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\circ}+\frac{0.059}{2} \log \frac{\left[\mathrm{H}^{+}\right]^{2}}{\left[\mathrm{Zn}^{2+}\right]\left(\mathrm{P}_{\mathrm{H}_{2}}\right)}$
$0.701=0.760+\frac{0.059}{2} \log _{10} \frac{\left[\mathrm{H}^{+}\right]^{2}}{\left[\mathrm{Zn}^{2+}\right]\left(\mathrm{P}_{\mathrm{H}_{2}}\right)}$
$0.701=0.760+\frac{0.059}{2} \log _{10} \frac{\left[\mathrm{H}^{+}\right]^{2}}{[0.1] \times 1}$
$\left[\mathrm{H}^{+}\right]=0.0316$ mole liter $^{-1}$
Since, $\mathrm{H}^{+}$must be used by NaOH
$\therefore \quad$ Meq. of $\mathrm{NaOH}=$ Meq. of $\left[\mathrm{H}^{+}\right]$
$(w / 40) \times 1000=0.0316 \times 1000(\because V=1$ liter $)$
$\therefore \quad \mathrm{w}=1.265 \mathrm{~g}$
After addition of NaOH to cathode solution $\left[\mathrm{H}^{+}\right]$ becomes $10^{-7}$ since both acid and base are neutralized completely. Thus, new e.m.f. of cell,

$$
\begin{aligned}
& \mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\circ}=\frac{0.059}{2} \log _{10} \frac{\left[\mathrm{H}^{+}\right]^{2}}{(0.1)} \\
& =0.760+\frac{0.059}{2} \log _{10} \frac{\left(10^{-7}\right)^{2}}{0.1} \mathrm{E}_{\text {cell }}=0.3765 \mathrm{~V}
\end{aligned}
$$

Example 6: For the galvanic cell:
$\mathrm{Ag} \left\lvert\, \begin{gathered}\left.\mathrm{AgCl}(\mathrm{s}) \mathrm{KCl}| | \begin{array}{cc}\mathrm{KBr} & \mathrm{AgBr}(\mathrm{s}) \\ 0.2 \mathrm{M} & \mathrm{Ag} \\ 0.001 \mathrm{M}\end{array} \right\rvert\,\end{gathered}\right.$
Calculate the e.m.f generated and assign correct polarity to each electrode for a spontaneous process after taking an account of cell reaction at $25^{\circ} \mathrm{C}$.
[Give, $K_{\text {sp }_{\mathrm{AgCl}}}=2.8 \times 10^{-10}, \mathrm{~K}_{\mathrm{sp}_{\mathrm{AgBr}}}=3.3 \times 10^{-13}$ ]
Sol: Write down the half-cell equation for both the cell. Here we are provided with solubility product of the two solution. From the value of solubility product first find out the concentration of silver ion in each solution. Now substitute this value in Nernst equation and calculate the e.m.f.

$$
\begin{align*}
& \mathrm{E}_{\mathrm{cell}=\mathrm{E}_{\mathrm{OP}_{\mathrm{Ag}}}+\mathrm{E}_{\mathrm{RP}_{\mathrm{Ag}}} ; \text { L.H.S. R.H.S. }}=\mathrm{E}_{\mathrm{OP}_{\mathrm{Ag}}^{\circ}}-\frac{0.059}{1} \log \left[\mathrm{Ag}^{+}\right]_{\text {L.H.S. }} \\
& +\mathrm{E}_{\mathrm{RP}_{\mathrm{Ag}}}+\frac{0.059}{1} \log \left[\mathrm{Ag}^{+}\right]_{\text {R.H.S. }} \\
& \mathrm{E}_{\text {cell }}=\frac{0.059}{1} \log \frac{\left[\mathrm{Ag}^{+}\right]_{\text {R.H.S. }}}{\left[\mathrm{Ag}^{+}\right]_{\text {L.H.S. }}}
\end{align*}
$$

For L.H.S. $\mathrm{K}_{\mathrm{sp}}$ of $\mathrm{AgCl}=2.8 \times 10^{-10}$
or $\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]=2.8 \times 10^{-10}$
or $\left[\mathrm{Ag}^{+}\right]=\frac{2.8 \times 10^{-10}}{\left[\mathrm{Cl}^{-}\right]}=\frac{2.8 \times 10^{-10}}{0.2}=1.4 \times 10^{-9} \mathrm{M}$
For R.H.S. $K_{\text {sp }}$ of $\mathrm{AgBr}=3.3 \times 10^{-13}$
or $\quad\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Br}^{-}\right]=3.3 \times 10^{-13}$
or $\left[\mathrm{Ag}^{+}\right]=\left(3.3 \times 10^{-13}\right) / 0.001=3.3 \times 10^{-10} \mathrm{M}$
$\therefore$ By Eq. (i),

$$
\mathrm{E}_{\text {cell }}=\frac{0.059}{1} \log \frac{3.3 \times 10^{-10}}{1.4 \times 10^{-9}}=-0.037 \mathrm{~V}
$$

Thus, to get cell reaction (i.e. $\mathrm{E}_{\text {cell }} \mathrm{E}_{\text {cell }}=+\mathrm{ve}$ ) polarity of cell

Example 7: $\mathrm{E}_{\text {cell }}^{\circ}$ values for
$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+}+2 \mathrm{e}^{-}$and $\mathrm{Fe} \rightarrow \mathrm{Fe}^{3+}+3 \mathrm{e}^{-}$are 0.440 and 0.036 V respectively:
(a) Design and point out the number of cells showing the overall reaction $\mathrm{Fe}+2 \mathrm{Fe}^{3+} \rightarrow 3 \mathrm{Fe}^{2+}$
(b) Also calculate $E_{\text {cell }}^{\circ}$ and $\Delta G^{\circ}$ values for each cell. Also comment on the result.

Sol: Standard free energy can be calculated using the equation
$\Delta G^{\circ}=-n E^{\circ} F$
$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+}+2 \mathrm{e}^{-} ;-\Delta \mathrm{G}_{1}^{\circ}=+0.440 \times 2 \times \mathrm{F}$
$\mathrm{Fe}^{3+}+3 \mathrm{e}^{-} \rightarrow \mathrm{Fe} ;-\Delta \mathrm{G}_{2}^{\circ}=-0.036 \times 3 \times \mathrm{F}$
$\therefore \mathrm{Fe}^{3+}+\mathrm{e}^{-} \rightarrow \mathrm{Fe}^{2+} ;-\Delta \mathrm{G}_{3}^{\circ}=-\left(\Delta \mathrm{G}_{2}^{\circ}+\Delta \mathrm{G}_{1}^{\circ}\right)$
$-n E^{\circ} F=[2 \times 0.440-3 \times 0.036] \times F(n=1)$
$\mathrm{E}^{\circ}=+0.772 \mathrm{~V}$
Cell no. I: $\mathrm{Fe}\left|\mathrm{Fe}^{+2}\right|\left|\mathrm{Fe}^{3+}\right| \mathrm{Fe}$

$$
3 \mathrm{Fe} \rightarrow 3 \mathrm{Fe}^{2+}+6 \mathrm{e}^{-}
$$

$$
2 \mathrm{Fe}^{3+}+6 \mathrm{e}^{-} \rightarrow 2 \mathrm{Fe}
$$

Redox $\quad \mathrm{Fe}+2 \mathrm{Fe}^{3+} \rightarrow 3 \mathrm{Fe}^{2+}$

$$
\mathrm{E}_{\mathrm{cell}}^{\circ}=\mathrm{E}_{\mathrm{Fe}^{\circ} \mathrm{Fe}}{ }^{2+}+\mathrm{E}_{\mathrm{Fe}^{3+}}^{\circ}{ }_{\mathrm{Fe}}=0.440-0.036=0.404 \mathrm{~V}
$$

Also, $\Delta G^{\circ}=-6 \times 0.404 \times F=-2.424 \mathrm{~F}$
Cell no. II: $\mathrm{Fe}\left|\mathrm{Fe}^{2+}\right|\left|\mathrm{Fe}^{3+}, \mathrm{Fe}^{2+}\right| \mathrm{Pt}$

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

$$
2 \mathrm{Fe}^{3+}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Fe}^{2+}
$$

Redox $\quad \mathrm{Fe}+2 \mathrm{Fe}^{3+} \rightarrow 3 \mathrm{Fe}^{2+}$

$$
\mathrm{E}_{\mathrm{cell}}^{\circ}=\mathrm{E}_{\mathrm{Oe} / \mathrm{Fe}^{2+}}^{\circ}+\mathrm{ERP}_{\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}}^{\circ}
$$

Example 8: Oxidizing power of $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}$ is more in acidic medium than in alkaline medium.

Sol: $\mathrm{E}_{\mathrm{RP}}^{\circ}$ in acidic medium is more than $\mathrm{E}_{\mathrm{RP}}^{\circ}$ in alkaline medium.

Acid: $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+14 \mathrm{H}^{+}+6 \mathrm{e}^{-} \rightarrow 2 \mathrm{Cr}^{3+}+7 \mathrm{H}_{2} \mathrm{O}$;

$$
\mathrm{E}_{\mathrm{RP}}^{\circ}=+1.33 \mathrm{~V}
$$

Alkali: $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+\mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{CrO}_{4}^{2-}+2 \mathrm{H}^{+}$
$\mathrm{CrO}_{4}^{2-}+4 \mathrm{H}_{2} \mathrm{O}+3 \mathrm{e}^{-} \rightarrow \mathrm{Cr}(\mathrm{OH})_{3}+5 \mathrm{OH}^{-} ; \mathrm{E}_{\mathrm{RP}}^{\circ}=-0.13 \mathrm{~V}$

Example 9: Color of KI solution containing starch turns blue when $\mathrm{Cl}_{2}$ water is added. Explain.

Sol: Chlorine placed below iodine in electrochemical series having lesser $\mathrm{E}_{\mathrm{OP}}^{\circ}$ than iodine and thus, shows reduction whereas $I^{-}$undergoes oxidation. The $I_{2}$ so formed gets absorbed in starch to give blue color.

$$
2 \mathrm{I}^{-} \rightarrow \mathrm{I}_{2}+2 \mathrm{e}^{-}
$$

$\mathrm{Cl}_{2}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Cl}^{-}$
$\mathrm{Cl}_{2}+2 \mathrm{I}^{-} \rightarrow \mathrm{I}_{2}+2 \mathrm{Cl}^{-}$

Example 10: Calculate the e.m.f of the cell.
$\mathrm{Mg}(\mathrm{s})\left|\mathrm{Mg}^{2+}(0.2 \mathrm{M})\right|\left|\mathrm{Ag}^{+}\left(1 \times 10^{-3}\right)\right| \mathrm{Ag}$

$$
\mathrm{E}_{\mathrm{Ag}^{+} \mid \mathrm{Ag}}^{\circ}=+0.8 \text { volt, } \mathrm{E}_{\mathrm{Mg}^{2+} / \mathrm{Mg}}^{\circ}=-2.37 \text { volt }
$$

What will be the effect on e.m.f if concentration of $\mathrm{Mg}^{2+}$ ion is decreased to 0.1 M ?

Sol: First calculate the standard potential for reaction which is calculated as $E_{\text {cell }}^{\circ}=E_{\text {oxidation }}^{\circ}-E_{\text {reduction }}^{\circ}$

After calculating $E_{\text {cell }}^{\circ}$ e.m.f of the cell can be easily calculated using following equation
$E_{\text {cell }}=E_{\text {cell }}^{\circ}-\frac{0.0591}{n} \log \frac{[\text { Products }]}{[\text { Reactants }]}$
$\mathrm{E}_{\text {Cell }}^{\circ}=\mathrm{E}_{\text {Cathode }}^{\circ}-\mathrm{E}_{\text {Anode }}^{\circ}=0.80-(-2.37)=3.17$ volt
Cell reaction, $\mathrm{Mg}+2 \mathrm{Ag}^{+} \rightarrow 2 \mathrm{Ag}+\mathrm{Mg}^{2+}$
$E_{\text {cell }}=E_{\text {cell }}^{\circ}-\frac{0.0591}{n} \log \frac{\mathrm{Mg}^{2+}}{\left[\mathrm{Ag}^{+}\right]^{2}}$
$=3.17-\frac{0.0591}{2} \log \frac{0.2}{\left[1 \times 10^{-3}\right]^{2}}$
$=3.17-0.1566=3.0134$ volt
When $\mathrm{Mg}^{2+}=0.1 \mathrm{M}$
$E_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\circ}-\frac{0.0591}{2} \log \frac{0.1}{\left(1 \times 10^{-3}\right)^{2}}$
$=(3.17-0.1477)$ volt $=3.0223$ volt

## JEE Main/Boards

## Exercise 1

Q. 1 Depict the galvanic cell in which the reaction $\mathrm{Zn}(\mathrm{s})$ $+2 \mathrm{Ag}^{+}(\mathrm{aq}) \rightarrow \mathrm{Zn}^{2+}(\mathrm{aq})+2 \mathrm{Ag}(\mathrm{s})$ takes place. Further show:
(i) Which of the electrode is negatively charged?
(ii) Individual reaction at each electrode.
Q. 2 Electrolytic conductivity of 0.20 mole $^{-1}$ solution of KCl at 298 K is $2.48 \times 10^{-2} \mathrm{ohm}^{-1} \mathrm{~cm}^{-1}$. Calculate its molar conductivity.
Q. 3 Write the Nernst equation and e.m.f of the following cells at 298K:
(i) $\mathrm{Mg}(\mathrm{s})\left|\mathrm{Mg}^{2+}(0.001 \mathrm{M})\right|\left|\mathrm{Cu}^{2+}(0.0001 \mathrm{M})\right| \mathrm{Cu}(\mathrm{s})$
(ii) $\mathrm{Fe}(\mathrm{s})\left|\mathrm{Fe}^{2+}(0.001 \mathrm{M})\right|\left|\mathrm{H}^{+}(1 \mathrm{M})\right| \mathrm{H}_{2}(\mathrm{~g})(1$ bar $) \mid \mathrm{Pt}(\mathrm{s})$
(iii) $\mathrm{Sn}(\mathrm{s})\left|\mathrm{Sn}^{2+}(0.050 \mathrm{M})\right|\left|\mathrm{H}^{+}(0.020 \mathrm{M})\right| \mathrm{H}_{2}(\mathrm{~g})(1$ bar) $\mid \operatorname{Pt}(\mathrm{s})$
(iv) $\mathrm{Pt}(\mathrm{s})\left|\mathrm{Br}_{2}(\mathrm{l})\right| \mathrm{Br}-(0.010 \quad \mathrm{M}) \quad \| \quad \mathrm{H}^{+}(0.030 \quad \mathrm{M}) \mid \mathrm{H}_{2}(\mathrm{~g})$ (1 bar) $\mid \operatorname{Pt}(\mathrm{s})$
Q. 4 In the button cells widely used in watches and other devices the following reaction takes place:
$\mathrm{Zn}(\mathrm{s})+\mathrm{Ag}_{2} \mathrm{O}(\mathrm{s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{Zn}^{2+}(\mathrm{aq})+2 \mathrm{Ag}(\mathrm{s})+2 \mathrm{OH}^{-}(\mathrm{aq})$ Determine $\Delta r G^{\prime}$ and $E^{\prime}$ for the reaction.
Q. 5 The conductivity of 0.20 M solution of KCl at 298 K is $0.0248 \mathrm{~S} \mathrm{~cm}^{-1}$. Calculate it molar conductivity.
Q. 6 How much electricity in terms of faraday is required to produce
(i) 20.0 g of Ca from molten $\mathrm{CaCl}_{2}$ ?
(ii) 40.0 g of Al from molten $\mathrm{Al}_{2} \mathrm{O}_{3}$ ?
Q. 7 How much electricity is required in coulomb for the oxidation of:
(i) 1 mole of $\mathrm{H}_{2} \mathrm{O}$ to $\mathrm{O}_{2}$ ?
(ii) 1 mole of FeO to $\mathrm{Fe}_{2} \mathrm{O}_{3}$ ?
Q. 8 The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is $1500 \Omega$. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is $0.146 \times 10^{-3} \mathrm{~S} \mathrm{~cm}^{-1}$ ?
Q. 9 Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \mathrm{~S} \mathrm{~cm}^{-1}$. Calculate its molar conductivity. If $\Lambda_{\infty}^{0}$ for acetic acid is $390.5 \mathrm{~S} \mathrm{~cm}^{2}$ mole $^{-1}$, what is its dissociation constant?
Q. 10 A solution of $\mathrm{Ni}\left(\mathrm{NO}_{3}\right)_{2}$ is electrolyzed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni deposited at the cathode?
Q. 11 The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

## Concentration M

$\begin{array}{lllll}0.001 & 0.010 & 0.020 & 0.050 & 0.100\end{array}$
$10^{2} \times \mathrm{k} / \mathrm{S} \mathrm{m}^{-1}$
$\begin{array}{lllll}1.237 & 11.85 & 23.15 & 55.53 & 106.74\end{array}$
Calculate $\Lambda_{\infty}$ for all concentrations and draw a plot between $\Lambda_{\infty}^{\infty}$ and $S$. Find the values of $\Lambda_{\infty}^{0}$
Q. 12 Three electrolytic cells $A, B, C$ containing solution of $\mathrm{ZnSO}_{4^{\prime}} \mathrm{AgNO}_{3}$ and $\mathrm{CuSO}_{4^{\prime}}$ respectively are connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?
Q. 13 Using the standard electrode potentials of electrochemical series, predict if the reaction between the following is feasible:
(i) $\mathrm{Fe}^{3+}$ (aq) and $\mathrm{I}^{-}$(aq)
(ii) $\mathrm{Ag}^{+}(\mathrm{aq})$ and $\mathrm{Cu}(\mathrm{s})$
(iii) $\mathrm{Fe}^{3+}(\mathrm{aq})$ an $\mathrm{Br}^{-}(\mathrm{aq})$
(iv) $\mathrm{Ag}(\mathrm{s})$ and $\mathrm{Fe}^{3+}(\mathrm{aq})$
(iv) $\mathrm{Br}_{2}(\mathrm{aq})$ and $\mathrm{Fe}^{2+}(\mathrm{aq})$.
Q. 14 The standard electrode potentials of $\mathrm{Cu}^{2+} \mid \mathrm{Cu}^{+}$an $\mathrm{Cu}^{+} \mid \mathrm{Cu}$ electrodes are +0.18 V and +0.50 V , respectively. Calculate the standard potential of $\mathrm{Cu}^{2+} \mid \mathrm{Cu}$ electrode.
Q. 15 Arrange $\mathrm{Zn}, \mathrm{Pb}$ and Al in the increasing order of their reducing power under standard conditions.

Given: $\mathrm{E}_{\mathrm{Zn}^{2+} \mid \mathrm{Zn}}^{\circ}=-0.76 \mathrm{~V}_{,}=-0.13 \mathrm{~V}_{\mathrm{V}^{-}}^{\mathrm{E}_{\left.\mathrm{Al}^{2+} \mid \mathrm{Al}\right]}^{\circ}}=-1.66 \mathrm{~V}$
Q. 16 The standard electrode potentials of $\mathrm{Ag}^{+} \mid \mathrm{Ag}$, $\mathrm{Cl}_{2} \mid \mathrm{Cl}^{-}$and $\mathrm{O}_{3} \mid \mathrm{O}_{2}$ electrodes are $+0.80 \mathrm{~V},+1.36 \mathrm{~V}$ and +2.07 V , respectively. Using these information, answer the following:
(i) Which of the following is strongest oxidizing agent:
$\mathrm{Ag}^{+}, \mathrm{Cl}_{2}$, and $\mathrm{O}_{3}$ ?
(ii) Which of the following is the strongest oxidizing agent: $\mathrm{Ag}, \mathrm{Ag}^{+}, \mathrm{O}_{3^{\prime}}$ and $\mathrm{O}_{2}$ ?
(iii) Which of the following is the strongest reducing agent: $\mathrm{Ag}_{\mathrm{g}} \mathrm{Cl}^{-}$, and $\mathrm{O}_{2}$
(iv) Which of the following is the strongest reducing agent: $\mathrm{Ag}, \mathrm{Ag}^{+}, \mathrm{O}_{3^{\prime}}$ and $\mathrm{O}_{2}$
Q. 17 The following reactions represent the reduction of $\mathrm{IO}^{-}$ion into $\mathrm{l}^{-i o n}$ in acidic and basic medium.
$\mathrm{IO}_{3}^{-}+6 \mathrm{H}^{+}+6 \mathrm{e}^{-} \rightarrow \mathrm{I}^{-}+3 \mathrm{H}_{2} \mathrm{O} ; \quad \mathrm{E}^{\circ}=+0.907 \mathrm{~V}$
$\mathrm{IO}_{3}^{-}+3 \mathrm{H}_{2} \mathrm{O}+6 \mathrm{e}^{-} \rightarrow \mathrm{I}^{-}+6 \mathrm{OH}^{-} ; \quad \mathrm{E}^{\circ}=+0.260 \mathrm{~V}$
[Acid Medium]
Q. 18 Can $\mathrm{Fe}^{3+}$ oxidize Br to Br under standard conditions?

Given: $\mathrm{E}_{\mathrm{Fe}^{3+}{ }_{\mid \mathrm{Fe}^{2+}}^{2+}}=+0.77 \mathrm{~V}_{1} \mathrm{E}_{\mathrm{Br}_{2} \mid \mathrm{Br}^{-}}^{\circ}=+1.09 \mathrm{~V}$
Q. 19 Calculate the electrode potential of the following electrodes at $25^{\circ} \mathrm{C}$ :
(i) $\mathrm{Cu}^{2+}(0.001 \mathrm{M}) \mid \mathrm{Cu}$; $\mathrm{E}_{\mathrm{Cu}^{3+} \mid \mathrm{Cu}}=+0.34 \mathrm{~V}$
(ii) $\mathrm{Zn} \mid \mathrm{Zn}^{2+}(0.02 \mathrm{M}) ; \mathrm{E}_{\mathrm{Zn}^{2+} \mid \mathrm{Zn}}=-0.76 \mathrm{~V}$
(iii) AgCl (stand. sol) $\mid \mathrm{Ag} ; \mathrm{E}_{\mathrm{Ag}^{+} \mid \mathrm{Ag}}=+0.80 \mathrm{~V}, \mathrm{~K}_{\mathrm{sp}}$ of $\mathrm{AgCl}=2 \times 10^{-10}$.
(iv) $\mathrm{Pt}\left|\mathrm{Cl}_{2}(0.5 \mathrm{~atm})\right| \mathrm{Cl}^{-}(0.02 \mathrm{M}) ; \mathrm{E}_{\mathrm{Cl}_{2} \mid \mathrm{Cl}^{-}}=1.36 \mathrm{~V}$
(v) $\mathrm{HCl}(\mathrm{pH}=4.4)\left|\mathrm{H}_{2}(2 \mathrm{~atm})\right| \mathrm{Pt}$
Q. 20 Calculate the reduction potential at $25^{\circ} \mathrm{C}$ for $\mathrm{Fe}^{3+} /$ $\mathrm{Fe}^{2+}$ electrode if the concentration of $\mathrm{Fe}^{2+}$ ion is five times that of $\mathrm{Fe}^{3+}$ ion.
$\mathrm{E}_{\mathrm{Fe}^{3+} \mid \mathrm{Fe}^{2+}}^{\circ}=0.77$ volt.
Q. 21 Calculate electrode potential for the half-cell $\mathrm{Pt}\left|\mathrm{H}_{2}(1 \mathrm{~atm})\right| 0.357 \mathrm{M}-\mathrm{CH}_{3} \mathrm{COOH}$. K a for $\mathrm{CH}_{3} \mathrm{COOH}=$ $1.74 \times 10^{-5}$.
Q. 22 The standard reduction potential for $\mathrm{Cu}^{2+} \mid \mathrm{Cu}$ is +
0.34 V . Calculate the reduction potential at $\mathrm{pH}=13$ for the above couple. $\mathrm{K}_{\mathrm{sp}}$ of $\mathrm{Cu}(\mathrm{OH})_{2}$ is $1.0 \times 10^{-10}$.
Q. 23 Calculate
(i) $\mathrm{E}_{\mathrm{Cl}^{+} \mid \mathrm{AgCl\mid Ag}}^{\circ} ; \mathrm{E}_{\mathrm{Ag}^{+} \mid \mathrm{Ag}}^{\circ}=0.80 \mathrm{~V}, \mathrm{~K}_{\mathrm{sp}}$ of $\mathrm{AgCl}=2 \times 10^{-10}$
(ii) $\mathrm{E}_{\mathrm{Cl}^{-}(0.004 \mathrm{M}) \mathrm{AgCl\mid Ag}}^{\circ} ; \mathrm{E}_{\mathrm{Ag}^{+} \mid \mathrm{Ag}}^{\circ}=+0.80 \mathrm{~V}$,
$\mathrm{K}_{\mathrm{sp}}$ of $\mathrm{AgCl}=2 \times 10^{-10}$
Q. 24 Calculate the e.m.f of the cell in which the following reaction takes place:
$\mathrm{Ni}(\mathrm{s})+2 \mathrm{Ag}^{+}(0.002 \mathrm{M}) \rightarrow \mathrm{Ni}^{2+}(0.160 \mathrm{M})+2 \mathrm{Ag}(\mathrm{s})$
Given that $\mathrm{E}_{\text {cell }}=1.05 \mathrm{~V}$
Q. 25 The molar conductivity of 0.025 mole methanoic acid is $46.1 \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mole}^{-1}$. Calculate its degree of dissociation and dissociation constant.
Given $\Lambda^{0}\left(\mathrm{H}^{+}\right)=349.6 \mathrm{~S} \mathrm{~cm}{ }^{2} \mathrm{~mol} / \mathrm{L}$ and
$\lambda^{\circ}\left(\mathrm{HCOO}^{-}\right)=54.6 \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mol} / \mathrm{L}$.
Q. 26 Suggest a list of metals that are extracted electrolytically.
Q. 27 Represent the cell in which following reaction takes place:
$\mathrm{Mg}(\mathrm{s})+2 \mathrm{Ag}^{+}(0.0001 \mathrm{M}) \rightarrow \mathrm{Mg}^{2+}(0.130 \mathrm{M})+2 \mathrm{Ag}(\mathrm{s})$ calculate its $\mathrm{E}_{\text {cell }}$ if $\mathrm{E}_{\text {cell }}^{\circ}=3.17 \mathrm{~V}$.
Q. 28 Calculate the reduction potential of the following electrodes:
(a) $\mathrm{Pt}_{2} \mathrm{H}_{2}(4 \mathrm{~atm}) \mid \mathrm{H}_{2} \mathrm{SO}_{4}(0.01 \mathrm{M})$
(b) $\mathrm{Pt}_{2} \mathrm{H}_{2}(1 \mathrm{~atm}) \mid \mathrm{HCl}(0.2 \mathrm{M})$
(c) Calculate the potential of hydrogen electrode in contact with a solution whose
(i) $\mathrm{pH}=5$ (ii) $\mathrm{pOH}=4$
Q. 29 Calculate the equivalent conductivity of $1 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}$ solution, if its conductivity is $26 \times 10^{-2} \mathrm{ohm}^{-1} \mathrm{~cm}^{-1}$.

## Exercise 2

## Single Correct Choice Type

Q. 1 One gm. metal $\mathrm{M}^{+2}$ was discharged by the passage of $1.81 \times 10^{22}$ electrons. What is the atomic weight of metal?
(A) 33.35
(B) 133.4
(C) 66.7
(D) 55
Q. 2 One mole of electron passes through each of the solution of $\mathrm{AgNO}_{3}, \mathrm{CuSO}_{4}$ and $\mathrm{AlCl}_{3}$ when $\mathrm{Ag}, \mathrm{Cu}$ and Al are deposited at cathode. The molar ratio of $\mathrm{Ag}, \mathrm{Cu}$ and Al deposited are:
(A) 1:1:1
(B) 6: 3: 2
(C) $6: 3: 1$
(D) 1:3:6
Q. 3 Salts of $A$ (atomic weight $=7$ ), $B$ (atomic weight $=$ 27) and $C$ (atomic weight $=48$ ) were electrolyzed under identical conditions using the same quantity of electricity. It was found that when 2.1 g of A was deposited, the weights of $B$ and $C$ deposited were 2.7 and 7.2 g . The valencies of $A, B$ and $C$ respectively are:
(A) 3, 1 and 2
(B) 1, 3 and 2
(C) 3, 1 and 3
(D) 2, 3 and 2
Q. 4 The density of Cu is $8.94 \mathrm{~g} \mathrm{~cm}^{-3}$. The quantity of electricity needed to plate an area $10 \mathrm{~cm} \times 10 \mathrm{~cm}$ to a thickness of $10^{-2} \mathrm{~cm}$ using $\mathrm{CuSO}_{4}$ solution would be
(A) 13586 C
(B) 27172 C
(C) 40758
(D) 20348 C
Q. 5 During electrolysis of an aqueous solution of sodium sulphate, 2.4 L of oxygen at STP was liberated at anode. The volume of hydrogen at STP, liberated at cathode would be
(A) 1.2 L
(B) 2.4 L
(C) 2.6 L
(D) 4.8 L
Q. 6 When an aqueous solution of lithium chloride is electrolyzed using graphite electrodes
(A) $\mathrm{Cl}_{2}$ is liberated at the anode
(B) Li is deposited at the cathode
(C) As the current flows, pH of the solution around the cathode remains constant
(D) As the current flows, pH of the solution around the cathode decreases.
Q. 7 A standard hydrogen electrons has zero electrode potential because
(A) Hydrogen is easier to oxidize
(B) This electrode potential is assumed to be zero
(C) Hydrogen atom has only one electron
(D) Hydrogen is the lightest element.
Q. 8 If the pressure of $\mathrm{H}_{2}$ gas is increased from 1 atm to 100 atm keeping $\mathrm{H}^{+}$concentration constant at 1 M , the change in reduction potential of hydrogen half-cell at $25^{\circ} \mathrm{C}$ will be
(A) 0.059 V
(B) 0.59 V
(C) 0.0295 V
(D) 0.118 V
Q. 9 The equilibrium constant for the reaction $\operatorname{Sr}(\mathrm{s})+$ $\mathrm{Mg}^{+2}(\mathrm{aq}) \rightarrow \mathrm{Sr}^{+2}(\mathrm{aq})+\mathrm{Mg}(\mathrm{s})$ is $2.69 \times 10^{12}$ at $25^{\circ} \mathrm{C}$

The $\mathrm{E}^{\circ}$ for a cell made up of the $\mathrm{Sr} / \mathrm{Sr}^{+2}$ and $\mathrm{Mg}^{+2} / \mathrm{Mg}$ half-cells
(A) 0.3667 V
(B) 0.7346 V
(C) 0.1836 V
(D) 0.1349 V
Q. 10 A silver wire dipped in 0.1 M HCl solution saturated with AgCl develop a potential of -0.25 V . If $\mathrm{E}_{\mathrm{Ag} / \mathrm{Ag}^{+}}^{\circ}=-0.799 \mathrm{~V}$, the $\mathrm{K}_{\mathrm{sp}}$ of AgCl in pure water will be:
(A) $2.95 \times 10^{-11}$
(B) $5.1 \times 10^{-11}$
(C) $3.95 \times 10^{-11}$
(D) $1.95 \times 10^{-11}$
Q. 11 During electrolysis of an aqueous solution of $\mathrm{CuSO}_{4}$ using copper electrodes, if 2.5 g of Cu is deposited at cathode, then at anode
(A) 890 ml of $\mathrm{Cl}_{2}$ at STP is liberated
(B) 445 ml of $\mathrm{O}_{2}$ at STP is liberated
(C) 2.5 g of copper is deposited
(D) A decrease of 2.5 g of mass takes place
Q. 12 The cost at 5 paise / KWH of operating an electric motor for 8 hours which takes 15 amp at 110 V is
(A) Rs 66
(B) 66 paise
(C) 37 paise
(D) Rs. 6.60
Q. 13 The resistance of 0.5 M solution of an electrolyte in a cell was found to be $50 \Omega$. If the electrodes in the cell are 2.2 cm apart and have an area of $4.4 \mathrm{~cm}^{2}$ then the molar conductivity (in $\mathrm{S} \mathrm{m}^{2}$ mole $^{-1}$ ) of the solution is
(A) 0.2
(B) 0.02
(C) 0.002
(D) None of these
Q. 14 Equivalent conductance of 0.1 M HA (weak acid) solution is $10 \mathrm{~S} \mathrm{~cm}^{2}$ equivalent ${ }^{-1}$ and that at infinite dilution is $200 \mathrm{~S} \mathrm{~cm}^{2}$ equivalent ${ }^{-1}$ Hence pH of HA solution is
(A) 1.3
(B) 1.7
(C) 2.3
(D) 3.7
Q. 15 If $x$ is specific resistance of the electrolyte solution and $y$ is the molarity of the solution, then $\Lambda_{m}$ is given by
(A) $\frac{1000 x}{y}$
(B) $1000 \frac{\mathrm{y}}{\mathrm{x}}$
(C) $\frac{1000}{x y}$
(D) $\frac{x y}{1000}$
Q. 16 The dissociation constant of $n$-butyric acid is $1.6 \times 10^{-5}$ and the molar conductivity at infinite dilution is $380 \times 10^{-4} \mathrm{~S} \mathrm{~m}^{2} \mathrm{~mol}^{-1}$. The specific conductance of the 0.01 M acid solution is
(A) $1.52 \times 10 \mathrm{~S} \mathrm{~m}^{-1}$
(B) $1.52 \times 10^{-2} \mathrm{~S} \mathrm{~m}^{-1}$
(C) $1.52 \times 10^{-3} \mathrm{~S} \mathrm{~m}^{-1}$
(D) None of these
Q. 17 Consider the reaction of extraction of gold from its ore
$\mathrm{Au}+2 \mathrm{CN}^{-}$(aq.) $+\frac{1}{4} \mathrm{O}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{Au}(\mathrm{CN})_{2}^{-}+\mathrm{OH}^{-}$
Use the following data to calculate $\Delta G^{\circ}$ for the reaction, $\mathrm{K}_{\mathrm{f}}\left\{\mathrm{Au}(\mathrm{CN})_{2}\right\}=\mathrm{X}$
$\mathrm{O}_{2}+2 \mathrm{H}_{2} \mathrm{O}+4 \mathrm{e}^{-} \rightarrow 4 \mathrm{OH}^{-} ; \mathrm{E}^{\circ}=+0.41$ volt
$\mathrm{Au}^{3+}+3 \mathrm{e}^{-} \rightarrow \mathrm{Au} ; \quad \mathrm{E}^{\circ}=+1.5$ volt
$\mathrm{Au}^{3+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Au}^{+} ; \quad \mathrm{E}^{\circ}=+1.4$ volt
(A) $-\mathrm{RT} \ln \mathrm{X}+1.29 \mathrm{~F}$
(B) $-R T \ln X-2.11 \mathrm{~F}$
(C) $-R \operatorname{Tln} \frac{1}{X}+2.11 \mathrm{~F}$
(D) $-R T \ln X-1.29 \mathrm{~F}$
Q. 18 Consider the following Galvanic cell


By what value the voltage change when concentration of ions in anodic and cathodic compartments both increases by factor of 10 at 298 K
(A) 0.0591
(B) -0.0591
(C) -0.1182
(D) 0
Q. 19 For the cell
$\mathrm{Pt}\left|\left|\mathrm{H}_{2}(0.4 \mathrm{~atm})\right| \mathrm{H}^{+}(\mathrm{pH}=1)\right|\left|\mathrm{H}^{+}(\mathrm{pH}=2)\right| \mathrm{H}_{2}(0.1 \mathrm{~atm}) \mid \mathrm{Pt}$ The measured potential at $25^{\circ} \mathrm{C}$ is
(A) -0.1 V
(B) -0.5
(C) -0.041
(D) None of these
Q. 20 For the fuel cell reaction:
$2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) ; \Delta_{\mathrm{f}} \mathrm{H}_{298}^{\circ}\left(\mathrm{H}_{2} \mathrm{O},(\mathrm{I})=-285.5 \mathrm{KJ} / \mathrm{mole}\right.$ What is $\Delta \mathrm{S}_{298}^{\circ}$ for the given fuel cell reaction?
Given $\mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{+}(\mathrm{aq})+4 \mathrm{e}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}$ (I) $\mathrm{E}^{\circ}=1.23 \mathrm{~V}$
(A) $-0.322 \mathrm{~J} / \mathrm{K}$
(B) $-0.635 \mathrm{~kJ} / \mathrm{K}$
(C) $3.51 \mathrm{~kJ} / \mathrm{K}$
(D) $-0.322 \mathrm{~kJ} / \mathrm{K}$
Q. 21 The standard reduction potentials of $\mathrm{Cu}^{2+} / \mathrm{Cu}$ and $\mathrm{Cu}^{2+} / \mathrm{Cu}^{+}$are 0.337 and 0.153 V respectively. The standard electrode potential of $\mathrm{Cu}^{+} / \mathrm{Cu}$ half-cell is:
(A) 0.184 V
(B) 0.827 V
(C) 0.521 V
(D) 0.490 V

## Previous Years' Questions

Q. 1 When the sample of copper with zinc impurity is to be purified by electrolysis, the appropriate electrodes are
(2002)

## Cathode

$\begin{array}{ll}\text { (a) Pure zinc } & \text { Pure copper } \\ \text { (b) Impure sample } & \text { Pure copper } \\ \text { (c) Impure zinc } & \text { Impure sample } \\ \text { (d) Pure copper } & \text { Impure sample }\end{array}$

## Anode

Q. 2 In the electrolytic cell, flow of electrons is from
(2003)
(A) Cathode to anode in solution
(B) Cathode to anode through external supply
(C) Cathode to anode through internal supply
(D) Anode to cathode through internal supply
Q. 3 During the electrolysis of a solution of $\mathrm{AgNO}_{3^{\prime}} 9650$ coulombs of charge pass through the electroplating both, the mass of silver deposited in the cathode will be
(2003)
(A) 1.08 g
(B) 10.8 g
(C) 21.6 g
(D) 108 g
Q. 4 During the process of electrolytic refining of copper, some metals present as impurity settle as 'anode mud.' These are
(2005)
(A) Sn and Ag
(B) Pb and Zn
(C) Ag and Au
(D) Fe and Ni
Q. 5 Conductivity (unit Siemen's) is directly proportional to area of the vessel and the concentration of the solution in it and is inversely proportional to the length of the vessel then the unit of the constant of proportionality is
(2002)
(A) $\mathrm{Sm} \mathrm{mole}^{-1}$
(B) $\mathrm{S} \mathrm{m}^{2} \mathrm{~mole}^{-1}$
(C) $\mathrm{S}^{-2} \mathrm{~m}^{2}$ mole
(D) $\mathrm{S}^{2} \mathrm{~m}^{2} \mathrm{~mole}^{-2}$
Q. 6 The highest electrical conductivity of the following aqueous solution is of
(2005)
(A) 0.1 M acetic acid
(B) 0.1 M chloroacetic acid
(C) 0.1 M fluoroacetic acid
(D) 0.1 M difluoroacetic acid
Q. 7 The equivalent conductance's of two strong electrolytes at infinite dilution in $\mathrm{H}_{2} \mathrm{O}$ (where ions move freely through a solution) at $25^{\circ} \mathrm{C}$ are given below: A t $25^{\circ} \mathrm{C}$ are given below:
(2007)
$\Lambda_{\mathrm{CH}_{3} \mathrm{COONa}}^{\circ}=91.0 \mathrm{~S} \mathrm{~cm}^{2} /$ equivalent
$\Lambda_{\mathrm{HCl}}^{\circ}=426.2 \mathrm{~S} \mathrm{~cm}^{2} /$ equivalent
What additional information/quantity one needs to calculate $\Lambda^{\circ}$ of an aqueous solution of acetic acid
(A) $\Lambda^{\circ}$ of NaCl
(B) $\Lambda^{\circ}$ of $\mathrm{CH}_{3} \mathrm{COOK}$
(C) The limiting equivalent conductance of $\mathrm{H}^{+}\left(\Lambda^{\circ} \mathrm{H}^{+}\right)$
(D) $\Lambda^{\circ}$ of chloroacetic acid $\left(\mathrm{Cl}_{2} / \mathrm{CH}_{2} \mathrm{COOH}\right)$
Q. 8 The molar conductivities $\lambda_{\mathrm{NaOAc}}^{\circ}$ and $\lambda_{\mathrm{HCl}}^{\circ}$ at infinity dilution in water at $25^{\circ} \mathrm{C}$ are 91.0 and $426.2 \mathrm{~S} \mathrm{~cm} /$ /mole respectively. To calculate $\lambda_{\text {HOAc }}^{\circ}$, the additional value required is
(2006)
(A) $\lambda_{\mathrm{H}_{2} \mathrm{O}}^{\circ}$
(B) $\lambda_{\mathrm{KCl}}^{\circ}$
(C) $\lambda_{\mathrm{NaOH}}^{\circ}$
(D) $\lambda_{\text {NaCl }}^{\circ}$
Q. 9 Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is $100 \Omega$. The conductivity of this solution is $1.29 \mathrm{~S} \mathrm{~m}^{-1}$. Resistance of the same cell when filled with 0.2 M of the same solution is $520 \Omega$. The molar conductivity of 0.02 M solution of the electrolyte will be
(2006)
(A) $12.4 \times 10^{-4} \mathrm{~S} \mathrm{~m}^{2} \mathrm{~mole}^{-1}$
(B) $1240 \times 10^{-4} \mathrm{~S} \mathrm{~m}^{2} \mathrm{~mole}^{-1}$
(C) $1.24 \times 10^{-4} \mathrm{~S} \mathrm{~m}^{2} \mathrm{~mol}^{-1}$
(D) $1.24 \times 10^{-4} \mathrm{Sm}^{2} \mathrm{~mole}^{-1}$
Q. 10 Saturated solution of $\mathrm{KNO}_{3}$ is used to make 'saltbridge' because
(2002)
(A) Velocity of $\mathrm{K}^{+}$is greater than that of $\mathrm{NO}_{3}^{-}$
(B) Velocity of $\mathrm{NO}_{3}^{-}$is greater than that of $\mathrm{K}^{+}$
(C) Velocities of both $\mathrm{K}^{+}$and $\mathrm{NO}_{3}^{-}$are nearly the same
(D) $\mathrm{KNO}_{3}$ is highly soluble in water
Q. 11 The reduction potential of hydrogen half-cell will be negative if
(2011)
(A) $\mathrm{P}_{\left(\mathrm{H}_{2}\right)}=1 \mathrm{~atm}$ and $\left[\mathrm{H}^{+}\right]=2.0 \mathrm{M}$
(B) $\mathrm{P}_{\left(\mathrm{H}_{2}\right)}=1 \mathrm{~atm}$ and $\left[\mathrm{H}^{+}\right]=1.0 \mathrm{M}$
(C) $\mathrm{P}_{\left(\mathrm{H}_{2}\right)}=2 \mathrm{~atm}$ and $\left[\mathrm{H}^{+}\right]=1.0 \mathrm{M}$
(D) $\mathrm{P}_{\left(\mathrm{H}_{2}\right)}=2 \mathrm{~atm}$ and $\left[\mathrm{H}^{+}\right]=2.0 \mathrm{M}$
Q. 12 The cell, $\mathrm{Zn}\left|\mathrm{Zn}^{2+}(1 \mathrm{M})\right|\left|\mathrm{Cu}^{2+}(1 \mathrm{M})\right| \mathrm{Cu}\left(\mathrm{E}_{\text {cell }}^{\circ}=1.10\right.$ V ) was allowed to be completely discharged at 298 K . The relative concentration of $\mathrm{Zn}^{2+}$ to
$\mathrm{Cu}^{2+}\left[\frac{\mathrm{Zn}^{2+}}{\left[\mathrm{Cu}^{2+}\right]}\right]$ is
(2007)
(A) Antilog (24.08)
(B) 37.3
(C) $10^{37.3}$
(D) $9.65 \times 10^{4}$
Q. 13 The standard reduction potential for $\mathrm{Fe}^{2+} / \mathrm{Fe}$ and $\mathrm{Sn}^{2+} / \mathrm{Sn}$ electrodes are -0.44 and -0.14 volt respectively, For the given cell reaction $\mathrm{Fe}^{2+}+\mathrm{Sn} \rightarrow \mathrm{Fe}+\mathrm{Sn}^{2+}$, the standard EMF is
(1990)
(A) +0.30 V
(B) -0.58 V
(C) +0.58 V
(D) -0.30 V
Q. 14 Given $\mathrm{E}_{\mathrm{Fe}^{3+} / \mathrm{Fe}}^{\circ}=-0.036 \mathrm{~V}$, $\mathrm{E}_{\mathrm{Fe}^{2+} / \mathrm{Fe}}^{-}=-0.439 \mathrm{~V}$

The value of standard electrode potential for the change, $\mathrm{Fe}_{(\mathrm{aq})}^{3+}+\mathrm{e}^{-} \rightarrow \mathrm{Fe}^{2+}(\mathrm{aq})$ will be
(A) -0.072 V
(B) 0.385 V
(C) 0.770 V
(D) -0.270 V
Q. 15 For the redox reaction:
$\mathrm{Zn}_{(\mathrm{s})}+\mathrm{Cu}^{2+}(0.1 \mathrm{M}) \rightarrow \mathrm{Zn}^{2+}(1 \mathrm{M})+\mathrm{Cu}_{(2)}$ taking place in a cell, $E_{\text {cell }}^{\circ}$ is 1.10 volt. $E_{\text {cell }}$ for the cell will be
$\left(2.303 \frac{R T}{F}=0.0591\right)$
(2003)
(A) 2.14 volt
(B) 1.80 volt
(C) 1.07 volt
(D) 0.82 volt
Q. 16 Given $\mathrm{E}_{\mathrm{Cr}^{3+} / \mathrm{Cr}}^{\circ}=-0.72 \mathrm{~V}, \mathrm{E}_{\mathrm{Fe}^{2+} / \mathrm{Fe}}^{\circ}=-0.42 \mathrm{~V}$.

The potential for the cell $\mathrm{Cr}^{2} \mathrm{Cr}^{3+}(0.1 \mathrm{M})| | \mathrm{Fe}^{2+}(0.01 \mathrm{M}) \mid \mathrm{Fe}$ is
(2008)
(A) 0.26 V
(B) 0.399 v
(C) -0.339 V
(D) -0.26 V
Q.17. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is
$\mathrm{CH}_{3} \mathrm{OH}(\ell)+\frac{3}{2} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\ell)$ at 298 K standard Gibb's energies of formation for $\mathrm{CH}_{3} \mathrm{OH}(\ell)$, $\mathrm{H}_{2} \mathrm{O}(\ell)$ and $\mathrm{CO}_{2}(\mathrm{~g})$ are -166.2, -237.2 and $394.4 \mathrm{~kJ} \mathrm{~mol}^{1}$ respectively. If standard enthalpy of combustion of methanol is $-726 \mathrm{~kJ} \mathrm{~mol}^{-1}$, efficiency of the fuel cell will be
(2009)
(A) $80 \%$
(B) $87 \%$
(C) $90 \%$
(D) $97 \%$
Q. 18 Given: $\mathrm{E}_{\mathrm{Fe}^{3+} / \mathrm{Fe}}^{\circ}=-0.036 \mathrm{~V}, \mathrm{E}_{\mathrm{Fe}^{2+} / \mathrm{Fe}}^{\circ}=-0.439 \mathrm{~V}$. The value of standard electron potential for the change, $\mathrm{Fe}_{(\mathrm{aq})}^{3+}+\mathrm{e}^{-} \longrightarrow \mathrm{Fe}^{2+}(\mathrm{aq})$ will be:
(2009)
(A) -0.072 V
(B) 0.385 V
(C) 0.770 V
(D) -0.270
Q. 19 The reduction potential of hydrogen half-cell will be negative if:
(2011)
(A) $\mathrm{p}\left(\mathrm{H}_{2}\right)=1 \mathrm{~atm}$ and $\left[\mathrm{H}^{+}\right]=1.0 \mathrm{M}$
(B) $\mathrm{p}\left(\mathrm{H}_{2}\right)=2 \mathrm{~atm}$ and $\left[\mathrm{H}^{+}\right]=1.0 \mathrm{M}$
(C) $\mathrm{p}\left(\mathrm{H}_{2}\right)=2 \mathrm{~atm}$ and $\left[\mathrm{H}^{+}\right]=2.0 \mathrm{M}$
(D) $\mathrm{p}\left(\mathrm{H}_{2}\right)=1 \mathrm{~atm}$ and $\left[\mathrm{H}^{+}\right]=2.0 \mathrm{M}$
Q. 20 The standard reduction potentials for $\mathrm{Zn}^{2+} / \mathrm{Zn}$, $\mathrm{Ni}^{2+} / \mathrm{Ni}$, and $\mathrm{Fe}^{2+} / \mathrm{Fe}$ are $-0.76,-0.23$ and -0.44 V respectively. The reaction $X+Y^{2+} \longrightarrow X^{2+}+Y$ will be spontaneous when:
(2012)
(A) $\mathrm{X}=\mathrm{Ni}, \mathrm{Y}=\mathrm{Fe}$
(B) $\mathrm{X}=\mathrm{Ni}, \mathrm{Y}=\mathrm{Zn}$
(C) $X=\mathrm{Fe}, \mathrm{Y}=\mathrm{Zn}$
(D) $\mathrm{X}=\mathrm{Zn}, \mathrm{Y}=\mathrm{Ni}$
Q. 21 Given: $\mathrm{E}_{\mathrm{Cr}^{3+} / \mathrm{Cr}^{3+}}^{\circ}=-0.74 \mathrm{~V} ; \mathrm{E}_{\mathrm{MnO}_{4}^{-} / \mathrm{Mn}^{2+}}^{\circ}=1.51 \mathrm{~V}$
$\mathrm{E}_{\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-} / \mathrm{Cr}^{3+}}^{\circ}=1.33 \mathrm{~V} ; \mathrm{E}_{\mathrm{Cl}_{\mathrm{Cl}}}^{\circ}=1.36 \mathrm{~V}$
Based on the data given above, strongest oxidising agent will be:
(2013)
(A) Cl
(B) $\mathrm{Cr}^{3+}$
(C) $\mathrm{Mn}^{2+}$
(D) $\mathrm{MnO}_{4}^{-}$
Q. 22 The equivalent conductance of NaCl at concentration C and at infinite dilution are $\lambda_{\mathrm{C}}$ and $\lambda_{\alpha^{\prime}}$ respectively. The correct relationship between $\lambda_{c}$ and $\lambda_{\alpha^{\prime}}$ is given as (Where the constant $B$ is positive)
(2014)
(A) $\lambda_{C}=\lambda_{\infty}+(B) C$
(B) $\lambda_{C}=\lambda_{\infty}-(B) C$
(C) $\lambda_{C}=\lambda_{\infty}-$
(B) $\sqrt{C}$
(D) $\lambda_{C}=\lambda_{\infty}+$ (B) $\sqrt{C}$
Q. 23 Given below are the half-cell reactions
(2014)
$\mathrm{Mn}^{2+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{Mn} ; \mathrm{E}^{\circ}=-1.18 \mathrm{~V}$
$\left(\mathrm{Mn}^{3+}+\mathrm{e}^{-} \longrightarrow \mathrm{Mn}^{2+}\right) ; \mathrm{E}^{\circ}=+1.51 \mathrm{~V}$
The $\mathrm{E}^{\circ}$ for $3 \mathrm{Mn}^{2+} \longrightarrow \mathrm{Mn}+2 \mathrm{Mn}^{3+}$ will be
(A) -2.69 V ; the reaction will not occur
(B) -2.69 V ; the reaction will occur
(C) -0.33 V ; the reaction will not occur
(D) -0.33 V ; the reaction will occur
Q. 24 Two Faraday of electricity is passed through a solution of $\mathrm{CuSO}_{4}$. The mass of copper deposited at the cathode is: (at. mass of $\mathrm{Cu}=63.5 \mathrm{amu}$ )
(2015)
(A) 0 g
(B) 63.5 g
(C) 2 g
(D) 127 g

## JEE Advanced/Boards

## Exercise 1

Q. 1 The standard reduction potential values, $\mathrm{E}^{\circ}\left(\mathrm{Bi}^{3+} \mid \mathrm{Bi}\right)$ and $\mathrm{E}^{\circ}\left(\mathrm{Cu}^{2+} \mid \mathrm{Cu}\right)$ are 0.226 V and 0.344 V respectively. A mixture of salts of bismuth and copper at unit concentration each is electrolyzed at $25^{\circ} \mathrm{C}$. To what value can $\left[\mathrm{Cu}^{2+}\right]$ be brought down before bismuth starts to deposit, in electrolysis.
Q. 2 The cell $\mathrm{Pt}, \mathrm{H}_{2}(1 \mathrm{~atm})\left|\mathrm{H}^{+}(\mathrm{pH}=\mathrm{x})\right| \mid$ Normal calomel electrode has an EMF of 0.67 V at $25^{\circ} \mathrm{C}$. Calculate the pH of the solution. The oxidation potential of the calomel electrode on hydrogen scale is -0.28 V .
Q. 3 Voltage of the cell $\mathrm{Pt}, \mathrm{H}_{2}(1 \mathrm{~atm}) \mid \mathrm{HOCN}\left(1.3 \times 10^{-3}\right.$ M) $\| \mathrm{Ag}^{+}(0.8 \mathrm{M}) \mid \mathrm{Ag}(\mathrm{s})$ is 0.982 V . Calculate the $\mathrm{K}_{\mathrm{a}}$ for HOCN . Neglect $\left[\mathrm{H}^{+}\right]$because of oxidation of $\mathrm{H}_{2}(\mathrm{~g})$.
$\mathrm{Ag}^{+}+\mathrm{e} \rightarrow \mathrm{Ag}(\mathrm{s})=0.8 \mathrm{~V}$.
Q. 4 Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contained $0.1 \mathrm{M} \mathrm{MnO}_{4}^{-}$and $0.8 \mathrm{M} \mathrm{H}^{+}$and which was treated with $90 \%$ of the $\mathrm{Fe}^{2+}$ necessary to reduce all the $\mathrm{MnO}_{4}^{-}$to $\mathrm{Mn}^{+2}$.

$$
\begin{aligned}
& \mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+}+5 \mathrm{e} \rightarrow \mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O} \\
& \mathrm{E}^{\circ}=1.51 \mathrm{~V}
\end{aligned}
$$

Q. 5 Calculate the e.m.f of the cell

Pt, $\mathrm{H}_{2}(1.0 \mathrm{~atm})\left|\mathrm{CH}_{3} \mathrm{COOH}(0.1 \mathrm{M})\right|\left|\mathrm{NH}_{3}(\mathrm{aq}, 0.01 \mathrm{M})\right|$ $\mathrm{H}_{2}(1.0 \mathrm{~atm}), \mathrm{Pt}$
$\mathrm{K}_{\mathrm{a}}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=1.8 \times 10^{-5}$,
$\mathrm{K}_{\mathrm{b}}\left(\mathrm{NH}_{3}\right)=1.8 \times 10^{-5}$.
Q. 6 The Edison storage cell is represented as $\mathrm{Fe}(\mathrm{s})$ | $\mathrm{FeO}(\mathrm{s})|\mathrm{KOH}(\mathrm{aq})| \mathrm{Ni}_{2} \mathrm{O}_{3}(\mathrm{~s}) \mid \mathrm{Ni}(\mathrm{s})$ the half-cell reaction are
$\mathrm{Ni}_{2} \mathrm{O}_{3}(\mathrm{~s})+\mathrm{H}_{2} \mathrm{O}$ (i) $+2 \mathrm{e}^{-} \mid 2 \mathrm{NiO}(\mathrm{s})+2 \mathrm{OH}^{-}$,

$$
\mathrm{E}^{\circ}=+0.40 \mathrm{~V}
$$

$\mathrm{FeO}(\mathrm{s})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})+2 \mathrm{e}^{-} \mathrm{IFe}(\mathrm{s})+2 \mathrm{OH}^{-}$,

$$
\mathrm{E}^{\circ}=-0.87 \mathrm{~V}
$$

(i) What is the cell reaction?
(ii) What is the cell e.m.f.? How does it depend on the concentration of KOH ?
(iii) What is the maximum amount of electrical energy that can be obtained from one mole of $\mathrm{Ni}_{2} \mathrm{O}_{3}$ ?
Q. 7 The standard reduction potential for $\mathrm{Cu}^{2+} / \mathrm{Cu}$ is 0.34 V . Calculate the reduction potential at $\mathrm{pH}=14$ for the above couple. $\mathrm{K}_{\text {sp }}$ of $\mathrm{Cu}(\mathrm{OH})_{2}$ is $1 \times 10^{-19}$.
Q. 8 Determine the degree of hydrolysis and hydrolysis constant of aniline hydrochloride in $\mathrm{M} / 32$ solution of salt at 298 K from the following cell data at 298 K .
$\mathrm{Pt}\left|\mathrm{H}_{2}(1 \mathrm{~atm})\right| \mathrm{H}^{+}(1 \mathrm{M})| | \mathrm{M} / 32 \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3} \mathrm{Cl\mid} \mathrm{H}_{2}(1 \mathrm{~atm}) \mid \mathrm{Pt} ;$ $\mathrm{E}_{\text {cell }}=-0.188 \mathrm{~V}$
Q. 9 The e.m.f of the cell, $\mathrm{Pt}\left|\mathrm{H}_{2}(1 \mathrm{~atm}),\right| \mathrm{H}^{+}(0.1 \mathrm{M}, 30 \mathrm{ml})$ $\| \mathrm{Ag}^{+}(0.8 \mathrm{M}) \mid \mathrm{Ag}$ is 0.9 V . Calculate the e.m.f when 40 ml of 0.05 M NaOH is added.
Q. 10 The e.m.f of the cell $\mathrm{Ag}|\mathrm{Agl}| \mathrm{KI}(0.05 \mathrm{M})\left|\mid \mathrm{AgNO}_{3}\right.$ $(0.05 \mathrm{M}) \mid \mathrm{Ag}$ is 0.788 V . Calculate the solubility product of Agl .

## Q. 11 Consider the cell

$\mathrm{Ag}\left|\mathrm{AgBr}(\mathrm{s}) \mathrm{Br}^{-}\right||\mathrm{AgCl}(\mathrm{s}), \mathrm{Ag}| \mathrm{Cl}^{-}$at $25^{\circ} \mathrm{C}$. The solubility product constants of $\mathrm{AgBr} \& \mathrm{AgCl}$ are respectively $5 \times$ $10^{-13} \& 1 \times 10^{-10}$. For what ratio of the concentration of $\mathrm{Br}^{-}$and $\mathrm{Cl}^{-}$ions would the e.m.f of the cell be zero?
Q. 12 The $\mathrm{pK}_{\text {sp }}$ of Agl is 16.07. If the $\mathrm{E}^{\circ}$ value for $\mathrm{Ag}^{+} \mid \mathrm{Ag}$ is 0.7991 V . Find the $\mathrm{E}^{\circ}$ for the half-cell reaction Agl (s) $+\mathrm{e}^{-} \rightarrow \mathrm{Ag}+\mathrm{I}^{-}$
Q. 13 For the galvanic cell: $\mathrm{Ag} \mathrm{AgCl}(\mathrm{s})|\mathrm{KCl}(0.2 \mathrm{M})| \mid \mathrm{KBr}$ $(0.001 \mathrm{M})|\mathrm{AgBr}(\mathrm{s})| \mathrm{Ag}$, Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at $25^{\circ} \mathrm{C}$.
$\left.\left[\mathrm{K}_{\text {sp (AgCl) }}\right]-2.8 \times 10^{-10} ; \mathrm{K}_{\text {sp (AgBr) }}-3.3 \times 10^{-13}\right]$
Q. 14 Given, $\mathrm{E}^{\circ}=-0.268 \mathrm{~V}$ for the $\mathrm{Cl}^{-}\left|\mathrm{PbCl}_{2}\right| \mathrm{Pb}$ couple and -0.126 V for the $\mathrm{Pb}^{2+} \mid \mathrm{Pb}$ couple, determine $\mathrm{K}_{\text {sp }}$ for $\mathrm{PbCl}_{2}$ a $25^{\circ} \mathrm{C}$ ?
Q. 15 Calculate the voltage, E , of the cell at $25^{\circ} \mathrm{C}$
$\mathrm{Mn}(\mathrm{s})\left|\mathrm{Mn}\left(\mathrm{OH}_{2}\right)(\mathrm{s})\right| \mathrm{Mn}^{2+}(\mathrm{xM}), \mathrm{OH}^{-}\left(1.00 \times 10^{-4} \mathrm{M}\right)| |$ $\mathrm{Cu}^{2+}(0.675 \mathrm{M}) \mid \mathrm{Cu}(\mathrm{s})$ given that $\mathrm{K}_{\mathrm{sp}}=1.9 \times 10^{-13}$ for Mn $(\mathrm{OH})_{2}(\mathrm{~s}) \mathrm{E}^{\circ}\left(\mathrm{Mn}^{2+} / \mathrm{Mn}\right)=-1.18 \mathrm{~V}$
Q. 16 Calculate the voltage, $E$, of the cell
$\mathrm{Ag}(\mathrm{s})\left|\mathrm{AgIO}_{3}(\mathrm{~s})\right| \mathrm{Ag}^{+}(\mathrm{x} \mathrm{M}), \mathrm{HIO}_{3}(0.300 \mathrm{M})| | \mathrm{Zn}^{2+}$ $(0.175 \mathrm{M}) \mid \mathrm{Zn}(\mathrm{s})$ if $\mathrm{K}_{\mathrm{sp}}=3.02 \times 10^{-8}$ for $\mathrm{AgIO}_{3}(\mathrm{~s})$ and $\mathrm{K}_{\mathrm{a}}$ $=0.162$ for $\mathrm{HIO}_{3}$.
Q. 17 The voltage of the cell
$\mathrm{Pb}(\mathrm{s})\left\|\mathrm{PbSO}_{4}(\mathrm{~s}) \mid \mathrm{NaHSO}_{4}(0.600 \mathrm{M})\right\| \mathrm{Pb}^{2+}(2.50 \times$ $\left.10^{-5} \mathrm{M}\right) \mid \mathrm{Pb}(\mathrm{s})$ is $\mathrm{E}=+0.061 \mathrm{~V}$. Calculate $\mathrm{K}_{2}=\left[\mathrm{H}^{+}\right]\left[\mathrm{SO}_{4}^{2-}\right.$ ]/ $\left[\mathrm{HSO}_{4}^{-}\right]$, the dissociation constant for $\mathrm{HSO}_{4}^{-}$. Given $\mathrm{Pb}(\mathrm{s})+\mathrm{SO}_{4}{ }^{2-}(\mathrm{aq}) \rightarrow \mathrm{PbSO}_{4}(\mathrm{~s})+2 \mathrm{e}^{-}\left(\mathrm{E}^{\circ}=0.356\right) \mathrm{E}^{\circ}\left(\mathrm{Pb}^{2+} /\right.$ $\mathrm{Pb})=-0.126 \mathrm{~V}$
Q. 18 The voltage of the cell
$\mathrm{Zn}(\mathrm{s})\left|\mathrm{Zn}(\mathrm{CN})_{4}{ }^{2-}(0.450 \mathrm{M}), \mathrm{CN}^{-}\left(2.65 \times 10^{-3} \mathrm{M}\right)\right| \mid \mathrm{Zn}^{2+}$ $\left(3.84 \times 10^{-4} \mathrm{M}\right) \mid \mathrm{Zn}(\mathrm{s})$ is $\mathrm{E}=+0.099 \mathrm{~V}$. Calculate the constant $\mathrm{K}_{\mathrm{f}}$ for
$\mathrm{Zn}^{2+}+4 \mathrm{CN}^{-} \rightarrow \mathrm{Zn}(\mathrm{CN})_{4}^{2-}$, the only $\mathrm{Zn}^{2+}+\mathrm{CN}^{-}$
complexation reaction of importance.
Q. 19 Given the standard reduction potentials $\mathrm{Ti}^{+}+\mathrm{e}^{-} \rightarrow$ $\mathrm{Ti}, \mathrm{E}^{\circ}=-0.34 \mathrm{~V}$ and $\mathrm{Ti}^{3+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Ti}^{+}, \mathrm{E}^{\circ}=1.25 \mathrm{~V}$. Examine the spontaneity of the reaction, $3 \mathrm{Ti}^{+} \rightarrow 2 \mathrm{Ti}+\mathrm{Ti}^{3+}$. Also find $E^{\circ}$ for this disproportionation.
Q. 20 Estimate the cell potential of a daniel cell having $1 \mathrm{M} \mathrm{Zn}^{++}$\& originally having $1 \mathrm{M} \mathrm{Cu}{ }^{++}$after sufficient $\mathrm{NH}_{3}$ has been added to the cathode compartment to make $\mathrm{NH}_{3}$ concentration 2 M . $\mathrm{K}_{\mathrm{f}}$ for $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$ $=1 . \times 10^{12}, \mathrm{E}^{\circ}$ for the reaction,
$\mathrm{Zn}+\mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+}+\mathrm{Cu}$ is 1.1 V .
Q. 21 The normal oxidation potential of Zn referred to SHE is 0.76 and that of Cu is -0.34 V at $25^{\circ} \mathrm{C}$. When excess of Zn is added to $\mathrm{CuSO}_{4^{\prime}} \mathrm{Zn}$ displaces $\mathrm{Cu}^{2+}$ till equilibrium is reached. What is the ratio of $\mathrm{Zn}^{2+}$ to $\mathrm{Cu}^{2+}$ ions at equilibrium?
Q. $22 \mathrm{~K}_{\mathrm{d}}$ for complete dissociation of $\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right]^{+}$into $\mathrm{Ag}^{+}$and $2 \mathrm{NH}_{3}$ is $6 \times 10^{-8}$. Calculate $\mathrm{E}^{\circ}$ for the following half reaction; $\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}+2 \mathrm{NH}_{3}$
$\mathrm{Ag}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}, \quad \mathrm{E}^{\circ}=0.799 \mathrm{~V}$
Q. 23 The overall formation constant for the reaction of 6 mole of $\mathrm{CN}^{-}$with cobalt (II) is $1 \times 10^{19}$. The standard reduction potential for the reaction
$\left[\mathrm{Co}(\mathrm{CN}]_{6}\right]^{3-} \mathrm{e}^{-} \rightarrow \mathrm{Co}(\mathrm{CN})_{6}{ }^{4-}$ is -0.83 V . Calculate the formation constant of $\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$ Given $\mathrm{Co}^{3+}+\mathrm{e}^{-} \rightarrow$ $\mathrm{Co}^{2+} ; \mathrm{E}^{\circ}=1.82 \mathrm{~V}$
Q. 24 Calculate $E^{\circ}$ for the following reactions at 298 K ,
$\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}{ }^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}+2 \mathrm{NH}_{3}$
$\mathrm{Ag}(\mathrm{CN})_{2}{ }^{-} \mathrm{e}^{-} \rightarrow \mathrm{Ag}+2 \mathrm{CN}^{-}$
Given: $\mathrm{E}_{\mathrm{Ag}^{\circ}{ }_{\mathrm{Ag}}}-0.7991 \mathrm{~V}$,
$\mathrm{K}_{\text {ins }}\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}^{+}\right]=6.02 \times 10^{-8}$ and
$\mathrm{K}_{\text {ins }}\left[\mathrm{Ag}(\mathrm{CN})_{2}{ }^{-}\right]=1.995 \times 10^{-19}$
Q. 25 Calculate the equilibrium constant for the reaction:
$3 \mathrm{Sn}(\mathrm{s})+2 \mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+28 \mathrm{H}^{+} \rightarrow 3 \mathrm{Sn}^{4+}+4 \mathrm{Cr}^{3+}+14 \mathrm{H}_{2} \mathrm{O}$
$\mathrm{E}^{\circ}$ for $\mathrm{Sn} / \mathrm{Sn}^{2+}=0.136 \mathrm{~V} \mathrm{E}^{\circ}$ for $\mathrm{Sn}^{2+} / \mathrm{Sn}^{4+}=-0.154 \mathrm{~V}$
$\mathrm{E}^{\circ}$ for $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-} / \mathrm{Cr}^{3+}=1.33 \mathrm{~V}$
Q. 26 Calculate the equilibrium concentration of all ions in an ideal solution prepared by mixing 25.00 mL of $0.100 \mathrm{M} \mathrm{Ti}^{+}$with 25.00 mL of $0.200 \mathrm{M} \mathrm{Co}^{3+}$.
$\mathrm{E}^{\circ}\left(\mathrm{Ti}^{+} / \mathrm{Ti}^{3+}\right)=-1.25 \mathrm{~V} ; \mathrm{E}^{\circ}\left(\mathrm{Co}^{3+} / \mathrm{Co}^{2+}\right)=1.84 \mathrm{~V}$
Q. 27 Same quantity of electricity is being used to liberate iodine (at anode) and a metal $x$ (cathode). The mass of $x$ deposited is 0.617 g and the iodine is completely reduced by 46.3 cc of 0.124 M sodium thiosulphate. Find the equivalent mass of $x$.
Q. 28 In a fuel cell, $\mathrm{H}_{2} \& \mathrm{O}_{2}$ react to produce electricity. In the process, $\mathrm{H}_{2}$ gas is oxidized at the anode $\& \mathrm{O}_{2}$ at the cathode. If 67.2 liter of $\mathrm{H}_{2}$ at STP react in 15 minutes, what is the average current produced? If the entire current is used for electrode deposition of Cu from Cu (II) solution, how many grams of Cu will be deposited?

Anode: $\quad \mathrm{H}_{2}+2 \mathrm{OH}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-}$
Cathode: $\quad \mathrm{O}_{2}+2 \mathrm{H}_{2} \mathrm{O}+4 \mathrm{e}^{-} \rightarrow 4 \mathrm{OH}^{-}$
Q. 29 One of the methods of preparation of per disulphuric acid, $\mathrm{H}_{2} \mathrm{~S}_{2} \mathrm{O}_{8}$, involve electrolytic oxidation of $\mathrm{H}_{2} \mathrm{~S} \mathrm{O}_{4}$ at anode $\left(2 \mathrm{H}_{2} \mathrm{~S} \mathrm{O}_{4} \rightarrow \mathrm{H}_{2} \mathrm{~S}_{2} \mathrm{O}_{8}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-}\right)$ with oxygen and hydrogen as by-products. In such an electrolysis, 9.722 L of $\mathrm{H}_{2}$ and 2.35 L of $\mathrm{O}_{2}$ were generated at STP. What is the weight of $\mathrm{H}_{2} \mathrm{~S}_{2} \mathrm{O}_{8}$ formed?
Q. 30 During the discharge of a lead storage battery the density of sulphuric acid fell from 1.294 to 1.139 g . $\mathrm{mL}^{-1} \mathrm{H}_{2} \mathrm{SO}_{4}$ of density $1.294 \mathrm{~g} \mathrm{~mL}^{-1}$ is $39 \%$ and that of density $1.139 \mathrm{~g} \mathrm{~mL}^{-1}$ is $20 \%$ by weight. The battery holds 3.5 L of acid and the volume practically remains constant during the discharge. Calculate the number of ampere hours for which the battery must have been used. The discharging reactions are:
$\mathrm{Pb}+\mathrm{SO}_{4}^{2-} \rightarrow \mathrm{PbSO}_{4}+2 \mathrm{e}^{-}$(anode)
$\mathrm{PbO}_{2}+4 \mathrm{H}^{+}+\mathrm{SO}_{4}^{2-}+2 \mathrm{e}^{-} \rightarrow \mathrm{PbSO}_{4}+2 \mathrm{H}_{2} \mathrm{O}$ (cathode)
Q. 31 A current of 3 amp was passed for 2 hour through a solution of $\mathrm{CuSO}_{4}{ }^{3} 3 \mathrm{~g}$ of $\mathrm{Cu}^{2+}$ ions were deposited as Cu at cathode. Calculate percentage current efficiency of the process.
Q. 32 An acidic solution of $\mathrm{Cu}^{2+}$ salt containing 0.4 g of $\mathrm{Cu}^{2+}$ is electrolyzed until all the copper is deposited. The electrolysis is continued for seven more minutes with the volume of solution kept at 100 ml and the current at 1.2 amp . Calculate the volume of gases evolved at NTP during the entire electrolysis.
Q. 33 In the refining of silver by electrolytic method what will be the weight of 100 gm . Ag anode if 5 ampere current is passed for 2 hours? Purity of silver is $95 \%$ by weight.
Q. 34 Dal Lake has water $8.2 \times 10^{12}$ liter approximately. A power reactor produces electricity at the rate of $1.5 \times 10^{6}$ coulomb per second at an appropriate voltage. How many years would it take to electrolyze the lake?
Q. 35 A lead storage cell is discharged which causes the $\mathrm{H}_{2} \mathrm{SO}_{4}$ electrolyte to change from a concentration of $34.6 \%$ by weight (density $1.261 \mathrm{~g} \mathrm{ml}^{-1}$ at $25^{\circ} \mathrm{C}$ ) to $27 \%$ by weight. The original volume of electrolyte is one liter. Calculate the total charge released at anode of the
battery. Note that the water is produced by the reaction as $\mathrm{H}_{2} \mathrm{SO}_{4}$ is used up. Overall reaction is

$$
\mathrm{Pb}(\mathrm{~s})+\mathrm{PbO}_{2}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{l}) \rightarrow 2 \mathrm{PbSO}_{4}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

Q. $36100 \mathrm{ml} \mathrm{CuSO}_{4}$ (aq) was electrolyzed using inert electrodes by passing 0.965 A till the pH of the resulting solution was 1 . The solution after electrolysis was neutralized, treated with excess KI and titrated with $0.04 \mathrm{M} \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$. Volume of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ required was 35 ml . Assuming no volume change during electrolysis, calculate:
(a) Duration of electrolysis if current efficiency is $80 \%$
(b) Initial concentration $(\mathrm{M})$ of $\mathrm{CuSO}_{4}$.
Q. 37 An external current source giving a current of 0.5 A was joined with Daniel cell and removed after 10 hrs. Before passing the current the LHE and RHE contained 1 L each of $1 \mathrm{M} \mathrm{Zn}{ }^{2+}$ and $\mathrm{Cu}^{2+}$ respectively. Find the EMF supplied by the Daniel cell after removal of the external current source. $\mathrm{E}^{\circ}$ of $\mathrm{Zn}^{2+} / \mathrm{Zn}$ and $\mathrm{Cu}^{2+} / \mathrm{Cu}$ at $25^{\circ} \mathrm{C}$ is
-0.76 and +0.34 V respectively.
Q. 38 Determine at 298 for cell

Pt | Q $\mathrm{QH}_{2^{\prime}} \mathrm{H}+\left||1 \mathrm{M} \mathrm{KCl}| \mathrm{Hg}_{2} \mathrm{Cl}_{2}(\mathrm{~s})\right| \mathrm{Hg}(\mathrm{I}) \mid \mathrm{Pt}$
(a) Its e.m.f when $\mathrm{pH}=5.0$
(b) The pH when $\mathrm{E}_{\text {cell }}=0$
(c) The positive electrode when $\mathrm{pH}=7.5$

Given $\mathrm{E}^{\circ}{ }_{\text {RP (RHS) }}=0.28, \mathrm{E}^{\circ}{ }_{\text {RP (LHS) }}=0.699$
Q. 39 At $25^{\circ} \mathrm{C}, \Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{H}_{2} \mathrm{O}, \mathrm{I}\right)=-56700 \mathrm{cal} / \mathrm{mole}$ and energy of ionization of $\mathrm{H}_{2} \mathrm{O}(\mathrm{I})=19050 \mathrm{Cal} / \mathrm{mol}$. What will be the reversible EMF at $25^{\circ} \mathrm{C}$ of the cell?
Pt | $\mathrm{H}_{2}(\mathrm{~g})(1 \mathrm{~atm})\left|\mathrm{H}^{+}\right|\left|\mathrm{OH}^{-}\right| \mathrm{O}_{2}(\mathrm{~g})(1 \mathrm{~atm}) \mid \mathrm{Pt}$, if at $26^{\circ} \mathrm{C}$ the e.m.f increase by 0.001158 V .
Q. 40 Calculate the cell potential of a cell having reaction: $\mathrm{Ag}_{2} \mathrm{~S}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Ag}+\mathrm{S}^{2-}$ in a solution buffered at $\mathrm{pH}=3$ and which is also saturated with $0.1 \mathrm{M} \mathrm{H}_{2} \mathrm{~S}$.
For $\mathrm{H}_{2} \mathrm{~S}: \mathrm{K}_{1}=10^{-8}$ and $\mathrm{K}_{2}=1.1 \times 10^{-13}, \mathrm{~K}_{\mathrm{sp}}\left(\mathrm{Ag}_{2} \mathrm{~S}\right)=2 \times$ $10^{-49}, \mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}^{\circ}=-0.8$.
Q.41The equivalent conductance of 0.10 N solution of $\mathrm{MgCl}_{2}$ is 97.1 mho $\mathrm{cm}^{2}$ equi- ${ }^{-1}$ at $25^{\circ} \mathrm{C}$. A cell with electrode that are $1.5 \mathrm{~cm}^{2}$ in surface area and 0.5 cm apart is filled with 0.1 N MgCl solution. How much current will flow when potential difference between the electrodes is 5 volt?
Q. 42 A dilute aqueous solution of KCl was placed between two electrodes 10 cm apart, across which a potential of 6 volt was applied. How far would the
$\mathrm{K}^{+}$ion move in 2 hours at $25^{\circ} \mathrm{C}$ ? lonic conductance of $\mathrm{K}^{+}$ ion at infinite dilution at $25^{\circ} \mathrm{C}$ is $73.52 \mathrm{ohm}^{-1} \mathrm{~cm}^{2} \mathrm{~mole}^{-1}$ ?
Q. 43 When a solution of specific conductance 1.342 ohm $^{-1}$ meter $^{-1}$ was placed in a conductivity cell with parallel electrodes, the resistance was found to be 170.5 ohm . Area of electrodes is $1.86 \times 10^{-4} \mathrm{~m}^{2}$. Calculate separation of electrodes.
Q. 44 The specific conductance at $25^{\circ} \mathrm{C}$ of a saturated solution of $\mathrm{SrSO}_{4}$ is $1.482 \times 10^{-4}$ ohm $^{-1} \mathrm{~cm}^{-1}$ while that of water used is $1.5 \times 10^{-6} \mathrm{mho} \mathrm{cm}^{-1}$. Determine at $25^{\circ} \mathrm{C}$ the solubility in gm. per liter of $\mathrm{SrSO}_{4}$ in water. Molar ionic conductance of $\mathrm{Sr}^{2+}$ and $\mathrm{SO}_{4}^{2-}$ ions at infinite dilution are 59.46 and $79.8 \mathrm{ohm}^{-1} \mathrm{~cm}^{2} \mathrm{~mole}^{-1}$ respectively. [ $\mathrm{Sr}=87.6, \mathrm{~S}=32, \mathrm{O}=16$ ]
Q. 45 Calculate the solubility and solubility product of $\mathrm{Co}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ in water at $25^{\circ} \mathrm{C}$ from the following data: Conductivity of a saturated solution of $\mathrm{Co}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]$ is $2.06 \times 10^{-6} \Omega^{-1} \mathrm{~cm}^{-1}$ and that of water used $4.1 \times 10^{-7} \Omega^{-1} \mathrm{~cm}^{-1}$. The ionic molar conductivities of $\mathrm{Co}^{2+}$ and $\mathrm{Fe}(\mathrm{CN})_{6}{ }^{4-}$ are $86.0 \Omega^{-1} \mathrm{~cm}^{2} \mathrm{~mole}^{-1}$ and $444.0 \Omega^{-1} \mathrm{~cm}^{-1} \mathrm{~mole}^{-1}$.
Q. 46 A sample of water from a large swimming pool has a resistance of $9200 \Omega$ at $25^{\circ} \mathrm{C}$ when placed in a certain conductance cell. When filled with 0.02 M KCl solution, the cell has a resistance of $85 \Omega$ at $25^{\circ} \mathrm{C} .500 \mathrm{gm}$. of NaCl were dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of $7600 \Omega$. Calculate the volume of water in the pool.
Given: Molar conductance of NaCl at that concentration is $126.5 \Omega^{-1} \mathrm{~cm}^{-1} \mathrm{~mol}^{-1}$ and molar conductivity of KCl at 0.02 M is $138 \Omega^{-1} \mathrm{~cm}^{2} \mathrm{~mole}^{-1}$.

## Exercise 2

## Single Correct Choice Type

Q. 1 An aqueous solution containing one mole per liter each of $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2} \mathrm{AgNO}_{3^{\prime}} \mathrm{Hg}_{2}\left(\mathrm{NO}_{3}\right)_{2^{\prime}} \mathrm{Mg}\left(\mathrm{NO}_{3}\right)_{2}$ is being electrolyzed by using inert electrodes. The value of standard potentials are

$$
\begin{aligned}
& \mathrm{E}_{\mathrm{Ag}^{+} \mid \mathrm{Ag}}^{\circ}-0.80 \mathrm{~V}, \mathrm{E}_{\mathrm{Hg}_{2}^{2+} \mid \mathrm{Hg}}^{\circ}-0.79 \mathrm{~V} \\
& \mathrm{E}_{\mathrm{Cu}^{2+} \mid \mathrm{Cu}}^{\circ}-0.34 \mathrm{~V} \text { and } \mathrm{E}_{\mathrm{Mg}^{2+} \mid \mathrm{Mg}}^{\circ}=-2.3 \mathrm{~V}
\end{aligned}
$$

With increasing voltage, the sequence of deposition of metals on the cathode will be
(A) Ag, Hg, Cu, Mg
(B) $\mathrm{Mg}, \mathrm{Cu}, \mathrm{Hg}, \mathrm{Ag}$
(C) $\mathrm{Ag}, \mathrm{Hg}, \mathrm{Cu}$
(D) $\mathrm{Cu}, \mathrm{Hg}, \mathrm{Ag}$
Q. 2 The charge required for the oxidation of one mole $\mathrm{Mn}_{3} \mathrm{O}_{4}$ into $\mathrm{MnO}_{4}{ }^{2-}$ in presence of alkaline medium is
(A) $5 \times 96500 C$
(B) 96500 C
(C) $10 \times 96500 \mathrm{C}$
(D) $2 \times 96500 \mathrm{C}$
Q. 3 A solution of sodium sulphate in water is electrolyzed using inert electrodes. The products at the cathode and anode are respectively.
(A) $\mathrm{H}_{2}, \mathrm{O}_{2}$
(B) $\mathrm{O}_{2}, \mathrm{H}_{2}$
(C) $\mathrm{O}_{2}, \mathrm{Na}$
(D) None
Q. 4 A hydrogen electrode $X$ was placed in a buffer solution of sodium acetate and acetic acid in the ratio $a$ : $b$ and another hydrogen electrode $Y$ was placed in a buffer solution of sodium acetate and acetic acid in the ratio b : a . If reduction potential values for two cells are found to be $E_{1}$ and $E_{2}$ respectively w.r.t. standard hydrogen electrode, the $\mathrm{pK}_{\mathrm{a}}$ value of the acid can be given as
(A) $\frac{E_{1}+E_{2}}{0.118}$
(B) $\frac{E_{2}-E_{1}}{0.118}$
(C) $-\frac{E_{1}+E_{2}}{0.118}$
(D) $\frac{E_{1}-E_{2}}{0.118}$
Q. 5 The conductivity of a saturated solution of $\mathrm{Ag}_{3} \mathrm{PO}_{4}$ is $9 \times 10^{-6} \mathrm{~S} \mathrm{~m}^{-1}$ and its equivalent conductivity is $1.50 \times 10^{-4} \mathrm{~S} \mathrm{~m}^{-2}$ equivalent ${ }^{-1}$. The $\mathrm{K}_{\text {sp }}$ of $\mathrm{Ag}_{3} \mathrm{PO}_{4}$ is:
(A) $4.32 \times 10^{-18}$
(B) $1.8 \times 10^{-9}$
(C) $8.64 \times 10^{-13}$
(D) None of these
Q. 6 Equal volumes of $0.015 \mathrm{M} \mathrm{CH}_{3} \mathrm{COOH} \& 0.015 \mathrm{M}$ NaOH are mixed together. What would be molar conductivity of mixture if conductivity of $\mathrm{CH}_{3} \mathrm{COONa}$ is $6.3 \times 10^{-4} \mathrm{~S} \mathrm{~cm}^{-1}$ ?
(A) $8.4 \mathrm{~S} \mathrm{~cm}^{2}$ mole $^{-1}$
(B) $84 \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mole}^{-1}$
(C) $4.2 \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mole}^{-1}$
(D) $42 \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mole}^{-1}$

## Multiple Correct Choice Type

Q. 7 Pick out the correct statements among the following from inspection of standard reduction potentials (Assume standard state conditions).

$$
\begin{aligned}
& \mathrm{Cl}_{2} \text { (aq.) }+2 \mathrm{e} \rightarrow 2 \mathrm{Cl}_{(\text {aq. })}^{-} \quad \mathrm{E}_{\mathrm{Cl}_{2} / \mathrm{Cl}^{-}}^{\circ}=+1.36 \text { volt } \\
& \mathrm{Br}_{2} \text { (aq.) }+2 \mathrm{e} \rightarrow \quad 2 \mathrm{Br} \text { (aq.) } \quad \mathrm{E}_{\mathrm{Br}_{2} / \mathrm{Br}^{-}}^{\circ}=+1.09 \text { volt } \\
& \mathrm{I}_{2} \text { (s) }+2 \mathrm{e} \rightarrow \quad 2 \mathrm{l}^{-} \text {(aq.) } \quad \mathrm{E}_{\mathrm{I}_{2} / \mathrm{I}^{-}}^{\circ}=+0.54 \text { volt } \\
& \mathrm{S}_{2} \mathrm{O}_{8}^{2-} \text { (aq.) }+2 \mathrm{e} \quad \rightarrow \quad 2 \mathrm{SO}_{4}^{2-} \text { (aq.) } \\
& \mathrm{E}_{\mathrm{S}_{2} \mathrm{O}_{3}^{2-} / \mathrm{SO}_{4}^{2-}}=+2.00 \text { volt }
\end{aligned}
$$

(A) $\mathrm{Cl}_{2}$ can oxidize $\mathrm{SO}_{4}^{2-}$ from solution
(B) $\mathrm{Cl}_{2}$ can oxidize $\mathrm{Br}^{-}$and $\mathrm{I}^{-}$from aqueous solution
(C) $\mathrm{S}_{2} \mathrm{O}_{8}^{2-}$ can oxidize $\mathrm{Cl}^{-}, \mathrm{Br}^{-}$and $\mathrm{I}^{-}$from aqueous solution
(D) $\mathrm{S}_{2} \mathrm{O}_{8}^{2-}$ is added slowly, $\mathrm{Br}^{-}$can be reduce in presence of $\mathrm{Cl}^{-}$
Q. 8 Which of the following arrangement will produce oxygen at anode during electrolysis?
(A) Dilute $\mathrm{H}_{2} \mathrm{SO}_{4}$ solution with Cu electrodes.
(B) Dilute $\mathrm{H}_{2} \mathrm{SO}_{4}$ solution with inert electrodes.
(C) Fused NaOH with inert electrodes.
(D) Dilute NaCl solution with inert electrodes.
Q. 9 If 270.0 of water is electrolyzed during an experiment performed by Miss Abhilasha with 75\% current efficiency then
(A) 168 L of $\mathrm{O}_{2}(\mathrm{~g})$ will be evolved at anode at $1 \mathrm{~atm} \&$ 273 K
(B) Total 504 L gases will be produced at 1 atm $\& 273 \mathrm{~K}$
(C) 336 L of $\mathrm{H}_{2}(\mathrm{~g})$ will be evolved at anode at $1 \mathrm{~atm} \&$ 273 K
(D) 45 F electricity will be consumed
Q. 10 During discharging of lead storage battery, which of the following is/are true?
(A) $\mathrm{H}_{2} \mathrm{SO}_{4}$ is produced
(B) $\mathrm{H}_{2} \mathrm{O}$ is consumed
(C) $\mathrm{PbSO}_{4}$ is formed at both electrodes
(D) Density of electrolytic solution decreases
Q. 11 The EMF of the following cell is 0.22 volt.
$\mathrm{Ag}(\mathrm{s})|\mathrm{AgCl}(\mathrm{s})| \mathrm{KCl}(1 \mathrm{M}) \mid \mathrm{H}^{+}$(1M) $\mid \mathrm{H}_{2}(\mathrm{~g})$ (1atm); $\mathrm{Pt}(\mathrm{s})$
Which of the following will decreases the EMF of cell
(A) Increasing pressure of $\mathrm{H}_{2}(\mathrm{~g})$ from 1 atm to 2 atm
(B) Increasing $\mathrm{Cl}^{-}$concentration in Anodic compartment
(C) Increasing $\mathrm{H}^{+}$concentration in cathodic compartment
(D) Decreasing KCl concentration in Anodic compartment.

## Assertion Reasoning Type

(A) Statement-I is true, statement-2 is true and statement-II is correct explanation for statement-I
(B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I.
(C) Statement-I is true, statement-II is false
(D) Statement-I is false, statement-II is true
Q. 12 Statement-I: The voltage of mercury cell remains constant for long period of time.

Statement-II: It because net cell reaction does not involve active species.
Q. 13 Statement-I: We can add the electrode potential in order to get electrode potential of net reaction.

Statement-II: Electrode potential is an intensive property.
Q. 14 Statement-I: The SRP of three metallic ions $A^{+}$, $\mathrm{B}^{2+} \mathrm{C}^{3+}$ are $-0.3,-0.5,0.8$ volt respectively, so oxidizing power of ions is $\mathrm{C}^{3+}>\mathrm{A}^{+}>\mathrm{B}^{2+}$.
Statement-II: Higher the SRP, higher the oxidizing power

## Comprehension type

Paragraph 1: A sample of water from a large swimming pool has a resistance of $10000 \Omega$ at $25^{\circ} \mathrm{C}$ when placed in a certain conductance cell. When filled with 0.02 M KCl solution, the cell has a resistance of $100 \Omega$ at $25^{\circ} \mathrm{C}$. 585 gm . of NaCl were dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of $8000 \Omega$.
[Given: Molar conductance of NaCl at that concentration is $125 \Omega^{-1} \mathrm{~cm}^{2}$ mole $^{-1}$ and molar conductivity of KCl at 0.02 M is $200 \Omega^{-1} \mathrm{~cm}^{2}$ mole $^{-1}$.]
Q. 15 Cell constant (in $\mathrm{cm}^{-1}$ ) of conductance cell is:
(A) 4
(B) 0.4
(C) $4 \times 10^{-2}$
(D) $4 \times 10^{-5}$
Q. 16 Conductivity $\left(\mathrm{Scm}^{-1}\right)$ of $\mathrm{H}_{2} \mathrm{O}$ is:
(A) $4 \times 10^{-2}$
(B) $4 \times 10^{-3}$
(C) $4 \times 10^{-5}$
(D) None of these
Q. 17 Volume (in Liters) of water in the pool is:
(A) $1.25 \times 10^{5}$
(B) 1250
(C) 12500
(D) None of these

Paragraph 2: Copper reduces $\mathrm{NO}_{3}^{-}$into NO and $\mathrm{NO}_{2}$ depending upon conc. Of $\mathrm{HNO}_{3}$ in solution. Assuming $\left[\mathrm{Cu}^{2+}\right]=0.1 \mathrm{M}_{2}$ and $\mathrm{P}_{\mathrm{NO}}=\mathrm{P}_{\mathrm{NO}_{2}}=10^{-3} \mathrm{~atm}$ and using given data answer the following questions:

$$
\begin{aligned}
& \mathrm{E}_{\mathrm{Cu}^{2+} / \mathrm{Cu}}^{\circ}=+0.34 \text { volt } \\
& \mathrm{E}_{\mathrm{NO}_{3}^{\circ} / \mathrm{NO}}=+0.96 \mathrm{volt} \\
& \mathrm{E}_{\mathrm{NO}_{3}^{\circ} / \mathrm{NO}_{2}}^{-}=+0.79 \mathrm{volt}
\end{aligned}
$$

At $298 \mathrm{~K} \frac{\mathrm{RT}}{\mathrm{F}}(2.303)=0.06 \mathrm{volt}$
Q. $18 \mathrm{E}_{\text {cell }}$ for reduction of $\mathrm{NO}_{3}^{-} \rightarrow \mathrm{NO}$ by $\mathrm{Cu}(\mathrm{s})$, when $\left[\mathrm{HNO}_{3}\right]=1 \mathrm{M}$ is $[\mathrm{At} \mathrm{T}=298]$
(A) $\sim 0.61$
(B) $\sim 0.71$
(C) ~ 0.51
(D) $\sim 0.81$
Q. 19 At what $\mathrm{HNO}_{3}$ concentration thermodynamic tendency for reduction of $\mathrm{NO}_{3}^{-}$into NO and $\mathrm{NO}_{2}$ by copper is same?
(A) $10^{1.23} \mathrm{M}$
(B) $10^{0.56} \mathrm{M}$
(C) $10^{0.66} \mathrm{M}$
(D) $10^{0.12} \mathrm{M}$

## Match the Columns

Q. 20

| Column I | Column II <br> (Electrolysis product using <br> inert electrode) |
| :--- | :--- |
| (A) Dilute solution of HCl | (p) $\mathrm{O}_{2}$ evolved at anode |
| (B) Dilute solution of NaCl | (q) $\mathrm{H}_{2}$ evolved at cathode |
| (C) Concentrated Solution <br> of NaCl | (r) $\mathrm{Cl}_{2}$ evolved at anode |
| (D) $\mathrm{AgNO}_{3}$ solution | (s) Ag deposition at cathode |

## Previous Years' Questions

Q. 1 In the electrolytic cell, flow of electrons is from
(2003)
(A) Cathode to anode is solution
(B) Cathode to anode through external supply
(C) Cathode to anode through internal supply
(D) Anode to cathode through internal supply
Q. $2 \mathrm{Zn}\left|\mathrm{Zn}^{2+}(\mathrm{a}=0.1 \mathrm{M}) \| \mathrm{Fe}^{2+}(\mathrm{a}=0.01 \mathrm{M})\right| \mathrm{Fe}$.

The e.m.f of the above cell is 0.2905 V . Equilibrium constant for the cell reaction is
(2004)
(A) $10^{0.32 / 0.059}$
(B) $10^{0.32 / 0.0295}$
(C) $100.26 / 0.0295$
(D) $10^{0.32 / 0.295}$
Q. 3 The half-cell reaction for rusting of iron are:
$2 \mathrm{H}^{+}+2 \mathrm{e}^{-}+\frac{1}{2} \mathrm{O}_{2} \rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) ; \mathrm{E}^{\circ}=+1.23 \mathrm{~V}$
$\mathrm{Fe}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Fe}(\mathrm{s}), \quad \mathrm{E}^{0}=-0.44 \mathrm{~V}$
$\Delta \mathrm{G}^{\circ}$ (in kJ ) for the reaction is
(2005)
(A) -76
(B) -322
(C) -122
(D) -176
Q. 4 Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 mA current. The time required to liberate 0.01 mole of $\mathrm{H}_{2}$ gas at the cathode is ( $1 \mathrm{~F}=96500 \mathrm{C} \mathrm{mole}^{-1}$ )
(2008)
(A) $9.65 \times 10^{4} \mathrm{~s}$
(B) $19.3 \times 10^{4} \mathrm{~s}$
(C) $28.95 \times 10^{4}$
(D) $38.6 \times 10^{4} \mathrm{~s}$
Q. $5 \mathrm{AgNO}_{3}$ (aqueous) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance ( $\Lambda$ ) versus the volume of $\mathrm{AgNO}_{3}$ is
(2011)

(R)


(S)
(A) (P)
(B) (Q)
(C) (R)
(D) $(\mathrm{S})$
Q. 6 Consider the following cell reaction,
$2 \mathrm{Fe}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{+}(\mathrm{aq}) \rightarrow$
$2 \mathrm{Fe}^{2+}(\mathrm{aq})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}), \mathrm{E}^{\circ}=1.67 \mathrm{~V}$
At $\left[\mathrm{Fe}^{2+}\right]=10^{-3} \mathrm{M}, \mathrm{P}\left(\mathrm{O}_{2}\right)=0.1$ atm and $\mathrm{pH}=3$, the cell potential at $25^{\circ} \mathrm{C}$ is
(2011)
(A) 1.47 V
(B) 1.77 V
(C) 1.87 V
(D) 1.57 V
Q. 7 For the reduction of $\mathrm{NO}_{3}^{-}$ion in an aqueous solution $\mathrm{E}^{\circ}$ is +0.96 V . Values of $\mathrm{E}^{\circ}$ for some metal ion are given below

$$
\begin{array}{ll}
\mathrm{V}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{V} & \mathrm{E}^{\circ}=-1.19 \mathrm{~V} \\
\mathrm{Fe}^{3+}(\mathrm{aq})+3 \mathrm{e}^{-} \rightarrow \mathrm{Fe} & \mathrm{E}^{\circ}=-0.04 \mathrm{~V} \\
\mathrm{Au}^{3+}(\mathrm{aq})+3 \mathrm{e}^{-} \rightarrow \mathrm{Au} & \mathrm{E}^{\circ}=+1.40 \mathrm{~V}
\end{array}
$$

$\mathrm{Hg}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Hg} \quad \mathrm{E}^{\circ}=+0.86 \mathrm{~V}$
The pair (s) of metals that is (are) oxidized by $\mathrm{NO}_{3}{ }^{-}$in aqueous solution is (are)
(2009)
(A) V and Hg
(B) Hg and Fe
(C) Fe and Au
(D) Fe and V

Paragraph 1: Tollen's reagent is used for the detection of aldehydes. When a solution of $\mathrm{AgNO}_{3}$ is added to glucose with $\mathrm{NH}_{4} \mathrm{OH}$ then gluconic acid is formed.
$\mathrm{Ag}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Ag} ; \mathrm{E}^{\circ}{ }_{\text {red }}=0.80 \mathrm{~V}$
[Use $2.303 \times \frac{R T}{F}=0.0592$ and $\frac{F}{R T}=38.92$ at 298 K ]
Q. $82 \mathrm{Ag}^{+}+\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{Ag}(\mathrm{s}) \mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{7}+2 \mathrm{H}^{+}$

Find in $K$ of this reaction.
(A) 66.13
(B) 58.38
(C) 28.30
(D) 46.29
Q. 9 When ammonia is added to the solution, pH is raised to 11 . Which half-cell reaction is affected by pH and by how much?
(A) $E_{\text {oxi }}$ will increase by a factor of 0.65 from $E_{o x i}^{\circ}$
(B) $E_{o x i}$ will decrease by a factor of 0.65 from $E_{o x i}^{\circ}$
(C) $E_{\text {red }}$ will increase by a factor of 0.65 from $E_{\text {red }}^{\circ}$
(D) $E_{\text {red }}$ will decrease by a factor of 0.65 from $E_{\text {red }}^{\circ}$
Q. 10 Ammonia is always added in this reaction. Which of the following must be incorrect?
(A) $\mathrm{NH}_{3}$ combines with $\mathrm{Ag}^{+}$to form a complex
(B) $\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}{ }^{+}$is a stronger oxidizing reagent than $\mathrm{Ag}^{+}$
(C) In absence of $\mathrm{NH}_{3}$ silver salt of gluconic acid is formed
(D) $\mathrm{NH}_{3}$ has no effect on the standard reduction potential of glucose/gluconic acid electrode

Paragraph 2: Chemical reactions involve interaction of atoms and molecules. A large number of atoms/ molecules (approximately $6.023 \times 10^{23}$ ) are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. This concept has implications in diverse areas such as analytical chemistry, biochemistry, electrochemistry and radiochemistry. The following example illustrates a typical case, involving chemical/ electrochemical reaction, which requires a clear understanding of the mole concept.

A 4.0 M aqueous solution of NaCl is prepared and 500 mL of this solution is electrolyzed. This lead to the evolution of chlorine gas at one of the electrodes
(Atomic mass: $\mathrm{Na}=23, \mathrm{Hg}=200,1 \mathrm{~F}=96500 \mathrm{C}$ ). (2007)
Q. 11 The total number of moles of chlorine gas evolved is
(A) 0.5
(B) 1.0
(C) 2.0
(D) 3.0
Q. 12 If the cathode is a Hg electrode, the maximum weight (in gram) of amalgam formed this solution is
(A) 200
(B) 255
(C) 400
(D) 446
Q. 13 The total charge (coulombs) required for complete electrolysis is
(A) 24125
(B) 48250
(C) 96500
(D) 193000

Paragraph 3: Redox reaction play a pivotal role in chemistry and biology. The values of standard redox potential ( $E^{\circ}$ ) of two half-cell
Reactions decide which way the reaction is expected to proceed. A simple example is a Daniel cell in which zinc goes into solution and copper gets deposited. Given below are a set of half-cell reaction (acidic medium) along with their $\mathrm{E}^{\circ}$ ( V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to

\[

\]

(2007)
Q. 14 Among the following, identify the correct statement
(A) Chloride ion is oxidized by $\mathrm{O}_{2}$
(B) $\mathrm{Fe}^{2+}$ is oxidized by iodine
(C) lodide ion is oxidized by chlorine
(D) $\mathrm{Mn}^{2+}$ is oxidized by chlorine
Q. 15 While $\mathrm{Fe}^{3+}$ is stable, $\mathrm{Mn}^{3+}$ is not stable in acid solution because
(A) $\mathrm{O}_{2}$ oxidizes $\mathrm{Mn}^{2+}$ to $\mathrm{Mn}^{3+}$.
(B) $\mathrm{O}_{2}$ oxidizes both $\mathrm{Mn}^{2+}$ to $\mathrm{Mn}^{3+}$ and $\mathrm{Fe}^{2+}$ to $\mathrm{Fe}^{3+}$
(C) $\mathrm{Fe}^{3+}$ oxidizes $\mathrm{H}_{2} \mathrm{O}$ to $\mathrm{O}_{2}$
(D) $\mathrm{Mn}^{3+}$ oxidizes $\mathrm{H}_{2} \mathrm{O}$ to $\mathrm{O}_{2}$
Q. 16 Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and $\mathrm{H}_{2} \mathrm{SO}_{4}$ in presence of air gives a Prussian blue precipitate. The blue color is due to the formation of
(A) $\mathrm{Fe}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{3}$
(B) $\mathrm{Fe}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{2}$
(C) $\mathrm{Fe}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{2}$
(D) $\mathrm{Fe}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{3}$

Paragraph 4: The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is:
$\mathrm{M}(\mathrm{s}) \mid \mathrm{M}^{+}$(aq; 0.05 molar) || $\mathrm{M}^{+}$(aq; 1 molar) | M (s)
For the above electrolytic cell the magnitude of the cell potential $\left|\mathrm{E}_{\text {cell }}\right|=70 \mathrm{mV}$.
(2010)
Q. 17 For the above cell
(A) $E_{\text {cell }}<0 ; \Delta G>0$
(B) $\mathrm{E}_{\text {cell }}>0 ; \Delta \mathrm{G}<0$
(C) $\mathrm{E}_{\text {cell }}<0 ; \Delta \mathrm{G}^{\circ}>0$
(D) $\mathrm{E}_{\text {cell }}>0 ; \Delta \mathrm{G}^{\circ}<0$
Q. 18 If the 0.05 molar solution of $\mathrm{M}^{+}$is replaced by a 0.0025 molar $\mathrm{M}^{+}$solution, then the magnitude of the cell potential would be
(A) 35 mV
(B) 70 mV
(C) 140 mV
(D) 700 mV
Q. 19 All the energy released from the reaction $0-1$
$X \longrightarrow Y \cdot \Delta_{\mathrm{r}} \mathrm{G}^{\circ}=-193 \mathrm{~kJ} \mathrm{~mol} / \mathrm{L}$
is used for oxidizing $\mathrm{M}^{+}$as $\mathrm{M}^{+} \longrightarrow \mathrm{M}^{3+}+2 \mathrm{e}^{-}$,
$\mathrm{E}^{\circ}=-0.25 \mathrm{~V}$.

Under standard conditions, the number of moles of $\mathrm{M}^{+}$ oxidized when one mole of $X$ is converted to $Y$ is
[ $\mathrm{F}=96500 \mathrm{Cmol} / \mathrm{L}]$
(2015)
Q. 20 The molar conductivity of a solution of a weak acid $\mathrm{HX}(0.01 \mathrm{M})$ is 10 times smaller than the molar conductivity of a solution of a weak acid HY ( 0.10 M ). If $\lambda_{\mathrm{x}^{-}}^{0} \approx \lambda_{\mathrm{Y}^{-}}^{0}$, the difference in their $\mathrm{pK}{ }_{\mathrm{a}}$ values, a $\mathrm{pK}{ }_{\mathrm{a}}$ $(H X)-p K_{\mathrm{a}}(H Y)$, is consider degree of ionization of both acids to be <<1)
(2015)
Q. 21 For the following electrochemical cell at 298 K ,
$\operatorname{Pt}(\mathrm{s})\left|\mathrm{H}_{2}(\mathrm{~g}, 1 \mathrm{bar})\right| \mathrm{H}^{+}(\mathrm{aq}, 1 \mathrm{M})| | \mathrm{M}^{4+}(\mathrm{aq}), \mathrm{M}^{2+}(\mathrm{aq}) \mid \mathrm{Pt}(\mathrm{s})$
$\mathrm{E}_{\text {cell }}=0.092 \mathrm{~V}$ when $\frac{\left[\mathrm{M}^{2+}(\mathrm{aq})\right]}{\left[\mathrm{M}^{4+}(\mathrm{aq})\right]}=10^{\mathrm{x}}$.
Given: $\mathrm{E}_{\mathrm{M}^{4+} / \mathrm{M}^{2+}}^{0}=0.151 \mathrm{~V} ; 2.303 \frac{\mathrm{RT}}{\mathrm{F}}=0.059 \mathrm{~V}$
The value of $x$ is
(2016)
(A) -2
(B) -1
(C) 1
(D) 2
Q. 22 In a galvanic cell, the salt bridge
(2014)
(A) Does not participate chemically in the cell reaction.
(B) Stops the diffusion of ions from one electrode to another.
(C) Is necessary for the occurrence of the cell reaction.
(D) Ensures mixing of the two electrolytic solutions.

## PlancEssential Questions

## JEE Main/Boards

## Exercise 1

| Q. 3 | Q. 4 | Q. 8 |
| :--- | :--- | :--- |
| Q. 9 | Q. 12 | Q. 16 |
| Q. 23 | Q. 30 |  |

## Exercise 2

Q. 3
Q. 12
Q. 5
Q. 15
Q. 20

## Previous Years' Questions

Q. 3
Q. 8

## JEE Advanced /Boards

## Exercise 1

| Q. 1 | Q. 6 | Q. 12 |
| :--- | :--- | :--- |
| Q. 19 | Q. 22 | Q. 30 |
| Q. 35 | Q. 42 | Q. 45 |

## Exercise 2

Q. 4
Q. 7
Q. 16
Q. 18

## Previous Years' Questions

Q. 5
Q. 7
Q. 17

## Answer Key

## JEE Main/Boards

## Exercise 1

Q. $2124 \mathrm{ohm}^{-1} \mathrm{~cm}^{2} \mathrm{~mole}^{-1}$
Q. $4 \Delta_{\mathrm{r}} G^{\circ}=-213.04 \mathrm{~kJ}, E_{\text {cell }}^{\circ}=+1.104 \mathrm{~V}$
Q. $5 \quad \lambda_{\mathrm{m}}=124 \Omega^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$
Q. $8 \quad 0.219 \mathrm{~cm}^{-1}$
Q. $9 \wedge_{\mathrm{m}}=32.765 \mathrm{~cm}^{2} \mathrm{~mol}^{-1}, \mathrm{k}_{\mathrm{a}}=2.2 \times 10^{-4}$
Q. 103.66 gm
Q. $14 E^{\circ}=0.34 \mathrm{~V}$
Q. 19 (i) 0.2515 V ; (ii) 0.8101 V (iii) 0.226 V (iv) 1.451 V ;

$$
\text { (v) }-0.268 \mathrm{~V}
$$

Q. 20 0.7288 V
Q. 21 0.1536 V
Q. $22-0.1615 \mathrm{~V}$
Q. 23 (i) 0.2278 V ; (ii) 0.3692
Q. 240.91 V
Q. $253.67 \times 10^{-4}$
Q. $26 \mathrm{Na}, \mathrm{Ca}, \mathrm{Mg}$ and Al .
Q. 27 2.96 V
Q. 28 (a) $-0.118 \mathrm{~V}_{\text {; }}$ (b) -0.0413 V ; (c) (i) -0.0295 V (ii) -0.59 V
Q. $291.3 \times 10^{2}$ ohm $^{-1} \mathrm{~cm}^{2}$ equi ${ }^{-1}$

## Exercise 2

## Single Correct Choice Type

Q. 1 C
Q. 2 B
Q. 3 B
Q. 4 B
Q. 5 D
Q. 6 D
Q. 7 B
Q. 8 A
Q. 9 A
Q. 10 B
Q. 11 B
Q. 12 B
Q. 13 C
Q. 14 C
Q. 15 C
Q. 16 B
Q. 17 A
Q. 18 C
Q. 19 C
Q. 20 D
Q. 21 C

## Previous Years Questions

| Q. 1 D | Q. 2 D | Q. 3 B | Q. 4 C | Q. 5 B | Q. 6 D |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Q. 7 A | Q. 8 D | Q. 9 A | Q. 10 C | Q. 11 C | Q. 12 C |
| Q. 13 D | Q. 14 C | Q. 15 C | Q. 16 A | Q. 17 D | Q. 18 C |
| Q. 19 B | Q. 20 D | Q. 21 D | Q. 22 C | Q. 23 A | Q. 24 A |

## JEE Advanced/Boards

## Exercise 1

Q. $1\left[\mathrm{Cu}^{2+}\right]=10^{-4} \mathrm{M}$
Q. $3 \quad \mathrm{~K}_{\mathrm{a}}=6.74 \times 10^{4}$
Q. $5-0.46 \mathrm{~V}$
Q. $7 E^{\circ}=-0.22 \mathrm{~V}$
Q. 90.95 V
Q. $2 \mathrm{pH}=6.61$
Q. 11 [ Br$]:\left[\mathrm{Cl}^{-}\right]=1: 200$
Q. $13-0.037 \mathrm{~V}$
Q. 151.66 V
Q. 17 10-2
Q. $19 \mathrm{E}^{\circ}=1.59 \mathrm{~V}$, non-spontaneous
Q. 41.39 V
Q. 6 (ii) 1.27 V (ii) 245.1 kJ
Q. $8 \mathrm{~h}=2.12 \times 10^{-2}, \mathrm{~K}_{\mathrm{h}}=1.43 \times 10^{-5} \mathrm{M}$
Q. $10 \quad \mathrm{~K}_{\mathrm{sp}}=1.1 \times 10^{-16}$
Q. $12 \mathrm{E}^{\circ}=-0.1511 \mathrm{~V}$
Q. $14 \quad 1.536 \times 10^{-5} \mathrm{M}^{3}$
Q. $16-1.188 \mathrm{~V}$
Q. $21\left[\mathrm{Zn}^{2+}\right] /\left[\mathrm{Cu}^{2+}\right]=1.941 \times 10^{37}$
Q. $18 \quad 5.24 \times 10^{16}$
Q. $20 E^{\circ}=0.71 \mathrm{~V}$
Q. $23 \mathrm{~K}_{\mathrm{f}}=8.227 \times 10^{63}$
Q. 220.373 V
Q. $25 K=10^{268}$
Q. $240.372 \mathrm{~V},-0.307 \mathrm{~V}$
Q. 27 Eq. wt. $=107.3$
Q. 2943.456 g
Q. $26 \mathrm{Ta}^{+}=5 \times 10^{-9} ; \mathrm{Co}^{3+}=10^{-8}$
Q. $28643.33 \mathrm{amp}, 190.5 \mathrm{~g}$
Q. 30265 Amp. Hr.
Q. 3142.2 \%
Q. $32 \mathrm{~V}\left(\mathrm{O}_{2}\right)=99.68 \mathrm{~mL}, \mathrm{~V}\left(\mathrm{H}_{2}\right)=58.46 \mathrm{~mL}$, Total vol. $=158.1 \mathrm{~mL}$
Q. 3357.5894 gm .
Q. $352.4 \times 10^{5}$ coulomb
Q. 371.143 V
Q. 390.4414 V
Q. $41 \quad 0.1456$ ampere
Q. 341.9 million year
Q. $361250 \mathrm{~s}, 0.064 \mathrm{M}$
Q. 38 (a) -0.124 V , (b) 7.1 (c) calomel electrode
Q. $40-0.167 \mathrm{~V}$
Q. 423.29 cm
Q. $434.25 \times 10^{-2}$ meter
Q. $45 K_{\text {sp }}=7.682 \times 10^{-17}$

## Exercise 2

## Single Correct Choice Type

Q. 1 C
Q. 2 C
Q. 3 A
Q. 4 C
Q. 5 A
Q. 6 B

## Multiple Correct Choice Type

Q. 7 B, C
Q. 8 B, C, D
Q. 9 A, B
Q. 10 C, D
Q. 11 D, C

## Assertion Reasoning Type

Q. 12 A
Q. 13 D
Q. 14 A

Comprehension Type

| Paragraph -1 | Q. 15 B | Q.16 C | Q. 17 A |
| :--- | :--- | :--- | :--- |
| Paragraph -2 | Q. 18 B | Q.19 C |  |

Match the Columns
Q. $20 \mathrm{~A} \rightarrow \mathrm{p}, \mathrm{q} ; \mathrm{B} \rightarrow \mathrm{p}, \mathrm{q} ; \mathrm{C} \rightarrow \mathrm{q}, \mathrm{r} ; \mathrm{D} \rightarrow \mathrm{p}, \mathrm{s}$

## Previous Years' Questions

| Q. 1 C | Q. 2 B | Q. 3 B | Q. 4 B | Q. 5 D | Q. 6 D |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Q. 7 A, B, D | Q. 8 B | Q. 9 C | Q. 10 D | Q. 11 B | Q. 12 D |
| Q. 13 D | Q. 14 C | Q. 15 D | Q. 16 A | Q. 17 B | Q. 18 C |
| Q. 21 D | Q. 22 A |  |  |  |  |

## Solutions

## JEE Main/Boards

## Exercise 1

Sol 1: $\mathrm{Zn}_{(\mathrm{s})}\left|\mathrm{Zn}_{\text {(aq) }}^{2+}\right|\left|\mathrm{Ag}_{\text {(aq) }}^{+}\right| \mathrm{Ag}_{(\mathrm{s})}$
(i) Zinc electrode is negatively charged
(ii) At anode:
$\mathrm{Zn}(\mathrm{s}) \rightarrow \mathrm{Zn}_{(\mathrm{aq})}^{2+}+2 \mathrm{e}^{-}$
At cathode
$\mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{e}^{-} \rightarrow \mathrm{Ag}(\mathrm{s})$
Sol 2: $\wedge_{\mathrm{m}}=\frac{\mathrm{k} \times 1000}{\mathrm{M}}=\frac{2.48 \times 10^{-2} \times 1000}{0.2}$ $\wedge_{\mathrm{m}}=124 \Omega^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$

Sol 3: (i) Reaction:

$$
\begin{aligned}
& \mathrm{Mg}(\mathrm{~s})+\mathrm{Cu}^{2+}(\text { aq. }) \rightarrow \mathrm{Cu}(\mathrm{~s})+\mathrm{Mg}^{2+}(\text { aq. }) \\
& \text { 0. } 0001 \mathrm{M} \\
& \text { 0. } 001 \mathrm{M} \\
& \mathrm{E}=\mathrm{E}^{\circ}-\frac{2.303 \mathrm{RT}}{\mathrm{nF}} \log \left(\frac{\left[\mathrm{Cu}^{2+}\right]}{\left[\mathrm{Mg}^{2+}\right]}\right)^{-1} \\
& E=E^{\circ}-\frac{0.0591}{2} \log \frac{0.001}{0.0001} \\
& \mathrm{E}=\mathrm{E}^{\circ}-0.02955 \\
& \mathrm{E}=\mathrm{E}^{\circ}-0.03 \\
& =2.70-0.03 \\
& \text { = } 2.67 \mathrm{~V} \\
& \text { (ii) } \mathrm{Fe}+2 \mathrm{H}^{+} \rightarrow \mathrm{Fe}^{2+}+\mathrm{H}_{2} \\
& 10.001 \\
& \mathrm{n}=2 \\
& \mathrm{E}=\mathrm{E}^{\circ}-\frac{0.0591}{2} \log \frac{\left[\mathrm{Fe}^{2+}\right] \mathrm{P}_{\mathrm{H}_{2}}}{\left[\mathrm{H}^{+}\right]^{2}} \\
& E=E^{\circ}-0.03 \log \frac{0.001 \times 1}{1} \\
& E=E^{\circ}+0.09=0.44+0.09 \\
& \Rightarrow \mathrm{E}=0.53 \mathrm{~V}
\end{aligned}
$$

(iii) $\mathrm{Sn}+2 \mathrm{H}^{+} \rightarrow \mathrm{Sn}^{2+}+\mathrm{H}_{2}$
0.02
0. 05
$\mathrm{n}=2$
$E=E^{\circ}-\frac{-0.0591}{2} \log \frac{\left[\mathrm{Sn}^{2+}\right]}{\left[\mathrm{H}^{+}\right]^{2}} \cdot \mathrm{P}_{\mathrm{H}_{2}}$
$E=E^{\circ}-0.03 \log \frac{0.05}{0.04}$
$\mathrm{E}=\mathrm{E}^{\circ}-0.0029$
$\mathrm{E}=0.14-0.0029$
$\Rightarrow \mathrm{E}=0.1371 \mathrm{~V}$
(iv) $\mathrm{Br}_{2}+\mathrm{H}_{2} \rightarrow 2 \mathrm{Br}^{-}+2 \mathrm{H}^{+}$
$\mathrm{E}=\mathrm{E}^{\circ}-\frac{0.0591}{2} \log \left[\mathrm{H}^{+}\right]^{2}[\mathrm{Br}]^{2}$
$=E^{\circ}-0.02955 \log (0.01)^{2}(0.03)^{2}$
$E=E^{\circ}+0.208$
$E=1.09+0.208$
$\mathrm{E}=1.298 \mathrm{~V}$

Sol 4: The formula of standard cell potential is
$E_{\text {cell }}^{\circ}=E_{\text {right }}^{\circ}-E_{\text {left }}^{\circ}$
Use this link to get all values
$\mathrm{E}_{\text {cell }}^{\circ}=0.344-(-0.76)$
$\mathrm{E}_{\text {cell }}^{\circ}=0.344+0.076 \mathrm{~V}$
$\mathrm{E}_{\text {cell }}^{\circ}=+1.104 \mathrm{~V}$
In balanced reaction there are 2 electron are transferring so that $\mathrm{n}=2$

Faraday constant, $\mathrm{F}=96500 \mathrm{C} \mathrm{mol}^{-1}$
$\mathrm{E}_{\text {cell }}^{\circ}=+1.104 \mathrm{~V}$
Use formula
$\Delta_{\mathrm{r}} \mathrm{G}^{\circ}=-\mathrm{nFE} \mathrm{c}_{\text {cell }}^{\circ}$
Plug the value we get
Then, $=-2 \times 96500 \mathrm{C} \mathrm{mol}^{-1} \times 1.104 \mathrm{~V}$
$=-212304 \mathrm{CV} \mathrm{mol}^{-1}$
$=-212304 \mathrm{~mol}^{-1}$
$=-212.304 \mathrm{~kJ} \mathrm{~mol}^{-1}=-213.04 \mathrm{~kJ}$
Sol 5: $\wedge_{m}=k \times \frac{1000}{C}$
$\wedge_{m}=\frac{0.0248 \times 1000}{0.2}=124 \Omega^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$

Sol 6: (i) $\mathrm{Ca}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Ca}$
Charge needed $=2 \times n F=2 \times \frac{20}{40} \mathrm{~F}=1 \mathrm{~F}=96500 \mathrm{C}$
(ii) $\mathrm{Al}^{3+}+3 \mathrm{e}^{-} \rightarrow \mathrm{Al}$

Charge needed $=\left(3 n_{A l}\right) \times 96500 C$
$=3 \times \frac{40}{27} \times 96500 \mathrm{C}=4.28 \times 10^{5} \mathrm{C}$

Sol 7: (i) $\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{O}_{2}$
We have, $\mathrm{H}_{2} \mathrm{O} \rightarrow \frac{1}{2} \mathrm{O}_{2}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-}$
Charge required $=2 \mathrm{~F}=1.93 \times 10^{5} \mathrm{C}$
(ii) $\mathrm{Fe}_{2} \mathrm{O}+\frac{1}{2} \mathrm{H}_{2} \mathrm{O} \rightarrow \frac{1}{2} \mathrm{Fe}_{2} \mathrm{O}_{3}+\mathrm{H}^{+}+\mathrm{e}^{-}$

Charge needed for 1 mole $\mathrm{FeO}=1 \mathrm{~F}=96500 \mathrm{C}$

Sol 8: $\mathrm{k}=0.146 \times 10^{-3} \mathrm{~s} \mathrm{~cm}^{-1}$
$R=1500 \Omega$
$G^{*}=R k=0.219 \mathrm{~cm}^{-1}$
Sol 9: $\wedge_{m}=1000 \times \frac{\mathrm{k}}{\mathrm{C}}=\frac{1000 \times 7.896 \times 10^{-5}}{0.00241}$
$\wedge_{m}=32.765 \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$
$\mathrm{q}=\frac{\wedge_{\mathrm{m}}}{\wedge^{{ }^{\circ}}{ }_{\mathrm{m}}}=\frac{32.76}{390.5}$
$\alpha=0.084$
$k_{a}=\frac{C \alpha^{2}}{1-\alpha} ; k_{a}=2.2 \times 10^{-4}$

Sol 10: $\mathrm{Ni}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Ni}$
Charge supplied $=5 \times 20 \times 60 \mathrm{C}=6000 \mathrm{C}$
Moles of Ni deposited $=\frac{6000}{96500}$
Mass of Ni deposited $=\frac{6000}{96500} \times 59=3.66 \mathrm{gm}$

Sol 11: We use the formula
$\wedge_{m}=\frac{\mathrm{k} \times 1000}{\mathrm{C}}$

| C/M | 0.001 | 0.010 | 0.02 | 0.05 | 0. 100 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $10^{2} \times \mathrm{k} / \mathrm{sm}^{-1}$ | 12.37 | 11.85 | 23.15 | 55. 53 | 106.74 |
| $\begin{aligned} & \wedge_{\mathrm{m}}^{0} \\ & \mathrm{~S} \mathrm{~cm}^{2} / \mathrm{mol} \end{aligned}$ | 12.37 | 11.85 | 11.575 | 11.106 | 10.674 |
| $\sqrt{C}$ | 0.03 | 0. 1 | 0. 14 | 0. 22 | 0. 31 |

$\wedge_{\mathrm{m}}$ vs C


We have
$\wedge_{m}=\wedge^{0}{ }_{m}-A \sqrt{C}$
At $C=0.01$,
$\wedge_{m}=11.85=\wedge^{o_{m}} . A \times 0.1$
At $C=0.02$
$\wedge_{m}=11.575=\wedge^{\circ}{ }_{m} . A \times 0.14$
Subtracting
$0.01 \mathrm{~A}=0.275$
$A=6.875$
$\wedge^{\circ}{ }_{m}=12.5375 \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$
(putting A in (i))

Sol 12: $\mathrm{Ag}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}$
$\mathrm{n}_{\mathrm{Ag}}=\frac{1.45}{108}=0.0134$
Charge, $\mathrm{Q}=\mathrm{n}_{\mathrm{Ag}} . \mathrm{F}=0.0134 \times 96500 \mathrm{C}$
$Q=1295.6 C$
$\mathrm{t}=\frac{\mathrm{Q}}{\mathrm{I}}=\frac{1295.6}{1.5}$
$\mathrm{t}=863.735 \mathrm{~s}$
$\mathrm{Zn}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Zn}$

Moles of $\mathrm{Zn}, \mathrm{n}_{\mathrm{Zn}}=\frac{\mathrm{Q}}{2 \mathrm{~F}}=\frac{\mathrm{n}_{\mathrm{Ag}}}{2}$
Wt. of $\mathrm{Zn}=\mathrm{n}_{\mathrm{Zn}} \times 65=\frac{\mathrm{w}_{\mathrm{Ag}}}{\mathrm{m}_{\mathrm{Ag}}} \times \frac{1}{2} \times 65$
Wt . of $\mathrm{Zn}=0.43 \mathrm{gm}$
For Cu,
$\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}$
$\mathrm{n}_{\mathrm{Cu}}=\frac{\mathrm{Q}}{2 \mathrm{~F}}=\mathrm{n}_{\mathrm{zn}}$
Wt. of copper $=\mathrm{n}_{\mathrm{Cu}} \times 63.5=0.426 \mathrm{gm}$
Sol 13: (i) $\mathrm{Fe}_{\text {(aq) }}^{3+}+\mathrm{I}_{\text {(aq) }}^{-} \rightarrow \mathrm{Fe}_{\text {(aq) }}^{2+}+\frac{1}{2} \mathrm{I}_{2}(\mathrm{~g})$ $\mathrm{E}^{\circ}=\mathrm{E}_{\mathrm{I}^{-} / \mathrm{I}_{2}}^{\circ}+\mathrm{E}_{\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}}^{\circ}=-0.54+0.77=+0.23>0$ This is feasible.
(ii) $\mathrm{Ag}_{(\mathrm{aq})}^{+}+\mathrm{Cu}_{(\mathrm{s})} \rightarrow \mathrm{Ag}_{(\mathrm{s})}+\mathrm{Cu}_{(\mathrm{aq})}^{+}$
$\mathrm{E}^{\circ}=\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}^{\circ}+\mathrm{E}_{\mathrm{Cu} / \mathrm{Cu}^{+}}^{\circ}=0.8-0.52=0.2870$
This is feasible.
(iii) $\mathrm{Fe}_{(\mathrm{aq})}^{3+}+\mathrm{Br}_{(\mathrm{aq})}^{-} \rightarrow \frac{1}{2} \mathrm{Br}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{Fe}^{2+}(\mathrm{g})$
$\mathrm{E}^{\circ}=\mathrm{E}_{\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}}^{\circ}-\mathrm{E}_{\mathrm{Br}_{2} / \mathrm{Br}^{-}}^{\circ}=0.77-(1.09)=-0.32<0$
So, this is not feasible
If $\mathrm{Fe}^{3+} \rightarrow \mathrm{Fe}$, then, $\mathrm{E}_{\mathrm{Fe}^{3+} / \mathrm{Fe}}=-0.036$
and $E^{\circ}=-1.126$, still not feasible.
(iv) $\mathrm{Ag}(\mathrm{s})+\mathrm{Fe}^{3+}(\mathrm{aq}) \rightarrow \mathrm{Fe}^{2+}(\mathrm{aq})+\mathrm{Ag}^{+}(\mathrm{aq})$
$\mathrm{E}^{\circ}=\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}^{+}}^{\circ}+\mathrm{E}_{\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}}^{\circ}=-0.8+0.77=-0.03<0$
So, this is not feasible

$E^{\circ}=-0.836$, still not feasible.
(v) $\mathrm{Br}_{2}(\mathrm{aq})+\mathrm{Fe}^{2+}(\mathrm{aq}) \rightarrow \frac{1}{2} \mathrm{Br}(\mathrm{aq})+\mathrm{Fe}^{3+}(\mathrm{aq})$
$\mathrm{E}^{\circ}=\mathrm{E}_{\mathrm{Br}_{2} / \mathrm{Br}^{+}}^{\circ}+\mathrm{E}_{\mathrm{Fe}^{2+} / \mathrm{Fe}^{3+}}^{\circ}=1.09-0.77=0.32>0$
This reaction is feasible.

Sol 14: $\mathrm{Cu}^{2+}+\mathrm{e} \rightarrow \mathrm{Cu}^{+}$
$\mathrm{E}^{\circ}=+0.18 \mathrm{~V}, \mathrm{n}=1$
$\Delta E_{1}=-n F E^{\circ}=-0.18 \mathrm{~F}$
$\mathrm{Cu}^{+}+\mathrm{e} \rightarrow \mathrm{Cu}$,
$\mathrm{E}^{\circ}=0.50 \mathrm{~V}, \mathrm{n}=1$
$\Delta G_{2}=-n F E^{\circ}=-0.5 \mathrm{~F}$
Adding
$\mathrm{Cu}^{2+}+2 \mathrm{e} \rightarrow \mathrm{Cu}$,
$\Delta G=\Delta G_{1}+\Delta G_{2^{\prime}} n=2$
$-2 F E^{\circ}=-0.18 F-0.5 F$
$\mathrm{E}^{\circ}=0.34 \mathrm{~V}$

Sol 15: Element with maximum oxidation potential will have highest reduction potential.
Now, $\mathrm{E}_{\mathrm{Zn} / \mathrm{Zn}^{2+}}=0.76 \mathrm{~V}$,
$\mathrm{E}_{\mathrm{Pb} / \mathrm{Pb}^{2+}}^{0}=0.13 \mathrm{~V}$
$\mathrm{E}_{{\mathrm{Al} / \mathrm{Al}^{2+}}_{\circ}=1.66 \mathrm{~V} .}$
$\therefore$ Reducing order: $\mathrm{Pb}<\mathrm{Zn}<\mathrm{Al}$

Sol 16: (i) Since $\mathrm{O}_{3}$ has the highest SRP, it is the strongest oxidising agent.
(ii) As Ag cannot get reduced, $\mathrm{O}_{3}$ is still the strongest oxidised agent.
(iii) Ag is the strongest reducing agent as it has the least negative oxidation potential.
(iv) Ag is still the strongest reducing agent.

Sol 17: $\mathrm{IO}_{3}{ }^{-}$will act as better oxidising agent in acidic medium due to its larger SRP in acidic medium then basic medium.

Sol 18: $\mathrm{Fe}^{3+}+\mathrm{Br}^{-} \rightarrow \frac{1}{2} \mathrm{Br}_{2}+\mathrm{Fe}^{2+}$
$\mathrm{E}^{\circ}=\mathrm{E}_{\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}}^{0}+\mathrm{E}_{\mathrm{Br}^{-} / \mathrm{Br}_{2}}^{0}$
$=0.77-1.09=-0.32<0$
$\therefore \mathrm{Fe}^{3+}$ cannot oxidise $\mathrm{Br}^{-}$to $\mathrm{Br}_{2}$.

Sol 19: (i) $\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}$
$E=E^{\circ}-\frac{0.0591}{2} \log \frac{1}{\left[\mathrm{Cu}^{2+}\right]}=0.34-0.0295 \log \frac{1}{0.001}$ $\mathrm{E}=0.2515 \mathrm{~V}$
(ii) $\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+}+2 \mathrm{e}^{-}$
0.02
$\mathrm{E}_{\mathrm{Zn} / \mathrm{Zn}^{2+}}^{\circ}=-\mathrm{E}_{\mathrm{Zn} / \mathrm{Zn}^{2+}}^{\circ}=0.76$
$E=E^{\circ}-\frac{0.0591}{2} \log \left[Z n^{2+}\right]=0.76-0.0295 \log (0.02)$
$\mathrm{E}=0.8101 \mathrm{~V}$
(iii) $\mathrm{AgCl}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}+\mathrm{Cl}^{-}$
$\mathrm{Ag}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}, \mathrm{E}_{1}^{\circ}=0.8, \mathrm{n}=1$
$\Delta G_{1}=-n F E_{1}^{\circ}$
$\Delta G_{1}=-0.8 \mathrm{~F}$
$\mathrm{AgCl} \rightleftharpoons \mathrm{Ag}^{+}+\mathrm{Cl}^{-}$,
$\mathrm{K}_{\mathrm{s}_{1}}=2 \times 10^{-10}$
$\Delta G_{2}=-R T \ln K_{s p}$
Adding
$\mathrm{AgCl}+\mathrm{e} \rightarrow \mathrm{Ag}+\mathrm{Cl}^{-}$
$\Delta G=\Delta G_{1}+\Delta G_{2^{\prime}} n=1$
$-F E^{\circ}=-0.8 F-2.303 R T \log \left(2 \times 10^{-10}\right)$
$\mathrm{E}^{\circ}=0.8+\frac{2.303 R T}{F} \log \left(2 \times 10^{-10}\right)$
$E^{\circ}=0.8-0.57$
$E^{\circ}=0.226 \mathrm{~V}$
(iv) $\frac{1}{2} \mathrm{Cl}_{2}+\mathrm{e}^{-} \rightarrow \mathrm{Cl}^{-}$
$\mathrm{E}_{\mathrm{Cl}_{2} / \mathrm{Cl}^{-}}^{\circ}=1.36 \mathrm{~V}$
$E=E^{\circ}-0.0591 \log \frac{\left[\mathrm{Cl}^{-}\right]}{\left(\mathrm{P}_{\mathrm{Cl}_{2}}\right)^{1 / 2}}$
$=1.36-0.0591 \log \frac{0.02}{(0.5)^{1 / 2}}=1.36-0.0591(-1.548)$
$\mathrm{E}=1.451 \mathrm{~V}$
(v) $\mathrm{H}^{+}+\mathrm{e}^{-} \rightarrow \frac{1}{2} \mathrm{H}_{2}$
$E^{\circ}=0$
$\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]$
$\left[\mathrm{H}^{+}\right]=10^{-4.4}$
$\mathrm{E}=0.0591 \log \frac{\mathrm{P}_{\mathrm{H} 2}^{1 / 2}}{\left[\mathrm{H}^{+}\right]}=-0.0591\left(\log \sqrt{2}-\log \left[\mathrm{H}^{+}\right]\right)$
$=-0.0591(0.15+4.4)$
$E=-0.268 \mathrm{~V}$

Sol 20: $\mathrm{Fe}^{3+}+\mathrm{e}^{-} \rightarrow \mathrm{Fe}^{2+}$
$\mathrm{E}_{\mathrm{Fe}^{3+} / \mathrm{Fe}^{2+}}^{0}=0.77 \mathrm{~V}$
$\mathrm{E}=\mathrm{E}^{\circ}-0.0591 \log \frac{\left[\mathrm{Fe}^{2+}\right]}{\left[\mathrm{Fe}^{3+}\right]}$
$E=0.77-0.0591 \log 5$
$\left(\because\left[\mathrm{Fe}^{2+}\right]=5 \times\left[\mathrm{Fe}^{3+}\right]\right)$
$\mathrm{E}=0.7287 \mathrm{~V}$

Sol 21: $\mathrm{CH}_{3} \mathrm{COOH} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}^{+}$
$\mathrm{k}_{\mathrm{a}}=\frac{\mathrm{C} \alpha^{2}}{1-\alpha}=\mathrm{Ca}^{2}$
$\alpha=\sqrt{\frac{\mathrm{k}_{\mathrm{a}}}{\mathrm{C}}}$
$\left[\mathrm{H}^{+}\right]=\mathrm{C} \alpha=\sqrt{\mathrm{Ck}_{\mathrm{a}}}$
$\left[\mathrm{H}^{+}\right]=\sqrt{0.357 \times 1.74 \times 10^{-5}}$
$\left[\mathrm{H}^{+}\right]=2.492 \times 10^{-3}$
$\frac{1}{2} \mathrm{H}_{2} \rightarrow \mathrm{H}^{+}+\mathrm{e}$
$\mathrm{E}^{\circ}=0$
$E=-0.0591 \log \left[H^{+}\right]=-0.0295 \log \left(2.492 \times 10^{-3}\right)$
$\mathrm{E}=0.1536 \mathrm{~V}$

Sol 22: $\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]$
$13=-\log \left[\mathrm{H}^{+}\right] \Rightarrow\left[\mathrm{H}^{+}\right]=10^{-13}$
$\left[\mathrm{OH}^{-}\right]=\frac{\mathrm{k}_{\mathrm{w}}}{\left[\mathrm{H}^{+}\right]}=\frac{10^{-14}}{10^{-13}}=\frac{1}{10}$
$\mathrm{Cu}(\mathrm{OH})_{2} \rightleftharpoons \mathrm{Cu}^{2+}+2 \mathrm{OH}^{-}$
$K_{\text {sp }}=\left[\mathrm{Cu}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2}$
$\left[\mathrm{Cu}^{2+}\right]=\frac{\mathrm{K}_{\mathrm{sp}}}{\left[\mathrm{OH}^{-}\right]^{2}}=\frac{1 \times 10^{-19}}{10^{-2}}$
$\left[\mathrm{Cu}^{2+}\right]=10^{-17} \mathrm{M}$
$\mathrm{Cu}^{2+}+2 \mathrm{e} \rightarrow \mathrm{Cu}$
$\mathrm{E}^{\circ}=0.34 \mathrm{~V}, \mathrm{n}=2$
$E=E^{\circ}-\frac{0.0591}{2} \log \frac{1}{\left[\mathrm{Cu}^{2+}\right]}$
$=0.34-0.0591 \log \frac{1}{10^{-17}}=0.34-0.5015$
$E=-0.1615 \mathrm{~V}$

Sol 23: (i) $\mathrm{Ag}^{+}+\mathrm{e} \rightarrow \mathrm{Ag} ; \mathrm{E}_{1}^{\circ}=0.80 \mathrm{~V}, \mathrm{n}=1$
$\Delta G_{1}=-n F^{\circ}{ }_{1}=-0.8 \mathrm{~F}$
$\mathrm{AgCl} \rightarrow \mathrm{Ag}^{+}+\mathrm{Cl}^{-}$
$\Delta G_{2}=-R T \ln k_{\mathrm{sp}}=-2.303 R T \log \left(2 \times 10^{-10}\right)$
Adding,
$\mathrm{AgCl}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}+\mathrm{Cl}^{-}$
$\Delta G=-n F E^{\circ}=\Delta G_{1}+\Delta G_{2^{\prime}} n=1$
$-F E^{\circ}=-0.8 F-2.303 R T \log \left(2 \times 10^{-10}\right)$
$E^{\circ}=0.8+\frac{2.303 R T}{F} \log \left(2 \times 10^{-10}\right)$
$\mathrm{E}^{\circ}=0.22 \mathrm{~V}$
(ii) $E=E^{\circ}-0.0591 \log \left[C l^{-}\right]=0.22-0.0591 \log \left(4 \times 10^{-3}\right)$
$\mathrm{E}=0.36 \mathrm{~V}$
Sol 24: $\mathrm{Ni}(\mathrm{s})+2 \mathrm{Ag}^{+}(0.002 \mathrm{M})$
$\rightarrow \mathrm{Ni}^{2+}(0.160 \mathrm{M})+2 \mathrm{Ag}(\mathrm{s})$
$\mathrm{n}=2$
$\therefore \mathrm{E}=\mathrm{E}_{1}^{\circ}-\frac{0.0591}{2} \log \frac{\left[\mathrm{Ni}^{2+}\right]}{\left[\mathrm{Ag}^{+}\right]^{2}}$
$=1.05-0.0295 \log \frac{0.16}{\left(2 \times 10^{-3}\right)^{2}}=1.05-0.135$
$\mathrm{E}=0.91 \mathrm{~V}$
Sol $25 \mathrm{HCOOH} \rightleftharpoons \mathrm{H}^{+}+\mathrm{HCOO}^{-}$
$\wedge_{\mathrm{m}}^{0}(\mathrm{HCOOH})=\wedge_{\mathrm{m}}^{0}\left(\mathrm{HCOO}^{-}\right)+\wedge_{\mathrm{m}}^{0}\left(\mathrm{H}^{+}\right)$
$=349.6+54.6$
$\wedge_{\mathrm{m}}^{0}=404.2 \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$
$\alpha=\frac{\wedge_{\mathrm{m}}}{\wedge_{\mathrm{m}}^{0}}=\frac{46.1}{404.2}$
$\alpha=0.114$
$k_{a}=\frac{C \alpha^{2}}{1-\alpha}=\frac{0.025(0.114)^{2}}{1-0.114}$
$k_{\mathrm{a}}=3.67 \times 10^{-4}$
Sol 26: (i) Potassium
(ii) Sodium
(iii) Calcium
(iv) Magnesium
(v) Aluminium

Sol 27: $\mathrm{Mg}(\mathrm{s})\left|\mathrm{Mg}^{2+}(\mathrm{aq})\right|\left|\mathrm{Ag}^{+}(\mathrm{aq})\right| \mathrm{Ag}(\mathrm{s})$
$\mathrm{Mg}(\mathrm{s})+2 \mathrm{Ag}^{+} \rightarrow \mathrm{Mg}^{2+}+2 \mathrm{Ag}$
$\mathrm{n}=2, \mathrm{E}^{\circ}=3.17 \mathrm{~V}$
$E=E^{\circ}-\frac{0.0591}{2} \log \frac{\left[\mathrm{Mg}^{2+}\right]}{\left[\mathrm{Ag}^{+}\right]^{2}}$
$=3.17-0.0295 \log \frac{(0.13)}{\left(10^{-4}\right)^{2}}=3.17-0.209$
$\mathrm{E}=2.96 \mathrm{~V}$
Sol 28: (a) $\mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow 2 \mathrm{H}^{+}+\mathrm{SO}_{4}{ }^{2-}$
$\left[\mathrm{H}^{+}\right]=2\left[\mathrm{H}_{2} \mathrm{SO}_{4}\right]=0.02 \mathrm{M}$
$\frac{1}{2} \mathrm{H}_{2} \rightarrow \mathrm{H}^{+}+\mathrm{e}^{-}$
$\mathrm{E}^{\circ}=0, \mathrm{n}=1$
$E=E^{\circ}-0.0591 \log \frac{\left[H^{+}\right]}{P_{H_{2}}{ }^{1 / 2}}=-0.0591 \log \frac{0.02}{\sqrt{4}}$
$E=-0.0591 \log (0.01)$
$\mathrm{E}=+0.1182, \mathrm{E}_{\mathrm{r}}=-0.1182$
(b) $\mathrm{HCl} \rightarrow \mathrm{H}^{+}+\mathrm{Cl}^{-}$
$\left[\mathrm{H}^{+}\right]=[\mathrm{HCl}]=0.2$
$\frac{1}{2} \mathrm{H}_{2} \rightarrow \mathrm{H}^{+}+\mathrm{e}^{-}$
$\mathrm{E}^{\circ}=0, \mathrm{n}=1$
$E=E^{\circ}-\frac{0.0591}{1} \log \frac{\left[H^{+}\right]}{P_{H_{2}}{ }^{1 / 2}}=0-0.0591 \log \frac{0.2}{1}$
$\mathrm{E}=0.0413 \mathrm{~V}, \mathrm{E}_{\mathrm{r}}=-0.0413 \mathrm{~V}$
(c) $\mathrm{E}=0, \mathrm{n}=1$
$\mathrm{E}^{\circ}=\frac{-0.0591}{1} \log \left[\mathrm{H}^{+}\right]=0.0591 \mathrm{p}[\mathrm{H}]$
(i) $\mathrm{pH}=5$
$\mathrm{E}=0.0591 \times 5=0.2955 \mathrm{~V}$
$\mathrm{E}_{\mathrm{r}}=-0.2955 \mathrm{~V}$
(ii) $\mathrm{pOH}=4$
$\mathrm{pH}=14-\mathrm{pOH}=10$
$\mathrm{E}=0.0591 \times 10=0.591 \mathrm{~V}$
$E_{r}=-E=-0.0591 \mathrm{~V}$
Sol 29: n for $\mathrm{H}_{2} \mathrm{SO}_{4}=2$
Normality $=$ Molarity $\times \mathrm{n}=2 \mathrm{M}$
$\wedge_{e}=\frac{k \times 1000}{N}=\frac{26 \times 1000 \times 10^{-2}}{2}=130 \mathrm{Scm}^{2}$ equiv $^{-1}$

## Exercise 2

## Single Correct Choice Type

Sol 1: (C) $M^{+2}+2 e \rightarrow M$
For one mole, charge required $=2 \mathrm{~F}$
If atomic weight is M .
Then, for M gm, 2F charge
For 1 gm , charge $=\frac{2 F}{M}=1.81 \times 10^{22} \times 1.6 \times 10^{-19}$
$\Rightarrow \mathrm{M}=66.7 \mathrm{gm}$

Sol 2: (B) Moles of $\mathrm{Ag}=1$
Moles of $\mathrm{Cu}=\frac{1}{2}$
Moles of $\mathrm{Al}=\frac{1}{3}$
1: $\frac{1}{2}: \frac{1}{3}=6: 3: 2$
Sol 3: (B) Moles of $A=\frac{2.1}{7}$
Molar ratio $=\frac{2.1}{7}: \frac{2.7}{27}: \frac{7.2}{78}=0.3: 0.1: 0.15$
= $3: 1: 1.5$
= 6: $2: 3$
$=1: \frac{1}{3}: \frac{1}{2}$
$\therefore$ Valency $=1,3$ and 2

Sol 4: (B) Volume of plate $=10 \times 10 \times 10^{-2} \mathrm{~cm}^{3}=1 \mathrm{~cm}^{3}$
Mass $=8.94 \mathrm{~g}$
Moles $=\frac{8.94}{63.5}$
Quantity of electricity $=\frac{8.94}{63.5} \times 2 \mathrm{~F}=27172 \mathrm{C}$
Sol 5: (D) $\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{2}+\frac{1}{2} \mathrm{O}_{2}$
$2 \mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{H}_{2}+\mathrm{O}_{2}$
Only water will be oxidised and reduced.
$\mathrm{V}_{\mathrm{H}_{2}}=2 \times \mathrm{V}_{\mathrm{O}_{2}}=4.8 \mathrm{~L}$
Sol 6: (D) At cathode, water will be reduced,
$2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2}+2 \mathrm{OH}^{-}(\mathrm{aq})$
pH of the solution around cathode will decrease.

Sol 7: (B) This is a convention.
Sol 8: (A) $\mathrm{H}^{+}+\mathrm{e}^{-} \rightarrow \frac{1}{2} \mathrm{H}_{2}$
$\mathrm{E}^{\circ}=0$
$E=\frac{-0.0591}{1} \log \frac{\left(\mathrm{P}_{\mathrm{H}_{2}}\right)^{1 / 2}}{\left[\mathrm{H}^{+}\right]}=-0.0591 \log 10=-0.0591 \mathrm{~V}$
$\Delta \mathrm{E}=0.0591 \mathrm{~V}$

Sol 9: (A) We have,
$E^{\circ}=\frac{0.0591}{2} \log k_{c}$
$E^{\circ}=\frac{0.0591}{2} \log \left(2.69 \times 10^{12}\right)=0.3667 \mathrm{~V}$

Sol 10: (B) $\mathrm{Ag}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}$
$E=E^{\circ}-0.0591 \log \frac{1}{\left[\mathrm{Ag}^{+}\right]}$
$0.25=0.799+0.059 \log \left[\mathrm{Ag}^{+}\right]$
$\left[\mathrm{Ag}^{+}\right]=5.13 \times 10^{-10}$
$k_{\text {sp }}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{Cl}^{-}\right]=5.1 \times 10^{-11}$
Sol 11: (B) At cathode
$\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}$
At anode
$2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{O}_{2}+4 \mathrm{H}^{+}+4 \mathrm{e}^{-}$
Moles $\mathrm{n}_{\mathrm{O}_{2}}=\frac{1}{2} \mathrm{nC}_{2}$
$\mathrm{V}_{\mathrm{O}_{2}}=22400 \mathrm{n}_{\mathrm{O}_{2}}=22400 \times \frac{1}{2} \times \frac{2.5}{63.5}=441 \mathrm{~mL}$
$\approx 445 \mathrm{~mL} \mathrm{O}_{2}$ is liberated
Sol 12: (B) $\mathrm{P}=\mathrm{VI}$
$P=1.65 \mathrm{~kW}$
$q=1.65 \times 8 \mathrm{kWh}=13.2 \mathrm{kWh}$
Cost $=13.2 \times 5$ paise $=66$ paise

Sol 13: (C) $\wedge_{m}=\frac{1}{R} \cdot \frac{\ell}{a} \cdot \frac{1000}{C}$
$=\frac{1}{50} \cdot \frac{2.2}{4.4 \times 10^{-2}} \times \frac{1}{0.5}=0.002 \mathrm{Sm}^{2} \mathrm{~mol}^{-1}$
Sol 14: (C) $\alpha=\frac{\wedge_{\mathrm{m}}}{\wedge_{\mathrm{m}}^{0}}=\frac{10}{200}=0.05$
$\left[\mathrm{H}^{+}\right]=\mathrm{C} \alpha=0.005$
$\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=\log [200]=2.3$

Sol 15: (C) $\wedge_{m}=k \times \frac{1000}{C}=\frac{1000}{x y}\left(k=\frac{1}{x}, C=y\right)$

Sol 16: (B) $\alpha=\sqrt{\frac{\mathrm{k}_{\mathrm{a}}}{\mathrm{C}}}=\sqrt{\frac{1.6 \times 10^{-5}}{0.01}}=0.04$
$\alpha=\frac{\wedge_{\mathrm{m}}}{\wedge_{\mathrm{m}}^{0}}$
$\Rightarrow \wedge_{\mathrm{m}}=380 \times 10^{-4} \times 0.04=1.52 \times 10^{-3}$
$\wedge_{m}=\frac{1000 \times \mathrm{k}}{\mathrm{C} \times 1000}$
$\mathrm{k}=1.52 \times 10^{-2} \mathrm{~S} \mathrm{~m}^{-1}$

Sol 17: (A) $\mathrm{Au}^{+}+2 \mathrm{CN}^{-}=\mathrm{Au}(\mathrm{CN})_{2}{ }^{-}$
$\Delta G_{1}=-R T \ln X$
$\mathrm{Au}^{3+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Au}^{+}$
$\Delta G_{2}=-n F E^{\circ}=-2.8 F$
$\mathrm{Au} \rightarrow \mathrm{Au}^{3+}+3 \mathrm{e}^{-}$
$\Delta G_{3}=-n F\left(-E^{\circ}\right)=4.5 F$
$\frac{1}{4} \mathrm{O}_{2}+\frac{1}{2} \mathrm{H}_{2} \mathrm{O}+\mathrm{e}^{-} \rightarrow \mathrm{OH}^{-}$
$\Delta G_{4}=-1 F\left(E^{\circ}\right)=-0.41 F$
Summing, $\Delta G=\sum_{i=1}^{4} \Delta G_{1}=-R T \ln X+1.29 F$
Sol 18: (C) At anode
$\frac{1}{2} \mathrm{H}_{2} \rightarrow \mathrm{H}^{+}+\mathrm{e}^{-}$
At cathode
$\frac{1}{2} \mathrm{Cl}_{2}+\mathrm{e}^{-} \rightarrow \mathrm{Cl}^{-}$
$\frac{1}{2} \mathrm{H}_{2}+\frac{1}{2} \mathrm{Cl}_{2} \rightarrow \mathrm{H}^{+}+\mathrm{Cl}^{-}$
$E=E^{\circ}-0.0591 \log \frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{Cl}^{-}\right]}{\mathrm{P}_{\mathrm{H}_{2}}{ }^{1 / 2} \cdot \mathrm{P}_{\mathrm{Cl}_{2}}{ }^{1 / 2}}$
$\mathrm{E}_{1}-\mathrm{E}_{2}=0.0591 \log \frac{\left[\mathrm{H}^{+}\right]_{2}\left[\mathrm{Cl}^{-}\right]_{2}}{\left[\mathrm{H}^{+}\right]_{1}\left[\mathrm{Cl}^{-}\right]_{1}}=0.0591 \times 2=0.1182$
$\therefore \mathrm{E}_{2}-\mathrm{E}_{1}=-0.1182$

Sol 19: (C) At cathode,
$\mathrm{H}^{+}+\mathrm{e}^{-} \rightarrow \frac{1}{2} \mathrm{H}_{2}$
At anode
$\frac{1}{2} \mathrm{H}_{2} \rightarrow \mathrm{H}^{+}+\mathrm{e}^{-}$
$\frac{1}{2} \mathrm{H}_{2}+\mathrm{H}^{+} \rightarrow \frac{1}{2} \mathrm{H}_{2}+\mathrm{H}^{+}$
0. $410^{-20 .} \rightarrow 10^{-1}$
$E=-0.0591 \log \frac{10^{-1} \cdot(0.1)^{1 / 2}}{10^{-2} \cdot(0.4)^{1 / 2}}$
$\mathrm{E}=-0.041 \mathrm{~V}$

Sol 20: (D) $\mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{+}(\mathrm{aq})+4 \mathrm{e}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}(\ell)$
$E^{\circ}=1.23 \mathrm{~V}$
$\Delta G^{\circ}=-n F E=-474.78 \mathrm{~kJ}$
$\Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{O}_{2}\right)=0$
$\Delta \mathrm{H}_{\mathrm{r}}=2 \Delta \mathrm{H}_{\mathrm{f}}\left(\mathrm{H}_{2} \mathrm{O}, \ell\right)=-2 \times 285.5 \mathrm{~kJ}=-571 \mathrm{~kJ}$
$\Delta \mathrm{G}=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S}$
$\Delta S=\frac{\Delta H-\Delta G}{T}=-0.322 \mathrm{~kJ} / \mathrm{k}$

Sol 21: (C) $\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu} ; \mathrm{E}^{\circ}=0.337$
$\Delta \mathrm{G}_{1}^{\circ}=-\mathrm{nFE} E^{\circ}=-0.674 \mathrm{~F}$
$\mathrm{Cu}^{2+}+\mathrm{eCu}^{+} ; \mathrm{E}^{\circ}=0.153$
$\mathrm{Cu}^{+} \rightarrow \mathrm{Cu}^{2+}+\mathrm{e}^{-} ; \mathrm{E}^{\circ}=-0.153$
$\Delta \mathrm{G}_{2}^{\circ}=-\mathrm{nFE}{ }^{\circ}=+0.153 \mathrm{~F}$
Adding,
$\mathrm{Cu}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Cu}$
$\Delta G=\Delta G_{1}^{\circ}+\Delta G_{2}^{\circ}$
$-F E^{\circ}=-0.674 F+0.153 F$
$E^{\circ}=0.521 \mathrm{~V}$

## Previous Years' Questions

Sol 1: (D) Impure metal made anode while pure metal made cathode.

Sol 2: (D) In electrolytic cell, cathode acts as source of electrons.

Sol 3: (B) $\mathrm{Ag}^{+} \xrightarrow{+\mathrm{e}^{-}} \mathrm{Ag}, 96500 \mathrm{C}$ will liberate silver $=108 \mathrm{gm}$.
9650C will liberate silver $=10.8$

Sol 4: (C) Gold (Au) and Silver(Ag) are present in the anode mud.

Sol 5 (B) $C=\frac{K[A] A}{1}, K=\frac{C \times I}{[A] A}=\frac{S ~ m}{\mathrm{~mol} \mathrm{~m}^{-3} \mathrm{~m}^{2}}$ $=S \mathrm{~m}^{2} \mathrm{~mol}^{-1}$.

Sol 6: (D) 0.1 M difluoroacetic acid has highest electrical conductivity among the given solutions.

Sol 7: (A) From Kohlraush's law
$\Lambda_{\mathrm{CH}_{3} \mathrm{COOH}}^{\circ}=\Lambda_{\mathrm{CH}_{3} \mathrm{COONa}}^{\circ}+\Lambda_{\mathrm{HCl}}^{\circ}-\Lambda_{\mathrm{NaCl}}^{\circ}$
Hence, $(A)$ is the correct answer.

Sol 8: (D) According to Kohlrausch's law, the molar conductivity of an electrolyte at infinite dilution is the sum of conductivities of its ions. Therefore to obtain $\wedge_{\mathrm{HOAc}}^{\circ}$ from the conductivity of $\wedge_{\mathrm{NaOAc}}^{\circ} \& \wedge_{\mathrm{HCl}}^{\circ}$, the conductivity value of NaCl i.e. $\wedge_{\mathrm{NaCl}}^{\circ}$ is also needed.
$\Lambda_{\mathrm{NaOAc}}^{\circ}+\Lambda_{\mathrm{HCl}}^{\circ}-\Lambda_{\mathrm{NaCl}}^{\circ}=\Lambda_{\mathrm{HOAc}}^{\circ}$
i.e. $\Lambda_{\mathrm{Na}^{+}}^{\circ}+\Lambda_{\mathrm{OAc}^{-}}^{\circ}+\Lambda_{\mathrm{H}^{+}}^{\circ}+\Lambda_{\mathrm{Cl}^{-}}^{\circ}-\left(\Lambda_{\mathrm{Na}^{+}}^{\circ}+\Lambda_{\mathrm{Cl}^{-}}^{\circ}\right)$
$=\Lambda_{\mathrm{OAc}^{-}}^{\circ}+\Lambda_{\mathrm{H}^{+}}^{\circ}=\Lambda_{\mathrm{HOAc}}^{\circ}$

Sol 9: (A) Cell constant
$=\frac{\text { Conductivity(I) }}{\text { Conductance(I) }}=\frac{\text { Conductivity(II) }}{\text { Conductance(II) }}$
Conductivity $(I I)=\frac{129}{520} \mathrm{Sm}^{-1}$
$0.2 \mathrm{M}=200 \mathrm{~mol} \mathrm{~m}^{-3}$.
Molar conductivity of 0.2 M solution
$=\frac{129 / 520}{200}=12.4 \times 10^{-4} \mathrm{~S} \mathrm{~m}^{2} \mathrm{~mol}^{-1}$.
Note: From given data it is not possible to calculate molar conductivity of 0.02 M solution exactly. However, it is sure that its molar conductivity will be slightly greater than $12.4 \times 10^{-4} \mathrm{Sm}^{2} \mathrm{~mol}^{-1}$. Assuming linear inverse variation of molar conductivity with concentration we can say that
$\therefore$ Molar conductivity of 0.02 M solution
$=1.24 \times 10^{-3} \times 10$
$=124 \times 10^{-4} \mathrm{~S} \mathrm{~m}^{2} \mathrm{~mol}^{-1}$.

Sol 10: (C) Velocities of both $\mathrm{K}^{+}$and $\mathrm{NO}_{3}^{-}$are nearly the same in $\mathrm{KNO}_{3}$ so it is used to make salt-bridge.

Sol 11: (C) $2 \mathrm{H}_{(\mathrm{aq})}^{+}+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2(\mathrm{~g})}$
$E_{\text {red }}=E_{\text {red }}^{\circ}-\frac{0.0591}{n} \log \frac{P_{\left(H_{2}\right)}}{\left(H^{+}\right)^{2}}$
$E_{\text {red }}=0-\frac{0.0591}{2} \log \frac{2}{(1)^{2}}$
$E_{\text {red }}=\frac{0.0591}{2} \log 2$
$\therefore \mathrm{E}_{\text {red }}$ is found to be negative for (c) option

Sol 12: (C) $E_{\text {cell }}=E_{\text {cell }}^{\circ}-\frac{0.0591}{n} \log Q$
Where, $\mathrm{Q}=\frac{\left[\mathrm{Zn}^{2+}\right]}{\left[\mathrm{Cu}^{2+}\right]}$
For complete discharge, $\mathrm{E}_{\text {cell }}=0$
So, $\mathrm{E}_{\text {cell }}^{\circ}=\frac{0.0591}{2} \log \frac{\left[\mathrm{Zn}^{2+}\right]}{\left[\mathrm{Cu}^{2+}\right]}$
$\Rightarrow\left[\frac{\left[\mathrm{Zn}^{2+}\right]}{\left[\mathrm{Cu}^{2+}\right]}\right]=10^{37.3}$.

Sol 13: (D) For the cell reaction, Fe acts as cathode and Sn as anode. Hence,
$\mathrm{E}_{\text {cell }}^{\circ}=\mathrm{E}_{\text {cathode }}^{\circ}-\mathrm{E}_{\text {anode }}^{\circ}=-0.44-(-0.14)=-0.30 \mathrm{~V}$
The negative EMF suggests that the reaction goes spontaneously in reverse direction.

Sol 14: (C) $\mathrm{Fe}^{3+}+3 \mathrm{e}^{-} \rightarrow \mathrm{Fe}$;
$\Delta \mathrm{G}_{1}=-3 \times \mathrm{F} \times \mathrm{E}_{\mathrm{Fe}^{\circ} / \mathrm{Fe}}^{\circ}$
$\mathrm{Fe}^{+2}+2 \mathrm{e}^{-} \rightarrow \mathrm{Fe} ; \Delta \mathrm{G}_{2}=-2 \times \mathrm{F} \times \mathrm{E}_{\mathrm{Fe}^{2+} / \mathrm{Fe}}^{\circ}$
$\mathrm{Fe}^{3+}+\mathrm{e}^{-} \rightarrow \mathrm{Fe}^{2+} ; \Delta \mathrm{G}=\Delta \mathrm{G}_{1}-\Delta \mathrm{G}_{2}$
$\Delta G=3 \times 0.036 G-2 \times 0.439 \times F$
$=-1 \times \mathrm{E}_{\left(\mathrm{Fe}^{3+} / \mathrm{Fe}^{+2}\right)}^{\circ} \times \mathrm{F}$
$\mathrm{E}_{\left(\mathrm{Fe}^{3+} / \mathrm{Fe}^{+2}\right)}^{\circ}=2 \times 0.439-3 \times 0.036$

$$
=0.878-0.108=0.770 \mathrm{~V}
$$

Sol 15: (C) $E=E^{\circ}-\frac{0.059}{n} \log \frac{\left[\mathrm{Zn}^{++}\right]}{\left[\mathrm{Cu}^{++}\right]}$
$=1.10-\frac{0.059}{2} \log \frac{1}{0.1}$
$=1.10-0.0295 \log 10=1.07$ volt.

## Sol 16: (A)

As $\mathrm{E}_{\mathrm{Cr}^{3+} / \mathrm{Cr}}^{\circ}=-0.72 \mathrm{~V}$ and $\mathrm{E}_{\mathrm{Fe}^{2+} / \mathrm{Fe}}^{\circ}=-0.42 \mathrm{~V}$
$2 \mathrm{Cr}+3 \mathrm{Fe}^{2+} \longrightarrow 3 \mathrm{Fe}+2 \mathrm{Cr}^{3+}$
$\mathrm{E}_{\text {cell }}=\mathrm{E}_{\text {cell }}^{\circ}-\frac{0.0591}{6} \log \frac{\left(\mathrm{Cr}^{3+}\right)^{2}}{\left(\mathrm{Fe}^{2+}\right)^{3}}$
$=(-0.42+0.72)-\frac{0.0591}{6} \log \frac{(0.1)^{2}}{(0.01)^{3}}=0.30-\frac{0.0591}{6} \log \frac{(0.1)^{2}}{(0.01)^{3}}$
$=0.30-\frac{0.0591}{6} \log \frac{10^{-2}}{10^{-6}}=0.30-\frac{0.0591}{6} \log 10^{4}$
$E_{\text {cell }}=0.2606 \mathrm{~V}$

Sol 17: (D)
$\mathrm{CH}_{3} \mathrm{OH}(\ell)+\frac{3}{2} \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\ell)$
$\Delta \mathrm{H}=-726 \mathrm{~kJ} \mathrm{~mol}^{-1}$
Also $\Delta \mathrm{G}_{\mathrm{f}}^{\circ} \mathrm{CH}_{3} \mathrm{OH}(\ell)=-166.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$
$\Delta \mathrm{G}_{\mathrm{f}}^{\circ} \mathrm{H}_{3} \mathrm{O}(\ell)=-237.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$
$\Delta \mathrm{G}_{\mathrm{f}}^{\circ} \mathrm{CO}_{2}(\ell)=-394.4 \mathrm{~kJ} \mathrm{~mol}^{-1}$
$\because \Delta G=\Sigma \Delta \mathrm{G}_{\mathrm{f}}^{\circ}$ products $-\Sigma \Delta \mathrm{G}_{\mathrm{f}}^{\circ}$ reactants
$=-394.4-2(237.2)+166.2$
$=-702.6 \mathrm{~kJ} \mathrm{~mol}^{-1}$
now Efficiency of fuel cell $=\frac{\Delta G}{\Delta H} \times 100$
$=\frac{702.6}{726} \times 100=97 \%$

Sol 18: (C)
$\mathrm{Fe}^{3+}+3 \mathrm{e}^{-} \longrightarrow \mathrm{Fe} ; \mathrm{E}^{\circ}=-0.036 \mathrm{~V}$
$\therefore \Delta \mathrm{G}_{1}^{\circ}=-\mathrm{nFE}^{\circ}=-3 \mathrm{~F}(-0.036)=+0.108 \mathrm{~F}$
Also $\mathrm{Fe}^{2+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{Fe}(\mathrm{aq}) ; \mathrm{E}^{\circ}=-0.439 \mathrm{~V}$
$\therefore \Delta \mathrm{G}_{1}^{\circ}=-\mathrm{nFE}^{\circ}=-2 \mathrm{~F}(-0.439)=0.878 \mathrm{~F}$
To find $\mathrm{E}^{\circ}$ for $\mathrm{Fe}_{(\mathrm{aq})}^{3+}+\mathrm{e}^{-} \longrightarrow \mathrm{Fe}^{2+}(\mathrm{aq})$
$\Delta \mathrm{G}_{1}^{\circ}=-\mathrm{nFE}^{\circ}=-1 \mathrm{FE}^{\circ}$
$\because \mathrm{G}^{\circ}=\mathrm{G}_{1}^{\circ}-\mathrm{G}_{2}^{\circ}$
$\therefore G^{\circ}=0.108 F-0.878 F$
$\therefore-\mathrm{FE}^{\circ}=+0.108 \mathrm{~F}-0.878 \mathrm{~F}$
$\therefore \mathrm{E}^{\circ}=0.878-0.108=0.77 v$

Sol 19: (B) $2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{H}_{2}(\mathrm{~g})$
$E=E^{\circ}-0.059 \log \left(\frac{P_{H_{2}}}{\left[\mathrm{H}^{+}\right]^{2}}\right)$ (here E is - ve when $\mathrm{P}_{\mathrm{H}_{2}}>\left[\mathrm{H}^{+}\right]^{2}$ )
$=\frac{-0.0591}{2} \log _{10}\left(\frac{2}{1}\right)=\frac{-0.0591}{2} \times 0.3010=$ negative value

## Sol 20: (D)

$\mathrm{Zn}+\mathrm{Fe}^{+2} \longrightarrow \mathrm{Zn}^{+2}+\mathrm{Fe}$
$\mathrm{Fe}+\mathrm{Ni}^{+2} \longrightarrow \mathrm{Fe}^{2+}+\mathrm{Ni}$
$\mathrm{Zn}+\mathrm{Ni}^{2+} \longrightarrow \mathrm{Zn}^{+2}+\mathrm{Ni}$
All these are spontaneous

## Sol 21: (D)

Higher the SRP, better is oxidising agent.
Hence, $\mathrm{MnO}_{4}^{-}$is strongest oxidising agent.

Sol 22: (C)
According to Debye Huckle onsager equation,
$\lambda_{C}=\lambda_{\infty}+(A) \sqrt{C}$
Here $\mathrm{A}=\mathrm{B}$

$$
\therefore \lambda_{C}=\lambda_{\infty}+(B) \sqrt{C}
$$

## Sol 23: (A)

(1) $\mathrm{Mn}^{2+}+2 \mathrm{e}^{-} \longrightarrow \mathrm{Mn} ; \mathrm{E}^{\circ}=-1.18 \mathrm{~V}$;
$\Delta \mathrm{G}_{1}^{\circ}=-2 \mathrm{~F}(-1.18)=2.36 \mathrm{~F}$
(2) $\mathrm{Mn}^{3+}+\mathrm{e}^{-} \longrightarrow \mathrm{Mn}^{2+} ; \mathrm{E}^{\circ}=+1.51 \mathrm{~V}$;
$\Delta G_{1}^{\circ}=-F(-1.51)=-1.51 F$
(1) $-2 \times(2)$
$3 \mathrm{Mn}^{2+} \longrightarrow \mathrm{Mn}+2 \mathrm{Mn}^{3+}$;
$\Delta G_{3}^{\circ}=\Delta G_{1}^{\circ}-2 \Delta G_{2}^{\circ}$
$=[2.36-2(-1.51)] \mathrm{F}$
$=(2.36+3.02) \mathrm{F}$
$=5.38 \mathrm{~F}$
But $\Delta \mathrm{G}_{3}^{\circ}=12 \mathrm{FE}^{\circ}$
$\Rightarrow 5.38 \mathrm{~F}=-2 \mathrm{FE}^{\circ}$
$\Rightarrow \mathrm{E}^{\circ}=-2.69 \mathrm{~V}$
As $\mathrm{E}^{\circ}$ value is negative reaction is non-spontaneous.

Sol 24: (A)


JEE Advanced/Boards

## Exercise 1

Sol 1: $\mathrm{Cu}^{2+}+2 \mathrm{e} \rightarrow \mathrm{Cu}$
$E^{\circ}=0.344$
$E=E^{\circ}-\frac{0.0591}{2} \log \frac{1}{\left[\mathrm{Cu}^{2+}\right]}=0.226$
As after $\mathrm{E}<0.226$, Bi will also start to deposit
$0.344-\frac{0.0591}{2} \log \frac{1}{\left[\mathrm{Cu}^{2+}\right]}=0.226$
$0.0295 \log \left[\mathrm{Cu}^{2+}\right]=-0.118$
$\log \left[\mathrm{Cu}^{2+}\right]=-4$
$\left[\mathrm{Cu}^{2+}\right]=10^{-4} \mathrm{M}$

Sol 2: Reduction potential of calomel electrode $=0.28 \mathrm{~V}$
$0.67=0.28-\mathrm{E}_{\mathrm{H}^{+} / \mathrm{H}_{2}}^{\circ}$
$\mathrm{E}_{\mathrm{H}^{+} / \mathrm{H}_{2}}^{\circ}=-0.39$
$\mathrm{H}^{+}+\mathrm{e} \rightarrow \frac{1}{2} \mathrm{H}_{2}$
$E=E^{\circ}-0.059 \log \frac{1}{\left[\mathrm{H}^{+}\right]}$
$-0.39=-0.059 \log \frac{1}{\left[\mathrm{H}^{+}\right]}$
$\frac{-0.039}{0.059}=\log \left[\mathrm{H}^{+}\right]$
$\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]$
$\mathrm{pH}=6.61$

Sol 3: $\mathrm{Ag}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}$
$\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}=\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}^{0}-\frac{0.0591}{1} \log \frac{1}{\left[\mathrm{Ag}^{+}\right]}$
$=0.8-0.0591 \log \frac{1}{0.8}$

$$
\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}=0.794
$$

$\mathrm{E}_{\mathrm{H}_{2} / \mathrm{H}^{+}}+\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}=0.982$
$\mathrm{E}_{\mathrm{H}_{2} / \mathrm{H}^{+}}=0.188$
$\frac{1}{2} \mathrm{H}_{2} \rightarrow \mathrm{H}^{+}+\mathrm{e}^{-}$
$0.188=0-0.059 \log \left[\mathrm{H}^{+}\right]$
$\left[\mathrm{H}^{+}\right]=6.6 \times 10^{-4}$
$C \alpha=6.6 \times 10^{-4}$
$\Rightarrow \alpha=\frac{6.6 \times 10^{-4}}{1.3 \times 10^{-3}}=0.5$
$\mathrm{k}_{\mathrm{a}}=\frac{\mathrm{C} \alpha^{2}}{1-\alpha}$
$k_{a}=6.74 \times 10^{-4}$
Sol 4: $\mathrm{E}=\mathrm{E}^{\circ}-\frac{0.0591}{5} \log \frac{\left[\mathrm{Mn}^{2+}\right]}{\left[\mathrm{H}^{+}\right]^{8}\left[\mathrm{MnO}_{4}^{-}\right]}$
$\mathrm{MnO}_{4}^{-}+8 \mathrm{H}^{+}+5 \mathrm{e}^{-} \rightarrow \mathrm{Mn}^{2+}+4 \mathrm{H}_{2} \mathrm{O}$
$\mathrm{t}=0 \begin{array}{lll}0 & 0.1 & 0.8\end{array}$
$\mathrm{t}=\mathrm{t} \quad 0.01 \quad 0.08$
0.09
$E=1.51-0.01182 \log \frac{0.09}{(0.08)^{8}(0.01)}=1.39 \mathrm{~V}$

Sol 5: $\mathrm{CH}_{3} \mathrm{COOH} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-}+\mathrm{H}^{+}$

$$
\begin{aligned}
& \alpha=\sqrt{\frac{\mathrm{k}_{\mathrm{a}}}{\mathrm{C}}}=\sqrt{\frac{1.8 \times 10^{-5}}{0.1}}=0.0134 \\
& {\left[\mathrm{H}^{+}\right]=\mathrm{C} \alpha=1.34 \times 10^{-3}} \\
& \frac{1}{2} \mathrm{H}_{2} \rightarrow \mathrm{H}^{+}+\mathrm{e}^{-} \\
& \mathrm{E}_{\mathrm{H}_{2} / \mathrm{H}^{+}}=\mathrm{E}_{\mathrm{H}_{2} / \mathrm{H}^{+}}^{\circ}-0.0591 \log \frac{\left[\mathrm{H}^{+}\right]}{\mathrm{P}_{\mathrm{H}_{2}}^{1 / 2}} \\
& \mathrm{E}_{\mathrm{H}_{2} / \mathrm{H}^{+}}=0-0.0591 \log 1.34 \times 10^{-3} \\
& \mathrm{E}_{\mathrm{H}_{2} / \mathrm{H}^{+}}=0.170 \mathrm{~V}
\end{aligned}
$$

At cathode,
$\mathrm{NH}_{3}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{4}^{+}+\mathrm{OH}^{-}$
$\alpha=\sqrt{\frac{k_{b}}{\mathrm{C}}}=\sqrt{\frac{1.8 \times 10^{-5}}{0.01}}$
$\alpha=0.042$
$\left[\mathrm{OH}^{-}\right]=\mathrm{C} \alpha=4.24 \times 10^{-4}$,
$\left[\mathrm{H}^{+}\right]=\frac{10^{-14}}{\left[\mathrm{OH}^{-}\right]}=2.35 \times 10^{-11}$
$\mathrm{H}^{+}+\mathrm{e}^{-} \rightarrow \frac{1}{2} \mathrm{H}_{2}$
$\mathrm{E}_{\mathrm{H}^{+} / \mathrm{H}_{2}}=\mathrm{E}_{\mathrm{H}_{2} / \mathrm{H}^{+}}^{\circ}-0.0591 \log \frac{1}{\left[\mathrm{H}^{+}\right]}$
$=0.0591 \log \frac{1}{2.35 \times 10^{-11}}=-0.628 \mathrm{~V}$
$E_{\text {cell }}=E_{H_{2} / H^{+}}+E_{H^{+} / \mathrm{H}_{2}}=0.170-0.628=0.458 \mathrm{~V}$
Sol 6: $\mathrm{Fe}(\mathrm{s})+2 \mathrm{OH}^{-} \rightarrow \mathrm{FeO}(\mathrm{s})+\mathrm{H}_{2} \mathrm{O}(\ell)+2 \mathrm{e}^{\Theta}$
$\mathrm{E}^{\circ}=0.87 \mathrm{~V}$
$\mathrm{Ni}_{2} \mathrm{O}_{3}(\mathrm{~s})+\mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{NiO}(\mathrm{s})+2 \mathrm{OH}^{-}$
$\mathrm{E}^{\circ}=+0.4 \mathrm{~V}$
(i) Cell reaction
$\mathrm{Fe}(\mathrm{s})+\mathrm{Ni}_{2} \mathrm{O}_{3}(\mathrm{~s}) \rightarrow \mathrm{FeO}(\mathrm{s})+2 \mathrm{NiO}(\mathrm{s})$
(ii) $\mathrm{E}^{\circ}=0.87+0.4=1.27 \mathrm{~V}$

It does not depend on $[\mathrm{KOH}]$
(iii) Maximum amount of electrical energy
$=\left|-n F E^{\circ}\right|$
$=|-2 \times 96.5 \times 1.27 \mathrm{~kJ}|$
$=245.1 \mathrm{~kJ}$

Sol 7: $\mathrm{Cu}(\mathrm{OH})_{2} \rightleftharpoons \mathrm{Cu}^{2+}+2 \mathrm{OH}^{-}$
We have $\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=14$
$\left[\mathrm{H}^{+}\right]=10^{-14}$
$\left[\mathrm{OH}^{-}\right]=\frac{10^{-14}}{\left[\mathrm{H}^{+}\right]}=1$
$\left[\mathrm{Cu}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2}=\mathrm{K}_{\mathrm{sp}}$
$\left[\mathrm{Cu}^{2+}\right]=1 \times 10^{-19}$
$\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}$
$E=E^{\circ}-\frac{0.0591}{2} \log \frac{1}{\left[\mathrm{Cu}^{2+}\right]}=0.34-0.0295 \log \frac{1}{10^{-19}}$
$=0.34-0.56=-0.22 \mathrm{~V}$

Sol 8: $\frac{1}{2} \mathrm{H}_{2}+\mathrm{H}^{+} \rightarrow \frac{1}{2} \mathrm{H}_{2}+\mathrm{H}^{+}$
All conditions are standard except $\left[\mathrm{H}^{+}\right]_{\text {anode }}$
$E=E^{\circ}-0.0591 \log \frac{1}{\left[\mathrm{H}^{+}\right]_{\text {cathode }}}$
$-0.188=0-0.0591 \log \frac{1}{\left[H^{+}\right]}$
$\log \left[\mathrm{H}^{+}\right]=6.59 \times 10^{-4}$
$\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3} \mathrm{Cl} \rightleftharpoons \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}+\mathrm{H}^{+}+\mathrm{Cl}^{-}$
$\mathrm{Ch}=\left[\mathrm{H}^{+}\right]$
$h=\frac{6.59 \times 10^{-4}}{(1 / 32)}=2.12 \times 10^{-2}$
$k_{h}=\frac{C \alpha^{2}}{1 . \alpha}$
$k_{h}=1.43 \times 10^{-5}$

Sol 9: m. equivalents of $\mathrm{OH}^{-}$added $=\mathrm{MV}$
$=40 \times 0.05=2 \mathrm{meq}$.
m. equivalents of $\mathrm{H}^{+}=\mathrm{MV}=30 \times 0.1=3 \mathrm{meq}$.
$\therefore$ m. equivalents of $\mathrm{H}^{+}$remaining $=1$ meq.
$\left[\mathrm{H}^{+}\right]=\frac{1}{40+30}=0.014$
$\frac{1}{2} \mathrm{H}_{2}+\mathrm{Ag}^{+} \rightarrow \mathrm{H}^{+}+\mathrm{Ag}$
$\mathrm{P}_{\mathrm{H}_{2}}=1 \mathrm{~atm}$,
$\therefore \mathrm{E}=\mathrm{E}^{\circ}-0.0591 \log \frac{\left[\mathrm{H}^{+}\right]}{\left[\mathrm{Ag}^{+}\right]}$
$\therefore \mathrm{E}_{2}-\mathrm{E}_{1}=0.0591 \log \frac{\left[\mathrm{H}^{+}\right]_{1}}{\left[\mathrm{H}^{+}\right]_{2}} \cdot \frac{\left[\mathrm{Ag}^{+}\right]_{2}}{\left[\mathrm{Ag}^{+}\right]_{1}}$
$E_{2}-0.9=0.0591 \log \frac{0.1}{0.014} .1$
$E_{2}-0.9=0.05$
$\mathrm{E}_{2}=0.95 \mathrm{~V}$

Sol 10: $\mathrm{E}^{\circ}=0$
$\mathrm{Ag}^{+}+\mathrm{Ag} \rightarrow \mathrm{Ag}^{+}+\mathrm{Ag}$
$\left[\mathrm{Ag}^{+}\right]_{c}=0.05 \mathrm{M}$
$E=\frac{-0.0591}{1} \log \frac{\left[\mathrm{Ag}^{+}\right]_{\mathrm{a}}}{\left[\mathrm{Ag}^{+}\right]_{\mathrm{c}}}$
$0.788=-0.0591 \log \frac{\left[\mathrm{Ag}^{+}\right]_{\mathrm{a}}}{0.05}$
$\log \frac{\left[\mathrm{Ag}^{+}\right]_{\mathrm{a}}}{0.05}=-13.3$
$\left[\mathrm{Ag}^{+}\right]=2.32 \times 10^{-15}$
$\mathrm{AgI} \rightleftharpoons \mathrm{Ag}^{+}+\mathrm{I}^{-}$
$\mathrm{k}_{\mathrm{sp}}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{I}^{-}\right]$
$\left[I^{-}\right]=[\mathrm{KI}]=0.05$
$\therefore \mathrm{k}_{\mathrm{sp}}=1.16 \times 10^{-16}$

Sol 11: $\mathrm{AgBr} \rightleftharpoons \mathrm{Ag}^{+}+\mathrm{Br}^{-}$
$k_{\text {sp }}=\left[\mathrm{Ag}^{+}\right]_{\mathrm{a}} \cdot[\mathrm{Br}]^{-}$
$\left[\mathrm{Ag}^{+}\right]_{\mathrm{a}}=\frac{\left(\mathrm{k}_{\mathrm{sp}}\right)_{\mathrm{AgBr}}}{\left[\mathrm{Br}^{-}\right]}$
Similarly, $\left[\mathrm{Ag}^{+}\right]_{c}=\frac{\left(\mathrm{k}_{\mathrm{sp}}\right)_{\mathrm{AgCl}}}{\left[\mathrm{Cl}^{-}\right]}$
$\mathrm{Ag}^{+}+\mathrm{Ag} \rightarrow \mathrm{Ag}^{+}+\mathrm{Ag}$
cathode anode
$E^{\circ}=0$
$E=-0.0591 \log \frac{\left[\mathrm{Ag}^{+}\right]_{\mathrm{a}}}{\left[\mathrm{Ag}^{+}\right]_{\mathrm{c}}}=0$
$\left[\mathrm{Ag}^{+}\right]_{\mathrm{a}}=\left[\mathrm{Ag}^{+}\right]_{c}$
$\frac{\left(\mathrm{k}_{\mathrm{sp}}\right)_{\mathrm{AgBr}}}{\left[\mathrm{Br}^{-}\right]}=\frac{\left(\mathrm{k}_{\mathrm{sp}}\right)_{\mathrm{AgCl}}}{\left[\mathrm{Cl}^{-}\right]}$
$\frac{\left[\mathrm{Br}^{-}\right]}{\left[\mathrm{Cl}^{-}\right]}=\frac{5 \times 10^{-13}}{1 \times 10^{-10}}$
$\frac{\left[\mathrm{Br}^{-}\right]}{\left[\mathrm{Cl}^{-}\right]}=5 \times 10^{-3}=\frac{1}{200}$
Sol 12: $\mathrm{AgI} \rightleftharpoons \mathrm{Ag}^{+}+1$
$\Delta G^{\circ}=-\mathrm{nFE}_{1}^{\circ}$
$\mathrm{Ag}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}$
$\Delta \mathrm{G}^{\circ}=-\mathrm{nFE}{ }_{1}^{\circ}$
$\mathrm{AgI}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}^{+}+\mathrm{I}^{-}$
$\Delta n=-n F E^{\circ}=-n F E_{1}^{\circ}-R T \ln k$
$E^{\circ}=E^{\circ}+\frac{R T}{n F} \ln k$
$\mathrm{E}^{\circ}=\mathrm{E}_{1}^{\circ}-\frac{2.303 R T}{\mathrm{nF}} \mathrm{pk}_{\mathrm{sp}}$
$\mathrm{E}^{\circ}=-0.15$

Sol 13: At anode
$\mathrm{AgCl} \rightleftharpoons \mathrm{Ag}^{+}+\mathrm{Cl}^{-}$
$k_{\text {sp }}=\left[\mathrm{Ag}^{+}\right]{ }_{\mathrm{a}}\left[\mathrm{Cl}^{-}\right]$
2. $8 \times 10^{-10}=\left[\mathrm{Ag}^{+}\right]_{\mathrm{a}} \times 0.2$
$\left[\mathrm{Ag}^{+}\right]_{\mathrm{a}}=1.4 \times 10^{-9}$
$\mathrm{Ag} \rightarrow \mathrm{Ag}^{+}+\mathrm{e}^{-}$
At cathode
$\mathrm{AgBr} \rightleftharpoons \mathrm{Ag}^{+}+\mathrm{Br}^{-}$
$\mathrm{k}_{\mathrm{sp}}=\left[\mathrm{Ag}^{+}\right]_{\mathrm{c}}\left[\mathrm{Br}^{-}\right]$
$\left[\mathrm{Ag}^{+}\right]_{c}=\frac{3.3 \times 10^{-13}}{10^{-3}}=3.3 \times 10^{-10}$
$\mathrm{Ag}+\mathrm{Ag}^{+}+\mathrm{Ag}+\mathrm{Ag}^{+}$
Cathode anode
$\mathrm{E}^{\circ}=0$
$E=-0.591 \log \frac{\left[\mathrm{Ag}^{+}\right]_{a}}{\left[\mathrm{Ag}^{+}\right]_{c}}=0.0591 \log \frac{1.4 \times 10^{-9}}{3.3 \times 10^{-10}}$
$\mathrm{E}=-0.037 \mathrm{~V}$
For a spontaneous process, electrodes should be reversed.

Sol 14: $\mathrm{Pb}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Pb}^{\circ}=-0.126 \mathrm{~V}$
$\mathrm{Pb} \rightarrow \mathrm{Pb}^{2+}+2 \mathrm{e}^{-} \mathrm{E}^{\circ}=0.126 \mathrm{~V}$
$\mathrm{PbCl}_{2}+2 \mathrm{e}^{-} \rightarrow \mathrm{Pb}+2 \mathrm{Cl}^{-} \mathrm{E}^{\circ}=-0.268$
$\mathrm{PbCl}_{2} \rightarrow \mathrm{~Pb}^{2+}+2 \mathrm{Cl}^{-} \mathrm{E}^{\circ}=-0.142 \mathrm{~V}$
$\Delta G^{\circ}=-F n E^{\circ}=-R T \ln k$
$\ln \mathrm{k}=\frac{\mathrm{nF}}{\mathrm{RT}} \mathrm{E}^{\circ}$
$\log k=\frac{n F}{R T \times 2.303} E^{\circ}$
$\log k=-4.8 n=2$
$k=1.536 \times 10^{-5}$

Sol 15: $\mathrm{Mn}(\mathrm{OH})_{2} \rightleftharpoons \mathrm{Mn}^{2+}+2 \mathrm{OH}^{-}$
$\mathrm{K}_{\mathrm{sp}}=\left[\mathrm{Mn}^{2+}\right]\left[\mathrm{OH}^{-}\right]^{2}$
$\left[\mathrm{Mn}^{2+}\right]=\frac{1.9 \times 10^{-13}}{\left(10^{-4}\right)^{2}}$
$\left[\mathrm{Mn}^{2+}\right]=1.9 \times 10^{-5}$
Cell reaction:
$\mathrm{Mn}+\mathrm{Cu}^{2} \rightarrow \mathrm{Mn}^{2+}+\mathrm{Cu}$
$\mathrm{E}_{\mathrm{Mn}^{2+} / \mathrm{Mn}}^{\circ}=-1.18 \mathrm{~V}$
$\mathrm{E}_{\mathrm{Cu}^{2+} / \mathrm{Cu}}^{\circ}=0.34 \mathrm{~V}$
$\mathrm{E}_{\text {cell }}^{\circ}=\mathrm{E}_{\mathrm{Cu}^{2+} / \mathrm{Cu}}^{0}-\mathrm{E}_{\mathrm{Mn}^{2+} / \mathrm{Mn}}^{\circ}$
$\mathrm{E}^{\circ}=0.34-(-1.18)$
$E^{\circ}=1.52 \mathrm{~V}$
$E=E^{\circ}-\frac{0.0591}{2} \log \frac{\left[\mathrm{Mn}^{2+}\right]}{\left[\mathrm{Cu}^{2+}\right]}$
$=1.52-0.0295 \log \frac{1.9 \times 10^{-5}}{6.75 \times 10^{-2}}=1.52-(-0.14)$
$\mathrm{E}=1.66 \mathrm{~V}$

Sol 16: $\mathrm{HIO}_{3} \rightleftharpoons \mathrm{H}^{+}+\mathrm{IO}_{3}$
$\left[\mathrm{IO}_{3}^{-}\right]=\mathrm{C} \alpha=\mathrm{C} \sqrt{\frac{\mathrm{k}_{\mathrm{a}}}{\mathrm{C}}}=\sqrt{\mathrm{Ck}_{\mathrm{a}}}$
$\left[\mathrm{IO}_{3}^{-}\right]=0.22 \mathrm{M}$
$\mathrm{AgIO}_{3} \rightleftharpoons \mathrm{Ag}^{+}+\mathrm{IO}_{3}^{-}$
$\mathrm{k}_{\mathrm{sp}}=\left[\mathrm{Ag}^{+}\right]\left[\mathrm{IO}_{3}^{-}\right]$
$\left[\mathrm{Ag}^{+}\right]=\frac{3.08 \times 10^{-8}}{0.22}$
$\left[\mathrm{Ag}^{+}\right]=1.37 \times 10^{-7}$
$2 \mathrm{Ag}+\mathrm{Zn}^{2+} \rightarrow 2 \mathrm{Ag}^{+}+\mathrm{Zn}$
$\mathrm{E}_{{\mathrm{Ag} / \mathrm{Ag}^{+}}_{\circ}=-0.80 \mathrm{~V} .{ }^{\circ} \mathrm{C}}$
$\mathrm{E}_{\mathrm{Zn}^{2+} / \mathrm{Zn}}^{\circ}=-0.76 \mathrm{~V}$
$\mathrm{E}_{\text {cell }}^{\circ}=\mathrm{E}_{\mathrm{Ag} / \mathrm{Ag}^{+}}^{\circ}+\mathrm{E}_{\mathrm{Zn}^{2+} / \mathrm{Zn}}^{\circ}=-1.56 \mathrm{~V}$
$E=E^{\circ}-\frac{0.0591}{2} \log \frac{\left[\mathrm{Ag}^{+}\right]^{2}}{\left[\mathrm{Zn}^{2+}\right]}$
$E=-1.56-0.0295 \log \frac{\left(1.37 \times 10^{-7}\right)^{2}}{0.175}$
$E=-1.56+0.372$
$\mathrm{E}=-1.188 \mathrm{~V}$

Sol 17: $\mathrm{Pb}+\mathrm{Pb}^{2+} \rightarrow \mathrm{Pb}+\mathrm{Pb}^{2+}$
$E^{\circ}=0$
$\mathrm{E}=0-\frac{0.0591}{2} \log \frac{\left[\mathrm{~Pb}^{2+}\right]_{\mathrm{a}}}{\left[\mathrm{Pb}^{2+}\right]_{\mathrm{c}}}+0.061$
$=\frac{0.0591}{2} \log \frac{\left[\mathrm{~Pb}^{2+}\right]_{\mathrm{a}}}{2.5 \times 10^{-3}}$
$\log \frac{\left[\mathrm{Pb}^{2+}\right]_{\mathrm{a}}}{2.5 \times 10^{-5}}=-2.06$
$\left[\mathrm{Pb}^{2+}\right]_{\mathrm{a}}=2.13 \times 10^{-7}$
At anode,
$\mathrm{Pb}+\mathrm{SO}_{4}^{2-} \rightarrow \mathrm{PbSO}_{4}+2 \mathrm{e}^{-} \mathrm{E}^{\circ}=0.356$
$\mathrm{Pb}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Pb}, \mathrm{E}^{\circ}=-0.126 \mathrm{~V}$
$\mathrm{Pb}^{2+}+\mathrm{SO}_{4}^{2-} \rightarrow \mathrm{PbSO}_{4} \mathrm{E}^{\circ}=0.230$
$\mathrm{PbSO}_{4} \rightarrow \mathrm{~Pb}^{2+}+\mathrm{SO}_{4}^{2-} \mathrm{E}^{\circ}=-0.230$
$\Delta G=-n F E^{\circ}=-R T \ln k$
$\ln \mathrm{k}=\frac{\mathrm{nF}}{\mathrm{RT}} \mathrm{E}^{\circ}$
$\log \mathrm{k}=\frac{\mathrm{nF}}{2.303 R T} \mathrm{E}^{\circ}$
$k=1.60 \times 10^{-8}$
$\mathrm{k}_{\mathrm{sp}}=1.6 \times 10^{-8}=\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{SO}_{4}^{-2}\right]$
$\left[\mathrm{SO}_{4}{ }^{2-}\right]=\frac{1.6 \times 10^{-8}}{2.13 \times 10^{-7}}$
$\left[\mathrm{SO}_{4}{ }^{2-}\right]=7.50 \times 10^{-2}$
$\mathrm{HSO}_{4}^{-} \rightleftharpoons \mathrm{H}^{+}+\mathrm{SO}_{4}^{2-}$
0. 5250.0750 .075
$\mathrm{k}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{SO}_{4}^{2-}\right]}{\left[\mathrm{HSO}_{4}^{-}\right]}$
$k_{a}=9.46 \times 10^{-3}$
$k_{a} \approx 10^{-2}$

Sol 18: Cell reaction
$\mathrm{Zn}+\mathrm{Zn}^{2+} \rightarrow \mathrm{Zn}+\mathrm{Zn}^{2+}$
Cathode anode
$\mathrm{E}^{\circ}=0$
$E=\frac{-0.0591}{2} \log \frac{\left[\mathrm{Zn}^{2+}\right]_{\mathrm{a}}}{\left[\mathrm{Zn}^{2+}\right]_{\mathrm{c}}}$
$0.099=\frac{-0.0591}{2} \log \frac{\left[\mathrm{Zn}^{2+}\right]_{\mathrm{a}}}{3.84 \times 10^{-4}}$
$\log \left(\frac{\left[\mathrm{Zn}^{2+}\right]_{\mathrm{a}}}{3.84 \times 10^{-4}}\right)=-3.356$
$\left[\mathrm{Zn}^{2+}\right]_{\mathrm{a}}=1.69 \times 10^{-7}$
At anode

$$
\begin{aligned}
& \mathrm{Zn}^{2+}+4 \mathrm{CN}^{-} \rightarrow \mathrm{Zn}(\mathrm{CN})_{4}^{2-} \\
& \mathrm{k}_{\mathrm{f}}=\frac{\left[\mathrm{Zn}(\mathrm{CN})_{4}^{2-}\right]}{\left[\mathrm{Zn}^{2+}\right]\left[\mathrm{CN}^{-}\right]^{4}} \\
& =\frac{0.450}{\left.1.69 \times 10^{-7} \times\left(2.65 \times 10^{-3}\right)\right)^{4}} \\
& \mathrm{k}_{\mathrm{f}}=5.24 \times 10^{16}
\end{aligned}
$$

Sol 19: $\mathrm{Ti}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Ti}^{\circ}=-0.34 \mathrm{~V}$
$\Delta G=-n F E^{\circ}$
$\mathrm{Ti}^{3+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Ti}^{+} \mathrm{E}^{\circ}=1.25 \mathrm{~V}$
$\mathrm{Ti}^{+} \rightarrow \mathrm{Ti}^{3+}+2 \mathrm{e}^{-} \mathrm{E}^{\circ}=-1.25 \mathrm{~V}$
$\Delta G_{1}=-n F E^{\circ}=-2 F(-1.25)$
$2 \mathrm{Ti}^{+}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Ti}$
$\Delta G_{2}=-2 n F E^{\circ}=-2 F(-0.34)$
$3 \mathrm{Ti}^{+} \rightarrow 2 \mathrm{Ti}+\mathrm{Ti}^{3+}$
$\Delta G=\Delta G_{1}+\Delta G_{2}$
$\Rightarrow-2 \mathrm{FE}^{\circ}=-2 \mathrm{FE}^{\circ}-2 \mathrm{FE}^{\circ}{ }_{2}$
$\mathrm{E}^{\circ}=\mathrm{E}^{\circ}{ }_{1}+\mathrm{E}_{2}$
$\mathrm{E}^{\circ}=-0.34-1.25$
$E^{\circ}=-1.59 \mathrm{~V}$
Since, $\mathrm{E}^{\circ}<0$, it is non spontaneous reaction.

Sol 20: $\mathrm{Cu}^{2+}+4 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}$
$\begin{array}{lll}t=0 & 1 & A \\ t=t & 1-x & A-4 x\end{array}$
We have, $A-4 x=2$
$K_{f}=\frac{\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right]^{2+}}{\left[\mathrm{Cu}^{2+}\right]\left[\mathrm{NH}_{3}\right]^{4}}$
$1 \times 10^{12}=\frac{x}{(1 \cdot x) \cdot 2^{4}}$
$\frac{1-x}{x}=6.25 \times 10^{-14}$
$\frac{1}{x}-1=6.25 \times 10^{-14}$
$x=\frac{1}{1+6.25 \times 10^{-14}}$
$1-x=\frac{6.25 \times 10^{-14}}{1+6.25 \times 10^{-14}} \approx 6.25 \times 10^{-14}$

Now for $\mathrm{Zn}+\mathrm{Cu}^{2} \rightarrow \mathrm{Cu}+\mathrm{Zn}^{2+}$
$E=E^{\circ}-\frac{0.0591}{2} \log \frac{\left[\mathrm{Zn}^{2+}\right]}{\left[\mathrm{Cu}^{2+}\right]}$
$E=1.1-\frac{0.0591}{2} \log \frac{1}{1-x}$
$=1.1-0.0295 \log \frac{1}{6.25 \times 10^{-14}}$
$\mathrm{E}=0.71 \mathrm{~V}$

Sol 21: $\mathrm{Zn}+\mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+}+\mathrm{Cu}$
we have, $\mathrm{E}^{\circ}=0.76-(-0.34)=1.1 \mathrm{~V}$
$\Delta G=-n F E^{\circ}=-R T \ln k$
$\log k=\frac{n F}{2.303 \times R T} E^{\circ}$
$\mathrm{k}=\frac{\left[\mathrm{Zn}^{2+}\right]}{\left[\mathrm{Cu}^{2+}\right]}$
$\log \frac{\left[\mathrm{Zn}^{2+}\right]}{\left[\mathrm{Cu}^{2+}\right]}=\frac{2}{0.0591} \times 1.1=37.28$
$\frac{\left[\mathrm{Zn}^{2+}\right]}{\left[\mathrm{Cu}^{2+}\right]}=1.941 \times 10^{37}$

Sol 22: $\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2} \rightleftharpoons \mathrm{Ag}^{+}+2 \mathrm{NH}_{3}$
$\mathrm{k}_{0}=6 \times 10^{-8}$
$\Delta G_{1}=-R T \ln k_{0}$
$\mathrm{Ag}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{Ag} \mathrm{E}^{\circ}=0.799 \mathrm{~V}$
$\Delta G_{2}=-n F E^{\circ}=-F \times 0.799$
( $\mathrm{n}=1$ )
Adding,
$\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}+\mathrm{e}^{-} \rightarrow \mathrm{Ag}+2 \mathrm{NH}_{3}$
$\Delta G=-n F E^{\circ}=\Delta G_{1}+\Delta G_{2}$
$-n E^{\circ}=-R T \ln k_{0}-0.799 F$
$E^{\circ}=\frac{R T}{F} \ln k_{0}+0.799=\frac{2.303 R T}{F} \log \left(6 \times 10^{-8}\right)+0.799$
$\mathrm{E}^{\circ}=0.373 \mathrm{~V}$

Sol 23: We have,
(i) $\mathrm{Co}^{2+}+6 \mathrm{CN}^{-} \rightarrow\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{4-}$
$k_{f}=1 \times 10^{14}$
$\Delta G_{1}=-R T \ln k_{f}=-43.757 R T$
(ii) $\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}+\mathrm{e}^{-} \rightarrow\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{4-}$
$E^{\circ}=-0.83 V, n=1$
$\Delta G_{2}=-n F E^{\circ}=0.83 \mathrm{~F}$
(iii) $\mathrm{Co}^{3+}+\mathrm{e}^{-} \rightarrow \mathrm{Co}^{2+}, \mathrm{E}^{\circ}=1.82 \mathrm{~V}, \mathrm{n}=1$
$\Delta G_{3}=-n F E^{\circ}=-1.82 \mathrm{~F}$
(iii) + (i). (ii) gives,
$\mathrm{Co}^{3+}+6 \mathrm{CN}^{-} \rightarrow\left[\mathrm{Co}(\mathrm{CN})_{6}\right]^{3-}$
$\Delta G=\Delta G_{3}+\Delta G_{1}-\Delta G_{2}$
$\Delta G=-R T \ln k_{f}=-1.82 F-43.757 R T-0.83 F$
$\Rightarrow \ln \mathrm{k}_{\mathrm{f}}=\frac{\mathrm{F}}{\mathrm{RT}} \times 1.82+43.757+\frac{\mathrm{F}}{\mathrm{RT}} 0.83$
$\log k_{f}=\frac{1.82+0.83}{0.059}+19$
$k_{f}=8.27 \times 10^{63}$

Sol 24: we have,
(i) $\mathrm{Ag}^{+}+\mathrm{e}^{-} \rightarrow \mathrm{AgE}=0.7991 \mathrm{~V}, \mathrm{n}=1$
$\Delta G^{\circ}{ }_{1}=-n F E^{\circ}=-0.7991 \mathrm{~F}$
(ii) $\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}{ }^{+}\right] \rightarrow \mathrm{Ag}^{+}+2 \mathrm{NH}_{3^{\prime}}$
$\mathrm{k}_{\text {ins }}=6.02 \times 10^{-8}$
$\Delta G_{2}=-R T \ln k_{\text {ins }}$
Adding (i) and (ii),
$\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}{ }^{+}\right]+\mathrm{e}^{-} \rightarrow \mathrm{Ag}+2 \mathrm{NH}_{3^{\prime}} \mathrm{n}=1$
$\Delta G=\Delta G_{1}+\Delta G_{2}$
$-F E^{\circ}=-0.7991 F-R T \ln k_{\text {ins }}$
$E^{\circ}=0.7991+\frac{2.303 R T}{F} \log k_{\text {ins }}$
$=0.7991+0.0591 \log \left(6.02 \times 10^{-8}\right)$
$\mathrm{E}^{\circ}=0.372 \mathrm{~V}$
Similarly for $\left[\mathrm{Ag}(\mathrm{CN})_{2}{ }^{-}\right]$
$\mathrm{E}^{\circ}=0.7991+0.0591 \log \left(1.995 \times 10^{-19}\right)$
$E^{\circ}=-0.307 \mathrm{~V}$

Sol 25: We have,
$\mathrm{Sn} \rightarrow \mathrm{Sn}^{2+}+2 \mathrm{e}, \mathrm{E}^{\circ}=0.136 \mathrm{~V}, \mathrm{n}=2$
$\Delta G_{1}^{\prime}=-n F E^{\circ}=-2 F \times 0.136=-0.272 \mathrm{~F}$
For, $3 \mathrm{Sn} \rightarrow 3 \mathrm{Sn}^{2+}+6 \mathrm{e}^{-}$
$\Delta G_{1}=3 \Delta G_{1}^{\prime}=-0.816 \mathrm{~F}$
$\mathrm{Sn}^{2+} \rightarrow \mathrm{Sn}^{4+}+2 \mathrm{e}^{-}, \mathrm{E}^{\circ}=-0.154 \mathrm{~V}, \mathrm{n}=2$
$\Delta G_{2}=-n F E^{\circ}=-2 \times F \times(-0.154)=0.308 \mathrm{~F}$
For, $3 \mathrm{Sn}^{2+} \rightarrow 3 \mathrm{Sn}^{4+}+6 \mathrm{e}^{-}$,
$\Delta G_{2}=3 \Delta G_{2}^{\prime}=0.924 \mathrm{~F}$
$\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}+14 \mathrm{H}^{+}+6 \mathrm{e}^{-} \rightarrow 2 \mathrm{Cr}^{3+}+7 \mathrm{H}_{2} \mathrm{O}$
$\mathrm{E}^{\circ}=1.33 \mathrm{~V}, \mathrm{n}=6$
$\Delta \mathrm{G}_{3}^{\prime}=-\mathrm{nFE}{ }^{\circ}=-6 \mathrm{~F}(1.33)=-7.98 \mathrm{~F}$
For, $2 \mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}+28 \mathrm{H}^{+}+12 \mathrm{e}^{-} \rightarrow \mathrm{HCr}^{3+} 14 \mathrm{H}_{2} \mathrm{O}$
$\Delta G_{3}=2 \Delta G_{3}^{\prime}$
$\Delta G_{3}=-15.96 \mathrm{~F}$
Now, (i) + (ii) + (iii) gives
$3 \mathrm{Sn}(\mathrm{s})+2 \mathrm{Cr}_{2} \mathrm{O}_{7}^{8-}+28 \mathrm{H}^{+} \rightarrow 3 \mathrm{Sn}^{4+}+4 \mathrm{Cr}^{+3}+14 \mathrm{H}_{2} \mathrm{O}$
$\Delta G=-R T \ln k=\Delta G_{1}+\Delta G_{2}+\Delta G_{3}$
$-R T \ln k=-0.816 F+0.924 F-15.96 F$
$\ln \mathrm{k}=\frac{\mathrm{F}}{\mathrm{RT}} \times 15.852$
$\log k=\frac{15.852}{0.0591}$
$\log k=268$
$k=10^{268}$

Sol 26: $\mathrm{Ti}^{+} \rightarrow \mathrm{Ti}^{3+}+2 \mathrm{e}^{-} ; \mathrm{E}^{\circ}=-1.25 \mathrm{~V}$
$\mathrm{Co}^{3+}+\mathrm{e}^{-} \rightarrow \mathrm{Co}^{2+}$
$2 \mathrm{Co}^{3+}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Co}^{2+} \mathrm{E}^{\circ}=1.84 \mathrm{~V}$
Adding,
$\mathrm{Ti}^{+}+2 \mathrm{Co}^{3+} \rightarrow \mathrm{Ti}^{3+}+2 \mathrm{Co}^{2+}$
$\mathrm{E}^{\circ}=0.59 \mathrm{~V}$
$\Delta G=-n F E^{\circ}=-R T \ln k, n=2$
$\log k=\frac{2 F}{2.303 R T} E^{\circ}=\frac{0.59}{0.0295}=20$
$\mathrm{k}=10^{20}$
Now, if $\mathrm{Ti}^{+}=0.1 \times 2.5=25$

Initial milimoles of $\mathrm{Co}^{3+}=25 \times 0.2=5$
$\mathrm{Ti}^{+}+2 \mathrm{Co}^{3+} \rightarrow \mathrm{Ti}^{3+}+2 \mathrm{Co}^{2+}$
$\mathrm{t}=0 \quad 2.5 \quad 5 \quad 0 \quad 0$
$\mathrm{t}=\mathrm{t} \quad 2.5-\mathrm{x} 5-2 \mathrm{x} \quad \mathrm{x} \quad 2 \mathrm{x}$
$\mathrm{k}=\frac{\left[\mathrm{Ti}^{3+}\right]\left[\mathrm{Co}^{2+}\right]^{2}}{\left[\mathrm{Co}^{3+}\right]^{2}\left[\mathrm{Ti}^{+}\right]}=10^{20}$
$\mathrm{~V}_{\text {final }}=50 \mathrm{ml}$
$\frac{\mathrm{x} .4 \mathrm{x}^{2} \cdot(50)^{2} \cdot(50)}{(50) .(50)^{2}(2.5-\mathrm{x})(5-2 \mathrm{x})^{2}}=10^{20}$
$\frac{\mathrm{x}^{3}}{(2.5-\mathrm{x})(2.5-\mathrm{x})^{2}}=10^{20}$
$\frac{x^{3}}{(2.5-x)^{3}}=10^{20}$
$x \approx 2.5$ as $\mathrm{k} \ggg 1$

Putting $x=2.5$
$(2.5-x)^{3}=\frac{(2.5)^{3}}{10^{20}}=1.5625 \times 10^{-3}$
2. $5-x=2.5 \times 10^{-7}$
$\left[\mathrm{Ti}^{+}\right]=\frac{2.5 . \mathrm{x}}{50}=5 \times 10^{-9}$
$\left[\mathrm{Co}^{3+}\right]=\frac{2(2.5-x)}{50}=10^{-8}$

Sol 27: For thiosulphate $\left(\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}\right), \mathrm{n}=2$
Number of equivalent $=\mathrm{n} . \mathrm{V} . \mathrm{M}$.
$=46.3 \times 0.124 \times 2 \times 10^{-9}=11.4824 \mathrm{~m}$. eq.
Equivalents of $x=$ eq. of $\mathrm{I}^{-}$
$=1 \times \frac{\text { eq. }}{2}$ of $\mathrm{I}_{2}=\frac{1}{2} \times$ eq. of $\mathrm{S}_{2} \mathrm{O}_{3}{ }^{2-}$
Eq. of $x=\frac{11.4824 \times 10^{-3}}{2}$
$\frac{0.617}{M}=\frac{11.4824 \times 10^{-3}}{2}$
$M=107.3 \mathrm{gm}$

Sol 28: At anode,
$\mathrm{H}_{2}+2 \mathrm{OH}^{-} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-}$
Moles of $\mathrm{H}_{2}$ reacted $=\frac{67.2}{22.4}=3$
Charge produced by 1 mole $\mathrm{H}_{2}=2 \mathrm{~F}$

Charge produced by 3 mole $\mathrm{H}_{2}=6 \mathrm{~F}$
Current, $I=\frac{6 F}{t}=\frac{6 \times 96500}{15 \times 60}$
$I=643.33 \mathrm{~A}$
$\mathrm{Cu}^{2+}+2 \mathrm{e} \rightarrow \mathrm{Cu}$
number of moles of Cu produced $=3$
$w t .=3 \times 63.5 \mathrm{~g}$
$\mathrm{wt} .=190.5 \mathrm{~g}$

Sol 29: At cathode, only reduction of water takes place
$2 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2}(\mathrm{~g})+2 \mathrm{OH}^{-}(\mathrm{aq})$
Moles of $\mathrm{H}_{2}$ produced $=\frac{9.722}{22.4}=0.434$
Charge needed, $\mathrm{Q}=2 \times 0.434=0.868$
At anode, for oxidation of water
$2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{+}+4 \mathrm{e}^{-}$
Moles of $\mathrm{O}_{2}$ produced, $\mathrm{n}_{\mathrm{O}_{2}}=\frac{2.35}{22.4}=0.105$
Charge needed, $\mathrm{q}=4 \times \mathrm{n}_{\mathrm{O}_{2}}=0.420$
Charge utilised for production of $\mathrm{H}_{2} \mathrm{~S}_{2} \mathrm{O}_{8}$
$=\mathrm{Q} . \mathrm{q}=0.998$
Moles of $\mathrm{H}_{2} \mathrm{~S}_{2} \mathrm{O}_{8}=\frac{\text { charge utilised }}{2}=0.224$
Weight of $\mathrm{H}_{2} \mathrm{~S}_{2} \mathrm{O}_{8}=0.224 \times 194=43.456 \mathrm{gm}$

Sol 30: Initially, mass of $\mathrm{H}_{2} \mathrm{SO}_{4}$ solution
$=1.294 \times 3.5 \times 1000 \mathrm{gm}=4.529 \mathrm{~kg}$
Wt. of $\mathrm{H}_{2} \mathrm{SO}_{4}=\frac{39}{100} \times 4.529=1.76631 \mathrm{~kg}$
Moles of $\mathrm{H}_{2} \mathrm{SO}_{4}=18.02$
$\left[\mathrm{H}_{2} \mathrm{SO}_{4}\right]=5.15 \mathrm{M}$
Finally, Mass $\mathrm{H}_{2} \mathrm{SO}_{4}$ solution $=1.139 \times 3.5 \mathrm{~kg}$
$=3.9865 \mathrm{~kg}$
Mass of $\mathrm{H}_{2} \mathrm{SO}_{4}=\frac{20}{100} \times 3.9865 \mathrm{~kg}=0.7973 \mathrm{~kg}$
Moles of $\mathrm{H}_{2} \mathrm{SO}_{4}=8.136$
$\left[\mathrm{H}_{2} \mathrm{SO}_{4}\right]=2.324 \mathrm{M}$
$\therefore \Delta \mathrm{n}_{\mathrm{SO}_{4}^{2-}}=9.884$
2 F charge consumes 2 moles of $\left[\mathrm{SO}_{4}{ }^{2-}\right]$

According to net reaction
Charge required $=9.884 \mathrm{~F}$
Ampere hours $=\frac{9.884 \times 96500}{3600}=265$ Amp. hr.

Sol 31: $\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}$
Moles of Cu deposited $=\frac{3}{63.5}=0.047$
Charge utilised $=2 \times 0.047 \times F=0.094 \mathrm{~F}=9071 \mathrm{C}$
Charge supplied $=3 \times 2 \times 3600=21600 C$
$\therefore$ Efficiency $=\frac{\text { Charge utilised }}{\text { Charge supplied }}=\frac{9071}{21600}=0.422$
$\therefore$ Efficiency $=42.2 \%$

Sol 32: At cathode,
$\mathrm{Cu}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}$
Moles of Cu deposited $=\frac{0.4}{63.5}=6.3 \times 10^{-3}$
Charge supplied $=2 \times 6.3 \times 10^{-3} \mathrm{~F}=1215.74 \mathrm{C}$
After deposition of copper,
$\mathrm{H}^{+}+\mathrm{e} \rightarrow \frac{1}{2} \mathrm{H}^{+}$(as solution is acidic)
Extra charge supplied $=1.2 \times 7 \times 60$
$=504 \mathrm{C}=5.22 \times 10^{-3} \mathrm{~F}$
Moles of $\mathrm{H}_{2}$ evolved $=\frac{5.22 \times 10^{-3}}{2}=2.61 \times 10^{-3}$
Volume of $\mathrm{H}_{2}$ evolved $=2.61 \times 10^{-3} \times 22400=58.46 \mathrm{~mL}$
At anode,
$2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{O}_{2}+4 \mathrm{H}^{+}+4 \mathrm{e}^{-}$
Total charge,
$Q=2 \times 6.3 \times 10^{-3} \times F+5.22 \times 10^{-2} \mathrm{~F}=1.78 \times 10^{-2} \mathrm{~F}$
Moles of $\mathrm{O}_{2}$ evolved $=\frac{\mathrm{Q}}{4}=4.45 \times 10^{-3}$
Volume of $\mathrm{O}_{2}$ evolved $=4.45 \times 10^{-3} \times 22400=99.68 \mathrm{~mL}$
Total volume $=158.14 \mathrm{~mL}$

Sol 33: $\mathrm{Ag} \rightarrow \mathrm{Ag}^{+}+\mathrm{e}^{-}$
Total charge supplied $=\frac{5 \times 2 \times 3600}{96500}=0.373 \mathrm{~F}$
Now, since purity of electrode is $95 \%$
Here, if charge will oxidise 0.95 moles of Ag , rather than 1 mole
$\therefore$ Moles of Ag oxidised $=\frac{0.373}{0.95}=0.392$
Mass of Ag oxidised $=0.392 \times 108=42.41 \mathrm{~g}$
Mass of electrode $=100-42.41=57.58 \mathrm{~g}$

Sol 34: Charge supplied per second
$=\frac{1.5 \times 10^{6}}{96500}=15.54 \mathrm{~F}$
Electrolysis:
$2 \mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{H}_{2}+\mathrm{O}_{2}$
$2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{O}_{2}+4 \mathrm{H}^{+}+4 \mathrm{e}^{-}$
4 F charges electrolysed 2 moles of $\mathrm{H}_{2} \mathrm{O}$.
$\therefore$ Moles of water electrolysed per second $=\frac{15.54}{2}$
$=7.77$
Total moles of water $=\frac{8.2 \times 10^{12} \times 10^{3}}{18}$
Time required in years $=\frac{8.2 \times 10^{15}}{18 \times 7.77} \times 86400 \times 365$
$=1.9$ million years

Sol 35: Initial mass of electrolyte
$=1.261 \times 1000=1261 \mathrm{~g}$
Wt. of $\mathrm{H}_{2} \mathrm{SO}_{4}=\frac{34.6}{100} \times 1261=436.306$
Moles of $\mathrm{H}_{2} \mathrm{SO}_{4}=\frac{436.306}{98}=4.45$
$\mathrm{Pb}(\mathrm{s})+\mathrm{PbO}_{2}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{SO}_{4}(\ell) \rightarrow 2 \mathrm{PbSO}_{4}(\mathrm{~s})+2 \mathrm{H}_{2} \mathrm{O}(\ell)$
$t=0$
4. 45
$t=t$
4. $45-x \quad x$
we have, wt. of $\mathrm{H}_{2} \mathrm{SO}_{4}=27$
$\therefore \frac{(4.45-x) 98}{12.61 \times 436.606+(4.45-x) 98+x .18}=0.27$
$\Rightarrow 436.608-98 x=0.27(1261-80 x)$
$463.608-98 x=340.47-21.6 x$
76. $4 x=96.138$
$x=1.258$
Change in moles of $\mathrm{SO}_{4}{ }^{2-}=x=1.258$
$\mathrm{Pb}+\mathrm{SO}_{4}{ }^{2-} \rightarrow \mathrm{PbSO}_{4}+2 \mathrm{e}$
Charge produced by 1 mole $\mathrm{SO}_{4}{ }^{2-}=2 \mathrm{~F}$
Charge produced by 1.258 moles $\mathrm{SO}_{4}{ }^{2-}$
$=2 \times 1.258 \mathrm{~F}=2.4 \times 10^{5} \mathrm{C}$

Sol 36: At anode,
$2 \mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{O}_{2}+4 \mathrm{H}^{+}+4 \mathrm{e}$
$\mathrm{pH}=1$
$\log \left[\mathrm{H}^{+}\right]=1$
$\left[\mathrm{H}^{+}\right]=0.1$
$\mathrm{n}_{\mathrm{H}^{+}}=\left[\mathrm{H}^{+}\right] \times \mathrm{v}=0.1 \times 10^{-1}=10^{-2}$
$\left[\mathrm{H}^{+}\right]_{\mathrm{i}}=10^{-7}$
$n_{\mathrm{H}^{+}}=10^{-7} \times 10^{-1}=10^{-8}$
Moles of $\mathrm{H}^{+}$produced $=10^{-2}-10^{-8}$
$\approx 10^{-2}$
Charge needed $=10^{-2} \mathrm{~F}=965 \mathrm{C}$
Theoretical time $=\frac{\mathrm{Q}}{\mathrm{I}}=\frac{96.5 \times 10}{0.965}=1000 \mathrm{~s}$
Current efficiency $=80 \%$
Therefore, actual time $=\frac{1000 \times 5}{4} \mathrm{~s}=1250 \mathrm{~s}$
Now, at cathode
$\mathrm{Cu}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Cu}(\mathrm{s})$
Current passed $=10^{-2} \mathrm{~F}$
$\therefore$ Moles of copper reduced $=\frac{10^{-2}}{2}=5 \times 10^{-3}$
After passing of current,
Equivalents of copper $=$ equivalents of $\mathrm{I}_{2}$
$=2$ equivalents of $\mathrm{S}_{2} \mathrm{O}_{3}^{-}$
Equivalents of copper
$=2 \times 0.04 \times 35 \times 10^{-3}$
Moles of copper $=31.4 \times 10^{-3}$
$\left(\because \mathrm{n}=2\right.$ for $\mathrm{Cu}^{2+}$ )
$\therefore$ Total moles of $\mathrm{Cu}^{2+}=6.4 \times 10^{-3}$
Molarity $=\frac{64 \times 10^{-3}}{100 \times 10^{-3}}=0.064 \mathrm{M}$
Sol 37: Current passed $=\frac{5 \times 10 \times 3600}{96500} \mathrm{~F}=1.861 \mathrm{~F}$
At anode
$\mathrm{Zn}^{2+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Zn}$
Moles of $\mathrm{Zn}^{2+}$ reduced $=\frac{\mathrm{Q}}{2}=0.9326$
Final, $\left[\mathrm{Zn}^{2+}\right]=1-0.9326=0.067$

At cathode,
$\mathrm{Cu} \rightarrow \mathrm{Cu}^{2+}+2 \mathrm{e}^{-}$
Final, $\left[\mathrm{Cu}^{2+}\right]=1+0.9326=1.9326$
Now, cell reaction,
$\mathrm{Zn}+\mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+}+\mathrm{Cu}$
$\mathrm{E}^{\circ}=1.1 \mathrm{~V}, \mathrm{n}=2$
$E=E^{\circ}-\frac{0.0591}{2} \log \frac{\left[\mathrm{Zn}^{2+}\right]}{\left[\mathrm{Cu}^{2+}\right]}=1.1-0.0295 \log \left(\frac{0.067}{1.9326}\right)$
$=1.1-(0.0295)(-1.45)$
$E=1.143 \mathrm{~V}$

Sol 38: At anode, for quinhydrone electrode,
$\mathrm{QH}_{2} \rightarrow \mathrm{Q}+2 \mathrm{H}^{+}+2 \mathrm{e}^{-}$
$E=E^{\circ}-\frac{0.0591}{2} \log \left[\mathrm{H}^{+}\right]^{2}$
$\mathrm{E}^{\circ}+0.0591 \mathrm{pH}=-0.699+0.0591 \mathrm{pH}$
$\left(\because \mathrm{E}_{\mathrm{OP}}=-\mathrm{E}_{\mathrm{RP}}{ }^{\prime}\right)$
At cathode,
$E=E^{\circ}=0.28$
$\therefore \mathrm{E}_{\text {cell }}=0.28-0.699+0.0591 \mathrm{pH}$
$\mathrm{E}_{\text {cell }}=-0.419+0.0591 \mathrm{pH}$
(a) At pH = 5. 0 ,
$\mathrm{E}_{\text {cell }}=-0.419+(0.0591) \times(5)=-0.124 \mathrm{~V}$
(b) When $\mathrm{E}_{\text {cell }}=0$,
$\mathrm{pH}=\frac{0.419}{0.0591}=7.1$
(c) At $\mathrm{pH}=7.5$
$\mathrm{E}_{\text {cell }}=0.0235 \mathrm{~V}$
Since, $\mathrm{E}_{\text {cell }}$ is positive, reaction takes place in the given direction and cathode (Calomel electrode) is positive electrode.

Sol 39: We have, at anode
$\frac{1}{2} \mathrm{H}_{2} \rightarrow \mathrm{H}^{+}+\mathrm{e}^{-}$
$2 \mathrm{H}_{2} \rightarrow 4 \mathrm{H}^{+}+4 \mathrm{e}^{-}$
$\mathrm{E}^{\circ}=0$
$E=-0.0591 \log \left[\mathrm{H}^{+}\right]$

At cathode
$\mathrm{O}_{2}+2 \mathrm{H}_{2} \mathrm{O}+4 \mathrm{e} \rightarrow 4 \mathrm{OH}^{-}$
Overall cell reaction
$2 \mathrm{H}_{2}+\mathrm{O}_{2}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{H}^{+}+4 \mathrm{OH}^{-}$
we have, $\frac{1}{2} \mathrm{H}_{2}+\mathrm{H}_{2} \mathrm{O}_{2} \rightarrow \mathrm{H}_{2} \mathrm{O} ; \Delta \mathrm{H}=-56.7 \mathrm{~kJ}$
$2 \mathrm{H}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O} ; \Delta \mathrm{H}=-2 \times 56.7 \mathrm{~kJ}=-113.4 \mathrm{~kJ}$
$\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}^{+}+\mathrm{OH}^{-} ; \Delta \mathrm{H}=19.05 \mathrm{~kJ}$
$4 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{H}^{+}+4 \mathrm{OH}^{-}$
$\Delta \mathrm{H}=4 \times 19.05 \mathrm{~kJ}=76.2 \mathrm{~kJ}$
Adding,
$2 \mathrm{H}_{2}+\mathrm{O}_{2}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{H}^{+}+4 \mathrm{OH}^{-}$
$\Delta H=-37.2 \mathrm{~kJ}$
$\Delta S=n F\left(\frac{\Delta E}{\Delta T}\right)_{P}=4 \times 96500 \times 0.001058$
$\Delta S=408.38$
$\Delta G=-n F E^{\circ}=\Delta H-T \Delta S$
$\mathrm{E}^{\circ}=\mathrm{T}\left(\frac{\Delta \mathrm{E}}{\Delta \mathrm{T}}\right)_{\mathrm{P}}-\frac{\Delta \mathrm{H}}{\Delta \mathrm{F}}$
$E^{\circ}=0.4414 V$

Sol 40: $\mathrm{Ag}_{2} \mathrm{~S}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Ag}+\mathrm{S}^{2-}$
$\mathrm{Ag}_{2} \mathrm{~S} \rightleftharpoons 2 \mathrm{Ag}^{2}+\mathrm{S}^{2-}$
$\Delta G_{1}=-R T \ln k_{s p}$
$\mathrm{Ag}^{+} \times \mathrm{e}^{-} \rightarrow \mathrm{Ag} ; \Delta \mathrm{G}_{2}=-\mathrm{FE}^{\circ}, \mathrm{n}=1$
$2 \mathrm{Ag}^{+}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Ag}$
$\Delta G_{2}=-2 F^{\circ}$
$\mathrm{Ag}_{2} \mathrm{~S}+2 \mathrm{e}^{-} \rightarrow 2 \mathrm{Ag}+\mathrm{S}^{2-}$
$\Delta G=\Delta G_{1}+\Delta G_{2}=-2 F^{\circ}-R T \ln k_{s p}$
$-n F E^{\circ}=-2 F^{\circ}-R T \ln k_{\text {sp }}$
$E^{\circ \circ}=E^{\circ}+\frac{2.303 R T}{n F} \log k_{s p}$
$E^{1 \circ}=-0.64 \mathrm{~V}$
$E=-0.64-\frac{0.0591}{2} \log \left[S^{2-}\right]$
We have,
$\mathrm{H}_{2} \mathrm{~S} \rightleftharpoons \mathrm{H}^{+}+\mathrm{HS}^{-}$
$\frac{\left[\mathrm{H}^{+}\right] \cdot\left[\mathrm{HS}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{~S}\right]}=\mathrm{k}_{1}$
$\mathrm{k}_{1}=10^{-8},\left[\mathrm{H}^{+}\right]=10^{-3},\left[\mathrm{H}_{2} \mathrm{~S}\right]=0.1$
$\therefore\left[\mathrm{HS}^{-}\right]=10^{-6} \mathrm{M}$
$\mathrm{HS}^{-} \rightleftharpoons \mathrm{H}^{+}+\mathrm{S}^{2-}$
$10^{-6} \quad 10^{-3}$
$\frac{\left[\mathrm{S}^{2-}\right] \cdot[\mathrm{H}]^{+}}{\left[\mathrm{HS}^{-}\right]}=\mathrm{k}_{2}$
$\left[\mathrm{H}^{+}\right]=10^{-3},\left[\mathrm{HS}^{-}\right]=10^{-6}, \mathrm{k}_{2}=1.1 \times 10^{-13}$
$\frac{\left[\mathrm{S}^{2-}\right] \cdot 10^{-3}}{10^{-6}}=1.1 \times 10^{-13}$
$\left[S^{2-}\right]=1.1 \times 10^{-16} \mathrm{M}$
$E=-0.64-0.0295 \log \left(1.1 \times 10^{-16}\right)$
$=-0.64-0.0295(-15.95)$
$\mathrm{E}=-0.167 \mathrm{~V}$

Sol 41: $\wedge_{\text {eq }}=k \times \frac{1000}{N}$
$\mathrm{k}=\frac{97.1 \times 0.1}{1000}=9.71 \times 10^{-3} \Omega^{-1} \mathrm{~cm}^{-1}$
and, $\mathrm{k}=\frac{1}{\mathrm{R}} \frac{\ell}{\mathrm{a}}$
$\mathrm{R}=\frac{\ell}{\mathrm{ka}}=\frac{0.5}{9.71 \times 10^{-3} \times 1.5}$
$R=34.32 \Omega$
$I=\frac{V}{R}=\frac{5}{34.32} Z$
$\mathrm{I}=0.1456 \mathrm{~A}$

Sol 42: $\mathrm{E}=\frac{\mathrm{V}}{\mathrm{L}}=\frac{6}{10 / 100}=60 \mathrm{~V} / \mathrm{m}=0.6 \mathrm{~V} / \mathrm{cm}$
Ionic mobility (drift speed) $=\frac{\wedge_{\infty}^{0}}{F} \times E$
$=\frac{73.52}{96500} \times 0.6 \mathrm{~cm} / \mathrm{s}=4.57 \times 10^{-4} \mathrm{~cm} / \mathrm{s}$
Distance in 2 hours $=4.57 \times 10^{-4} \times 2 \times 3600=3.29 \mathrm{~cm}$
Sol 43: $R=\frac{1}{k} \frac{\ell}{\mathrm{a}}$
$\ell=\mathrm{kRa}=1.342 \times 170.5 \times 1.86 \times 10^{-4}=0.0425 \mathrm{~m}$ $\ell=4.25 \mathrm{~cm}$

Sol 44: $\wedge_{\mathrm{m}}^{0} \mathrm{SrSO}_{4}=\wedge_{\mathrm{m}}^{0} \mathrm{Sr}^{2+}+\wedge_{\mathrm{m}}^{0} \mathrm{SO}_{4}{ }^{2-}$
$=59.46+79.8=139.26$ ohm $^{-1} \mathrm{~cm}^{2}$ mole $^{-1}$
$\wedge_{\mathrm{m}}^{0} \mathrm{SrSO}_{4}=1000 \times \frac{\mathrm{k}_{\mathrm{SrSO}_{4}}}{\mathrm{C}}$
$C=\frac{1000 \times 1.482 \times 10^{-4}}{139.26}$
$C=1.064 \times 10^{-3}$
$C=S=1.064 \times 10^{-3} \mathrm{~mole} / \mathrm{L}$
$=1.064 \times 10^{-3} \times 183.6 \mathrm{gm} / \mathrm{L}$
$S=0.1953 \mathrm{gm} / \mathrm{L}$
Sol 45: $\wedge_{m}^{0}\left(\mathrm{Co}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]\right)$
$=2 \wedge_{\mathrm{m}}^{0}\left(\mathrm{Co}^{2+}\right)+\wedge_{\mathrm{m}}^{0}\left(\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{+}\right)$
$=2 \times 86+444=616 \Omega^{-1} \mathrm{~cm}^{-1} \mathrm{~mol}^{-1}$
$\mathrm{k}_{\mathrm{Co}_{2}}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]=\mathrm{k}_{\text {solution }}-\mathrm{k}_{\text {water }}$
$=2.06 \times 10^{-6}-0.41 \times 10^{-6}$
$=1.65 \times 10^{-6} \Omega^{-1} \mathrm{~cm}^{-1}$
$=1.65 \times 10^{-6} \Omega^{-1} \mathrm{~cm}^{-1}$
$\wedge_{m}^{0}=k \times \frac{1000}{C}$
$C=\frac{\mathrm{k} \times 1000}{\wedge_{\mathrm{m}}^{0}}=\frac{1.65 \times 10^{-6} \times 1000}{616}$
$C=2.59 \times 10^{-6} \mathrm{~mol} / \mathrm{L}$
$S=C=2.59 \times 10^{-6} \mathrm{~mol} / \mathrm{L}$
$\mathrm{Co}_{2}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right] \rightleftharpoons 2 \mathrm{Co}^{2+}+\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}$
$\mathrm{k}_{\mathrm{sp}}=(2 \mathrm{~s})^{2} \cdot \mathrm{~S}=4 \mathrm{~S}^{3}$
$k_{\text {sp }}=7.682 \times 10^{-17}$

Sol 46: For $\mathrm{KCl}, \wedge_{\mathrm{m}}^{0}=138 \Omega^{-1} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$
$\therefore \wedge_{m}=\mathrm{k} \times \frac{1000}{\mathrm{C}}$
$\mathrm{k}=\frac{138 \times 0.02}{1000}=2.76 \times 10^{-3} \Omega^{-1} \mathrm{~cm}^{-1}$
$G^{*}=R k$
$=2.76 \times 10^{-3} \times 85=0.2346 \mathrm{~cm}^{-1}$
$\mathrm{k}_{\text {water }}=\frac{\mathrm{G}^{*}}{\mathrm{R}}=\frac{0.2346}{9200}$
$\mathrm{k}_{\text {water }}=2.55 \times 10^{-5} \Omega^{-1} \mathrm{~cm}^{-1}$
$\mathrm{n}_{\mathrm{NaCl}}=\frac{500}{58.5}=8.547$
$\mathrm{k}_{\mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}}=\frac{0.2346}{7600}=3.08 \times 10^{-5}$
$\mathrm{k}_{\mathrm{NaCl}}=\mathrm{k}_{\mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}} \cdot \mathrm{k}_{\mathrm{H}_{2} \mathrm{O}}$
$=(3.08-2.55) \times 10^{-5}$
$=5.3 \times 10^{-6} \Omega^{-1} \mathrm{~cm}^{-1}$
$C_{\mathrm{NaCl}}=\frac{\mathrm{k}_{\mathrm{NaCl}} \times 1000}{\wedge_{\mathrm{m}}}$
$=\frac{5.3 \times 10^{-6} \times 1000}{126.5}=4.190 \times 10^{-5} \mathrm{~mole} / \mathrm{L}$
$C=\frac{n}{V}$
$V=\frac{n}{C}=\frac{8.547}{4.19 \times 10^{-5}}\left(1 \mathrm{~L}=1 \mathrm{dm}^{3}\right)$
$V \approx 2 \times 10^{5} \mathrm{dm}^{3}$.

## Exercise 2

## Single Correct Choice Type

Sol 1: (C) As $\mathrm{E}_{\mathrm{Ag}^{+} / \mathrm{Ag}}^{\circ}>\mathrm{E}_{\mathrm{Hg}_{2} / \mathrm{Hg}}^{\circ}>\mathrm{E}_{\mathrm{Cu}^{2+} / \mathrm{Cu}}^{\circ}$
Sol 2: (C) $\mathrm{Mn}_{3} \mathrm{O}_{4}+16 \mathrm{OH}^{-} \rightarrow 3 \mathrm{MnO}_{4}^{2-}+8 \mathrm{H}_{2} \mathrm{O}+10 \mathrm{e}^{-}$
$\therefore$ Charge required $=10 \mathrm{~F}$

Sol 3: (A) Only water will be oxidised and reduced at anode and cathode respectively because SRP of $\mathrm{SO}_{4}{ }^{2-}$ is very high (magnitude).

## Sol 4: (C) At X

$\mathrm{pH}=\mathrm{pk}_{\mathrm{a}}+\log \frac{\left[\mathrm{A}^{+}\right]}{\left[\mathrm{H}_{\mathrm{A}}\right]}=\mathrm{pk}_{\mathrm{a}}+\log \frac{\mathrm{a}}{\mathrm{b}}$
$\mathrm{H}^{+}+\mathrm{e}^{-}+\frac{1}{2} \mathrm{H}_{2}$
$\mathrm{E}_{1}=0+0.0591 \log \left[\mathrm{H}^{+}\right]=-0.0591 \mathrm{pH}$
$\frac{E_{1}}{0.0591}=-p k_{a}-\log \frac{a}{b}$
At $Y$
$\mathrm{pH}=\mathrm{pk}_{\mathrm{a}}+\log \frac{\mathrm{b}}{\mathrm{a}}$
$\mathrm{E}_{2}=-0.0591 \mathrm{pH}$
$\frac{E_{2}}{0.0591}=-p k_{a}-\log \frac{b}{a}=-p k_{a}+\log \frac{a}{b}$
$\frac{E_{1}+E_{2}}{0.0591}=-2 p k_{a}$
$p k_{a}=-\frac{E_{1}+E_{2}}{0.118}$
Sol 5: $(A) \wedge_{\text {eq }}=\frac{k \times t}{C}$
$C=\frac{9 \times 10^{-6}}{1.5 \times 10^{-4}} \times 10^{-3}=6 \times 10^{-5} \mathrm{M}$
$\mathrm{Ag}_{3} \mathrm{PO}_{4} \rightleftharpoons 3 \mathrm{Ag}^{+}+\mathrm{PO}_{4}^{3-}$
$\left[\mathrm{Ag}^{+}\right]=3 \mathrm{C}=1.8 \times 10^{-4} \mathrm{M}$
$\left[\mathrm{PO}_{4}{ }^{3-}\right]=6 \times 10^{-5} \mathrm{M}$
$\mathrm{k}_{\mathrm{sp}}=\left[\mathrm{Ag}^{+}\right]^{3}\left[\mathrm{PO}_{4}{ }^{3-}\right]$
$k_{\text {sp }}=4.32 \times 10^{-18}$

Sol 6: (B) $\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{NaOH} \rightarrow \mathrm{CH}_{3} \mathrm{COONa}+\mathrm{H}_{2} \mathrm{O}$
$\left[\mathrm{CH}_{3} \mathrm{COONa}\right]=\frac{0.015}{2}=0.0075$
$\wedge_{m}=\mathrm{k} \times \frac{1000}{\mathrm{C}}$
$=\frac{6.3 \times 10^{-4} \times 1000}{0.0075}=84 \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$

## Multiple Correct Choice Type

Sol 7: (B,C) $\mathrm{E}_{\mathrm{S}_{2} \mathrm{O}_{2} / \mathrm{SO}_{4}^{2-}}^{\circ}>\mathrm{E}_{\mathrm{Cl}_{2} / \mathrm{Cl}^{-}}^{\circ}>\mathrm{E}_{\mathrm{Br}_{2} / \mathrm{Br}^{-}}^{\circ}>\mathrm{E}_{\mathrm{I}_{2} / \mathrm{I}_{1}}^{\circ}$ species with higher $\mathrm{E}^{\circ}$ can oxidise a species with lower $\mathrm{E}^{\circ}$.

Sol 8: (B, C, D) In all case $\mathrm{H}_{2} \mathrm{O}$ will oxidise at anode to give $\mathrm{O}_{2}$.

Sol 9: (A, B) $\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{2}+\frac{1}{2} \mathrm{O}_{2}$
$\mathrm{n}_{\mathrm{H}_{2} \mathrm{O}}=\frac{270}{18}=15$
$\mathrm{V}_{\mathrm{H}_{2}}=15 \times 22.1=33.6 \mathrm{~L}$
$\mathrm{V}_{\mathrm{O}_{2}}=168 \mathrm{~L}$, evolved at anode
$V_{T}=504 \mathrm{~L}$

Sol 10: (C, D) Refer text

Sol 11: $(\mathbf{D}, \mathrm{C}) \mathrm{Ag}+\mathrm{Cl}^{-} \rightarrow \mathrm{AgCl}+\mathrm{e}$
Cell reaction
$\frac{1}{2} \mathrm{H}_{2}+\mathrm{Ag}+\mathrm{Cl}^{-} \rightarrow \mathrm{AgCl}=\mathrm{H}^{+}$
$E=E^{\circ}-0.0591 \log \frac{\left[\mathrm{H}^{+}\right]}{\left[\mathrm{Cl}^{-}\right]\left[\mathrm{P}_{\mathrm{H}_{2}}\right]^{1 / 2}}$
on increasing $\left[\mathrm{H}^{+}\right]$or decreasing $\left[\mathrm{Cl}^{-}\right]$, E will decrease.

## Assertion Reasoning Type

Sol 12: (A) Cell Reaction:
$\mathrm{Zn}(\mathrm{Hg})+\mathrm{HgO}(\mathrm{s}) \rightarrow \mathrm{ZnO}(\mathrm{s})+\mathrm{Hg}(\ell)$

Sol 13: (D) $\mathrm{E}^{\circ}=\mathrm{E}_{\text {left }}^{\circ}-\mathrm{E}_{\text {right }}^{\circ}$
$E^{\circ}$ is intensive.

Sol 14: (A) These are facts.

## Comprehension Type

## Paragraph 1

Sol 15: (B) $R=\rho G^{*}$
for $\mathrm{KCl}, \wedge_{\mathrm{m}}=200 \mathrm{~S} \mathrm{~cm}^{2} \mathrm{~mol}^{-1}$
$\mathrm{k}=\frac{\mathrm{C} \wedge_{\mathrm{m}}}{1000}=\frac{0.02 \times 200}{1000}$
$\mathrm{k}=4 \times 10^{-3}$
$\mathrm{G}^{*}=\mathrm{Rk}=100 \times 4 \times 10^{-3}$
$G^{*}=0.4$
Sol 16: (C) $k_{\text {water }}=\frac{G^{*}}{R}=\frac{0.4}{10^{4}}=4 \times 10^{-5}$

Sol 17: (A) $\mathrm{n}_{\mathrm{NaCl}}=\frac{585}{58.8}=10$
$\mathrm{k}_{\mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}}=\frac{\mathrm{G}^{*}}{\mathrm{R}}=\frac{0.4}{8000}=5 \times 10^{-5}$
$\mathrm{k}_{\mathrm{NaCl}}=\mathrm{k}_{\mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}}-\mathrm{k}_{\mathrm{H}_{2} \mathrm{O}}=10^{-5}$
$\therefore \mathrm{C}_{\mathrm{NaCl}}=\frac{\mathrm{k}_{\mathrm{NaCl}} \times 1000}{\wedge_{\mathrm{m}}}$
$=\frac{10^{-5} \times 1000}{125}=8 \times 10^{-5}$
$C_{\mathrm{NaCl}}=\frac{10}{\mathrm{~V}}$
$V=\frac{10}{8 \times 10^{-5}}=1.25 \times 10^{5} \mathrm{~L}$

## Paragraph 2

Sol 18: (B) $\mathrm{NO}_{3}^{-}+4 \mathrm{H}^{+} \rightarrow \mathrm{NO}+2 \mathrm{H}_{2} \mathrm{O}+3 \mathrm{e}(\mathrm{a})$
$\mathrm{NO}_{3}^{-}+2 \mathrm{H}^{+}+\mathrm{e} \rightarrow \mathrm{NO}_{2}+\mathrm{H}_{2} \mathrm{O}(b)$
For (a),
$E=-\frac{0.06}{3} \log \frac{P_{N O}}{\left[H^{+}\right]^{4}\left[\mathrm{NO}_{3}^{-}\right]}$
For (b),
$\mathrm{E}=\mathrm{E}^{\circ}-\frac{0.06}{1} \log \frac{\mathrm{P}_{\mathrm{NO}_{2}}}{\left[\mathrm{H}^{+}\right]^{2}\left[\mathrm{NO}_{3}^{-}\right]}$
For (a), $\left[\mathrm{NO}_{3}^{-}\right]=\left[\mathrm{H}^{+}\right]=1 \mathrm{M}, \mathrm{P}_{\mathrm{NO}}=10^{-3}$
$E_{R}=0.96-\frac{0.06}{3} \log 10^{-3}=1.02$
$\mathrm{Cu} \rightarrow \mathrm{Cu}^{2+}+2 \mathrm{e}$
$E_{L}=-0.34-\frac{0.06}{2} \log \left[\mathrm{Cu}^{2+}\right]$
$=-0.34-0.03 \log \left[\mathrm{Cu}^{2+}\right]$
$E_{L}=-0.34+0.03 \log 10^{-1}$
$=-0.31$
$\mathrm{E}=\mathrm{E}_{\mathrm{R}}+\mathrm{E}_{\mathrm{L}} \approx 0.71 \mathrm{~V}$
E for $\mathrm{NO}_{3} \rightarrow \mathrm{NO}$,
$\mathrm{E}_{1}=0.65-0.02 \log \frac{10^{-3}}{\left[\mathrm{H}^{+}\right]\left[\mathrm{NO}_{3}^{-}\right]}$
$\mathrm{E}_{2}=0.48-0.06 \log \frac{10^{-3}}{\left[\mathrm{H}^{+}\right]^{2}\left[\mathrm{NO}_{3}^{-}\right]}$
Sol 19: (C) $E_{1}=E_{2}$
$0.65-0.02\left(-3-5 \log \left[\mathrm{HNO}_{3}\right]\right)$
$=0.48-0.06\left(-3-3 \log \left[\mathrm{HNO}_{3}\right]\right)$
$0.65+0.06+0.1 \log \left[\mathrm{HNO}_{3}\right]$
$=0.48+0.18+0.18 \log \left[\mathrm{HNO}_{3}\right]$
$0.08 \log \left[\mathrm{HNO}_{3}\right]=0.71-0.66=0.05$
$\log \left[\mathrm{HNO}_{3}\right]=\frac{5}{8}$
$\left[\mathrm{HNO}_{3}\right]=10^{0.625} \approx 10^{0.66}$

## Match the Columns

Sol $20(A) \rightarrow p, q$
$\mathrm{Cl}^{-}$will not oxidise at low concentration.
$\frac{1}{2} \mathrm{Cl}^{-} \rightarrow \mathrm{Cl}_{2}+\mathrm{e}^{-}$
$\mathrm{E}=\mathrm{E}^{\circ}-0.06 \log \frac{\mathrm{P}_{\mathrm{Cl}_{2}}}{\left[\mathrm{Cl}^{-}\right]^{1 / 2}}$
(B) $\rightarrow \mathrm{p}, \mathrm{q}$

SEP of $\mathrm{Na}^{+}<\mathrm{SEP}$ of $\mathrm{H}_{2} \mathrm{O}$
$\therefore$ Water will get reduced to $H_{2}$ at cathode
(C) $\rightarrow q, r$
$\mathrm{Cl}^{-}$will be oxidised as concentrated solution
(D) $\rightarrow \mathrm{p}, \mathrm{s}$

SEP of $\mathrm{Ag}^{+}<$SEP of $\mathrm{H}_{2} \mathrm{O}$
$\therefore \mathrm{Ag}^{+}$will be reduced to deposit Ag at cathode.

## Previous Years' Questions

Sol 1: (C) In electrolytic cell, electrolysis occur at the cost of electricity :
At cathode: $\mathrm{M}^{\mathrm{n+}}+\mathrm{ne} \rightarrow \mathrm{M}$ (electron gone in solution)
At anode : $\mathrm{X}^{\mathrm{n-}} \rightarrow \mathrm{X}+$ ne $^{-}$(electron supplied to anode)
Therefore, electron is moving from cathode to anode via internal circuit.

Sol 2: (B) The cell reaction is :
$\mathrm{n}+\mathrm{Fe}^{2+} \longrightarrow \mathrm{Zn}^{+}+\mathrm{Fe} ; \mathrm{E}_{\text {cell }}=0.2905 \mathrm{~V}$
$\Rightarrow \mathrm{E}=\mathrm{E}^{\circ}-\frac{0.059}{2} \log \frac{\left[\mathrm{Zn}^{2+}\right]}{\left[\mathrm{Fe}^{2+}\right]}$
$\Rightarrow \mathrm{E}^{\circ}=0.2905+\frac{0.059}{2} \log \frac{0.1}{0.01}=0.32 \mathrm{~V}$
Also, $E^{\circ}=\frac{0.059}{n} \log K$
$\Rightarrow \log \mathrm{K}=\frac{2 \mathrm{E}^{\circ}}{0.059}=\frac{0.32}{0.0295}$
$\Rightarrow \mathrm{K}=(10)^{0.32 / 0.0295}$

Sol 3: (B) The net reaction is
$2 \mathrm{H}^{+}+\frac{1}{2} \mathrm{O}_{2}+\mathrm{Fe} \rightarrow \mathrm{H}_{2} \mathrm{O}+\mathrm{Fe}^{2+}+\mathrm{E}^{\circ}=1.67 \mathrm{~V}$
$\Delta G^{\circ}=-n E^{\circ} F$
$=\frac{2 \times 1.67 \times 96500}{1000} \mathrm{~kJ}$
$=-322.31 \mathrm{~kJ}$

Sol 4: (B) $0.01 \mathrm{~mol} \mathrm{H}_{2}=0.02 \mathrm{~g}$ equivalent
$\Rightarrow$ Coulombs required $=0.02 \times 96500=1930 C$
$\Rightarrow \mathrm{Q}=\mathrm{It}=1930 \mathrm{C}$
$\Rightarrow t=\frac{1930}{10 \times 10^{-3}}=19.3 \times 10^{4} \mathrm{~s}$

Sol 5: (D) $\mathrm{As}_{\mathrm{AgNO}}^{3}$ is added to solution, KCl will be displaced according to following reaction
$\mathrm{AgNO}_{3}(\mathrm{aq})+\mathrm{KCl}(\mathrm{aq}) \rightarrow \mathrm{AgCl}(\mathrm{s})+\mathrm{KNO}_{3}(\mathrm{aq})$
For every mole of KCl displaced from solution, one mole of $\mathrm{KNO}_{3}$ comes in solution resulting in almost constant conductivity. As the end point is reached, added $\mathrm{AgNO}_{3}$ remain in solution increasing ionic concentration, hence conductivity increases.

Sol 6: (D) The half reactions are
$\mathrm{Fe}(\mathrm{s}) \rightarrow \mathrm{Fe}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \times 2$
$\mathrm{O}_{2}(\mathrm{~g})+4 \mathrm{H}^{+} \rightarrow 2 \mathrm{Fe}^{2+}(\mathrm{aq})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
$E=E^{\circ}-\frac{0.059}{4} \log \frac{\left(10^{-3}\right)^{2}}{\left(10^{-3}\right)^{4}(0.1)}=1.57 \mathrm{~V}$
Sol 7: (A, B, D) Metals with $E^{\circ}$ value less than 0.96 V will abletoreduce $\mathrm{NO}_{3}$-inaqueoussolution. Therefore, metals $\mathrm{V}\left(\mathrm{E}^{\circ}=-1.19 \mathrm{~V}\right)$,
$\mathrm{Fe}\left(\mathrm{E}^{\circ}=-0.04 \mathrm{~V}\right), \mathrm{Hg}\left(\mathrm{E}^{\circ}=0.86 \mathrm{~V}\right)$ will all reduce $\mathrm{NO}_{3}^{-}$ but $\mathrm{Au}\left(\mathrm{E}^{\circ}=1.40 \mathrm{~V}\right.$ ) cannot reduce $\mathrm{NO}_{3}^{-}$in aqueous solution.

## Paragraph 1

Sol 8: (B) $\mathrm{E}^{\circ}$ for $2 \mathrm{Ag}^{+}+\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}+\mathrm{H}_{2} \mathrm{O} \longrightarrow 2 \mathrm{Ag}(\mathrm{s})+$ $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{7}+2 \mathrm{H}^{+}$is 0.75 V

Also, $E^{\circ}=\frac{0.0592}{2} \log K$
$\Rightarrow \log \mathrm{K}=\frac{2 \mathrm{E}^{\circ}}{0.0592}=25.33$
$\Rightarrow \ln K=2.303 \log K=58.35$

Sol 9: (C) On increasing concentration of $\mathrm{NH}_{3}$ the concentration of $\mathrm{H}^{+}$ion decreases, therefore,
$\mathrm{E}_{\text {red }}=\mathrm{E}_{\text {red }}^{\circ}-\frac{0.0592}{2} \log \left[\mathrm{H}^{+}\right]^{2}$
$=0-\frac{0.0592}{2} \times 2 \log 10^{-11}=0.65 \mathrm{~V}$
i.e. $\mathrm{E}_{\text {red }}$ increases by 0.65 V .

Sol 10: (D) $\mathrm{NH}_{3}$ has no effect on the $\mathrm{E}^{\circ}$ of glucose/ gluconic acid electrode.

## Paragraph 2

Sol 11: (B) Moles of NaCl electrolysed $=4 \times \frac{500}{1000}=2.0$
$\Rightarrow$ Moles of $\mathrm{Cl}_{2}$ produced $=1.0$
$2 \mathrm{Cl}^{-} \rightarrow+2 \mathrm{e}^{-}$

Sol 12: (D) At cathode: $\mathrm{Na}^{+}+\mathrm{e}^{-} \xrightarrow{\mathrm{Hg}} \underset{\text { amalgam }}{\mathrm{Na}(\mathrm{Hg})}$
Two moles of Na formed during electrolysis would produce two moles of $\mathrm{Na}(\mathrm{Hg})$ amalgam.
$\Rightarrow$ Mass of amalgam $=2 \times(23+200)=446 \mathrm{~g}$

Sol 13: (D) Two Faraday of electric charge would be required for electrolysis of 2.0 moles of NaCl .
$\Rightarrow$ total coulombs $=2 \times 96500=193000 C$

## Paragraph 3

Sol 14: (C) For spontaneous redox reaction: $\mathrm{E}_{\text {cell }}^{\circ}>0$
For $2 \mathrm{I}^{-}+\mathrm{Cl}_{2} \rightarrow 2 \mathrm{Cl}^{-}+\mathrm{I}_{2}$
$\mathrm{E}^{\circ}=1.36-0.54=0.82 \mathrm{~V}>0$
i.e. $\mathrm{Cl}_{2}$ will spontaneously oxidize $\mathrm{I}^{-}$.

Sol 15: (D) In other cases $\mathrm{E}_{\text {cell }}^{\circ}<0$, they are nonspontaneous.

For the reaction:
(i) $4 \mathrm{Fe}^{3+}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{Fe}^{2+}+4 \mathrm{H}^{+}+\mathrm{O}_{2}$;
$\mathrm{E}^{\circ}=-0.46 \mathrm{~V}$
(ii) $4 \mathrm{Mn}^{3+}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{Mn}^{2+}+4 \mathrm{H}^{+}+\mathrm{O}_{2}$ i
$E^{\circ}=+0.27 V$

Sol 16: (A) As evidenced above, reaction (i) is nonspontaneous, therefore, $\mathrm{Fe}^{3+}$ is stable in acid solution. However, reaction (ii) is spontaneous $\mathrm{Mn}^{3+}$ oxidises $\mathrm{H}_{2} \mathrm{O}$ to $\mathrm{O}_{2}$ and itself reduced to $\mathrm{Mn}^{2+}$ in acidic medium.
Sodium fusion extract from aniline produces NaCN which reacts with $\mathrm{Fe}^{2+}$ to form $\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4-}$. The complex ion then reacts with $\mathrm{Fe}^{3+}$ give blue precipitate of Prussian blue.
$\mathrm{Fe}^{3+}+\left[\mathrm{Fe}(\mathrm{CN})_{6}{ }^{4-} \rightarrow \underset{\text { Prussian blue }}{\mathrm{Fe}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{3}}\right.$

## Paragraph 4

Sol 17: (B) $M(s)+M^{+}(a q, 1 M) \rightarrow M^{+}(a q, 0.05 M)+M(s)$
$E_{\text {cell }}=0-\frac{2.303 R T}{F} \log \frac{0.05}{1}>0$
Hence, $\left|E_{\text {cell }}\right|=E_{\text {cell }}=0.70 \mathrm{~V}$ and $\Delta G<0$ for spontaneity of reaction.

Sol 18: (C) $E_{\text {cell }}=E^{\circ}-\frac{0.0538}{1} \log 0.0025=0.139 \mathrm{~V}$
$=139 \mathrm{~V}$

Sol 19: $\mathrm{X} \longrightarrow \mathrm{Y} . \Delta_{\mathrm{r}} \mathrm{G}^{0}=-193 \mathrm{~kJ} \mathrm{~mol}^{-1}$
$\mathrm{M}^{+} \longrightarrow \mathrm{M}^{3+}+2 \mathrm{e}^{-} \quad \mathrm{E}^{0}=-0.25 \mathrm{~V}$
$\Delta G^{0}$ for the this reaction is
$\Delta G^{0}=-n F E^{0}=-2 \times(-0.25) \times 96500=48250 \mathrm{~J} / \mathrm{mol}$
$48.25 \mathrm{~kJ} / \mathrm{mole}$
So the number of moles of $M+$ oxidized using $X \longrightarrow$ $Y$ will be
$=\frac{193}{48.25}=4$ moles

Sol 20: $\mathrm{HK} \rightleftharpoons \mathrm{H}^{+}+\mathrm{X}^{-}$
$\mathrm{Ka}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{X}^{-}\right]}{[\mathrm{HX}]}$
$\mathrm{HY} \rightleftharpoons \mathrm{H}^{+}+\mathrm{Y}^{-}$
$\mathrm{Ka}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{X}^{-}\right]}{[\mathrm{HX}]}$
$\Lambda_{m}$ for $\mathrm{HX}=\Lambda_{\mathrm{m}_{1}}$
$\Lambda_{m}$ for $\mathrm{HX}=\Lambda_{\mathrm{m}_{2}}$
$\Lambda_{\mathrm{m}_{1}}=\frac{1}{10} \Lambda_{\mathrm{m}_{2}}$
$\mathrm{Ka}=\mathrm{C} \propto^{2}$
$\mathrm{Ka}_{1}=\mathrm{C}_{1} \times\left(\frac{\Lambda_{\mathrm{m}_{1}}}{\Lambda_{\mathrm{m}_{1}}^{0}}\right)^{2}$
$\mathrm{Ka}_{2}=\mathrm{C}_{2} \times\left(\frac{\Lambda_{\mathrm{m}_{2}}}{\Lambda_{\mathrm{m}_{2}}^{0}}\right)^{2}$
$\frac{\mathrm{Ka}_{1}}{\mathrm{Ka}_{2}}=\frac{\mathrm{C}_{1}}{\mathrm{C}_{2}} \times\left(\frac{\Lambda_{\mathrm{m}_{2}}}{\Lambda_{\mathrm{m}_{2}}^{0}}\right)^{2}=\frac{0.01}{0.1} \times\left(\frac{1}{10}\right)^{2}=0.001$
$\mathrm{pKa}_{1}-\mathrm{pKa}_{2}=3$

Sol 21: (D) Anode: $\mathrm{H}_{2}(\mathrm{~s}) \longrightarrow 2 \mathrm{H}^{+}+2 \mathrm{e}^{-}$
Cathode: $\quad \frac{\mathrm{Mn}^{+4}+2 \mathrm{e}^{-} \longrightarrow \mathrm{Mn}^{+2}}{\mathrm{Mn}^{+4}+\mathrm{H}^{2} \longrightarrow \mathrm{Mn}^{+2}+2 \mathrm{H}^{+}}$
$\mathrm{E}=\mathrm{E}^{\circ}-\frac{0.059}{2} \log 10\left(\frac{\left[\mathrm{Mn}^{+2}\right]\left[\mathrm{H}^{+}\right]^{2}}{\left[\mathrm{Mn}^{+4}\right] \mathrm{P}_{\mathrm{H}_{2}}}\right)$
$0.092=0.151-\frac{0.059}{2} \log 10\left(10^{x}\right)$
$0.092=0.151-\frac{0.059}{2} x$
$\Rightarrow \quad X=2$

Sol 22: (A) In a galvanic cell, the salt bridge does not participate chemically in the cell reaction.

