17. ELECTROCHEMISTRY

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 metallic lattice, e.g., Cu, Ag, etc.	Passage of current by ions in molten state or in aqueous solution 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 passage of current due to increase in temperature. Thermal motion of metal ions hindering the flow of electrons increases with increase in temperature.	It generally shows a decrease in resistance due to decrease in viscosity of the medium and degree of hydration of ions with 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 $CdBr_2$, $HgCl_2$), mineral acids like HCl, H_2SO_4, HNO_3, etc. and bases like NaOH, KOH, 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 HCN, H_3BO_3, etc. and bases like 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 $CuCl_2$ solution	Pt	$Cu^{2+} + 2e^- \longrightarrow Cu$	$2Cl^- \longrightarrow Cl_2 + 2e^-$
Molten $PbBr_2$	Pt	$Pb^{2+} + 2e^- \longrightarrow Pb$	$2Br^- \longrightarrow Br_2 + 2e^-$
Sodium chloride solution	Hg	$2Na^+ + 2e^- \longrightarrow 2Na$	$2Cl^- \longrightarrow Cl_2 + 2e^-$
Silver nitrate solution	Pt	$Ag^+ + e^- \longrightarrow Ag$	$2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$
Sodium nitrate solution	Pt	$2H^+ + 2e^- \longrightarrow H_2$	$2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$

Illustration 1: Find the charge in coulomb on 1 g-ion of 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 6.02×10^{23} ions. So, charge on one g-ion of N^{3-} can be calculated by multiplying charge.

Charge on one ions of N^{3-} into Avogadro number.

Charge on one ions of $N^{3-} = 3 \times 1.6 \times 10^{-19}$ coulomb One g-ion = 6.02×10^{23} ions

Thus, charge on one g-ion of $N^{3-} = 3 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{23} = 2.89 \times 10^5$ coulomb

Illustration 2: Explain the reaction: (a) $2KI + Cl_2 \longrightarrow 2KCl + I_2$, (b) $2KClO_3 + I_2 \longrightarrow 2KIO_3 + Cl_2$

Sol: Compound which undergoes oxidation acts as a reducing agent and compound which undergoes reduction acts as an oxidizing agent.

(a) Cl_2 acts as oxidizing agent: $2e^- + Cl_2 \longrightarrow 2Cl^-$; $2I^- \longrightarrow I_2 + 2e^-$

(b) I_2 acts as reducing agent: $2Cl^{5+} + 10e^- \longrightarrow Cl_2$; $I_2^0 \longrightarrow 2I^{5+} + 10e^-$

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.

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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: $W \propto Q$

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

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, $Q = 96500$ 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 $V = \frac{ItV_e}{96500}$

Where, V = Volume of gas evolved at STP at an electrode

V_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 s). Determine the mass of iron and the volume of chlorine gas (measured at 25ºC 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): $2Cl^- \to Cl_2(g) + 2e^-$ **Cathode (reduction):** $Fe^{3+} + 3e^- \to Fe(s)$

2. Calculate the number of moles of electrons.

   $$40.0\,\text{amps} \times 36{,}000\,\text{s} = 1.44 \times 10^6\,\text{C}$$

   $$1.44 \times 10^6\,\text{C} \times \frac{1\text{F}}{96{,}485\,\text{C}} = 14.9\text{F}\,;\ 14.9\text{F} \times \frac{1\text{mole e}^-}{1\text{F}} = 14.9\,\text{mole e}^-$$

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.

   $$14.9\,\text{mole e}^- \times \frac{1\text{mole Fe}}{3\text{mole e}^-} = 4.97\,\text{mole Fe};\quad 14.9\,\text{mole e}^- \times \frac{1\text{mole Cl}_2}{2\text{mole e}^-} = 7.45\,\text{mole Cl}_2$$

4. Calculate the mass of iron using the molar mass and calculate the volume of chlorine gas using the ideal gas law (PV = nRT).

   $$4.97\,\text{mole Fe} \times \frac{55.847\text{ gFe}}{1\text{mole Fe}} = 278\,\text{gFe};\quad \frac{(7.45\,\text{mole Cl}_2)(0.0821\,\text{atm L / mole K})(298\text{K})}{1\,\text{atm}} = 182\,\text{L Cl}_2$$

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 $ZnSO_4$ 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.

$$25.00\,\text{g Zn} \times \frac{1\text{mole Zn}}{65.39\,\text{g Zn}} = 0.3823\,\text{mole Zn}$$

(ii) Write the half-reaction for the production of Zn at the cathode. $Zn^{2+}(aq) + 2e^- \to Zn(s)$

(iii) Calculate the moles of e^- required to produce the moles of Zn using the stoichiometry of the balanced half-reaction. According to the equation, 2 moles of electrons will produce one mole of zinc.

$$0.3823\,\text{mole Zn} \times \frac{2\text{mole e}^-}{1\text{mole Zn}} = 0.7646\,\text{mole e}^-$$

(iv) Convert the moles of electrons into coulombs of charge using Faraday's constant.

$$0.76\text{mole e}^- \times \frac{1\text{F}}{1\text{mole e}^-} = 0.7646\text{F};\ \ 0.7646\text{F} \times \frac{96,485\text{C}}{1\text{F}} = 73,770\text{C}$$

(v) Calculate the time using the current and the coulombs of charge.

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

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 H_2. (Remember, at STP, 1 mole of any gas occupies 22.4 L)

$$400.0\text{L } H_2 \times \frac{1\text{mole } H_2}{22.4\text{L } H_2} = 17.9\text{mole } H_2$$

(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:

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

(iii) Calculate the number of moles of electrons. According to the stoichiometry of the equation, 4 mole of e^- are required to produce 2 moles of hydrogen gas, or 2 moles of e^-s for every one mole of hydrogen gas.

$$17.9\text{mole } H_2 \times \frac{2\text{mole e}^-}{1\text{mole } H_2} = 35.8\text{mole e}^-$$

(iv) Convert the moles of electrons into coulombs of charge.

$$35.8\text{mole e}^- \times \frac{1\text{F}}{1\text{mole e}^-} = 35.8\text{F};\ \ 35.8\text{F} \times \frac{96,485\text{C}}{1\text{F}} = 3.45 \times 10^6\ \text{C}$$

(v) Calculate the current required. $I \times 3600\,\text{s} = 3.45 \times 10^6\ \text{C};\ I = 958\,\text{C/s} = 958\,\text{amps}$

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., $Z = \dfrac{\text{Eq.wt. of the substance}}{96500}$

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., $\text{Eq.wt.} = \dfrac{W}{Q} \times 96500$

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 × 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:-

$$W = ZQ = \frac{E}{F} \times Q = \frac{Q}{F} \times E = \frac{Q}{F} \times \frac{M}{z} = \frac{C \times t}{F} \times \frac{M}{z}$$

z = Electrochemical equivalent; Q = Quantity of electricity passed, E = Eq. wt. of the metal,

F = 1 Faraday, M = Atomic mass of the metal; z = Valency of the metal; C = Current passed,

t = Time for which current is passed.

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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 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: $\underset{71.0g}{2Cl^-} \longrightarrow \underset{\substack{71.0g \\ 1mole}}{Cl_2} + \underset{2\times96500\ coulomb}{2e^-}$ $Q = I \times t = 100 \times 5 \times 60 \times 60$ 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 Cl_2 liberated at NTP $= 9.3264 \times 22.4 = 201L$

Illustration 4: How much electric charge is required to oxidize (a) 1 mole of H_2O to O_2 and

(b) 1 mole of FeO to Fe_2O_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: $\underset{1mole}{H_2O} \longrightarrow \frac{1}{2}O_2 + 2H^+ + \underset{2mole}{2e^-}$ **;** $Q = 2 \times F = 2 \times 96500 = 193000$ coulomb

(b) The oxidation reaction is: $FeO + \frac{1}{2}H_2O \longrightarrow \frac{1}{2}Fe_2O_3 + H^+ + e^-$; $O = F = 96500$ coulomb

Illustration 5: An aqueous solution of sodium chloride on electrolysis gives $H_2(g), Cl_2(g)$ and NaOH according to the reaction. $2Cl^-(aq.) + 2H_2O \longrightarrow 2OH^-(aq.) + H_2(g) + Cl_2(g)$.

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 kg of 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 Cl_2 present in 1 kg.

Reactions at anode and cathode are: $2Cl^- \longrightarrow Cl_2 + 2e^-$ (at anode)

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \ \text{(at cathode)} \quad 1\text{kg of } Cl_2 = \frac{1000}{71.0} = 14.08 \text{ mole}$$

Charge to produce one mole of Cl_2=2 x 96500

Charge to produce 14.08 mole of Cl_2=2x96500x14.08

Effective current = $\frac{62}{100} \times 25.0 = 15.5$ ampere

$$\text{Time} = \frac{\text{Charge}}{\text{Current}} = \frac{2 \times 96500 \times 14.08}{15.5} = 175318.7 \text{ second} = 48.699 \text{ hour}$$

OH^- ions produced = 2 × moles of Cl_2 = 2x14.08 = 28.16

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

Illustration 6: An acidic solution of Cu^{2+} salt containing 0.4 g of 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: $0.4 \text{ g of } Cu^{2+} = \frac{0.4}{31.75} = 0.0126\text{g} - \text{equivalent}$

$$\text{At the same time, the oxygen deposited at anode} = \frac{8}{32} \times 0.0126\text{g} = 0.00315\text{g} - \text{mole}$$

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 $= \frac{1}{96500} \times 504 = 0.00523\text{g} - \text{equivalent} \ = \frac{8}{32} \times 0.00523 = 0.001307\text{g} - \text{mole}$

Hydrogen liberated $= 0.00523\text{g} - \text{equivalent} = \frac{1}{2} \times 0.00523 = 0.00261\text{g} - \text{mole}$

Total gases evolved $= (0.00315 + 0.001307 + 0.00261)\text{g} - \text{mole} \ = 0.007067\text{g} - \text{mole}$

Volume of gases evolved at NTP $= 22400 \times 0.007067\text{mL} \ = 158.3\text{mL}$

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.

$$A^+B^- + aq. \longrightarrow A^+(aq.) + B^-(aq.)$$

(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 'α'

(c) $\alpha = \dfrac{\text{Number of molecules dissociated into ions}}{\text{Total number of molecules}}$

(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. $AB \rightleftharpoons A^+ + B^-$

(e) Applying the law of mass action to the above equilibrium $\dfrac{[A^+][B^-]}{[AB]} = K$. 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.

$AB \rightleftharpoons A^+ + B^-$	(Both ions are equal)
$NaCl \rightleftharpoons Na^+ + Cl^-$	(Both ions are equal)
$AB_2 \rightleftharpoons A^{2+} + 2B^-$	(Anions are double that of cations)
$BaCl_2 \rightleftharpoons Ba^{2+} + 2Cl^-$	(Anions are double that of cations)
$A_2B \rightleftharpoons 2A^+ + B^{2-}$	(Cations are double that of anions)
$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$	(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 H^+ ions while basic solution contains OH^- ions and characteristic properties of solutions are those of H^+ ions and 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.

$$\text{Conductance} = \frac{1}{\text{Resistance}} = \frac{1}{R} \qquad \text{... (i)}$$

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. $R \propto \frac{l}{a}$ or $R = \rho\frac{l}{a}$ .... (ii)

Where, ρ is called the specific resistance. If l = 1 cm and a = 1cm^2, then $R = \rho$ ... (iii)

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 κ, Thus,

$\kappa = \frac{1}{\rho}, \kappa = \text{kappa}$ – The specific conductance ... (iv)

Specific conductance is also called conductivity.

From eq. (ii), we have $\rho = \frac{a}{l}\cdot R$ or $\frac{1}{\rho} = \frac{l}{a}\cdot\frac{1}{R}$; $\kappa = \frac{l}{a}\times C$ $\left(\frac{l}{a} = \text{cell constant}\right)$

or Specific conductance = conductance × 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 Λ.

In general $\Lambda = \kappa \times V$ ... (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 $\Lambda = \kappa \times \frac{1000}{c}$ ... (vi)

$\Lambda = \kappa \times \frac{1000}{N}$; where, N = normality. The unit of equivalent conductance is $\text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$.

5.3 Molar Conductance

The molar conductance is defined as the conductance of all the ions produced by ionization of **1 g-mole** of an electrolyte when present in V ml of solution. It is denoted by μ.

Molar conductance $\mu = \kappa \times V$ ... (vii)

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 $\mu = \kappa \times \frac{1000}{c}$ Its unit is $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

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 sq. 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 $= \kappa \times V$

In order to find equivalent conductivity we have to calculate specific conductance.

Specific conductance (κ) is given as $\kappa = \frac{l}{a} \cdot \frac{1}{R}$

Given, l = 2.1 cm, a = 4.2 sq. cm, R = 50 ohm. Specific conductance, $\kappa = \frac{l}{a} \cdot \frac{1}{R}$

Or $\kappa = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01\ \text{ohm}^{-1}\ \text{cm}^{-1}$; Equivalent conductivity $= \kappa \times V$

V = The volume containing 1 g-equivalent = 1000 mL

So, Equivalent conductivity $= 0.01 \times 1000 = 10\ \text{ohm}^{-1}\ \text{cm}^2\ \text{eq}^{-1}$

Illustration 8: The specific conductivity of $0.02\text{M}\ \text{KCl}$ solution at 25°C is $2.768 \times 10^{-3}\ \text{ohm}^{-1}\ \text{cm}^{-1}$. The resistance of this solution at 25°C when measured with a particular cell was 250.2 ohm. The resistance of $0.01\ \text{M}\ \text{CuSO}_4$ solution at 25°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 $= \text{Sp. cond.} \times \frac{1000}{C}$ 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 = $\frac{\text{Sp. cond. of KCl}}{\text{Conductance of KCl}} = \frac{2.768 \times 10^{-3}}{1/250.2} = 2.768 \times 10^{-3} \times 250.2$

For 0.01 M CuSO_4 solution

Sp. Conductivity = Cell constant × Conductance $= 2.768 \times 10^{-3} \times 250.2 \times \frac{1}{8331}$

Molar conductance $= \text{Sp. cond.} \times \frac{1000}{C} = \frac{2.768 \times 10^{-3} \times 250.2}{8331} \times \frac{1000}{1/100} = 8.312\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

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., $\Lambda = \lambda_+ + \lambda_-$ λ_C and λ_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, $\lambda_C = ku_C$ and $\lambda_a = ku_a$, where, u_C and u_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, μ: It is the distance travelled by an ions per second under a potential gradient of 1 volt per meter.

1. For an, $\mu = \lambda^o / F$
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:

   $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+; F^- < Cl^- < Br^- < I^-; Al^{3+} < Mg^{2+} < Na^+$
4. The size of gaseous 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 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 Λ_m^0 of a weak electrolyte: In order to calculate Λ_m^0 of a weak electrolyte say CH_3COOH, we determine experimentally Λ_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 CH_3COONa

(iii) A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

Λ_m^0 of CH_3COOH is then given as: $\Lambda_m^0(CH_3COOH) = \Lambda_m^0(HCl) + \Lambda_m^0(CH_3COONa) - \Lambda_m^0(NaCl)$

Proof: $\Lambda_m^0(HCl) = \lambda_H^0 + \lambda_{Cl^-}$ ... (i)

$\Lambda_m^0(CH_3COONa) = \lambda^0_{CH_3COO^-} + \lambda_{Na^+}$ ... (ii)

$\Lambda_m^0(NaCl) = \lambda^0_{Na^+} + \lambda^0_{Cl^-}$ ... (iii)

Adding equation (I) and equation (II) and subtracting (III) from them:

$$\Lambda^0_{(HCl)} + \Lambda^0_{(CH_3COONa)} - \Lambda^0_{(NaCl)} = \lambda^0_{(H^+)} + \lambda^0_{(CH_3COO^-)} = \Lambda_{0(CH_3COOH)}$$

(b) Determination of degree of dissociation (α): $\alpha = \frac{\text{No. of molecules ionised}}{\text{Total number of molecules dissolved}} = \frac{\Lambda_m}{\Lambda_m^0}$

(c) Determination of solubility of sparingly soluble salt: $\Lambda_m^0 = \frac{1000\kappa}{C}$,

Where C is the molarity of solution and hence the solubility.

(d) Determination of ionic product of water: From Kohlrausch's law, we determine Λ_m^0 of H_2O where Λ_m^0 is the molar conductance of water at infinite dilution when one mole of water is completely ionized to give one mole of H^+ and one mole of OH^- ions i.e. $\Lambda_m^0(H_2O) = \lambda^0_{H^+} + \lambda^0_{OH^-}$

Again using the following $\Lambda_m = \frac{\kappa \times 1000}{C}$, where C=molar concentration i.e. mole L^{-1} or mole dm^{-3}

$\Rightarrow \quad \Lambda_m = \frac{\kappa}{C}$, where C = concentration in mole m^{-3}

Assuming that Λ_m differs very little from Λ_m^0; $\Lambda_m^0 = \frac{\kappa}{C} \Rightarrow C = \frac{\kappa}{\Lambda_m^0}$

Specific conductance (κ) of pure water is determined experimentally. Thereafter, molar concentration of dissociated water is determined using the above equation. K_w is then calculated as: $K_w = C^2$

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. $AB \rightleftharpoons A^+ + B^-$

(ii) The Concept of chemical equilibrium and law of mass action can be applied to ionic equilibrium also.

	AB	A^+ + B^-
t = 0	C	0 0

$t_{eq.} \quad C - C\alpha \quad C\alpha \quad C\alpha;\ K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)};\quad K = \frac{C\alpha^2}{1-\alpha}$ ... (i)

For weak electrolytes, $\alpha << 1 \quad \therefore \quad (1-\alpha) \approx 1$

Thus, equation (i) can be written as: $K = C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K}{C}}$ ... (ii)

From eq. (ii), it is clear that on dilution concentration decreases, as a result of which degree of ionization 'α' increases. Both equivalent and molar conductance increase when at a high degree of ionization.

(iii) Degree of ionization can be calculated as: $\alpha = \frac{\Lambda_e^C}{\Lambda_e^\infty} = \frac{\Lambda_m^C}{\Lambda_m^\infty}$ ... (iii)

Λ_e^C, Λ_m^C = Equivalent and molar conductance at concentration 'C'

$\Lambda_e^\infty, \Lambda_m^\infty$ = Equivalent and molar conductance at infinite dilution.

Substituting the values of 'α' from eq. (iii) in eq. (i), we get $K = \frac{C \times \left(\frac{\Lambda_e^C}{\Lambda_e^\infty}\right)^2}{1 - \frac{\Lambda_e^C}{\Lambda_e^\infty}} = \frac{C(\Lambda_e^C)^2}{\Lambda_e^\infty(\Lambda_e^\infty - \Lambda_e^C)}$ ... (iv)

Similarly $K = \frac{C(\Lambda_m^C)^2}{\Lambda_m^\infty(\Lambda_m^\infty - \Lambda_m^C)}$ ... (v)

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 Na^+ and Cl^- ions at the same temperature are 43.0 and 65.0 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 Λ_∞

Λ_v . Λ_∞ is determined by summing up ionic conductance of each ion. Λ_v is product of specific conductance and dilution.

Equivalent conductance of N/10 NaCl solution

$\Lambda_v = \text{Sp.conductivity} \times \text{dilution} = 0.0092 \times 10{,}000 = 92\ ohm^{-1}$;

$\Lambda_\infty = \lambda_{Na^+} + \lambda_{Cl^-} = 43.0 + 65.0 = 108\ ohm^{-1}$

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

Illustration 10: At 18°C, the conductivities at infinite dilution of $NH_4Cl, NaOH$ and $NaCl$ are 129.8, 217.4 and 108.9 mho respectively. If the equivalent conductivity of N/100 solution of NH_4OH is 9.93 mho, calculate the degree of dissociation of NH_4OH 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. Λ_v is given. Λ_∞ is determined by summing up ionic conductance of each ion

$\Lambda_{\infty NH_4Cl} = \lambda_{NH_4^+} + \lambda_{Cl^-} = 129.8$ ... (i)

$\Lambda_{\infty NaOH} = \lambda_{Na^+} + \lambda_{OH^-} = 217.4$ ... (ii)

Adding eqs. (i) and (ii) and subtracting eq. (iii),

$$\Lambda_{NH_4^+} + \lambda_{Cl^-} + \lambda_{Na^+} + \lambda_{OH^-} - \lambda_{Na^+} - \lambda_{Cl^-} = \lambda_{NH_4^+} + \lambda_{OH^-} = 129.8 + 217.4 - 108.9$$

$\Lambda_{\infty NH_4OH} = 238.3\text{ mho}$. Degree of dissociation, $\alpha = \frac{\Lambda_v}{\Lambda_\infty} = \frac{9.93}{238.3} = 0.04167$ 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

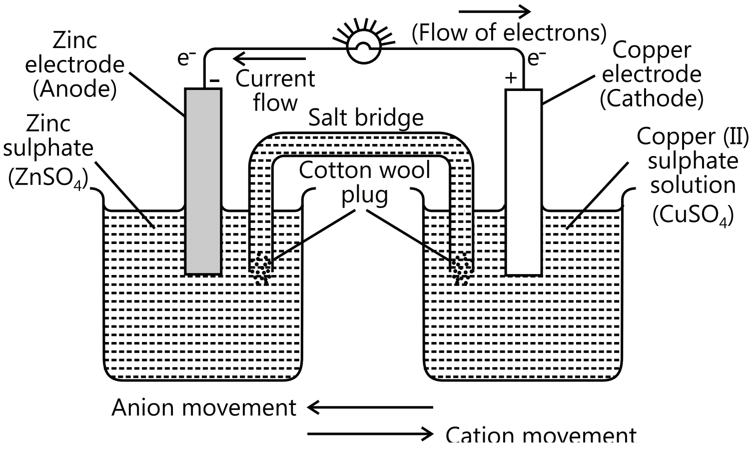

Figure 17.1: Representation of a daniel cell

Oxidation half reaction, $Zn(s) \longrightarrow Zn^{2+}(aq.) + 2e^-$

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

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

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.

$Zn | Zn^{2+} || Cu^{2+} | Cu$

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.

$M \longrightarrow Mn^+ + ne^-$

Reduction potential: It is the tendency of an electrode to get reduced, i.e., to accept electrons.

$Mn^+ + ne^- \longrightarrow M$

Standard Electrode Potential: The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 M) at 25ºC (278 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 M) at 25ºC (298 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°_{cell}

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ or $E^\circ_{cell} = E^\circ_{right\ electrode} - E^\circ_{left\ electrode}$

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.

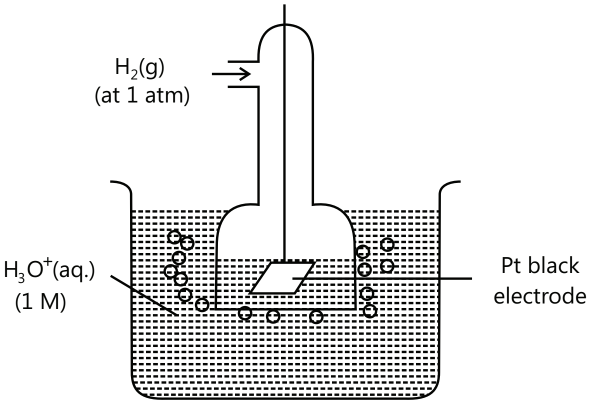

Figure 17.2: Representation of reference electrode

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	Electrode potential
$H_2 \longrightarrow 2H^+ + 2e^-$	0.0 V (Anode)
$2H^+ + 2e^- \longrightarrow H_2$	0.0 V (Cathode)

8.5 Some other Reference Electrodes

(i) Calomel Electrode:

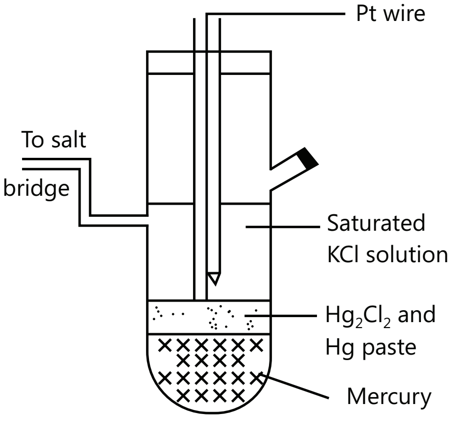

Figure 17.3: Representation of calomel electrode

Reaction when electrode act as cathode: $\frac{1}{2}Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl$

(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: Ag | AgCl | Cl^-

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

PLANCESS CONCEPTS

In $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$, oxidant should be taken as $[MnO_4^-][H^+]^8$, i.e., 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 Zn^{2+} in the Zn/Cu cell from its unit-activity value of around 0.5 M to a much smaller value:

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

This will reduce the value of Q for the cell reaction $Zn(s) + Cu^{2+} \longrightarrow Zn^{2+} + Cu(s)$

The free energy change ΔG more negative than ΔG^0, so than E would be more positive than E^o.

The relation between the actual cell potential E and the standard potential E^o is developed in the following way.

According to cell potential and Gibb's free energy change: $\Delta G^0 = -nE^oF$; $\Delta G = -nEF$

These expressions can then be substituted into the relation $\Delta G = \Delta G^0 + RT\ln Q$

Which gives $-nEF = -nE^oF + RT\ln Q$. Which can be rearranged to $E = E^\circ - \frac{RT}{nF}\ln Q$

This is Nernst Equation, which relates the cell potential to the standard potential E^o. If Q is unity then at 25°C

Nernst Equation will be $E = E^o - \frac{0.059}{n}\log Q$

And for a general electrochemical reaction of the type aA+bBcC+dD

Nernst equation can be written as: $E_{cell} = E^\circ_{(cell)} - \frac{RT}{nF}\ln Q = E^\circ_{(cell)} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$

PLANCESS CONCEPTS

- The overall reaction and ΔG^o for each cell is same.
- E^o_{cell} and 'n' values are different for each cell.
- $E^o_{cell} \times n$ is same for each cell.
- ΔG^o depends on cell reaction and E^o_{cell} depends upon making up of a cell.

B Rajiv Reddy (JEE 2010 AIR 11)

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 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 Fe, Pb, Sn, Ni, 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. $K^+, Ca^{2+}, Na^+, Mg^{+2}, Al^{+3}, \ Zn^{+2}, Fe^{+2}, H^+, Cu^{+2}, Ag^+, Au^{+3}$ 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 + ne^-)	**$\rightarrow$ Reduced form**		**E°/V**
Increasing strength of oxidizing agent	$F_2(g) + 2e^-$	$\rightarrow 2F^-$	Increasing strength of reducing agent	2.87
	$Co^{3+} + e^-$	$\rightarrow Co^{2+}$		1.81
	$H_2O_2 + 2H^+ + 2e^-$	$\rightarrow 2H_2O$		1.78
	$MnO_4^- + 8H^+ + 5e^-$	$\rightarrow Mn^{2+} + 4H_2O$		1.51
	$Au^{3+} + 3e^-$	$\rightarrow Au(s)$		1.40
	$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$		1.36
	$Cr_2O_7^{2-} + 14H^+ + 6e^-$	$\rightarrow 2Cr^{3+} + 7H_2O$		1.33
	$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$		1.23
	$MnO_2(s) + 4H^+ + 2e^-$	$\rightarrow Mn^{2+} + 2H_2O$		1.23
	$Br_2 + 2e^-$	$\rightarrow 2Br^-$		1.09
	$NO_3^- + 4H^+ + 3e^-$	$\rightarrow NO(g) + 2H_2O$		0.97
	$2Hg^{2+} + 2e^-$	$\rightarrow Hg_2^{2+}$		0.92
	$Ag^+ + e^-$	$\rightarrow Ag(s)$		0.80
	$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$		0.77
	$O_2(g) + 2H^+ 2e^-$	$\rightarrow H_2O_2$		0.68
	$I_2 + 2e^-$	$\rightarrow 2I^-$		0.54
	$Cu^+ + e^-$	$\rightarrow Cu(s)$		0.52
	$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$		0.34
	$AgCl(s) + e^-$	$\rightarrow Ag(s) + Cl^-$		0.22
	$AgBr(s) + e^-$	$\rightarrow Ag(s) + Br^-$		0.10
	$2H^+ + 2e^-$	**$\rightarrow H_2(g)$**		**0.00**
	$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$		-0.13
	$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$		-0.14
	$Ni^{2+} + 2e^-$	$\rightarrow Ni(s)$		-0.25

	Reaction (Oxidized form + ne^-)	**$\rightarrow$ Reduced form**		**E°/V**
↑ Increasing strength of oxidizing agent	$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$	Increasing strength of reducing agent ↓	-0.44
	$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$		-0.74
	$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$		-0.76
	$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$		-0.83
	$Al^{3+} + 3e^-$	$\rightarrow Al(s)$		-1.66
	$Mg^{2+} + 2e^-$	$\rightarrow Mg(s)$		-2.36
	$Na^+ + e^-$	$\rightarrow Na(s)$		-2.71
	$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$		-2.87
	$K^+ + e^-$	$\rightarrow K(s)$		-2.93
	$Li^+ + e^-$	$\rightarrow Li(s)$		-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°_{cell}
2. Determining the standard state free energy change from E°_{cell}
3. Determining the non-standard free energy change

Determining the Equilibrium Constant from E°_{cell}

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. $E^{\circ}_{cell} = \frac{RT}{nF}\ln Q$

At equilibrium Q = K, Substituting in K for Q and the values for R, T and F we get:

$$E^{\circ}_{cell} = \frac{0.0257}{n}\ln K = \frac{0.0592}{n}\log K$$

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

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

$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$ $\qquad E^{\circ}_{reduction} = +0.799\,V$

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $\qquad E^{\circ}_{oxidation} = -0.518\,V$

$2Ag^+(aq) + Al(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$ $\qquad E^{\circ}_{cell} = +0.281\,V$

n = 2 moles of electrons

(ii) Substitute into the above equations and solve for K.

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

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

Determining the Standard State Free Energy Change from E°_{cell}

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

1. Determine the E°_{cell}
2. Determine the number of moles of electrons transferred in the reaction.
3. Solve for ΔG° using the equation $\Delta G^{\circ} = -nFE^{\circ}_{cell}$

$\Delta G^{o} =$ standard state free energy change (joules); n = number of moles of electrons transferred

F = Faraday's constant (96,485 C/mole e^{-}); $E^{\circ}_{cell} =$ standard state cell potential (volts or joules/C)

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

(The solution for the determination of the E°_{cell} and the number of moles of electrons, n, are shown in the example in the previous section.)

1. Determine the E°_{cell}. $E^{\circ}_{cell} = +0.281\,\text{volts}$
2. Determine the number of moles of electrons transferred. n = 2 moles of e^{-}
3. Substitute into the equation and solve.

$$\Delta G^{\circ} = -(2\,\text{mol}\,e^{-})(96,485\,C/\text{mol}\,e^{-})0.281\,J/C;\ \Delta G^{\circ} = -54,200\,J \text{ or } -54.2\,kJ$$

Determining the Non-Standard State Free Energy Change

To determine the non-standard state free energy change:

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

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

$$Zn(s)\,|\,Zn^{2+}(1.50M)\,||\,Cu^{2+}(0.25M)\,|\,Cu(s)$$

1. Calculate E°_{cell}.

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ $\qquad E^{\circ}_{oxidiation} = +0.762\,\text{volts}$

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $\qquad E^{\circ}_{reduction} = +0.339\,\text{volts}$

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ $\qquad E^{\circ}_{cell} = +1.101\,\text{volts}$

2. Determine "n". n = 2 moles of electrons

3. Calculate Q; $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1.50}{0.25} = 6.0$

4. Calculate E_{cell}; $E_{cell} = 1.101\,\text{volts} - \frac{0.0257}{2}\ln 6 = 1.078\,\text{volt}$

5. Calculate ΔG.

$\Delta G = -nFE_{cell} = -(2\text{mole } e^-)(96,485\,C/\text{mole } e^-)(1.078 \text{ volts})$; $\Delta G = -208,000$ 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.

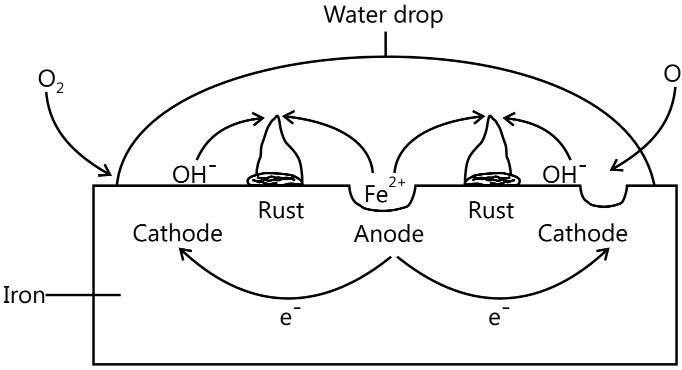

Figure 17.4 : Process of corrosion

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

Reduction: $O_2 + 4H^+(aq.) + 4e^- \longrightarrow 2H_2O(l)$

Atmospheric: $4Fe^{2+} + O_2 + 4H_2O(l) \longrightarrow 2Fe_2O_3(s) + 8H^+(aq.)$

Oxidation: $Fe_2O_3 + xH_2O \longrightarrow \underset{\text{Rust}}{Fe_2O_3.xH_2O}$

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 Zn^{2+}; $Zn \longrightarrow Zn^{2+} + 2e^-$ (Anode reaction)

The electrons are utilized at carbon rod (cathode) as the ammonium ions are reduced.

$2NH_4^+ + 2e^- \longrightarrow 2NH_3 + H_2$ (Cathode reaction)

The cell reaction is $Zn + 2NH_4^+ \longrightarrow Zn^{2+} + 2NH_3 + H_2$

Hydrogen is oxidized by MnO_2 in the cell. $2MnO_2 + H_2 \longrightarrow 2MnO(OH)$

Ammonia produced at cathode combines with zinc ions to form complex ion.

$Zn^{2+} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$; E_{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 $[OH^-]$.
- Alkaline cells retards corrosion as corrosion is favored more in H^+ ions.
- Alkaline cells show more efficient ion transport because of alkaline electrolyte and thus give rise to more stable current and voltage.

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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: $[H_2(g) + 2OH^-(aq.) \longrightarrow 2H_2O(l) + 2e^-] \times 2$

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

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

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.

$$\underset{\text{Anode}}{\underline{\text{Pt}, H_2(\text{Pr essure } p_1)}}[H^+]\underset{\text{Cathode}}{\underline{H_2(\text{Pressure } p_2)\text{Pt}}}$$

If $p_1 > p_2$, oxidation occurs at LHS electrode and reduction occurs at RHS electrode.

$$E_{cell} = \frac{0.0591}{2}\log\frac{(p_1)}{(p_2)} \text{at } 25^oC$$

In the amalgam cells, two amalgams of the same metal at two different concentrations are immersed in the same electrolytic solution. $M(HgC_1)|M^{n+}|Zn(HgC_2)$

The e.m.f of the cell is given by the expression $E_{cell} = \frac{0.0591}{n}\log\frac{C_1}{C_2}$ at $25^\circ C$

(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: (C_2 is greater than C_1).

$$M|M^{n+}(C_1)||M^{n+}(C_2)|M \text{ or } \underbrace{Zn|Zn^{2+}(C_1)}_{\text{Anode}}||\underbrace{Zn^{2+}(C_2)|Zn}_{\text{Cathode}}$$

The e.m.f of the cell is given by the following expression: $E_{cell} = \frac{0.0591}{n}\log\frac{C_{2(RHS)}}{C_{1(LHS)}}$ at 25°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.

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

Sol:

(i) Write the half-reactions for each process. $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$; $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

(ii) Look up the standard potentials for the reduction half-reaction. $E^\circ_{reduction}$ of $Cu^{2+} = +0.339\,V$

(iii) Look up the standard reduction potential for the reverse of the oxidation reaction and change the sign.

$E^\circ_{reduction}$ of $Zn^{2+} = -0.762\,V$, $E^\circ_{oxidation}$ of $Zn = -(-0.762\,V) = +0.762\,V$

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

Oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $\quad E^\circ_{oxidation} = -E^\circ_{reduction} = -(-0.762\,V) = +0.762\,V$

Reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad E^\circ_{reduction} = +0.339\,V$

Overall: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ $\quad E^\circ_{cell} = +1.101\,V$

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.

$O_2(g) + 4H^+(aq) + 4Br^-(aq) \rightarrow 2H_2O(l) + 2Br_2(l)$

Sol: (i) Calculate the standard cell potential for the reaction, $E^\circ_{cell,}$ using the tabled values:

Oxidation: $4Br^-(aq) \rightarrow 2Br_2(l) + 4e^-$ $\quad E^\circ_{oxidation} = -E^\circ_{reduction} = -(+1.077\,V) = -1.077\,V$

Reduction: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$ $\quad E^\circ_{reduction} = +1.229\,V$

Overall: $O_2(g) + 4H^+(aq) + 4Br^-(aq) \rightarrow 2H_2O(l) + 2Br_2(l)$ $\quad E^\circ_{cell} = +0.152\,V$

(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.)

$$Q=\frac{1}{P_{O_2}[H^+]^4[Br^-]^4};\ Q=\frac{1}{(2.50\,atm)(0.10\ M)^4(0.25M)^4};\ Q=1.02\times10^6$$

(iv) Calculate the number of moles of electrons transferred in the balanced equation, n.

n = 4 moles of electrons

(v) Substitute values into the Nernst equation and solve for the non-standard cell potential, E_{cell}.

$$E_{cell}=+0.152\,V-(0.0257/4)\ln(1.02\times10^6), E_{cell}=0.063\,V$$

Illustration 11: Reaction $\rightarrow 2Ag+Cd^{2+}$. The standard electrode potentials for $Ag^+\rightarrow Ag$ and $Cd^{2+}\rightarrow Cd$ couples are 0.80 volt and -0.40 volt respectively

(i) What is the standard potential E° 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° 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: $2Ag^+ + \underset{\substack{\text{Reduction}\\\text{(Cathode)}}}{2e^-}\longrightarrow 2Ag$

$E^\circ_{Ag^+/Ag}=0.80\,\text{volt}$ (Reduction potential); $Cd\longrightarrow \underset{\substack{\text{Oxidation}\\(\text{Anode})}}{Cd^{2+}}+2e^-$

$E^\circ_{Cd^{2+}/Cd}=-0.40\,\text{volt}$ (Reduction potential) or $E^\circ_{Cd/Cd^{2+}}=+0.40\,\text{volt}$

$$E^o=E^\circ_{Cd/Cd^{2+}}+E^\circ_{Ag^+/Ag}=0.40+0.80=1.20\,\text{volt}$$

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:

$Zn\,|\,\underset{0.25M}{Zn(NO_3)_2}\,||\,\underset{0.1M}{AgNO_3}\,|\,Ag$ At 25°C. **(JEE MAIN)**

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

$$E^\circ_{cell}=E^\circ_{oxidation}-E^\circ_{reduction}$$

After calculating E°_{cell} e.m.f of the cell can be easily calculated using following equation

$$E_{cell}=E^\circ_{cell}-\frac{0.0591}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]}$$

The cell reaction is $Zn+2Ag^+\longrightarrow 2Ag+Zn^{2+}$; $E^\circ_{oxidation}$ of $Zn=0.76\,\text{volt}$

$E^\circ_{reduction}$ of $Ag=0.80\,\text{volt}$; $E^\circ_{cell}=E^\circ_{oxidation}$ of $Zn+E^\circ_{reduction}$ of $Ag=0.76+0.80=1.56\,\text{volt}$

We know that, $E_{cell}=E^\circ_{cell}-\frac{0.0591}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]}$

$$=E^\circ_{cell}-\frac{0.0591}{n}\log\frac{0.25}{0.1\times0.1}=1.56-\frac{0.0591}{2}\times1.3979=(1.56-0.0413)\,\text{volt}=1.5187\,\text{volt}.$$

Illustration 13: Calculate the e.m.f of the cell. $Mg(s)\,|\,Mg^{2+}(0.2M)\,||\,Ag^{+}(1\times10^{-3})\,|\,Ag$

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

What will be the effect on e.m.f if concentration of Mg^{2+} ion is decreased to 0.1 M? **(JEE MAIN)**

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

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

After calculating E°_{cell} e.m.f of the cell can be easily calculated using following equation

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

$E^{\circ}_{cell} = E^{\circ}_{Cathode} - E^{\circ}_{Anode} = 0.80-(-2.37) = 3.17\,\text{volt}$

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

$$= 3.17 - \frac{0.0591}{2}\log\frac{0.2}{[1\times10^{-3}]^{2}} = 3.17 - 0.1566 = 3.0134\,\text{volt} \text{ when } Mg^{2+} = 0.1M$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{2}\log\frac{0.1}{(1\times10^{-3})^{2}} = (3.17-0.1477)\,\text{volt} = 3.0223\text{ volt.}$$

Illustrations 14: To find the standard potential of M^{3+} / M electrode, the following cell is constituted:

$Pt\,|\,M\,|\,M^{3+}(0.0018\,mol^{-1}L)\,||\,Ag^{+}(0.01\,mol^{-1}L)\,|\,Ag$

The e.m.f of this cell is found to be 0.42 volt. Calculate the standard potential of the half reaction

$M^{3+} + 3e^{-} \longrightarrow M.\ E^{\circ}_{Ag^{+}/Ag} = 0.80\,\text{volt.}$ **(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

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

The cell reaction is $M + 3Ag^{+} \longrightarrow 3Ag + M^{3+}$

Applying Nernst equation, $E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{3}\log\frac{[M^{3+}]}{[Ag^{+}]^{3}}$

$$0.42 = E^{\circ}_{cell} - \frac{0.0591}{3}\log\frac{(0.0018)}{(0.01)^{3}} = E^{\circ}_{cell} - 0.064\ ;\ E^{\circ}_{cell} = (0.42+0.064) = 0.484\,\text{volt}$$

$$E^{\circ}_{cell} = E^{\circ}_{Cathode} - E^{\circ}_{Anode} \text{ or } E^{\circ}_{Anode} = E^{\circ}_{Cathode} - E^{\circ}_{Cell} = (0.80-0.484) = 0.32\,\text{volt}.$$

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 × 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 25ºC.

(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, $E^{\circ}_{\text{reduction,}}$ 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, $E^{\circ}_{\text{oxidation}} = -E^{\circ}_{\text{reduction}}$.

(v) Add the potentials of the half-cells to get the overall standard cell potential.

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

(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 $E_{cell,}$ the cell potential at the non-standard state conditions using the Nernst equation.

$$E_{cell} = E^{\circ}_{cell} - (RT / nF)\ln Q$$

E_{cell} = cell potential at non-standard state conditions; E°_{cell} = standard state cell potential

R = constant (8.31 J/mole K); T = absolute temperature (Kelvin scale)

F = Faraday's constant (96,485 C/mole e^-)

n = Number of moles of electrons transferred in the balanced equation for the reaction occurring in the cell;

Q = Reaction quotient for the reaction. $aA + bB \rightarrow cC + dD,\ Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

If the temperature of the cell remains at 25ºC, the equation simplifies to:

$E_{cell} = E^{\circ}_{cell} - (0.0257 / n)\ln Q$ or in terms of $\log_{10}$; $E_{cell} = E^{\circ}_{cell} - (0.0592 / n)\log Q$

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 (NaCl, HCl, NaOH) or weak (NH_4OH, CH_3COOH, HF). 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. **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: $CaCl_2(s) + H_2O \rightarrow Ca^{+2}(aq) + 2Cl^-(aq)$.
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 non-metallic part of the circuit (usually an electrolyte). b. Anode: The electrode at which oxidation occurs. c. Cathode: The electrode at which reduction occurs. d. Electrolyte: A liquid, paste, or gel that serves to conduct charge by moving ions in the cell. e. Half-cell: A single electrode immersed in a solution of its ions. f. Salt bridge: A device (porous disk or bridge i.e. U-tube containing inert electrolytic solution, KCl, NH_4NO_3, etc.) placed between the cells which maintains electrical neutrality by allowing ions to migrate between the cells. g. External circuit: The part of the cell where charge is conducted as a current of moving electrons. h. Standard Electrode Reduction Potential E°: The measurement, in volts, of the tendency for a half reaction to occur as a reduction half reaction.

<table>
<tr><th>S.No.</th><th></th><th colspan="3">Description</th></tr>
<tr><td>6</td><td>Voltaic/Galvanic Cells</td><td colspan="3">Redox reactions are spontaneous and chemical energy is transformed into electrical energy. The cell potential E° is positive and the anode is the negative electrode. i.e. batteries
$Zn(s)\,|\,Zn^{+2}(1M)\,||\,Cu^{+2}(1M)\,|\,Cu(s)$
anode || cathode</td></tr>
<tr><td>7</td><td>Electrolytic Cells</td><td colspan="3">Cell in which an external electric current is required to drive a non-spontaneous redox reaction. The cell potential (E^o) is negative and the anode is the positive electrode. i.e. electrolysis, electroplating, etc.
$Cu(s)\,|\,Cu^{+2}(1M)\,||\,Cu^{+2}(1M)\,|\,Cu(s)$
anode || cathode</td></tr>
<tr><td>8</td><td>Quick Comparison of Electrolytic Cells</td><td>Type of redox reaction cell potential (E^o_{cell}) Electron flow
Site of oxidation
Site of reduction
Positive electrode
Negative electrode
Flow of electrons</td><td>Galvanic/Voltaic
Spontaneous
(E^o_{cell} is positive)
Creates one
Anode
Cathode
Cathode
Anode
Anode to cathode
(negative to positive)
Batteries</td><td>Electrolytic
Non-spontaneous
(E^o_{cell} is negative)
Requires one
Anode
Cathode
Anode
Cathode
Anode to cathode
(positive to negative)
Electrolysis, electroplating</td></tr>
<tr><td>9</td><td>Faraday's First law of Electrolysis</td><td colspan="3">The amount of electrolyte discharged at an electrode is directly proportional to the quantity of electricity passed:
$W \propto Q$ where, = I. t
I = Current strength in ampere
T = time in seconds
$\Rightarrow$ $W = ZQ = Zit$
Z is a constant called electrochemical equivalence (ECE)</td></tr>
<tr><td>10</td><td>Electrochemical Equivalent</td><td colspan="3">It is the amount of an electrolyte discharged on passing one coulomb of electricity.</td></tr>
<tr><td>11</td><td>Faraday's Constant</td><td colspan="3">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.
$\Rightarrow$ $W = E\left(\frac{Q}{96500}\right)$ where, E = Equivalent weight</td></tr>
<tr><td>12</td><td>Faraday's Second Law</td><td colspan="3">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:
$\Rightarrow$ $\frac{W_1}{W_2} = \frac{E_1}{E_2}$
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.</td></tr>
</table>

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

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 E°_{OP} than Cu, whereas Pt and Au have less E°_{OP}

Example 2: Which of the following metals cannot be obtained by the electrolysis of their aqueous salt solution and why?

Al, Na, Cu, Ag.

Sol: Al and Na cannot be obtained because they have higher E°_{OP} than H and thus, reduction of Cu^{2+} and Ag^+ will give Cu and Ag.

Example 3: Calculate the no. of electron lost or gained during electrolysis of 2 g Cl^- from NaCl (aq) to give Cl_2 at anode.

Sol: First calculate the equivalent of Cl^- used during the reaction and on multiplying it with avogadro number will give us the no of electron lost during the reaction

$\because\ 2Cl^- \rightarrow Cl_2 + 2e^-$

Eq. of 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

$= \frac{N \times 2}{35.5}$ electrons $= \frac{6.023 \times 10^{23} \times 2}{35.5}$

$= 3.4 \times 10^{22}$ electrons

Example 4: Evaluate the $E^\circ_{Ag^+/Ag}$ and $E^\circ_{Zn^{2+}/Zn}$ from the given values:

$$\underset{1bar}{Pt(H_2)}\left|\underset{a=1}{H^+}\right|\left|\underset{a=1}{Ag^+}\right| Ag \quad E^o_{cell} = 0.7991\ V$$

Sol: Since platinum electrode has zero reduction potential the standard electrode potential will be equal to the standard electrode potential of the cell.

$$E^\circ_{cell} = E^\circ_{OP_{H/H^+}} + E^\circ_{RP_{Ag^+/Ag}}$$

Or $0.7991 = 0 + E^\circ_{RP_{Ag^+/Ag}}$ $\therefore E^\circ_{RP_{Ag^+/Ag}} = 0.7991$ V

Example 5: Standard reduction potential of the Ag^+/Ag electrode at 298 K is 0.799 V. Given that for AgI, $K_{sp} = 8.7 \times 10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI. Also calculate the standard reduction potential of I^- / AgI/Ag electrode.

Sol: Here solubility product is given from this calculate the concentration of silver ions. Now substituting this value in Nernst equation determine $E_{Ag^+/Ag}$

As we have found out $E_{Ag^+/Ag}$, $E^\circ_{I/AgI/Ag}$ can find out by using the value of solubility product.

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} + (0.059/1)\log[Ag^+] \qquad \text{... (i)}$$

Also, $K_{sp_{AgI}} = [Ag^+][I^-]$

$\because [Ag]^+ = [I^-]$ (for a saturated solution)

$\therefore [Ag^+] = \sqrt{(K_{sp_{AgI}})} = \sqrt{(8.7 \times 10^{-17})}$

$= 9.32 \times 10^{-19}$ ... (ii)

$\therefore$ By Eq. (i),

$E_{Ag^+/Ag}$ = 0.799 + (0.059/1) log (9.32 × 10^{-9})

= 0.799 – 0.474 = 0.32 V

Also, $E^\circ_{I/AgI/Ag} = E^\circ_{Ag^+/Ag}$ + (0.059/1) log $K_{sp_{AgI}}$

= 0.799 + (0.059/1) log [8.7 × 10^{-17}]

= 0.799 – 0.948 = – 0.149 V

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

$$\begin{tikzcd}
Cu^{2+} \arrow[r, "+0.15\text{ V}"] \arrow[rr, bend right, "E^\circ = X\text{ volt}"'] & Cu^{+} \arrow[r, "+0.50\text{ V}"] & Cu
\end{tikzcd}$$

Calculate X. Does Cu^+ disproportionate in solution?

Sol: Given;

$Cu^{2+} + e^- \rightarrow Cu^+$; $E^\circ_1 = 0.15V$

$-\Delta G^\circ_1 = 1\times E^\circ_1 \times F$ ... (i)

$Cu^+ + e^- \rightarrow Cu$; $E^\circ_2 = 0.5$ V

$-\Delta G^\circ_2 = 1\times E^\circ_2 \times F$ ... (ii)

$Cu^{2+} + 2e^- \rightarrow Cu$; E°_3 =?

$-\Delta G^\circ_3 = 2\times E^\circ_3 \times F$ ... (iii)

Adding Eqs. (i) and (ii)

$Cu^{2+} + 2e^- \rightarrow Cu ; -(\Delta G^\circ_1 + \Delta G^\circ_2)$ ... (iv)

i.e., $-\Delta G^\circ_3 = -(\Delta G^\circ_1 + \Delta G^\circ_2)$

$2\times E^\circ_3 \times F = [1 \times 0.15 \times F + 1 \times 0.5 \times F]$

$\therefore \quad E^\circ_3 = 0.325V$

Example 7: The standard oxidation potential of Ni/Ni^{2+} electrode is 0.236 V. If this is combined with a hydrogen electrode in acid solution, at what pH of the solution will the measured e.m.f. be zero at 25ºC?

(Assume $[Ni^{2+}]$ = 1 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

pH= $-\log H^+$

$Ni \rightarrow Ni^{2+} + 2e^-$; $E^\circ_{OP} = 0.236V$

$2H^+ + 2e^- \rightarrow H_2$; $E^\circ_{RP} = 0$

$\therefore E^\circ_{Cell} = E^\circ_{OP_{Ni}} + E^\circ_{RP_H} = 0.236 + 0.0 = 0.236$ V

$$\therefore \quad E_{cell} = E^\circ_{cell} + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{[Ni^{2+}]}$$

$$0 = 0.236 + \frac{0.059}{2}\log_{10}[H^+]^2$$

or $\quad -\log H^+ = 4$

$\therefore \quad$ pH = 4

Example 8: A current of 3 ampere was passed for 2 hour through a solution of $CuSO_4$.3g of Cu^{2+} ions were discharged at cathode. Calculate current efficiency. (At wt. of Cu = 63.5)

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

Current efficiency =

$$\frac{\text{Current passed actually}}{\text{Total current passed experimentally}}\times 100$$

$\because \quad w_{Cu} = E.\ i.\ t/96500$

$\therefore 3 = \dfrac{63.5\times i\times 2\times 60\times 60}{2\times 96500}$ or i = 1.266 ampere

Current efficiency

$$= \frac{\text{Current passed actually}}{\text{Total current passed experimentally}}\times 100$$

= (1.266/3)×100 = 42.2%

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 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

$$(I) = \frac{w}{E \times t} \times 96500$$

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

∴ $i = 0.536$ ampere

Thus, error in (I) = 0.536 – 0.525 = 0.011

$$\therefore \text{ \% error in ammeter} = \frac{0.011 \times 100}{0.536} = 2.05\%$$

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

Sol: For the reduction: $Pd^{n+} + ne^- \rightarrow Pd$

Eq. of Pd or (w/E) = (I × t)/96500

$$\text{or} \quad \frac{2.977}{106.4/n} = \frac{3 \times 1 \times 60 \times 60}{96500}$$

∴ n = 4 (an integer).

JEE Advanced/Boards

Example 1: Calculate the quantity of electricity that will be required to liberate 710g of Cl_2 gas by electrolyzing a conc. solution of NaCl. What weight of NaOH and what volume of H_2 at 27°C and 1 atm pressure is obtained during this process?

Sol: Quantity of electricity can be calculated using

Simple relationship

$$W = \frac{E \times i \times t}{96500} \quad (\because Q = i \times t)$$

Similarly calculate w_{NaOH} and w_{H_2} from the value of w_{H_2} volume can be calculated using ideal gas equation.

$\because \quad 2Cl^- \rightarrow Cl_2 + 2e;\ 2H^+ + 2e \rightarrow H_2$

$\therefore \quad$ Eq. wt. of Cl_2 = M. Wt./2

$$\text{Now } w = \frac{E \times i \times t}{96500} = \frac{E \times Q}{96500} \quad (\because Q = i \times t)$$

$$\therefore \quad Q = \frac{w}{E} \times 96500 = \frac{710}{71/2} \times 96500$$

$$= 1.93 \times 10^6 \text{ coulomb}$$

Also Eq. of NaOH formed

= Eq. of H^+ discharged = Eq. of Cl_2 formed

$\therefore \quad w_{NaOH}$ = {710[71/2]} × 40 = 800 g

And $\quad w_{H_2}$ = {710/[71/2]} × 1 = 20g

$\therefore \quad V_{H_2} = wRT/mp$

= [20 × 0.0821 × 300] / [2 × 1] = 246.3 liter

Example 2: 50 mL 0.1 M $CuSO_4$ 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 $[Cu^{2+}]$, $[H^+]$ and $[SO_4^{2-}]$ after electrolysis. What will be the concentration of each species, if current is passed using Cu electrodes?

Sol: Meq. Of $CuSO_4$ in solution = Meq. Of Cu^{2+}

= 50 × 0.1 × 2 = 10 (∵ Meq. Of N× V in mL)

The redox changes are:

$Cu^{2+} + 2e \rightarrow Cu$ (at cathode)

$2H_2O \rightarrow 4H^+ + O_2 + 4e$ (at anode)

$\because \quad$ w/E = i.t/96500

And Eq. of Cu^{2+} lost = Equivalent of H^+ formed

$$= \frac{i.\ t.}{96500} = \frac{0.965 \times 1 \times 60}{96500} = 6 \times 10^{-4}$$

Or Meq. Of Cu^{2+} lost = 0.6

∴ Meq. of Cu^{2+} or Meq. of $CuSO_4$ left in solution = 10 – 0.6 = 9.4

$$\therefore [Cu^{2+}] = \frac{N_{Cu^{2+}}}{2} = \frac{\text{Meq. of } Cu^{2+}}{2 \times \text{Volume of solution (in mL)}}$$

$$= \frac{9.4}{2 \times 50} = 0.094 \text{ M}$$

$[H^+] = (N_{H^+}/1)$ = (0.6/50) = 0.012 M

$[SO_4^{2-}] = 0.1M$

($\because SO_4^{2-}$ is not involved in redox changes)

Also, if Cu electrodes are used, Cu^{2+} ions are discharged at cathode and Cu^{2+} are formed at anode and thus no changes in molarity of $CuSO_4$ solution. Anode $Cu \rightarrow Cu^{2+} + 2e^-$
Cathode $Cu^{2+} + 2e \rightarrow Cu$

Example 3: Two students use same stock solution $ZnSO_4$ and a solution of $CuSO_4$. The e.m.f., of one cell is 0.03 V higher than the other. The conc. of $CuSO_4$ in the cell with higher e.m.f. value is 0.5 M. Find out the conc. of $CuSO_4$ in the other cell.

$$\left(\frac{2.303RT}{F} = 0.06\right)$$

Sol: First write down the half-cell reaction and nernst equation for both the half cell. By comparing both the equation, value of C_2 can be calculated.

Cell I: $Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$

$$(C_2 = 0.5\ M);\ E_{cell} = E^{\circ}_{cell} + \frac{0.060}{2}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$$

$$= E^{o}_{cell} + \frac{0.060}{2}\log\frac{[C_2]}{[C_1]} \quad \text{... (i)}$$

Cell II: $Zn \mid \underset{C_1}{ZnSO_4} \parallel \underset{C_2^{'}}{CuSO_4} \mid Cu$

$$E^{'}_{cell} = E^{\circ}_{cell} + \frac{0.06}{2}\log\frac{[C_2^{'}]}{[C_1]} \quad \text{... (ii)}$$

By Eqs. (i) and (ii) $E_{cell} - E^{'}_{cell} = \frac{0.06}{2}\log\frac{[C_2]}{[C_2^{'}]}$

$$0.03 = \frac{0.06}{2}\log\frac{0.5}{C_2^{'}} \quad \text{or} \quad C_2^{'} = 0.05M$$

Example 4: Two weak acid solutions HA_1 and HA_2 each with the same concentration and having pK_a values 3 and 5 are placed in contact with hydrogen electrode (1 atm at 25°C)) and are interconnected through a salt bridge. Find e.m.f. of cell.

Sol: First write down the nernst equation for two half-cell 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

$$Pt\ H_{2(1\ atm)} \mid HA_2 \parallel HA_1 \mid (H_2)_{(1\ atm)} Pt$$

At L.H.S. $E_{H/H^+} = E^{\circ}_{OP_{H/H^+}} - \frac{0.059}{1}\log[H^+]_2$

$\because \quad -\log H^+ = pH$

$$\therefore \quad E_{H/H^+} = E^{\circ}_{OP_{H/H^+}} + 0.059(pH)_2 \quad \text{..... (i)}$$

At R.H.S. $E_{H^+/H} = E^{\circ}_{RP_{H^+/H}} + \frac{0.059}{1}\log[H^+]_1$

$$E_{H^+/H} = E^{\circ}_{RP_{H^+/H}} - 0.059(pH)_1 \quad \text{... (ii)}$$

For acid $HA_1 \quad HA_1 \rightleftharpoons H^+ + A_1^-$

$[H^+] = C\,\alpha = \sqrt{K_a\,.\,C}$

$\therefore\ pH_1 = \frac{1}{2}pK_{a_1} - \frac{1}{2}\log\ C$

Similarly, $pH_2 = \frac{1}{2}pK_{a_2} - \frac{1}{2}\log\ C$

($\because$ C are same) By Eqs. (i) and (ii), E_{cell}

$$= E^{\circ}_{OP_{H/H^+}} + E^{\circ}_{RP_{H/H^+}} + 0.059\left[\frac{1}{2}pK_{a_2} - \frac{1}{2}pK_{a_1}\right]$$

$= 0 + 0.059 \times 5[5 - 3]/2 = +\ 0.059$ volt

Example 5: Calculate the minimum weight of NaOH required to added in RHS to consume all the H^+ present in RHS of cell of e.m.f. +0.701 V at 25°C before its use. Also report the e.m.f. of cell after addition of NaOH.

$$Zn \left| \begin{matrix} Zn^{2+} \\ 0.1M \end{matrix} \right| \begin{matrix} HCl \\ 1\ litre \end{matrix} \left| \begin{matrix} Pt_{(H_2)} \\ 1\ atm \end{matrix} \right. \quad E^{\circ}_{Zn|Zn^{2+}} = +0.760V$$

Sol: For given cell $\because\ E_{OP_{Zn/Zn^{2+}}} > E_{OP_{H/H^+}}$

$\therefore$ Redox changes will be: $Zn \rightarrow Zn^{2+} + 2e$

$2H^+ + 2e \rightarrow H_2$, $E_{cell} = E_{OP_{Zn/Zn^{2+}}} + E_{RP_{H+/H}}$

$$= E^{\circ}_{OP_{Zn/Zn^{2+}}} - \frac{0.059}{2}\log_{10}[Zn^{2+}]$$

$$+\ E^{\circ}_{RP_{H^+/H}} + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{(P_{H_2})}$$

$$E_{cell} = E^{\circ}_{cell} + \frac{0.059}{2}\log\frac{[H^+]^2}{[Zn^{2+}](P_{H_2})}$$

$$0.701 = 0.760 + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{[Zn^{2+}](P_{H_2})}$$

$$0.701 = 0.760 + \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{[0.1]\times 1}$$

$[H^+] = 0.0316$ mole liter^{-1}

Since, H^+ must be used by NaOH

$\therefore \quad$ Meq. of NaOH = Meq. of $[H^+]$

(w/40) × 1000 = 0.0316 × 1000 ($\because$ V = 1 liter)

$\therefore \quad$ w = 1.265 g

After addition of NaOH to cathode solution $[H^+]$ becomes 10^{-7} since both acid and base are neutralized completely. Thus, new e.m.f. of cell,

$$E_{cell} = E^{\circ}_{cell} = \frac{0.059}{2}\log_{10}\frac{[H^+]^2}{(0.1)}$$

$$= 0.760 + \frac{0.059}{2}\log_{10}\frac{(10^{-7})^2}{0.1} \quad E_{cell} = 0.3765\text{ V}$$

Example 6: For the galvanic cell:

$$Ag\left|\begin{matrix}AgCl(s)\ KCl\\ 0.2\text{ M}\end{matrix}\right\|\begin{matrix}KBr\ \ AgBr(s)\\ 0.001\text{ M}\end{matrix}\left|Ag\right.$$

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 25ºC.

[Give, $K_{sp_{AgCl}} = 2.8\times10^{-10}, K_{sp_{AgBr}} = 3.3\times10^{-13}$]

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.

$E_{cell} = E_{OP_{Ag}} + E_{RP_{Ag}}$; L.H.S. R.H.S.

$$= E^{\circ}_{OP_{Ag}} - \frac{0.059}{1}\log\,[Ag^+]_{L.H.S.}$$

$$+ E^{\circ}_{RP_{Ag}} + \frac{0.059}{1}\log[Ag^+]_{R.H.S.}$$

$$E_{cell} = \frac{0.059}{1}\log\frac{[Ag^+]_{R.H.S.}}{[Ag^+]_{L.H.S.}} \qquad \text{.... (i)}$$

For L.H.S. K_{sp} of AgCl = 2.8×10^{-10}

or $[Ag^+][Cl^-] = 2.8 \times 10^{-10}$

or $[Ag^+] = \dfrac{2.8\times10^{-10}}{[Cl^-]} = \dfrac{2.8\times10^{-10}}{0.2} = 1.4\times10^{-9}$ M

For R.H.S. K_{sp} of AgBr = 3.3×10^{-13}

or $[Ag^+][Br^-] = 3.3 \times 10^{-13}$

or $[Ag^+] = (3.3 \times 10^{-13}) / 0.001 = 3.3 \times 10^{-10}$ M

∴ By Eq. (i),

$$E_{cell} = \frac{0.059}{1}\log\frac{3.3\times10^{-10}}{1.4\times10^{-9}} = -0.037\text{V}$$

Thus, to get cell reaction (i.e. E_{cell}, E_{cell} = +ve) polarity of cell

Example 7: E°_{cell} values for

$Fe \rightarrow Fe^{2+} + 2e^-$ and $Fe \rightarrow Fe^{3+} + 3e^-$ are 0.440 and 0.036 V respectively:

(a) Design and point out the number of cells showing the overall reaction $Fe + 2Fe^{3+} \rightarrow 3Fe^{2+}$

(b) Also calculate E°_{cell} and ΔG° values for each cell. Also comment on the result.

Sol: Standard free energy can be calculated using the equation

$\Delta G^{\circ} = -n\,E^{\circ}F$

$Fe \rightarrow Fe^{2+} + 2e^-$; $-\Delta G^{\circ}_1 = +0.440 \times 2 \times F$

$Fe^{3+} + 3e^- \rightarrow Fe$; $-\Delta G^{\circ}_2 = -0.036 \times 3 \times F$

∴ $Fe^{3+} + e^- \rightarrow Fe^{2+}$; $-\Delta G^{\circ}_3 = -(\Delta G^{\circ}_2 + \Delta G^{\circ}_1)$

$-n\,E^{\circ}F = [2 \times 0.440 - 3 \times 0.036] \times F$ (n = 1)

$E^o = +0.772$ V

Cell no. I: $Fe \mid Fe^{+2} \| Fe^{3+} \mid Fe$

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

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

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

$$E^{\circ}_{cell} = E^{\circ}_{OP_{Fe|Fe^{2+}}} + E^{\circ}_{RP_{Fe^{3+}|Fe}} = 0.440 - 0.036 = 0.404\text{V}$$

Also, $\Delta G^{\circ} = -6 \times 0.404 \times F = -2.424$ F

Cell no. II: $Fe \mid Fe^{2+} \| Fe^{3+}, Fe^{2+} \mid Pt$

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

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

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

$$E^{\circ}_{cell} = E^{\circ}_{OP_{Fe/Fe^{2+}}} + E^{\circ}_{RP_{Fe^{3+}/Fe^{2+}}}$$

Example 8: Oxidizing power of $Cr_2O_7^{2-}$ is more in acidic medium than in alkaline medium.

Sol: E°_{RP} in acidic medium is more than E^{o}_{RP} in alkaline medium.

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

$E^{o}_{RP} = +1.33$V

Alkali: $Cr_2O_7^{2-} + H_2O \rightarrow 2CrO_4^{2-} + 2H^+$

$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^-$; $E^{\circ}_{RP} = -0.13$V

Example 9: Color of KI solution containing starch turns blue when Cl_2 water is added. Explain.

Sol: Chlorine placed below iodine in electrochemical series having lesser E°_{OP} than iodine and thus, shows reduction whereas I^- undergoes oxidation. The I_2 so formed gets absorbed in starch to give blue color.

$2I^- \rightarrow I_2 + 2e^-$

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

$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$

Example 10: Calculate the e.m.f of the cell.

$Mg(s) \mid Mg^{2+}(0.2\ M) \parallel Ag^+\ (1 \times 10^{-3}) \mid Ag$

$E^o_{Ag^+|Ag} = +\ 0.8$ volt, $E^o_{Mg^{2+}/Mg} = -\ 2.37$ volt

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

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

After calculating E°_{cell} e.m.f of the cell can be easily calculated using following equation

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]}$$

$E^\circ_{Cell} = E^\circ_{Cathode} - E^\circ_{Anode} = 0.80-(-2.37) = 3.17$ volt

Cell reaction, $Mg + 2Ag^+ \rightarrow 2Ag + Mg^{2+}$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{Mg^{2+}}{[Ag^+]^2}$$

$$= 3.17 - \frac{0.0591}{2}\log\frac{0.2}{[1\times10^{-3}]^2}$$

$= 3.17 - 0.1566 = 3.0134$ volt

When $Mg^{2+} = 0.1$ M

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{0.1}{(1\times10^{-3})^2}$$

$= (3.17 - 0.1477)$ volt$= 3.0223$ volt

JEE Main/Boards

Exercise 1

Q.1 Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+\ (aq) \rightarrow Zn^{2+}\ (aq) + 2Ag(s)$ 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 L^{-1} solution of KCl at 298 K is $2.48 \times 10^{-2}\ ohm^{-1}cm^{-1}$. Calculate its molar conductivity.

Q.3 Write the Nernst equation and e.m.f of the following cells at 298K:

(i) $Mg(s)|Mg^{2+}\ (0.001M)||Cu^{2+}(0.0001\ M)|Cu(s)$

(ii) $Fe(s)|Fe^{2+}(0.001M)||H^+(1M)|H_2(g)(1bar)|Pt(s)$

(iii) $Sn(s)|Sn^{2+}(0.050\ M)||H^+\ (0.020\ M)|H_2(g)(1\ bar)|Pt(s)$

(iv) $Pt(s)|Br_2(l)|Br^-(0.010\ M)\ ||\ H^+(0.030\ M)|H_2(g)$ (1 bar)|Pt(s)

Q.4 In the button cells widely used in watches and other devices the following reaction takes place:

$Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$

Determine $\Delta rG'$ and E′ for the reaction.

Q.5 The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S 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 $CaCl_2$?

(ii) 40.0 g of Al from molten Al_2O_3?

Q.7 How much electricity is required in coulomb for the oxidation of:

(i) 1 mole of H_2O to O_2?

(ii) 1 mole of FeO to Fe_2O_3?

Q.8 The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is 0.146×10^{-3} S cm^{-1}?

Q.9 Conductivity of 0.00241 M acetic acid is 7.896×10^{-5} S cm^{-1}. Calculate its molar conductivity. If Λ_{∞}^{0} for acetic acid is 390.5 S cm^{2} mole^{-1}, what is its dissociation constant?

Q.10 A solution of $Ni(NO_3)_2$ 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	0.001	0.010	0.020	0.050	0.100
$10^2 \times k$/S m^{-1}	1.237	11.85	23.15	55.53	106.74

Calculate Λ_{∞} for all concentrations and draw a plot between Λ_{∞} and S. Find the values of Λ_{∞}^{0}

Q.12 Three electrolytic cells A, B, C containing solution of $ZnSO_4$, $AgNO_3$ and $CuSO_4$, 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) Fe^{3+}(aq) and I^- (aq) (ii) Ag^+(aq) and Cu(s)

(iii) Fe^{3+}(aq) an Br^-(aq) (iv) Ag(s) and Fe^{3+}(aq)

(iv) Br_2(aq) and Fe^{2+}(aq).

Q.14 The standard electrode potentials of $Cu^{2+}|Cu^+$ an $Cu^+|Cu$ electrodes are +0.18 V and +0.50 V, respectively. Calculate the standard potential of $Cu^{2+}|$ Cu electrode.

Q.15 Arrange Zn, Pb and Al in the increasing order of their reducing power under standard conditions.

Given: $E^{\circ}_{Zn^{2+}|Zn}$ = –0.76 V, = –0.13 V, $E^{\circ}_{Al^{2+}|Al]}$ = –1.66 V

Q.16 The standard electrode potentials of $Ag^+|Ag$, $Cl_2|Cl^-$ and $O_3|O_2$ electrodes are +0.80V, +1.36V and +2.07 V, respectively. Using these information, answer the following:

(i) Which of the following is strongest oxidizing agent: Ag^+, Cl_2, and O_3?

(ii) Which of the following is the strongest oxidizing agent: Ag, Ag^+, O_3, and O_2?

(iii) Which of the following is the strongest reducing agent: Ag, Cl^-, and O_2

(iv) Which of the following is the strongest reducing agent: Ag, Ag^+, O_3, and O_2

Q.17 The following reactions represent the reduction of IO^- ion into I^-ion in acidic and basic medium.

$$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O \;;\quad E^o = +\,0.907\text{ V}$$

$$IO_3^- + 3H_2O + 6e^- \rightarrow I^- + 6OH^- \;;\quad E^o = +\,0.260\text{ V}$$

[Acid Medium]

Q.18 Can Fe^{3+} oxidize Br^- to Br under standard conditions?

Given: $E^{\circ}_{Fe^{3+}|Fe^{2+}}$ = + 0.77 V, $E^{\circ}_{Br_2|Br^-}$ = + 1.09 V

Q.19 Calculate the electrode potential of the following electrodes at 25ºC:

(i) Cu^{2+} (0.001 M) | Cu ; $E^{\circ}_{Cu^{3+}|Cu}$ = + 0.34 V

(ii) Zn | Zn^{2+} (0.02 M) ; $E^{\circ}_{Zn^{2+}|Zn}$ = –0.76 V

(iii) AgCl (stand. sol) | Ag ; $E^{\circ}_{Ag^+|Ag}$ = +0.80 V, K_{sp} of AgCl = 2×10^{-10}.

(iv) Pt | Cl_2 (0.5 atm) | Cl^- (0.02 M); $E^{\circ}_{Cl_2|Cl^-}$ = 1.36 V

(v) HCl (pH = 4.4) | H_2(2 atm) | Pt

Q.20 Calculate the reduction potential at 25ºC for Fe^{3+}/Fe^{2+} electrode if the concentration of Fe^{2+} ion is five times that of Fe^{3+} ion.

$E^{\circ}_{Fe^{3+}|Fe^{2+}}$ = 0.77 volt.

Q.21 Calculate electrode potential for the half-cell Pt|H_2 (1 atm) | 0.357M – CH_3COOH. K_a for CH_3COOH = 1.74×10^{-5}.

Q.22 The standard reduction potential for $Cu^{2+}|$ Cu is +

0.34 V. Calculate the reduction potential at pH = 13 for the above couple. K_{sp} of $Cu(OH)_2$ is 1.0×10^{-10}.

Q.23 Calculate

(i) $E^\circ_{Cl^+|AgCl|Ag}$; $E^\circ_{Ag^+|Ag} = 0.80$ V, K_{sp} of AgCl $= 2 \times 10^{-10}$

(ii) $E^\circ_{Cl^-(0.004M)AgCl|Ag}$; $E^\circ_{Ag^+|Ag} = +\ 0.80$ V,

K_{sp} of AgCl $= 2 \times 10^{-10}$

Q.24 Calculate the e.m.f of the cell in which the following reaction takes place:

$Ni(s) + 2Ag^+(0.002\ M) \rightarrow Ni^{2+}\ (0.160\ M) + 2Ag(s)$

Given that $E^\circ_{cell} = 1.05$ V

Q.25 The molar conductivity of 0.025 mole methanoic acid is 46.1 S cm^2 mole^{-1}. Calculate its degree of dissociation and dissociation constant.
Given $\Lambda^0\ (H^+) = 349.6$ S cm^2 mol/L and

$\lambda^\circ(HCOO^-) = 54.6$ S cm^2 mol/L.

Q.26 Suggest a list of metals that are extracted electrolytically.

Q.27 Represent the cell in which following reaction takes place:

$Mg(s) + 2Ag^+\ (0.0001\ M) \rightarrow Mg^{2+}(0.130\ M) + 2Ag(s)$ calculate its E_{cell} if $E^o_{cell} = 3.17V$.

Q.28 Calculate the reduction potential of the following electrodes:

(a) $Pt_2\ H_2$ (4 atm) | H_2SO_4 (0.01 M)

(b) $Pt_2\ H_2$ (1 atm) | HCl (0.2 M)

(c) Calculate the potential of hydrogen electrode in contact with a solution whose

(i) pH = 5 (ii) pOH = 4

Q.29 Calculate the equivalent conductivity of 1M H_2SO_4 solution, if its conductivity is 26×10^{-2} ohm^{-1} cm^{-1}.

Exercise 2

Single Correct Choice Type

Q.1 One gm. metal M^{+2} was discharged by the passage of 1.81×10^{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 $AgNO_3$, $CuSO_4$ and $AlCl_3$ when Ag, Cu and Al are deposited at cathode. The molar ratio of Ag, Cu and Al deposited are:

(A) 1: 1: 1 (B) 6: 3: 2 (C) 6: 3: 1 (D) 1: 3: 6

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 g cm^{-3}. The quantity of electricity needed to plate an area 10 cm × 10 cm to a thickness of 10^{-2} cm using $CuSO_4$ 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, 2.4L 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) 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 H_2 gas is increased from 1 atm to 100 atm keeping H^+ concentration constant at 1 M, the change in reduction potential of hydrogen half-cell at 25°C will be

(A) 0.059 V (B) 0.59 V (C) 0.0295 V (D) 0.118 V

Q.9 The equilibrium constant for the reaction Sr(s) + Mg^{+2} (aq) → Sr^{+2} (aq) + Mg(s) is 2.69×10^{12} at 25°C

The E° for a cell made up of the Sr/Sr^{+2} and Mg^{+2}/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 E°_{Ag/Ag^+} = –0.799 V, the K_{sp} of AgCl in pure water will be:

(A) 2.95×10^{-11} (B) 5.1×10^{-11}

(C) 3.95×10^{-11} (D) 1.95×10^{-11}

Q.11 During electrolysis of an aqueous solution of $CuSO_4$ using copper electrodes, if 2.5 g of Cu is deposited at cathode, then at anode

(A) 890 ml of Cl_2 at STP is liberated

(B) 445 ml of O_2 at STP is liberated

(C) 2.5 g of copper is deposited

(D) A decrease of 2.5 g of mass takes place

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 50Ω. If the electrodes in the cell are 2.2 cm apart and have an area of 4.4 cm^2 then the molar conductivity (in S m^2 $mole^{-1}$) 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 S cm^2 $equivalent^{-1}$ and that at infinite dilution is 200 S 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 Λ_m is given by

(A) $\frac{1000x}{y}$ (B) $1000\frac{y}{x}$

(C) $\frac{1000}{xy}$ (D) $\frac{xy}{1000}$

Q.16 The dissociation constant of n-butyric acid is 1.6×10^{-5} and the molar conductivity at infinite dilution is 380×10^{-4} S m^2 mol^{-1}. The specific conductance of the 0.01 M acid solution is

(A) 1.52×10 S m^{-1} (B) 1.52×10^{-2} S m^{-1}

(C) 1.52×10^{-3} S m^{-1} (D) None of these

Q.17 Consider the reaction of extraction of gold from its ore

$Au + 2CN^-(aq.) + \frac{1}{4} O_2(g) + \frac{1}{2} H_2O \rightarrow Au(CN)_2^- + OH^-$

Use the following data to calculate ΔG° for the reaction, $K_f\{Au(CN)_2\}$ = X

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$; E° = + 0.41 volt

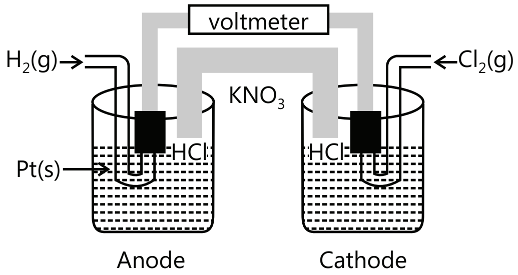
$Au^{3+} + 3e^- \rightarrow Au$; E° = + 1.5 volt

$Au^{3+} + 2e^- \rightarrow Au^+$; E°= + 1.4 volt

(A) –RT ln X + 1.29 F (B) –RTln X –2.11 F

(C) $-RT\ln\frac{1}{X}$ + 2.11 F (D) –RTln X –1.29 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

Pt||H_2 (0.4 atm) | H^+ (pH=1) || H^+ (pH =2) | H_2 (0.1 atm) | Pt

The measured potential at 25°C is

(A) –0.1 V (B) –0.5 (C) –0.041 (D) None of these

Q.20 For the fuel cell reaction:

$2H_2$ (g) + O_2 (g) → $2H_2O$ (l); $\Delta_f H^\circ_{298}$ (H_2O,(l)= –285.5 KJ/mole

What is ΔS°_{298} for the given fuel cell reaction?

Given O_2 (g) + $4H^+$ (aq) + $4e^-$ → $2H_2O$ (l) E° = 1.23 V

(A) –0.322 J/K (B) –0.635kJ/K

(C) 3.51 kJ/K (D) –0.322 kJ/K

Q.21 The standard reduction potentials of Cu^{2+}/Cu and Cu^{2+}/Cu^{+} are 0.337 and 0.153 V respectively. The standard electrode potential of Cu^{+}/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	**Anode**
(a) Pure zinc	Pure copper
(b) Impure sample	Pure copper
(c) Impure zinc	Impure sample
(d) Pure copper	Impure sample

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 $AgNO_3$, 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) $S\ m\ mole^{-1}$ (B) $S\ m^2\ mole^{-1}$

(C) $S^{-2}\ m^2\ mole$ (D) $S^2\ m^2\ mole^{-2}$

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 H_2O (where ions move freely through a solution) at 25ºC are given below: At 25ºC are given below: ***(2007)***

$\Lambda^{\circ}_{CH_3COONa}$ = 91.0 S cm^2 / equivalent

Λ°_{HCl} = 426.2 S cm^2/equivalent

What additional information/quantity one needs to calculate Λ° of an aqueous solution of acetic acid

(A) Λ° of NaCl

(B) Λ° of CH_3COOK

(C) The limiting equivalent conductance of H^{+} $(\Lambda^{\circ}H^{+})$

(D) Λ° of chloroacetic acid (Cl/CH_2COOH)

Q.8 The molar conductivities λ°_{NaOAc} and λ°_{HCl} at infinity dilution in water at 25ºC are 91.0 and 426.2 S cm^2/mole respectively. To calculate λ°_{HOAc}, the additional value required is ***(2006)***

(A) $\lambda^{\circ}_{H_2O}$ (B) λ°_{KCl} (C) λ°_{NaOH} (D) λ°_{NaCl}

Q.9 Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 Ω. The conductivity of this solution is 1.29 S m^{-1}. Resistance of the same cell when filled with 0.2 M of the same solution is 520 Ω. The molar conductivity of 0.02 M solution of the electrolyte will be ***(2006)***

(A) $12.4 \times 10^{-4}\ S\ m^2\ mole^{-1}$

(B) $1240 \times 10^{-4}\ S\ m^2\ mole^{-1}$

(C) $1.24 \times 10^{-4}\ S\ m^2\ mol^{-1}$

(D) $1.24 \times 10^{-4}\ Sm^2\ mole^{-1}$

Q.10 Saturated solution of KNO_3 is used to make 'salt-bridge' because ***(2002)***

(A) Velocity of K^{+} is greater than that of NO_3^{-}

(B) Velocity of NO_3^{-} is greater than that of K^{+}

(C) Velocities of both K^{+} and NO_3^{-} are nearly the same

(D) KNO_3 is highly soluble in water

Q.11 The reduction potential of hydrogen half-cell will be negative if ***(2011)***

(A) $P_{(H_2)} = 1$ atm and [H$^+$] = 2.0 M

(B) $P_{(H_2)} = 1$ atm and [H$^+$] = 1.0 M

(C) $P_{(H_2)} = 2$ atm and [H$^+$] = 1.0 M

(D) $P_{(H_2)} = 2$ atm and [H$^+$] = 2.0 M

Q.12 The cell, Zn|Zn^{2+} (1M) ||Cu^{2+} (1M) |Cu (E°_{cell} = 1.10 V) was allowed to be completely discharged at 298 K. The relative concentration of Zn^{2+} to

Cu^{2+} $\left[\dfrac{Zn^{2+}}{[Cu^{2+}]}\right]$ is ***(2007)***

(A) Antilog (24.08) (B) 37.3

(C) $10^{37.3}$ (D) 9.65×10^4

Q.13 The standard reduction potential for Fe^{2+}/ Fe and Sn^{2+}/Sn electrodes are –0.44 and –0.14 volt respectively, For the given cell reaction Fe^{2+} + Sn → Fe + 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 $E^\circ_{Fe^{3+}/Fe} = -0.036V,\ E^\circ_{Fe^{2+}/Fe} = -0.439V$

The value of standard electrode potential for the change, $Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}(aq)$ will be

(A) –0.072 V (B) 0.385 V

(C) 0.770 V (D) –0.270 V

Q.15 For the redox reaction:

$Zn_{(s)} + Cu^{2+}(0.1M) \rightarrow Zn^{2+}(1M) + Cu_{(2)}$ taking place in a cell, E°_{cell} is 1.10 volt. E_{cell} for the cell will be

$\left(2.303\dfrac{RT}{F} = 0.0591\right)$ ***(2003)***

(A) 2.14 volt (B) 1.80 volt

(C) 1.07 volt (D) 0.82 volt

Q.16 Given $E^\circ_{Cr^{3+}/Cr} = -0.72V, E^\circ_{Fe^{2+}/Fe} = -0.42V$.

The potential for the cell Cr|Cr^{3+} (0.1M)||Fe^{2+}(0.01M)|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

$CH_3OH(\ell) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$ at 298K

standard Gibb's energies of formation for $CH_3OH(\ell)$, $H_2O(\ell l)$ and CO_2 (g) are -166.2, -237.2 and 394.4 kJ mol^{1} respectively. If standard enthalpy of combustion of methanol is -726kJ mol^{-1}, efficiency of the fuel cell will be ***(2009)***

(A) 80 % (B) 87% (C) 90% (D) 97%

Q.18 Given: $E^\circ_{Fe^{3+}/Fe} = -0.036V, E^\circ_{Fe^{2+}/Fe} = -0.439V$.

The value of standard electron potential for the change, $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}(aq)$ 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) p(H_2) = 1 atm and [H$^+$] =1.0 M

(B) p (H_2) =2 atm and [H$^+$] =1.0 M

(C) p (H_2) = 2 atm and [H$^+$] = 2.0 M

(D) p (H_2) =1 atm and [H$^+$] = 2.0 M

Q.20 The standard reduction potentials for Zn^{2+}/ Zn, Ni^{2+}/ Ni, and Fe^{2+}/ Fe are –0.76, –0.23 and –0.44 V respectively. The reaction X + Y^{2+} $\longrightarrow$ X^{2+} + Y will be spontaneous when: ***(2012)***

(A) X = Ni, Y = Fe (B) X = Ni, Y = Zn

(C) X = Fe, Y = Zn (D) X = Zn, Y = Ni

Q.21 Given: $E^\circ_{Cr^{3+}/Cr^{3+}} = -0.74V;\ E^\circ_{MnO_4^-/Mn^{2+}} = 1.51\,V$

$E^\circ_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\ V;\ E^\circ_{Cl/Cl^-} = 1.36V$

Based on the data given above, strongest oxidising agent will be: ***(2013)***

(A) Cl (B) Cr^{3+} (C) Mn^{2+} (D) MnO_4^-

Q.22 The equivalent conductance of NaCl at concentration C and at infinite dilution are λ_C and λ_∞, respectively. The correct relationship between λ_C and λ_∞, is given as (Where the constant B is positive) ***(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)***

$Mn^{2+} + 2e^- \longrightarrow Mn$; E° = — 1.18 V

$(Mn^{3+} + e^- \longrightarrow Mn^{2+})$; E° = + 1.51 V

The E° for $3\,Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$ 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 $CuSO_4$. The mass of copper deposited at the cathode is: (at. mass of Cu = 63.5 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, E° ($Bi^{3+}|Bi$) and E° ($Cu^{2+}|Cu$) are 0.226 V and 0.344 V respectively. A mixture of salts of bismuth and copper at unit concentration each is electrolyzed at 25ºC. To what value can $[Cu^{2+}]$ be brought down before bismuth starts to deposit, in electrolysis.

Q.2 The cell Pt, H_2 (1 atm) | H^+ (pH = x) || Normal calomel electrode has an EMF of 0.67 V at 25°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 Pt, H_2 (1 atm) |HOCN (1.3×10^{-3} M) ||Ag^+ (0.8 M)| Ag(s) is 0.982 V. Calculate the K_a for HOCN. Neglect $[H^+]$ because of oxidation of H_2 (g).

$Ag^+ + e \rightarrow Ag(s) = 0.8$ V.

Q.4 Calculate the potential of an indicator electrode versus the standard hydrogen electrode, which originally contained 0.1 M MnO_4^- and 0.8 M H^+ and which was treated with 90% of the Fe^{2+} necessary to reduce all the MnO_4^- to Mn^{+2}.

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

E° = 1.51 V

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

Pt, H_2 (1.0 atm) | CH_3COOH (0.1 M) || NH_3 (aq, 0.01M) | H_2 (1.0 atm), Pt

K_a (CH_3COOH) = 1.8×10^{-5},
K_b (NH_3) = 1.8×10^{-5}.

Q.6 The Edison storage cell is represented as Fe(s) | FeO(s) | KOH (aq) | Ni_2O_3(s) |Ni(s) the half-cell reaction are

$Ni_2O_3(s) + H_2O\ (i) + 2e^-$ l $2NiO(s) + 2OH^-$,

E° = +0.40 V

$FeO(s) + H_2O\ (l) + 2e^-$ l $Fe(s) + 2OH^-$,

E° = –0.87 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 Ni_2O_3?

Q.7 The standard reduction potential for Cu^{2+}/Cu is 0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $Cu(OH)_2$ is 1×10^{-19}.

Q.8 Determine the degree of hydrolysis and hydrolysis constant of aniline hydrochloride in M/32 solution of salt at 298 K from the following cell data at 298 K.

Pt|H_2 (1 atm) | H^+ (1M) ||M/32 $C_6H_5NH_3Cl$|H_2 (1 atm) | Pt; E_{cell} = –0.188 V

Q.9 The e.m.f of the cell, Pt|H_2(1 atm), | H^+ (0.1 M, 30 ml) || Ag^+(0.8 M)|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 Ag | AgI | KI (0.05 M) || $AgNO_3$ (0.05 M) | Ag is 0.788 V. Calculate the solubility product of AgI.

Q.11 Consider the cell

$Ag \mid AgBr(s)\ Br^- \parallel AgCl(s), Ag \mid Cl^-$ at 25°C. The solubility product constants of AgBr & AgCl are respectively 5×10^{-13} & 1×10^{-10}. For what ratio of the concentration of Br^- and Cl^- ions would the e.m.f of the cell be zero?

Q.12 The pK_{sp} of AgI is 16.07. If the E° value for $Ag^+|Ag$ is 0.7991 V. Find the E° for the half-cell reaction $AgI\ (s) + e^- \rightarrow Ag + I^-$

Q.13 For the galvanic cell: $Ag\ AgCl(s) \mid KCl\ (0.2\ M) \parallel KBr\ (0.001\ M) \mid AgBr(s) \mid Ag$, Calculate the EMF generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25°C.

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

Q.14 Given, E° = –0.268 V for the $Cl^-|PbCl_2|Pb$ couple and –0.126 V for the $Pb^{2+}|Pb$ couple, determine K_{sp} for $PbCl_2$ a 25°C?

Q.15 Calculate the voltage, E, of the cell at 25°C

$Mn(s) \mid Mn\ (OH_2)\ (s) \mid Mn^{2+}\ (xM),\ OH^-\ (1.00 \times 10^{-4} M) \parallel Cu^{2+}\ (0.675\ M) \mid Cu(s)$ given that $K_{sp} = 1.9 \times 10^{-13}$ for $Mn\ (OH)_2(s)$ $E^\circ\ (Mn^{2+}/Mn) = –1.18$ V

Q.16 Calculate the voltage, E, of the cell

$Ag(s) \mid AgIO_3(s) \mid Ag^+(x\ M),\ HIO_3\ (0.300\ M) \parallel Zn^{2+}\ (0.175\ M) \mid Zn(s)$ if $K_{sp} = 3.02 \times 10^{-8}$ for $AgIO_3(s)$ and $K_a = 0.162$ for HIO_3.

Q.17 The voltage of the cell

$Pb(s) \parallel PbSO_4(s) \mid NaHSO_4\ (0.600\ M) \parallel Pb^{2+}\ (2.50 \times 10^{-5} M) \mid Pb(s)$ is E = +0.061 V. Calculate $K_2 = [H^+]\ [SO_4^{2-}]/\ [HSO_4^-]$, the dissociation constant for HSO_4^-. Given $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$ (E° = 0.356) E° $(Pb^{2+}/Pb) = –0.126$ V

Q.18 The voltage of the cell

$Zn(s) \mid Zn(CN)_4^{2-}(0.450M),\ CN^-(2.65 \times 10^{-3}M) \parallel Zn^{2+}\ (3.84 \times 10^{-4}M) \mid Zn(s)$ is E = + 0.099 V. Calculate the constant K_f for

$Zn^{2+} + 4CN^- \rightarrow Zn(CN)_4^{2-}$, the only $Zn^{2+} + CN^-$ complexation reaction of importance.

Q.19 Given the standard reduction potentials $Ti^+ + e^- \rightarrow Ti$, E° = –0.34 V and $Ti^{3+} + 2e^- \rightarrow Ti^+$, E° = 1.25 V. Examine the spontaneity of the reaction, $3Ti^+ \rightarrow 2Ti + Ti^{3+}$. Also find E° for this disproportionation.

Q.20 Estimate the cell potential of a daniel cell having 1 M Zn^{++} & originally having 1 M Cu^{++} after sufficient NH_3 has been added to the cathode compartment to make NH_3 concentration 2M. K_f for $[Cu\ (NH_3)_4]^{2+} = 1. \times 10^{12}$, E° for the reaction,

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ 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°C. When excess of Zn is added to $CuSO_4$, Zn displaces Cu^{2+} till equilibrium is reached. What is the ratio of Zn^{2+} to Cu^{2+} ions at equilibrium?

Q.22 K_d for complete dissociation of $[Ag(NH_3)_2]^+$ into Ag^+ and $2NH_3$ is 6×10^{-8}. Calculate E° for the following half reaction; $Ag(NH_3)_2^+ + e^- \rightarrow Ag + 2NH_3$

$Ag^+ + e^- \rightarrow Ag$, E° = 0.799 V

Q.23 The overall formation constant for the reaction of 6 mole of CN^- with cobalt (II) is 1×10^{19}. The standard reduction potential for the reaction

$[Co(CN]_6]^{3-}\ e^- \rightarrow Co(CN)_6^{4-}$ is –0.83 V. Calculate the formation constant of $[Co(CN)_6]^{3-}$ Given $Co^{3+} + e^- \rightarrow Co^{2+}$; E° =1.82 V

Q.24 Calculate E° for the following reactions at 298 K,

$Ag(NH_3)_2^+ + e^- \rightarrow Ag + 2NH_3$

$Ag(CN)_2^-\ e^- \rightarrow Ag + 2CN^-$

Given: $E^\circ_{Ag^+|Ag}$ – 0.7991 V,

$K_{ins}\ [Ag(NH_3)_2^+] = 6.02 \times 10^{-8}$ and

$K_{ins}[Ag(CN)_2^-] = 1.995 \times 10^{-19}$

Q.25 Calculate the equilibrium constant for the reaction:

$3Sn(s) + 2Cr_2O_7^{2-} + 28H^+ \rightarrow 3Sn^{4+} + 4Cr^{3+} + 14H_2O$

E° for Sn/Sn^{2+} = 0.136 V E° for Sn^{2+}/Sn^{4+} = – 0.154 V

E° for $Cr_2O_7^{2-}/Cr^{3+}$ = 1.33 V

Q.26 Calculate the equilibrium concentration of all ions in an ideal solution prepared by mixing 25.00 mL of 0.100 M Ti^+ with 25.00 mL of 0.200M Co^{3+}.

E° (Ti^+/Ti^{3+}) =–1.25 V; E° (Co^{3+}/Co^{2+}) = 1.84 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, H_2 & O_2 react to produce electricity. In the process, H_2 gas is oxidized at the anode & O_2 at the cathode. If 67.2 liter of 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: $H_2 + 2OH^- \rightarrow 2H_2O + 2\ e^-$

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

Q.29 One of the methods of preparation of per disulphuric acid, $H_2S_2O_8$, involve electrolytic oxidation of $H_2S\ O_4$ at anode ($2H_2S\ O_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^-$) with oxygen and hydrogen as by-products. In such an electrolysis, 9.722 L of H_2 and 2.35 L of O_2 were generated at STP. What is the weight of $H_2S_2O_8$ formed?

Q.30 During the discharge of a lead storage battery the density of sulphuric acid fell from 1.294 to 1.139 g. mL^{-1} H_2SO_4 of density 1.294 g mL^{-1} is 39% and that of density 1.139 g 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:

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

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

Q.31 A current of 3 amp was passed for 2 hour through a solution of $CuSO_4$, 3g of Cu^{2+} ions were deposited as Cu at cathode. Calculate percentage current efficiency of the process.

Q.32 An acidic solution of Cu^{2+} salt containing 0.4 g of 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 8.2×10^{12} liter approximately. A power reactor produces electricity at the rate of 1.5×10^6 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 H_2SO_4 electrolyte to change from a concentration of 34.6% by weight (density 1.261 g ml^{-1} at 25ºC) 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 H_2SO_4 is used up. Overall reaction is

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

Q.36 100ml $CuSO_4$ (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 M $Na_2S_2O_3$. Volume of $Na_2S_2O_3$ required was 35 ml. Assuming no volume change during electrolysis, calculate:

(a) Duration of electrolysis if current efficiency is 80%

(b) Initial concentration (M) of $CuSO_4$.

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 1L each of 1M Zn^{2+} and Cu^{2+} respectively. Find the EMF supplied by the Daniel cell after removal of the external current source. E° of Zn^{2+}/Zn and Cu^{2+}/Cu at 25ºC is – 0.76 and + 0.34 V respectively.

Q.38 Determine at 298 for cell

$Pt \mid Q, QH_2, H+ \parallel 1M\ KCl \mid Hg_2Cl_2(s) \mid Hg\ (l) \mid Pt$

(a) Its e.m.f when pH = 5.0

(b) The pH when $E_{cell} = 0$

(c) The positive electrode when pH = 7.5

Given $E^\circ_{RP\ (RHS)} = 0.28$, $E^\circ_{RP\ (LHS)} = 0.699$

Q.39 At 25ºC, ΔH_f (H_2O, l) = –56700 cal/mole and energy of ionization of H_2O (l) = 19050 Cal/mol. What will be the reversible EMF at 25ºC of the cell?

$Pt \mid H_2\ (g)\ (1\ atm) \mid H^+ \parallel OH^- \mid O_2\ (g)\ (1\ atm) \mid Pt$, if at 26ºC the e.m.f increase by 0.001158 V.

Q.40 Calculate the cell potential of a cell having reaction: $Ag_2S + 2e^- \rightarrow 2Ag + S^{2-}$ in a solution buffered at pH = 3 and which is also saturated with 0.1 M H_2S.

For H_2S: $K_1 = 10^{-8}$ and $K_2 = 1.1 \times 10^{-13}$, $K_{sp}\ (Ag_2S) = 2 \times 10^{-49}$, $E^\circ_{Ag^+/Ag} = -0.8\cdot$

Q.41 The equivalent conductance of 0.10N solution of $MgCl_2$ is 97.1 mho cm^2 $equi^{-1}$ at 25ºC. A cell with electrode that are 1.5 cm^2 in surface area and 0.5 cm apart is filled with 0.1 N $MgCl_2$ solution. How much current will flow when potential difference between the electrodes is 5 volt?

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

K^+ ion move in 2 hours at 25°C? Ionic conductance of K^+ ion at infinite dilution at 25°C is 73.52 ohm^{-1} cm^2 $mole^{-1}$?

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 $1.86 \times 10^{-4} m^2$. Calculate separation of electrodes.

Q.44 The specific conductance at 25°C of a saturated solution of $SrSO_4$ is 1.482×10^{-4} ohm^{-1} cm^{-1} while that of water used is 1.5×10^{-6} mho cm^{-1}. Determine at 25°C the solubility in gm. per liter of $SrSO_4$ in water. Molar ionic conductance of Sr^{2+} and SO_4^{2-} ions at infinite dilution are 59.46 and 79.8 ohm^{-1} cm^2 $mole^{-1}$ respectively. [Sr = 87.6, S =32, O = 16]

Q.45 Calculate the solubility and solubility product of Co_2 $[Fe(CN)_6]$ in water at 25°C from the following data: Conductivity of a saturated solution of $Co_2[Fe(CN)_6]$ is $2.06 \times 10^{-6} \Omega^{-1} cm^{-1}$ and that of water used $4.1 \times 10^{-7} \Omega^{-1} cm^{-1}$.The ionic molar conductivities of Co^{2+} and $Fe(CN)_6^{4-}$ are 86.0 $\Omega^{-1} cm^2$ $mole^{-1}$ and 444.0 $\Omega^{-1} cm^{-1}$ $mole^{-1}$.

Q.46 A sample of water from a large swimming pool has a resistance of 9200 Ω at 25°C when placed in a certain conductance cell. When filled with 0.02 M KCl solution, the cell has a resistance of 85 Ω at 25°C. 500 gm. of NaCl were dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of 7600 Ω. Calculate the volume of water in the pool.

Given: Molar conductance of NaCl at that concentration is 126.5 $\Omega^{-1} cm^{-1} mol^{-1}$ and molar conductivity of KCl at 0.02 M is 138 Ω^{-1} cm^2 $mole^{-1}$.

Exercise 2

Single Correct Choice Type

Q.1 An aqueous solution containing one mole per liter each of $Cu(NO_3)_2$ $AgNO_3$, $Hg_2(NO_3)_2$, $Mg(NO_3)_2$ is being electrolyzed by using inert electrodes. The value of standard potentials are

$$E^\circ_{Ag^+|Ag} - 0.80V,\ E^\circ_{Hg_2^{2+}|Hg} - 0.79V,$$

$$E^\circ_{Cu^{2+}|Cu} - 0.34V \text{ and } E^\circ_{Mg^{2+}|Mg} = -2.3V$$

With increasing voltage, the sequence of deposition of metals on the cathode will be

(A) Ag, Hg, Cu, Mg (B) Mg, Cu, Hg, Ag

(C) Ag, Hg, Cu (D) Cu, Hg, Ag

Q.2 The charge required for the oxidation of one mole Mn_3O_4 into MnO_4^{2-} in presence of alkaline medium is

(A) 5 × 96500C (B) 96500 C

(C) 10 × 96500 C (D) 2 × 96500 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) H_2, O_2 (B) O_2, H_2 (C) O_2, 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 pK_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 Ag_3PO_4 is 9×10^{-6} S m^{-1} and its equivalent conductivity is 1.50×10^{-4} S m^{-2} $equivalent^{-1}$. The K_{sp} of Ag_3PO_4 is:

(A) 4.32×10^{-18} (B) 1.8×10^{-9}

(C) 8.64×10^{-13} (D) None of these

Q.6 Equal volumes of 0.015 M CH_3COOH & 0.015 M NaOH are mixed together. What would be molar conductivity of mixture if conductivity of CH_3COONa is 6.3×10^{-4} S $cm^{-1?}$

(A) 8.4 S cm^2 $mole^{-1}$ (B) 84 S cm^2 $mole^{-1}$

(C) 4.2 S cm^2 $mole^{-1}$ (D) 42 S cm^2 $mole^{-1}$

Multiple Correct Choice Type

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

Cl_2 (aq.) + 2e → $2Cl^-_{(aq.)}$ $E^\circ_{Cl_2/Cl^-} = +1.36$ volt

Br_2 (aq.) + 2e → $2Br^-$(aq.) $E^\circ_{Br_2/Br^-} = +1.09$ volt

I_2(s) + 2e → $2I^-$(aq.) $E^\circ_{I_2/I^-} = +0.54$ volt

$S_2O_8^{2-}$(aq.) + 2e → $2SO_4^{2-}$(aq.)

$E_{S_2O_3^{2-}/SO_4^{2-}} = +2.00$ volt

(A) Cl_2 can oxidize SO_4^{2-} from solution

(B) Cl_2 can oxidize Br^- and I^- from aqueous solution

(C) $S_2O_8^{2-}$ can oxidize Cl^-, Br^- and I^- from aqueous solution

(D) $S_2O_8^{2-}$ is added slowly, Br^- can be reduce in presence of Cl^-

Q.8 Which of the following arrangement will produce oxygen at anode during electrolysis?

(A) Dilute H_2SO_4 solution with Cu electrodes.

(B) Dilute H_2SO_4 solution with inert electrodes.

(C) Fused NaOH with inert electrodes.

(D) Dilute NaCl solution with inert electrodes.

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 O_2 (g) will be evolved at anode at 1 atm & 273 K

(B) Total 504 L gases will be produced at 1 atm & 273 K

(C) 336 L of H_2(g) will be evolved at anode at 1 atm & 273 K

(D) 45 F electricity will be consumed

Q.10 During discharging of lead storage battery, which of the following is/are true?

(A) H_2SO_4 is produced

(B) H_2O is consumed

(C) $PbSO_4$ is formed at both electrodes

(D) Density of electrolytic solution decreases

Q.11 The EMF of the following cell is 0.22 volt.

Ag(s) | AgCl(s) |KCl (1M) |H^+ (1M) |H_2 (g) (1atm); Pt(s)

Which of the following will decreases the EMF of cell

(A) Increasing pressure of H_2 (g) from 1 atm to 2 atm

(B) Increasing Cl^- concentration in Anodic compartment

(C) Increasing H^+ concentration in cathodic compartment

(D) Decreasing KCl concentration in Anodic compartment.

Assertion Reasoning Type

(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^+, B^{2+} C^{3+} are –0.3, –0.5, 0.8 volt respectively, so oxidizing power of ions is $C^{3+} > A^+ > B^{2+}$.

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 Ω at 25ºC when placed in a certain conductance cell. When filled with 0.02 M KCl solution, the cell has a resistance of 100 Ω at 25ºC. 585 gm. of NaCl were dissolved in the pool, which was thoroughly stirred. A sample of this solution gave a resistance of 8000 Ω.

[Given: Molar conductance of NaCl at that concentration is 125 $\Omega^{-1}cm^2$ $mole^{-1}$ and molar conductivity of KCl at 0.02 M is 200 Ω^{-1} cm^2 $mole^{-1}$.]

Q.15 Cell constant (in cm^{-1}) of conductance cell is:

(A) 4 (B) 0.4 (C) 4×10^{-2} (D) 4×10^{-5}

Q.16 Conductivity (Scm^{-1}) of H_2O is:

(A) 4×10^{-2} (B) 4×10^{-3}

(C) 4×10^{-5} (D) None of these

Q.17 Volume (in Liters) of water in the pool is:

(A) 1.25×10^5 (B) 1250

(C) 12500 (D) None of these

Paragraph 2: Copper reduces NO_3^- into NO and NO_2 depending upon conc. Of HNO_3 in solution. Assuming $[Cu^{2+}] = 0.1\ M_2$ and $P_{NO} = P_{NO_2} = 10^{-3}$ atm and using given data answer the following questions:

$E^\circ_{Cu^{2+}/Cu} = +\ 0.34$ volt

$E^\circ_{NO_3^-/NO} = +\ 0.96$ volt

$E^\circ_{NO_3^-/NO_2} = +0.79$ volt

At 298 K $\frac{RT}{F}(2.303) = 0.06$ volt

Q.18 E_{Cell} for reduction of $NO_3^- \rightarrow NO$ by Cu(s), when $[HNO_3] = 1$ M is [At T = 298]

(A) ~0.61 (B) ~0.71 (C) ~ 0.51 (D) ~0.81

Q.19 At what HNO_3 concentration thermodynamic tendency for reduction of NO_3^- into NO and NO_2 by copper is same?

(A) $10^{1.23}$ M (B) $10^{0.56}$ M (C) $10^{0.66}$ M (D) $10^{0.12}$ M

Match the Columns

Q.20

Column I	**Column II (Electrolysis product using inert electrode)**
(A) Dilute solution of HCl	(p) O_2 evolved at anode
(B) Dilute solution of NaCl	(q) H_2 evolved at cathode
(C) Concentrated Solution of NaCl	(r) Cl_2 evolved at anode
(D) $AgNO_3$ solution	(s) Ag deposition at cathode

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 $Zn|Zn^{2+}$ (a = 0.1 M) || Fe^{2+} (a = 0.01 M) | 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) $10^{0.26/0.0295}$ (D) $10^{0.32/0.295}$

Q.3 The half-cell reaction for rusting of iron are:

$2H^+ + 2e^- + \frac{1}{2}O_2 \rightarrow H_2O\ (l);\ E^\circ = +\ 1.23$ V

$Fe^{2+} + 2e^- \rightarrow Fe(s),\quad E^\circ = -0.44$ V

ΔG° (in kJ) for the reaction is ***(2005)***

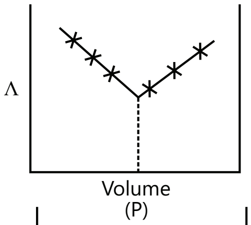
(A) –76 (B) –322 (C) –122 (D) –176

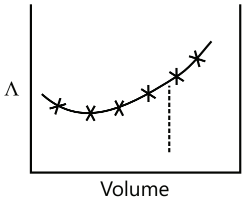
Q.4 Electrolysis of dilute aqueous NaCl solution was carried out by passing 10 mA current. The time required to liberate 0.01 mole of H_2 gas at the cathode is
(1 F = 96500 C $mole^{-1}$) ***(2008)***

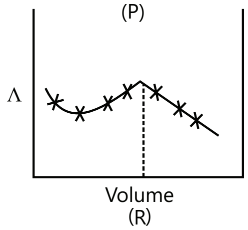
(A) 9.65×10^4 s (B) 19.3×10^4 s

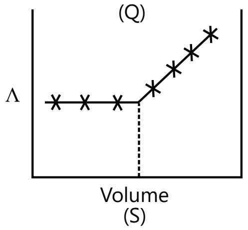
(C) 28.95×10^4 (D) 38.6×10^4 s

Q.5 $AgNO_3$ (aqueous) was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance (Λ) versus the volume of $AgNO_3$ is ***(2011)***









(A) (P) (B) (Q) (C) (R) (D) (S)

Q.6 Consider the following cell reaction,

$2Fe(s) + O_2\ (g) + 4H^+\ (aq) \rightarrow$

$2Fe^{2+}\ (aq) + 2H_2O\ (l),\ E^\circ = 1.67$ V

At $[Fe^{2+}] = 10^{-3}$ M, P $(O_2) = 0.1$ atm and pH = 3, the cell potential at 25°C is ***(2011)***

(A) 1.47 V (B) 1.77 V (C) 1.87 V (D) 1.57 V

Q.7 For the reduction of NO_3^- ion in an aqueous solution E° is + 0.96 V. Values of E° for some metal ion are given below

$V^{2+}\ (aq) + 2e^- \rightarrow V \qquad E^\circ = -1.19$ V

$Fe^{3+}\ (aq) + 3e^- \rightarrow Fe \qquad E^\circ = -0.04$ V

$Au^{3+}\ (aq) + 3e^- \rightarrow Au \qquad E^\circ = +\ 1.40$ V

Hg^{2+} (aq) +2e$^-$ $\rightarrow$ Hg E° = + 0.86 V

The pair (s) of metals that is (are) oxidized by 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 $AgNO_3$ is added to glucose with NH_4OH then gluconic acid is formed.

$Ag^+ + e^- \rightarrow Ag$; $E^\circ_{red} = 0.80$ V

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

Q.8 $2Ag^+ + C_6H_{12}O_6 + H_2O \rightarrow 2Ag(s)\ C_6H_{12}O_7 + 2H^+$

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_{oxi} will increase by a factor of 0.65 from E°_{oxi}

(B) E_{oxi} will decrease by a factor of 0.65 from E°_{oxi}

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

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

Q.10 Ammonia is always added in this reaction. Which of the following must be incorrect?

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

(B) $Ag(NH_3)_2^+$ is a stronger oxidizing reagent than Ag^+

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

(D) 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 6.023×10^{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: Na = 23, Hg = 200, 1 F = 96500C). ***(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°) 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 E° (V with respect to normal hydrogen electrode) values. Using this data obtain the correct explanations to

$I_2 + 2e^- \rightarrow 2I^-$ $E^\circ = 0.54$

$Cl_2 + 2e^- \rightarrow 2Cl^-$ $E^\circ = 1.36$

$Mn^{3+} + e^- \rightarrow Mn^{2+}$ $E^\circ = 1.50$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E^\circ = 0.77$

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $E^\circ = 1.23$ ***(2007)***

Q.14 Among the following, identify the correct statement

(A) Chloride ion is oxidized by O_2

(B) Fe^{2+} is oxidized by iodine

(C) Iodide ion is oxidized by chlorine

(D) Mn^{2+} is oxidized by chlorine

Q.15 While Fe^{3+} is stable, Mn^{3+} is not stable in acid solution because

(A) O_2 oxidizes Mn^{2+} to Mn^{3+}.

(B) O_2 oxidizes both Mn^{2+} to Mn^{3+} and Fe^{2+} to Fe^{3+}

(C) Fe^{3+} oxidizes H_2O to O_2

(D) Mn^{3+} oxidizes H_2O to O_2

Q.16 Sodium fusion extract, obtained from aniline, on treatment with iron (II) sulphate and H_2SO_4 in presence of air gives a Prussian blue precipitate. The blue color is due to the formation of

(A) $Fe_4\,[Fe\,(CN)_6]_3$ (B) $Fe_3\,[Fe\,(CN)_6]_2$

(C) $Fe_4\,[Fe\,(CN)_6]_2$ (D) $Fe_3\,[Fe\,(CN)_6]_3$

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:

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

For the above electrolytic cell the magnitude of the cell potential | E_{cell} | = 70 mV. ***(2010)***

Q.17 For the above cell

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

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

Q.18 If the 0.05 molar solution of M^+ is replaced by a 0.0025 molar M^+ solution, then the magnitude of the cell potential would be

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

Q.19 All the energy released from the reaction 0 –1

X $\longrightarrow$ Y. $\Delta_r G^\circ$ = -193 kJ mol/L

is used for oxidizing M^+ as $M^+ \longrightarrow M^{3+} + 2e^-$,

E° = -0.25V.

Under standard conditions, the number of moles of M^+ oxidized when one mole of X is converted to Y is

[F = 96500 C mol/L] ***(2015)***

Q.20 The molar conductivity of a solution of a weak acid HX (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid HY (0.10 M). If $\lambda^0_{X^-} \approx \lambda^0_{Y^-}$, the difference in their pK_a values, a pK_a (HX) - pK_a (HY), is consider degree of ionization of both acids to be << 1) ***(2015)***

Q.21 For the following electrochemical cell at 298 K,

Pt(s) | H_2(g, 1 bar) | H^+ (aq, 1M)|| M^{4+}(aq), M^{2+} (aq) | Pt(s)

E_{cell} = 0.092 V when $\dfrac{\left[M^{2+}(aq)\right]}{\left[M^{4+}(aq)\right]} = 10^x$.

Given: $E^\circ_{M^{4+}/M^{2+}} = 0.151\,V;\ 2.303\dfrac{RT}{F} = 0.059\ V$

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.5
Q.9
Q.12
Q.15
Q.18
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.2 124 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mole}^{-1}$

Q.4 $\Delta_r G° = -213.04$ kJ, $E^{\circ}_{cell} = +1.104$ V

Q.5 $\lambda_m = 124\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$

Q.8 0.219cm^{-1}

Q.9 $\wedge_m = 32.765\ \text{cm}^2\ \text{mol}^{-1}$, $k_a = 2.2 \times 10^{-4}$

Q.10 3. 66 gm

Q.14 $E^{\circ} = 0.34$ V

Q.19 (i) 0.2515 V; (ii) 0.8101 V (iii) 0.226 V (iv) 1.451 V; (v) –0.268 V

Q.20 0.7288 V

Q.21 0.1536 V

Q.22 –0.1615 V

Q.23 (i) 0.2278 V ; (ii) 0.3692

Q.24 0.91 V

Q.25 3.67×10^{-4}

Q.26 Na, Ca, Mg and Al.

Q.27 2.96 V

Q.28 (a) –0.118 V; (b) –0.0413 V; (c) (i) –0.0295 V (ii) –0.59 V

Q.29 $1.3 \times 10^2\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equi}^{-1}$

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 $[Cu^{2+}] = 10^{-4}$ M

Q.2 pH = 6.61

Q.3 $K_a = 6.74 \times 10^4$

Q.4 1.39 V

Q.5 – 0.46 V

Q.6 (ii) 1.27V (ii) 245.1 kJ

Q.7 $E^o = -0.22$ V

Q.8 h =2.12×10^{-2}, $K_h = 1.43 \times 10^{-5}$ M

Q.9 0.95 V

Q.10 $K_{sp} = 1.1 \times 10^{-16}$

Q.11 $[Br^-]: [Cl^-] = 1: 200$

Q.12 $E^o = -0.1511$ V

Q.13 –0.037 V

Q.14 1.536×10^{-5} M^3

Q.15 1.66 V

Q.16 –1.188V

Q.17 10^{-2}

Q.18 5.24×10^{16}

Q.19 $E^o = 1.59$ V, non–spontaneous

Q.20 $E^o = 0.71$ V

Q.21 $[Zn^{2+}]/[Cu^{2+}] = 1.941 \times 10^{37}$

Q.22 0.373 V

Q.23 $K_f = 8.227 \times 10^{63}$

Q.24 0.372 V, –0.307 V

Q.25 $K = 10^{268}$

Q.26 $Ta^+ = 5x10^{-9}$; $Co^{3+} = 10^{-8}$

Q.27 Eq. wt. = 107.3

Q.28 643.33 amp, 190.5 g

Q.29 43.456 g

Q.30 265 Amp. Hr.

Q.31 42.2 %

Q.32 V (O_2) = 99.68 mL, V (H_2) = 58.46 mL, Total vol. = 158.1 mL

Q.33 57.5894 gm.

Q.34 1.9 million year

Q.35 2.4×10^5 coulomb

Q.36 1250 s, 0.064 M

Q.37 1.143 V

Q.38 (a) –0.124 V, (b) 7.1 (c) calomel electrode

Q.39 0.4414 V

Q.40 –0.167 V

Q.41 0.1456 ampere

Q.42 3.29 cm

Q.43 4.25×10^{-2} meter   **Q.44** 0.1934 gm. /liter

Q.45 $K_{sp} = 7.682 \times 10^{-17}$ **Q.46** $2 \times 10^5 dm^3$

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 A → p, q; B → p, q; C → q, r; D → p, 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: $Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Ag^{+}_{(aq)} \mid Ag_{(s)}$

(i) Zinc electrode is negatively charged

(ii) At anode:

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

At cathode

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

Sol 2: $\wedge_m = \dfrac{k \times 1000}{M} = \dfrac{2.48 \times 10^{-2} \times 1000}{0.2}$

$\wedge_m = 124\ \Omega^{-1}\ cm^2\ mol^{-1}$

Sol 3: (i) Reaction:

$$\underset{0.\ 0001\ M}{Mg(s) + Cu^{2+}(aq.)} \rightarrow \underset{0.\ 001\ M}{Cu(s) + Mg^{2+}(aq.)}$$

$$E = E^{\circ} - \frac{2.303\ RT}{nF} \log\left(\frac{[Cu^{2+}]}{[Mg^{2+}]}\right)^{-1}$$

$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{0.001}{0.0001}$$

$E = E^{\circ} - 0.\ 02955$

$E = E^{\circ} - 0.\ 03$

$= 2.\ 70 - 0.\ 03$

$= 2.\ 67\ V$

(ii) $Fe + 2H^{+} \rightarrow Fe^{2+} + H_2$

1 0.001

$n = 2$

$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{[Fe^{2+}]P_{H_2}}{[H^{+}]^2}$$

$$E = E^{\circ} - 0.\ 03 \log \frac{0.001 \times 1}{1}$$

$E = E^{\circ} + 0.\ 09 = 0.\ 44 + 0.\ 09$

$\Rightarrow E = 0.\ 53\ V$

(iii) $Sn + 2H^{+} \rightarrow Sn^{2+} + H_2$

0. 02 0. 05

$n = 2$

$$E = E^{\circ} - \frac{-0.0591}{2} \log \frac{[Sn^{2+}]}{[H^{+}]^2} . P_{H_2}$$

$$E = E^{\circ} - 0.\ 03 \log \frac{0.05}{0.04}$$

$E = E^{\circ} - 0.\ 0029$

$E = 0.\ 14 - 0.\ 0029$

$\Rightarrow E = 0.\ 1371\ V$

(iv) $Br_2 + H_2 \rightarrow 2Br^{-} + 2H^{+}$

$$E = E^{\circ} - \frac{0.0591}{2} \log\ [H^{+}]^{2} [Br^{-}]^{2}$$

$= E^{\circ} - 0.\ 02955 \log\ (0.\ 01)^2 (0.\ 03)^2$

$E = E^{\circ} + 0.\ 208$

$E = 1.\ 09 + 0.\ 208$

$E = 1.\ 298\ V$

Sol 4: The formula of standard cell potential is

$E^{\circ}_{cell} = E^{\circ}_{right} - E^{\circ}_{left}$

Use this link to get all values

$E^{\circ}_{cell} = 0.344 - (-0.76)$

$E^{\circ}_{cell} = 0.344 + 0.076\ V$

$E^{\circ}_{cell} = +1.104\ V$

In balanced reaction there are 2 electron are transferring so that n = 2

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

$E^{\circ}_{cell} = +1.104\ V$

Use formula

$\Delta_r G^{\circ} = -n\ FE^{\circ}_{cell}$

Plug the value we get

Then, $= -2 \times 96500\ C\ mol^{-1} \times 1.104\ V$

$= -212304\ CV\ mol^{-1}$

$= -212304\ mol^{-1}$

$= -212.304 \text{ kJ mol}^{-1} = -213.04 \text{ kJ}$

Sol 5: $\wedge_m = k \times \dfrac{1000}{C}$

$\wedge_m = \dfrac{0.0248 \times 1000}{0.2} = 124\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$

Sol 6: (i) $Ca^{2+} + 2e^- \rightarrow Ca$

Charge needed $= 2 \times nF = 2 \times \dfrac{20}{40} F = 1 F = 96500$ C

(ii) $Al^{3+} + 3e^- \rightarrow Al$

Charge needed $= (3n_{Al}) \times 96500C$

$= 3 \times \dfrac{40}{27} \times 96500 \text{ C} = 4.28 \times 10^5$ C

Sol 7: (i) $H_2O \rightarrow O_2$

We have, $H_2O \rightarrow \dfrac{1}{2}O_2 + 2H^+ + 2e^-$

Charge required $= 2 F = 1.93 \times 10^5$ C

(ii) $Fe_2O + \dfrac{1}{2}H_2O \rightarrow \dfrac{1}{2}Fe_2O_3 + H^+ + e^-$

Charge needed for 1 mole FeO = 1 F = 96500 C

Sol 8: $k = 0.146 \times 10^{-3}\ \text{s cm}^{-1}$

$R = 1500\ \Omega$

$G^* = Rk = 0.219\ \text{cm}^{-1}$

Sol 9: $\wedge_m = 1000 \times \dfrac{k}{C} = \dfrac{1000 \times 7.896 \times 10^{-5}}{0.00241}$

$\wedge_m = 32.765\ \text{cm}^2\ \text{mol}^{-1}$

$q = \dfrac{\wedge_m}{\wedge^{o}_m} = \dfrac{32.76}{390.5}$

$\alpha = 0.084$

$k_a = \dfrac{C\alpha^2}{1-\alpha}$; $k_a = 2.2 \times 10^{-4}$

Sol 10: $Ni^{2+} + 2e^- \rightarrow Ni$

Charge supplied = 5 × 20 × 60 C = 6000 C

Moles of Ni deposited $= \dfrac{6000}{96500}$

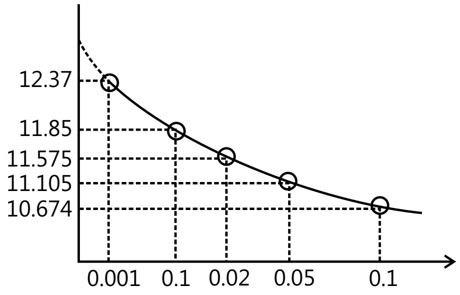
Mass of Ni deposited $= \dfrac{6000}{96500} \times 59 = 3.66$ gm

Sol 11: We use the formula

$\wedge_m = \dfrac{k \times 1000}{C}$

C/M	0.001	0.010	0. 02	0. 05	0. 100
$10^2 \times k/\text{sm}^{-1}$	12.37	11.85	23. 15	55. 53	106.74
$\wedge^{o}_m$ S cm^2/mol	12.37	11.85	11.575	11.106	10.674
$\sqrt{C}$	0. 03	0. 1	0. 14	0. 22	0. 31

$\wedge_m$ vs C



We have

$\wedge_m = \wedge^{o}_m - A\sqrt{C}$

At C = 0. 01,

$\wedge_m = 11.85 = \wedge^{o}_m . A \times 0.1$ ...(i)

At C = 0. 02

$\wedge_m = 11.575 = \wedge^{o}_m . A \times 0.14$ ...(ii)

Subtracting

0. 01 A = 0. 275

A = 6. 875

$\wedge^{o}_m = 12.5375\ \text{cm}^2\ \text{mol}^{-1}$

(putting A in (i))

Sol 12: $Ag^+ + e^- \rightarrow Ag$

$n_{Ag} = \dfrac{1.45}{108} = 0.0134$

Charge, $Q = n_{Ag}.\ F = 0.0134 \times 96500$ C

Q = 1295. 6 C

$t = \dfrac{Q}{I} = \dfrac{1295.6}{1.5}$

t = 863. 735 s

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

Moles of Zn, $n_{Zn} = \frac{Q}{2F} = \frac{n_{Ag}}{2}$

Wt. of Zn = $n_{Zn} \times 65 = \frac{w_{Ag}}{m_{Ag}} \times \frac{1}{2} \times 65$

Wt. of Zn = 0. 43 gm

For Cu,

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

$n_{Cu} = \frac{Q}{2F} = n_{Zn}$

Wt. of copper = $n_{Cu} \times 63.5 = 0.426$ gm

Sol 13: (i) $Fe^{3+}_{(aq)} + I^-_{(aq)} \rightarrow Fe^{2+}_{(aq)} + \frac{1}{2}I_2(g)$

$E^\circ = E^\circ_{I^-/I_2} + E^\circ_{Fe^{3+}/Fe^{2+}} = -0.54 + 0.77 = +0.23 > 0$

This is feasible.

(ii) $Ag^+_{(aq)} + Cu_{(s)} \rightarrow Ag_{(s)} + Cu^+_{(aq)}$

$E^\circ = E^\circ_{Ag^+/Ag} + E^\circ_{Cu/Cu^+} = 0.8 - 0.52 = 0.2870$

This is feasible.

(iii) $Fe^{3+}_{(aq)} + Br^-_{(aq)} \rightarrow \frac{1}{2}Br_2(g) + \frac{1}{2}Fe^{2+}(g)$

$E^o = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Br_2/Br^-} = 0.77 - (1.09) = -0.32 < 0$

So, this is not feasible

If $Fe^{3+} \rightarrow Fe$, then, $E_{Fe^{3+}/Fe} = -0.036$

and $E^\circ = -1.126$, still not feasible.

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

$E^\circ = E^\circ_{Ag^+/Ag^+} + E^\circ_{Fe^{3+}/Fe^{2+}} = -0.8 + 0.77 = -0.03 < 0$

So, this is not feasible

if $Fe^{3+} \rightarrow Fe$, $E^\circ_{Fe^{3+}/Fe} = -0.03$,

$E^\circ = -0.836$, still not feasible.

(v) $Br_2(aq)+Fe^{2+}(aq) \rightarrow \frac{1}{2}Br^-(aq)+Fe^{3+}(aq)$

$E^\circ = E^\circ_{Br_2/Br^+} + E^\circ_{Fe^{2+}/Fe^{3+}} = 1.09 - 0.77 = 0.32 > 0$

This reaction is feasible.

Sol 14: $Cu^{2+} + e \rightarrow Cu^+$

$E^\circ = +0.18$ V, n = 1

$\Delta E_1 = -nFE^o = -0.18\ F$

$Cu^+ + e \rightarrow Cu$,

$E^\circ = 0.50$ V, n = 1

$\Delta G_2 = -nF\ E^\circ = -0.5\ F$

Adding

$Cu^{2+} + 2e \rightarrow Cu$,

$\Delta G = \Delta G_1 + \Delta G_2$, n = 2

$-2F\ E^\circ = -0.18\ F - 0.5\ F$

$E^\circ = 0.34$ V

Sol 15: Element with maximum oxidation potential will have highest reduction potential.

Now, $E^\circ_{Zn/Zn^{2+}} = 0.76$ V,

$E^\circ_{Pb/Pb^{2+}} = 0.13$ V

$E^\circ_{Al/Al^{2+}} = 1.66$ V

$\therefore$ Reducing order: Pb < Zn < Al

Sol 16: (i) Since O_3 has the highest SRP, it is the strongest oxidising agent.

(ii) As Ag cannot get reduced, 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: IO_3^- will act as better oxidising agent in acidic medium due to its larger SRP in acidic medium then basic medium.

Sol 18: $Fe^{3+} + Br^- \rightarrow \frac{1}{2}Br_2 + Fe^{2+}$

$E^\circ = E^\circ_{Fe^{3+}/Fe^{2+}} + E^\circ_{Br^-/Br_2}$

$= 0.77 - 1.09 = -0.32 < 0$

$\therefore$ Fe^{3+} cannot oxidise Br^- to Br_2.

Sol 19: (i) $Cu^{2+} + 2e^- \rightarrow Cu$

$E = E^\circ - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]} = 0.34 - 0.0295 \log \frac{1}{0.001}$

E = 0. 2515 V

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

0. 02

$E^\circ_{Zn/Zn^{2+}} = -E^\circ_{Zn/Zn^{2+}} = 0. 76$

$E = E^\circ - \frac{0.0591}{2}\log[Zn^{2+}] = 0. 76 - 0. 0295 \log (0. 02)$

$E = 0. 8101$ V

(iii) $AgCl + e^- \rightarrow Ag + Cl^-$

$Ag^+ + e^- \rightarrow Ag,\ E^\circ_1 = 0. 8,\ n = 1$

$\Delta G_1 = - nFE^\circ_1$

$\Delta G_1 = -0. 8\ F$

$AgCl \rightleftharpoons Ag^+ + Cl^-,$

$K_{s_1} = 2 \times 10^{-10}$

$\Delta G_2 = -RT \ln K_{sp}$

Adding

$AgCl + e \rightarrow Ag + Cl^-$

$\Delta G = \Delta G_1 + \Delta G_2,\ n = 1$

$-F\ E^\circ = -0. 8\ F - 2. 303RT \log (2\times10^{-10})$

$E^\circ = 0. 8 + \frac{2.303RT}{F} \log (2 \times 10^{-10})$

$E^\circ = 0. 8 - 0. 57$

$E^\circ = 0. 226$ V

(iv) $\frac{1}{2}Cl_2 + e^- \rightarrow Cl^-$

$E^\circ_{Cl_2/Cl^-} = 1. 36$ V

$E = E^\circ - 0. 0591 \log \frac{[Cl^-]}{(P_{Cl_2})^{1/2}}$

$= 1. 36 - 0. 0591 \log \frac{0.02}{(0.5)^{1/2}} = 1. 36 - 0. 0591(-1. 548)$

$E = 1. 451$ V

(v) $H^+ + e^- \rightarrow \frac{1}{2}H_2$

$E^\circ = 0$

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

$[H^+] = 10^{-4. 4}$

$E = 0. 0591 \log \frac{P_{H2}^{\ 1/2}}{[H^+]} = -0. 0591(\log\sqrt{2} - \log[H^+])$

$= -0. 0591(0. 15 + 4. 4)$

$E = -0. 268$ V

Sol 20: $Fe^{3+} + e^- \rightarrow Fe^{2+}$

$E^\circ_{Fe^{3+}/Fe^{2+}} = 0. 77$ V

$E = E^\circ - 0. 0591 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$

$E = 0. 77 - 0. 0591 \log 5$

$(\because [Fe^{2+}] = 5 \times [Fe^{3+}])$

$E = 0. 7287$ V

Sol 21: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$k_a = \frac{C\alpha^2}{1-\alpha} = C\alpha^2$

$\alpha = \sqrt{\frac{k_a}{C}}$

$[H^+] = C\alpha = \sqrt{Ck_a}$

$[H^+] = \sqrt{0.357\times1.74\times10^{-5}}$

$[H^+] = 2. 492 \times 10^{-3}$

$\frac{1}{2}H_2 \rightarrow H^+ + e$

$E^\circ = 0$

$E = -0. 0591 \log[H^+] = -0. 0295 \log (2. 492 \times 10^{-3})$

$E = 0. 1536$ V

Sol 22: $pH = -\log[H^+]$

$13 = -\log[H^+] \Rightarrow [H^+] = 10^{-13}$

$[OH^-] = \frac{k_w}{[H^+]} = \frac{10^{-14}}{10^{-13}} = \frac{1}{10}$

$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-$

$K_{sp} = [Cu^{2+}]\ [OH^-]^{\ 2}$

$[Cu^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1\times10^{-19}}{10^{-2}}$

$[Cu^{2+}] = 10^{-17}$ M

$Cu^{2+} + 2e \rightarrow Cu$

$E^\circ = 0. 34$ V, $n = 2$

$E = E^\circ - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]}$

$= 0. 34 - 0. 0591 \log\frac{1}{10^{-17}} = 0. 34 - 0. 5015$

$E = -0. 1615$ V

Sol 23: (i) $Ag^+ + e \rightarrow Ag$; $E^\circ_1 = 0.80$ V, n = 1

$\Delta G_1 = -nFE^\circ_1 = -0.8F$

$AgCl \rightarrow Ag^+ + Cl^-$

$\Delta G_2 = -RT \ln k_{sp} = -2.303\ RT \log(2\times10^{-10})$

Adding,

$AgCl + e^- \rightarrow Ag + Cl^-$

$\Delta G = -nF\ E^\circ = \Delta G_1 + \Delta G_2$, n = 1

$-F\ E^\circ = -0.8\ F - 2.303\ RT \log(2\times10^{-10})$

$$E^\circ = 0.8 + \frac{2.303RT}{F}\log(2\times10^{-10})$$

$E^\circ = 0.22$ V

(ii) $E = E^\circ - 0.0591\log[Cl^-] = 0.22 - 0.0591\log(4\times10^{-3})$

E = 0.36 V

Sol 24: $Ni(s) + 2Ag^+(0.002\ M)$

$\rightarrow Ni^{2+}(0.160\ M) + 2\ Ag(s)$

n = 2

$$\therefore E = E^\circ_1 - \frac{0.0591}{2}\log\frac{[Ni^{2+}]}{[Ag^+]^2}$$

$$= 1.05 - 0.0295\log\frac{0.16}{(2\times10^{-3})^2} = 1.05 - 0.135$$

E = 0.91 V

Sol 25 $HCOOH \rightleftharpoons H^+ + HCOO^-$

$\wedge_m^0(HCOOH) = \wedge_m^0(HCOO^-) + \wedge_m^0(H^+)$

= 349.6 + 54.6

$\wedge_m^0 = 404.2\ S\ cm^2\ mol^{-1}$

$$\alpha = \frac{\wedge_m}{\wedge_m^0} = \frac{46.1}{404.2}$$

$\alpha = 0.114$

$$k_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.025(0.114)^2}{1-0.114}$$

$k_a = 3.67\times10^{-4}$

Sol 26: (i) Potassium

(ii) Sodium

(iii) Calcium

(iv) Magnesium

(v) Aluminium

Sol 27: $Mg(s)|Mg^{2+}(aq)||Ag^+(aq)|Ag(s)$

$Mg(s) + 2Ag^+ \rightarrow Mg^{2+} + 2Ag$

n = 2, E° = 3.17 V

$$E = E^\circ - \frac{0.0591}{2}\log\frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$= 3.17 - 0.0295\log\frac{(0.13)}{(10^{-4})^2} = 3.17 - 0.209$$

E = 2.96 V

Sol 28: (a) $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

$[H^+] = 2[H_2SO_4] = 0.02$ M

$\frac{1}{2}H_2 \rightarrow H^+ + e^-$

E° = 0, n = 1

$$E = E^\circ - 0.0591\log\frac{[H^+]}{P_{H_2}^{1/2}} = -0.0591\log\frac{0.02}{\sqrt{4}}$$

$E = -0.0591\log(0.01)$

$E = +0.1182$, $E_r = -0.1182$

(b) $HCl \rightarrow H^+ + Cl^-$

$[H^+] = [HCl] = 0.2$

$\frac{1}{2}H_2 \rightarrow H^+ + e^-$

E° = 0, n = 1

$$E = E^\circ - \frac{0.0591}{1}\log\frac{[H^+]}{P_{H_2}^{1/2}} = 0 - 0.0591\log\frac{0.2}{1}$$

$E = 0.0413$ V, $E_r = -0.0413$ V

(c) E = 0, n = 1

$$E^\circ = \frac{-0.0591}{1}\log[H^+] = 0.0591\ p[H]$$

(i) pH = 5

E = 0.0591 × 5 = 0.2955 V

$E_r = -0.2955$ V

(ii) pOH = 4

pH = 14 – pOH = 10

E = 0.0591 × 10 = 0.591 V

$E_r = -E = -0.0591$ V

Sol 29: n for $H_2SO_4 = 2$

Normality = Molarity × n = 2M

$$\wedge_e = \frac{k\times1000}{N} = \frac{26\times1000\times10^{-2}}{2} = 130\ Scm^2\ equiv^{-1}$$

Exercise 2

Single Correct Choice Type

Sol 1: (C) $M^{+2} + 2e \rightarrow M$

For one mole, charge required = 2F

If atomic weight is M.

Then, for M gm, 2F charge

For 1 gm, charge = $\frac{2F}{M}$ = $1.81 \times 10^{22} \times 1.6 \times 10^{-19}$

$\Rightarrow$ M = 66. 7 gm

Sol 2: (B) Moles of Ag = 1

Moles of Cu = $\frac{1}{2}$

Moles of 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 = $10 \times 10 \times 10^{-2}$ cm^3 = 1 cm^3

Mass = 8. 94 g

Moles = $\frac{8.94}{63.5}$

Quantity of electricity = $\frac{8.94}{63.5} \times 2F$ = 27172 C

Sol 5: (D) $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

$2H_2O \rightarrow 2H_2 + O_2$

Only water will be oxidised and reduced.

$V_{H_2} = 2 \times V_{O_2} = 4.8$ L

Sol 6: (D) At cathode, water will be reduced,

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

pH of the solution around cathode will decrease.

Sol 7: (B) This is a convention.

Sol 8: (A) $H^+ + e^- \rightarrow \frac{1}{2}H_2$

E° = 0

$$E = \frac{-0.0591}{1}\log\frac{(P_{H_2})^{1/2}}{[H^+]} = -0.0591 \log 10 = -0.0591 \text{ V}$$

ΔE = 0. 0591 V

Sol 9: (A) We have,

$$E^\circ = \frac{0.0591}{2}\log k_C$$

$$E^\circ = \frac{0.0591}{2}\log(2.69 \times 10^{12}) = 0.3667 \text{ V}$$

Sol 10: (B) $Ag^+ + e^- \rightarrow Ag$

$$E = E^\circ - 0.0591 \log \frac{1}{[Ag^+]}$$

$0.25 = 0.799 + 0.059 \log [Ag^+]$

$[Ag^+] = 5.13 \times 10^{-10}$

$k_{sp} = [Ag^+][Cl^-] = 5.1 \times 10^{-11}$

Sol 11: (B) At cathode

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

At anode

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

Moles $n_{O_2} = \frac{1}{2}nC_2$

$$V_{O_2} = 22400\ n_{O_2} = 22400 \times \frac{1}{2} \times \frac{2.5}{63.5} = 441 \text{ mL}$$

$\approx$ 445 mL O_2 is liberated

Sol 12: (B) P = VI

P = 1. 65 kW

q = 1. 65 × 8 kWh = 13. 2 kWh

Cost = 13. 2 × 5 paise = 66 paise

Sol 13: (C) $\wedge_m = \frac{1}{R}.\frac{\ell}{a}.\frac{1000}{C}$

$$= \frac{1}{50}.\frac{2.2}{4.4 \times 10^{-2}} \times \frac{1}{0.5} = 0.002 \text{ Sm}^2 \text{ mol}^{-1}$$

Sol 14: (C) $\alpha = \frac{\wedge_m}{\wedge_m^0} = \frac{10}{200} = 0.05$

$[H^+] = C\alpha = 0.\ 005$

$pH = -\log[H^+] = \log[200] = 2.\ 3$

Sol 15: (C) $\wedge_m = k \times \frac{1000}{C} = \frac{1000}{xy}\ (k = \frac{1}{x}, C = y)$

Sol 16: (B) $\alpha = \sqrt{\frac{k_a}{C}} = \sqrt{\frac{1.6\times10^{-5}}{0.01}} = 0.\ 04$

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

$\Rightarrow \wedge_m = 380 \times 10^{-4} \times 0.\ 04 = 1.\ 52 \times 10^{-3}$

$\wedge_m = \frac{1000\times k}{C\times1000}$

$k = 1.\ 52 \times 10^{-2}\ S\ m^{-1}$

Sol 17: (A) $Au^+ + 2CN^- = Au(CN)_2^-$

$\Delta G_1 = -RT\ ln\ X$

$Au^{3+} + 2e^- \rightarrow Au^+$

$\Delta G_2 = -nFE^o = -2.\ 8F$

$Au \rightarrow Au^{3+} + 3e^-$

$\Delta G_3 = -nF(-E^o) = 4.\ 5F$

$\frac{1}{4}O_2 + \frac{1}{2}H_2O + e^- \rightarrow OH^-$

$\Delta G_4 = -1F(E^o) = -0.\ 41F$

Summing, $\Delta G = \sum_{i=1}^{4}\Delta G_1 = -RT\ ln\ X + 1.\ 29\ F$

Sol 18: (C) At anode

$\frac{1}{2}H_2 \rightarrow H^+ + e^-$

At cathode

$\frac{1}{2}Cl_2 + e^- \rightarrow Cl^-$

$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow H^+ + Cl^-$

$E = E^o - 0.\ 0591 \log \frac{[H^+][Cl^-]}{P_{H_2}^{\ 1/2}.P_{Cl_2}^{\ 1/2}}$

$E_1 - E_2 = 0.\ 0591 \log \frac{[H^+]_2[Cl^-]_2}{[H^+]_1[Cl^-]_1} = 0.\ 0591 \times 2 = 0.\ 1182$

$\therefore E_2 - E_1 = -0.\ 1182$

Sol 19: (C) At cathode,

$H^+ + e^- \rightarrow \frac{1}{2}H_2$

At anode

$\frac{1}{2}H_2 \rightarrow H^+ + e^-$

$\frac{1}{2}H_2 + H^+ \rightarrow \frac{1}{2}H_2 + H^+$

$0.\ 410^{-20.} \rightarrow 10^{-1}$

$E = -0.\ 0591 \log \frac{10^{-1}.(0.1)^{1/2}}{10^{-2}.(0.4)^{1/2}}$

$E = -0.\ 041\ V$

Sol 20: (D) $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(\ell)$

$E^\circ = 1.\ 23\ V$

$\Delta G^\circ = -nFE = -474.\ 78\ kJ$

$\Delta H_f\ (O_2) = 0$

$\Delta H_r = 2\Delta H_f(H_2O, \ell) = -2 \times 285.\ 5\ kJ = -571\ kJ$

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

$\Delta S = \frac{\Delta H - \Delta G}{T} = -0.\ 322\ kJ/k$

Sol 21: (C) $Cu^{2+} + 2e^- \rightarrow Cu;\ E^o = 0.\ 337$

$\Delta G^\circ_1 = -nFE^\circ = -0.\ 674\ F$

$Cu^{2+} + e\ Cu^+;\ E^\circ = 0.\ 153$

$Cu^+ \rightarrow Cu^{2+} + e^-;\ E^\circ = -0.\ 153$

$\Delta G^\circ_2 = -nFE^\circ = +\ 0.\ 153\ F$

Adding,

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

$\Delta G = \Delta G^\circ_1 + \Delta G^\circ_2$

$-F\ E^\circ = -0.\ 674\ F + 0.\ 153\ F$

$E^\circ = 0.\ 521\ V$

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) $Ag^+ \xrightarrow{+e^-} Ag$, 96500 C will liberate silver = 108 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 = $\frac{C \times l}{[A]A}$ = $\frac{S\ m}{mol\ m^{-3} m^2}$

= S m^2 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

$$\Lambda^{o}_{CH_3COOH} = \Lambda^{o}_{CH_3COONa} + \Lambda^{o}_{HCl} - \Lambda^{o}_{NaCl}$$

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 $\wedge^{o}_{HOAc}$ from the conductivity of $\wedge^{o}_{NaOAc}$ & $\wedge^{o}_{HCl}$,the conductivity value of NaCl i.e. $\wedge^{o}_{NaCl}$ is also needed.

$$\Lambda^{o}_{NaOAc} + \Lambda^{o}_{HCl} - \Lambda^{o}_{NaCl} = \Lambda^{o}_{HOAc}$$

i.e. $\Lambda^{o}_{Na^+} + \Lambda^{o}_{OAc^-} + \Lambda^{o}_{H^+} + \Lambda^{o}_{Cl^-} - (\Lambda^{o}_{Na^+} + \Lambda^{o}_{Cl^-})$

= $\Lambda^{o}_{OAc^-} + \Lambda^{o}_{H^+} = \Lambda^{o}_{HOAc}$

Sol 9: (A) Cell constant

= $\frac{\text{Conductivity(I)}}{\text{Conductance(I)}} = \frac{\text{Conductivity(II)}}{\text{Conductance(II)}}$

Conductivity (II) = $\frac{129}{520} Sm^{-1}$

0.2 M = 200 mol m^{-3}.

Molar conductivity of 0.2 M solution

= $\frac{129/520}{200}$ = 12.4 × 10^{-4} S m^2 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 × 10^{-4} Sm^2 mol^{-1}. Assuming linear inverse variation of molar conductivity with concentration we can say that

∴ Molar conductivity of 0.02M solution

= 1.24 × 10^{-3} × 10

= 124 × 10^{-4} S $m^2 mol^{-1}$.

Sol 10: (C) Velocities of both K^+ and NO_3^- are nearly the same in KNO_3 so it is used to make salt-bridge.

Sol 11: (C) $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

$$E_{red} = E^{\circ}_{red} - \frac{0.0591}{n} \log \frac{P_{(H_2)}}{(H^+)^2}$$

$$E_{red} = 0 - \frac{0.0591}{2} \log \frac{2}{(1)^2}$$

$$E_{red} = \frac{0.0591}{2} \log 2$$

∴ E_{red} is found to be negative for (c) option

Sol 12: (C) $E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log Q$

Where, Q = $\frac{[Zn^{2+}]}{[Cu^{2+}]}$

For complete discharge, E_{cell} = 0

So, $E^{\circ}_{cell} = \frac{0.0591}{2} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$

$\Rightarrow \left[\frac{[Zn^{2+}]}{[Cu^{2+}]}\right] = 10^{37.3}$.

Sol 13: (D) For the cell reaction, Fe acts as cathode and Sn as anode. Hence,

$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = -0.44 - (-0.14) = -0.30V$

The negative EMF suggests that the reaction goes spontaneously in reverse direction.

Sol 14: (C) $Fe^{3+} + 3e^- \rightarrow Fe$;

$\Delta G_1 = -3 \times F \times E^{\circ}_{Fe^{3+}/Fe}$

$Fe^{+2} + 2e^- \rightarrow Fe$; $\Delta G_2 = -2 \times F \times E^{\circ}_{Fe^{2+}/Fe}$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$; $\Delta G = \Delta G_1 - \Delta G_2$

$\Delta G = 3 \times 0.036G - 2 \times 0.439 \times F$

$= -1 \times E^{\circ}_{(Fe^{3+}/Fe^{+2})} \times F$

$E^{\circ}_{(Fe^{3+}/Fe^{+2})} = 2 \times 0.439 - 3 \times 0.036$

= 0.878 – 0.108 = 0.770 V

Sol 15: (C) E = $E^{\circ} - \frac{0.059}{n} \log \frac{[Zn^{++}]}{[Cu^{++}]}$

= $1.10 - \frac{0.059}{2} \log \frac{1}{0.1}$

= 1.10 – 0.0295 log 10 = 1.07 volt.

Sol 16: (A)

As $E^{\circ}_{Cr^{3+}/Cr} = -0.72V$ and $E^{\circ}_{Fe^{2+}/Fe} = -0.42V$

$2Cr + 3Fe^{2+} \longrightarrow 3Fe + 2Cr^{3+}$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{6}\log\frac{(Cr^{3+})^2}{(Fe^{2+})^3}$$

$$= (-0.42 + 0.72) - \frac{0.0591}{6}\log\frac{(0.1)^2}{(0.01)^3} = 0.30 - \frac{0.0591}{6}\log\frac{(0.1)^2}{(0.01)^3}$$

$$= 0.30 - \frac{0.0591}{6}\log\frac{10^{-2}}{10^{-6}} = 0.30 - \frac{0.0591}{6}\log 10^4$$

E_{cell}=0.2606 V

Sol 17: (D)

$CH_3OH(\ell) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$

$\Delta H = -726\,kJ\ mol^{-1}$

Also $\Delta G^{\circ}_f CH_3OH(\ell) = -166.2\ kJ\ mol^{-1}$

$\Delta G^{\circ}_f H_3O(\ell) = -237.2\ kJ\ mol^{-1}$

$\Delta G^{\circ}_f CO_2(\ell) = -394.4\ kJ\ mol^{-1}$

$\because\ \Delta G = \Sigma\Delta G^{\circ}_f$ products $- \Sigma\Delta G^{\circ}_f$ reactants

$=-394.4-2(237.2) + 166.2$

$=-702.6$ kJ mol^{-1}

now Efficiency of fuel cell = $\frac{\Delta G}{\Delta H} \times 100$

$$= \frac{702.6}{726} \times 100 = 97\%$$

Sol 18: (C)

$Fe^{3+} + 3e^- \longrightarrow Fe;\ E^{\circ} = -0.036\ V$

$\therefore\ \Delta G^{\circ}_1 = -nFE^{\circ} = -3F(-0.036) = +0.108F$

Also $Fe^{2+} + 2e^- \longrightarrow Fe(aq);\ E^{\circ} = -0.439\ V$

$\therefore\ \Delta G^{\circ}_1 = -nFE^{\circ} = -2F(-0.439) = 0.878F$

To find E° for $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}(aq)$

$\Delta G^{\circ}_1 = -nFE^{\circ} = -1FE^{\circ}$

$\because\ G^{\circ} = G^{\circ}_1 - G^{\circ}_2$

$\therefore\ G^{\circ} = 0.108F - 0.878F$

$\therefore\ -FE^{\circ} = +0.108F - 0.878F$

$\therefore\ E^{\circ} = 0.878 - 0.108 = 0.77v$

Sol 19: (B) $2H^+ + 2e^- \longrightarrow H_2(g)$

$E = E^{o} - 0.059\log\left(\frac{P_{H_2}}{\left[H^+\right]^2}\right)$ (here E is – ve when $P_{H_2} > \left[H^+\right]^2$)

$$= \frac{-0.0591}{2}\log_{10}\left(\frac{2}{1}\right) = \frac{-0.0591}{2} \times 0.3010 = \text{negative value}$$

Sol 20: (D)

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

$Fe + Ni^{+2} \longrightarrow Fe^{2+} + Ni$

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

All these are spontaneous

Sol 21: (D)

Higher the SRP, better is oxidising agent.

Hence, MnO_4^- is strongest oxidising agent.

Sol 22: (C)

According to Debye Huckle onsager equation,

$\lambda_C = \lambda_{\infty} + (A)\sqrt{C}$

Here A = B

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

Sol 23: (A)

(1) $Mn^{2+} + 2e^- \longrightarrow Mn;\ E° = -1.18V;$

$\Delta G^{\circ}_1 = -2F(-1.18) = 2.36F$

(2) $Mn^{3+} + e^- \longrightarrow Mn^{2+};\ E° = +1.51\ V;$

$\Delta G^{\circ}_1 = -F(-1.51) = -1.51F$

(1) - 2 × (2)

$3Mn^{2+} \longrightarrow Mn + 2Mn^{3+};$

$\Delta G^{\circ}_3 = \Delta G^{\circ}_1 - 2\Delta G^{\circ}_2$

= [2.36 – 2(–1.51)] F

= (2.36 + 3.02) F

= 5.38 F

But $\Delta G^{\circ}_3 = 12FE^{\circ}$

$\Rightarrow 5.38F = -2FE^{\circ}$

$\Rightarrow E^\circ = -2.69\,V$

As E° value is negative reaction is non-spontaneous.

Sol 24: (A) $Cu^{2+} + \underset{2F}{2e^-} \longrightarrow \underset{\substack{1\,\text{mole}\\ =63.5\text{g}}}{Cu}$

JEE Advanced/Boards

Exercise 1

Sol 1: $Cu^{2+} + 2e \rightarrow Cu$

$E^\circ = 0.344$

$$E = E^\circ - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]} = 0.226$$

As after E < 0. 226, Bi will also start to deposit

$$0.344 - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]} = 0.226$$

$0.0295 \log [Cu^{2+}] = -0.118$

$\log [Cu^{2+}] = -4$

$[Cu^{2+}] = 10^{-4}\ M$

Sol 2: Reduction potential of calomel electrode = 0. 28 V

$0.67 = 0.28 - E^\circ_{H^+/H_2}$

$E^\circ_{H^+/H_2} = -0.39$

$H^+ + e \rightarrow \frac{1}{2}H_2$

$$E = E^\circ - 0.059 \log \frac{1}{[H^+]}$$

$$-0.39 = -0.059 \log \frac{1}{[H^+]}$$

$$\frac{-0.039}{0.059} = \log[H^+]$$

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

$pH = 6.61$

Sol 3: $Ag^+ + e^- \rightarrow Ag$

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} - \frac{0.0591}{1}\log\frac{1}{[Ag^+]}$$

$$= 0.8 - 0.0591 \log \frac{1}{0.8}$$

$E_{Ag^+/Ag} = 0.794$

$E_{H_2/H^+} + E_{Ag^+/Ag} = 0.982$

$E_{H_2/H^+} = 0.188$

$\frac{1}{2}H_2 \rightarrow H^+ + e^-$

$0.188 = 0 - 0.059 \log[H^+]$

$[H^+] = 6.6 \times 10^{-4}$

$C\alpha = 6.6 \times 10^{-4}$

$$\Rightarrow \alpha = \frac{6.6\times10^{-4}}{1.3\times10^{-3}} = 0.5$$

$$k_a = \frac{C\alpha^2}{1-\alpha}$$

$k_a = 6.74 \times 10^{-4}$

Sol 4: $E = E^\circ - \dfrac{0.0591}{5}\log\dfrac{[Mn^{2+}]}{[H^+]^8[MnO_4^-]}$

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

t = 0   0. 1   0. 8

t = t   0. 01   0. 08   0. 09

$$E = 1.51 - 0.01182 \log \frac{0.09}{(0.08)^8(0.01)} = 1.39\ V$$

Sol 5: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$\alpha = \sqrt{\frac{k_a}{C}} = \sqrt{\frac{1.8\times10^{-5}}{0.1}} = 0.0134$$

$[H^+] = C\alpha = 1.34 \times 10^{-3}$

$\frac{1}{2}H_2 \rightarrow H^+ + e^-$

$$E_{H_2/H^+} = E^\circ_{H_2/H^+} - 0.0591 \log \frac{[H^+]}{P_{H_2}^{\ 1/2}}$$

$E_{H_2/H^+} = 0 - 0.0591 \log 1.34 \times 10^{-3}$

$E_{H_2/H^+} = 0.170\ V$

At cathode,

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$$\alpha = \sqrt{\frac{k_b}{C}} = \sqrt{\frac{1.8\times10^{-5}}{0.01}}$$

$\alpha = 0.042$

$[OH^-] = C\alpha = 4.24 \times 10^{-4}$,

$$[H^+] = \frac{10^{-14}}{[OH^-]} = 2.35 \times 10^{-11}$$

$H^+ + e^- \rightarrow \frac{1}{2}H_2$

$$E_{H^+/H_2} = E^\circ_{H_2/H^+} - 0.0591 \log \frac{1}{[H^+]}$$

$$= 0.0591 \log \frac{1}{2.35\times10^{-11}} = -0.628 \text{ V}$$

$$E_{cell} = E_{H_2/H^+} + E_{H^+/H_2} = 0.170 - 0.628 = 0.458 \text{ V}$$

Sol 6: $Fe(s) + 2OH^- \rightarrow FeO(s) + H_2O(\ell) + 2e^\ominus$

$E^\circ = 0.87$ V

$Ni_2O_3(s) + H_2O + 2e^- \rightarrow 2NiO(s) + 2OH^-$

$E^\circ = +0.4$ V

(i) Cell reaction

$Fe(s) + Ni_2O_3(s) \rightarrow FeO(s) + 2NiO(s)$

(ii) $E^\circ = 0.87 + 0.4 = 1.27$ V

It does not depend on [KOH]

(iii) Maximum amount of electrical energy

$= |-n\,F\,E^\circ|$

$= |-2 \times 96.5 \times 1.27 \text{ kJ}|$

$= 245.1$ kJ

Sol 7: $Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-$

We have pH = $-\log[H^+] = 14$

$[H^+] = 10^{-14}$

$$[OH^-] = \frac{10^{-14}}{[H^+]} = 1$$

$[Cu^{2+}]\,[OH^-]^2 = K_{sp}$

$[Cu^{2+}] = 1 \times 10^{-19}$

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

$$E = E^\circ - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]} = 0.34 - 0.0295 \log \frac{1}{10^{-19}}$$

$= 0.34 - 0.56 = -0.22$ V

Sol 8: $\frac{1}{2}H_2 + H^+ \rightarrow \frac{1}{2}H_2 + H^+$

All conditions are standard except $[H^+]_{\text{anode}}$

$$E = E^\circ - 0.0591 \log \frac{1}{[H^+]_{\text{cathode}}}$$

$$-0.188 = 0 - 0.0591 \log \frac{1}{[H^+]}$$

$\log [H^+] = 6.59 \times 10^{-4}$

$C_6H_5NH_3Cl \rightleftharpoons C_6H_5NH_2 + H^+ + Cl^-$

$Ch = [H^+]$

$$h = \frac{6.59\times10^{-4}}{(1/32)} = 2.12 \times 10^{-2}$$

$$k_h = \frac{C\alpha^2}{1.\alpha}$$

$k_h = 1.43 \times 10^{-5}$

Sol 9: m. equivalents of OH^- added = MV

$= 40 \times 0.05 = 2$ meq.

m. equivalents of H^+ = MV = 30×0.1 = 3meq.

$\therefore$ m. equivalents of H^+ remaining = 1 meq.

$$[H^+] = \frac{1}{40+30} = 0.014$$

$\frac{1}{2}H_2 + Ag^+ \rightarrow H^+ + Ag$

$P_{H_2} = 1$ atm,

$$\therefore E = E^\circ - 0.0591 \log \frac{[H^+]}{[Ag^+]}$$

$$\therefore E_2 - E_1 = 0.0591 \log \frac{[H^+]_1}{[H^+]_2} \cdot \frac{[Ag^+]_2}{[Ag^+]_1}$$

$$E_2 - 0.9 = 0.0591 \log \frac{0.1}{0.014} \cdot 1$$

$E_2 - 0.9 = 0.05$

$E_2 = 0.95$ V

Sol 10: $E^\circ = 0$

$Ag^+ + Ag \rightarrow Ag^+ + Ag$

$[Ag^+]_c = 0.05$ M

$$E = \frac{-0.0591}{1}\log\frac{[Ag^+]_a}{[Ag^+]_c}$$

$$0.788 = -0.0591 \log \frac{[Ag^+]_a}{0.05}$$

$$\log \frac{[Ag^+]_a}{0.05} = -13.3$$

$[Ag^+] = 2.\ 32 \times 10^{-15}$

$AgI \rightleftharpoons Ag^+ + I^-$

$k_{sp} = [Ag^+]\ [I^-]$

$[I^-] = [KI] = 0.\ 05$

$\therefore\ k_{sp} = 1.\ 16 \times 10^{-16}$

Sol 11: $AgBr \rightleftharpoons Ag^+ + Br^-$

$k_{sp} = [Ag^+]_a.\ [Br]^-$

$[Ag^+]_a = \dfrac{(k_{sp})_{AgBr}}{[Br^-]}$

Similarly, $[Ag^+]_c = \dfrac{(k_{sp})_{AgCl}}{[Cl^-]}$

$Ag^+ + Ag \rightarrow Ag^+ + Ag$

cathode anode

$E^\circ = 0$

$E = -0.\ 0591 \log \dfrac{[Ag^+]_a}{[Ag^+]_c} = 0$

$[Ag^+]_a = [Ag^+]_c$

$$\frac{(k_{sp})_{AgBr}}{[Br^-]} = \frac{(k_{sp})_{AgCl}}{[Cl^-]}$$

$$\frac{[Br^-]}{[Cl^-]} = \frac{5\times10^{-13}}{1\times10^{-10}}$$

$$\frac{[Br^-]}{[Cl^-]} = 5 \times 10^{-3} = \frac{1}{200}$$

Sol 12: $AgI \rightleftharpoons Ag^+ + I$

$\Delta G^\circ = -nFE_1^\circ$

$Ag^+ + e^- \rightarrow Ag$

$\Delta G^\circ = -nFE_1^\circ$

$AgI + e^- \rightarrow Ag^+ + I^-$

$\Delta n = -nFE^\circ = -nFE_1^\circ - RT \ln k$

$E^\circ = E^\circ + \dfrac{RT}{nF} \ln k$

$E^\circ = E_1^\circ - \dfrac{2.303RT}{nF} pk_{sp}$

$E^o = -0.\ 15$

Sol 13: At anode

$AgCl \rightleftharpoons Ag^+ + Cl^-$

$k_{sp} = [Ag^+]_a [Cl^-]$

$2.\ 8 \times 10^{-10} = [Ag^+]_a \times 0.\ 2$

$[Ag^+]_a = 1.\ 4 \times 10^{-9}$

$Ag \rightarrow Ag^+ + e^-$

At cathode

$AgBr \rightleftharpoons Ag^+ + Br^-$

$k_{sp} = [Ag^+]_c [Br^-]$

$[Ag^+]_c = \dfrac{3.3\times10^{-13}}{10^{-3}} = 3.\ 3 \times 10^{-10}$

$Ag + Ag^+ + Ag + Ag^+$

Cathode anode

$E^\circ = 0$

$E = -0.\ 591 \log \dfrac{[Ag^+]_a}{[Ag^+]_c} = 0.\ 0591 \log \dfrac{1.4\times10^{-9}}{3.3\times10^{-10}}$

$E = -0.\ 037\ V$

For a spontaneous process, electrodes should be reversed.

Sol 14: $Pb^{2+} + 2e^- \rightarrow Pb\ \ E^\circ = -0.\ 126\ V$

$Pb \rightarrow Pb^{2+} + 2e^-\ \ E^\circ = 0.\ 126\ V$

$PbCl_2 + 2e^- \rightarrow Pb + 2Cl^-\ E^\circ = -0.\ 268$

$PbCl_2 \rightarrow Pb^{2+} + 2Cl^-\ \ E^\circ = -0.\ 142\ V$

$\Delta G^\circ = -FnE^\circ = -RT \ln k$

$\ln k = \dfrac{nF}{RT} E^\circ$

$\log k = \dfrac{nF}{RT\times2.303} E^\circ$

$\log k = -4.\ 8n = 2$

$k = 1.\ 536 \times 10^{-5}$

Sol 15: $Mn(OH)_2 \rightleftharpoons Mn^{2+} + 2OH^-$

$K_{sp} = [Mn^{2+}]\ [OH^-]^2$

$[Mn^{2+}] = \dfrac{1.9\times10^{-13}}{(10^{-4})^2}$

$[Mn^{2+}] = 1.\ 9 \times 10^{-5}$

Cell reaction:

$Mn + Cu^2 \rightarrow Mn^{2+} + Cu$

$E^\circ_{Mn^{2+}/Mn} = -1.\ 18\ V$

$E^{\circ}_{Cu^{2+}/Cu} = 0.34\ V$

$E^{o}_{cell} = E^{\circ}_{Cu^{2+}/Cu} - E^{\circ}_{Mn^{2+}/Mn}$

$E^{o} = 0.34 - (-1.18)$

$E^{o} = 1.52\ V$

$$E = E^{o} - \frac{0.0591}{2}\log\frac{[Mn^{2+}]}{[Cu^{2+}]}$$

$$= 1.52 - 0.0295\log\frac{1.9\times10^{-5}}{6.75\times10^{-2}} = 1.52 - (-0.14)$$

$E = 1.66\ V$

Sol 16: $HIO_3 \rightleftharpoons H^+ + IO_3$

$$[IO_3^-] = C\alpha = C\sqrt{\frac{k_a}{C}} = \sqrt{Ck_a}$$

$[IO_3^-] = 0.22\ M$

$AgIO_3 \rightleftharpoons Ag^+ + IO_3^-$

$k_{sp} = [Ag^+][IO_3^-]$

$$[Ag^+] = \frac{3.08\times10^{-8}}{0.22}$$

$[Ag^+] = 1.37 \times 10^{-7}$

$2Ag + Zn^{2+} \rightarrow 2Ag^+ + Zn$

$E^{\circ}_{Ag/Ag^+} = -0.80\ V$

$E^{\circ}_{Zn^{2+}/Zn} = -0.76\ V$

$E^{\circ}_{cell} = E^{\circ}_{Ag/Ag^+} + E^{\circ}_{Zn^{2+}/Zn} = -1.56\ V$

$$E = E^{\circ} - \frac{0.0591}{2}\log\frac{[Ag^+]^2}{[Zn^{2+}]}$$

$$E = -1.56 - 0.0295\log\frac{(1.37\times10^{-7})^2}{0.175}$$

$E = -1.56 + 0.372$

$E = -1.188\ V$

Sol 17: $Pb + Pb^{2+} \rightarrow Pb + Pb^{2+}$

$E^{\circ} = 0$

$$E = 0 - \frac{0.0591}{2}\log\frac{[Pb^{2+}]_a}{[Pb^{2+}]_c} + 0.061$$

$$= \frac{0.0591}{2}\log\frac{[Pb^{2+}]_a}{2.5\times10^{-3}}$$

$$\log\frac{[Pb^{2+}]_a}{2.5\times10^{-5}} = -2.06$$

$[Pb^{2+}]_a = 2.13 \times 10^{-7}$

At anode,

$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-\ E^{\circ} = 0.356$

$Pb^{2+} + 2e^- \rightarrow Pb,\ E^{\circ} = -0.126\ V$

$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4\ E^{\circ} = 0.230$

$PbSO_4 \rightarrow Pb^{2+} + SO_4^{2-}\ E^{\circ} = -0.230$

$\Delta G = -nF E^{\circ} = -RT \ln k$

$$\ln k = \frac{nF}{RT}E^{\circ}$$

$$\log k = \frac{nF}{2.303RT}E^{\circ}$$

$k = 1.60 \times 10^{-8}$

$k_{sp} = 1.6 \times 10^{-8} = [Pb^{2+}][SO_4^{-2}]$

$$[SO_4^{2-}] = \frac{1.6\times10^{-8}}{2.13\times10^{-7}}$$

$[SO_4^{2-}] = 7.50 \times 10^{-2}$

$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$

0. 525 0. 075 0. 075

$$k_a = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$$

$k_a = 9.46 \times 10^{-3}$

$k_a \approx 10^{-2}$

Sol 18: Cell reaction

$Zn + Zn^{2+} \rightarrow Zn + Zn^{2+}$

Cathode anode

$E^{\circ} = 0$

$$E = \frac{-0.0591}{2}\log\frac{[Zn^{2+}]_a}{[Zn^{2+}]_c}$$

$$0.099 = \frac{-0.0591}{2}\log\frac{[Zn^{2+}]_a}{3.84\times10^{-4}}$$

$$\log\left(\frac{[Zn^{2+}]_a}{3.84\times10^{-4}}\right) = -3.356$$

$[Zn^{2+}]_a = 1.69 \times 10^{-7}$

At anode

$Zn^{2+} + 4CN^- \rightarrow Zn(CN)_4^{2-}$

$$k_f = \frac{[Zn(CN)_4^{2-}]}{[Zn^{2+}][CN^-]^4}$$

$$= \frac{0.450}{1.69\times10^{-7}\times(2.65\times10^{-3}))^4}$$

$k_f = 5.24 \times 10^{16}$

Sol 19: $Ti^+ + e^- \rightarrow Ti$ $E° = -0.34$ V

$\Delta G = -nF E°$

$Ti^{3+} + 2e^- \rightarrow Ti^+$ $E° = 1.25$ V

$Ti^+ \rightarrow Ti^{3+} + 2e^-$ $E° = -1.25$ V

$\Delta G_1 = -nF E° = -2F(-1.25)$

$2Ti^+ + 2e^- \rightarrow 2Ti$

$\Delta G_2 = -2nF E° = -2F(-0.34)$

$3Ti^+ \rightarrow 2Ti + Ti^{3+}$

$\Delta G = \Delta G_1 + \Delta G_2$

$\Rightarrow -2FE^o = -2FE^o{}_1 - 2FE^o{}_2$

$E^o = E°{}_1 + E°{}_2$

$E^o = -0.34 - 1.25$

$E^o = -1.59$ V

Since, E° < 0, it is non spontaneous reaction.

Sol 20: $Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}$

t = 0   1   A

t = t   1 – x   A – 4x   x

We have, A – 4x = 2

$$K_f = \frac{[Cu(NH_3)_4]^{2+}}{[Cu^{2+}][NH_3]^4}$$

$$1 \times 10^{12} = \frac{x}{(1.x).2^4}$$

$$\frac{1-x}{x} = 6.25 \times 10^{-14}$$

$$\frac{1}{x} - 1 = 6.25 \times 10^{-14}$$

$$x = \frac{1}{1+6.25\times10^{-14}}$$

$$1 - x = \frac{6.25\times10^{-14}}{1+6.25\times10^{-14}} \approx 6.25\times10^{-14}$$

Now for $Zn + Cu^2 \rightarrow Cu + Zn^{2+}$

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

$$E = 1.1 - \frac{0.0591}{2}\log\frac{1}{1-x}$$

$$= 1.1 - 0.0295 \log \frac{1}{6.25\times10^{-14}}$$

E = 0.71 V

Sol 21: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

we have, E° = 0.76 – (–0.34) = 1.1 V

$\Delta G = -nF E° = -RT \ln k$

$$\log k = \frac{nF}{2.303\times RT} E°$$

$$k = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

$$\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{2}{0.0591} \times 1.1 = 37.28$$

$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = 1.941 \times 10^{37}$$

Sol 22: $Ag(NH_3)_2 \rightleftharpoons Ag^+ + 2NH_3$

$k_0 = 6 \times 10^{-8}$

$\Delta G_1 = -RT \ln k_0$

$Ag^+ + e^- \rightarrow Ag$ $E° = 0.799$ V

$\Delta G_2 = -nFE° = -F \times 0.799$

(n = 1)

Adding,

$Ag(NH_3)_2 + e^- \rightarrow Ag + 2NH_3$

$\Delta G = -nF E° = \Delta G_1 + \Delta G_2$

$-n E° = -RT \ln k_0 - 0.799 F$

$$E^o = \frac{RT}{F}\ln k_0 + 0.799 = \frac{2.303\, RT}{F}\log(6 \times 10^{-8}) + 0.799$$

$E^o = 0.373$ V

Sol 23: We have,

(i) $Co^{2+} + 6CN^- \rightarrow [Co(CN)_6]^{4-}$

$k_f = 1 \times 10^{14}$

$\Delta G_1 = -RT \ln k_f = -43.757\ RT$

(ii) $[Co(CN)_6]^{3-} + e^- \rightarrow [Co(CN)_6]^{4-}$

$E^\circ = -0.83$ V, n=1

$\Delta G_2 = -nF E^\circ = 0.83$ F

(iii) $Co^{3+} + e^- \rightarrow Co^{2+}$, $E^o = 1.82$ V, n=1

$\Delta G_3 = -nF E^\circ = -1.82$ F

(iii) + (i). (ii) gives,

$Co^{3+} + 6CN^- \rightarrow [Co(CN)_6]^{3-}$

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

$\Delta G = -RT \ln k_f = -1.82F - 43.757RT - 0.83\ F$

$\Rightarrow \ln k_f = \frac{F}{RT} \times 1.82 + 43.757 + \frac{F}{RT} 0.83$

$\log k_f = \frac{1.82+0.83}{0.059} + 19$

$k_f = 8.27 \times 10^{63}$

Sol 24: we have,

(i)$Ag^+ + e^- \rightarrow Ag$ $E^\circ = 0.7991$ V, n=1

$\Delta G^\circ{}_1 = -nFE^\circ = -0.7991$ F

(ii) $[Ag(NH_3)_2{}^+] \rightarrow Ag^+ + 2NH_3$,

$k_{ins} = 6.02 \times 10^{-8}$

$\Delta G_2 = -RT \ln k_{ins}$

Adding (i) and (ii),

$[Ag(NH_3)_2{}^+] + e^- \rightarrow Ag + 2NH_3$, n = 1

$\Delta G = \Delta G_1 + \Delta G_2$

$-F E^\circ = -0.7991\ F - RT \ln k_{ins}$

$E^\circ = 0.7991 + \frac{2.303RT}{F} \log k_{ins}$

$= 0.7991 + 0.0591 \log (6.02\times10^{-8})$

$E^\circ = 0.372$ V

Similarly for $[Ag(CN)_2{}^-]$

$E^\circ = 0.7991 + 0.0591 \log (1.995\times10^{-19})$

$E^\circ = -0.307$ V

Sol 25: We have,

$Sn \rightarrow Sn^{2+} + 2e$, $E^\circ = 0.136$ V, n = 2

$\Delta G'_1 = -nF E^\circ = -2F \times 0.136 = -0.272\ F$

For, $3Sn \rightarrow 3Sn^{2+} + 6e^-$

$\Delta G_1 = 3\Delta G'_1 = -0.816\ F$

$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$, $E^\circ = -0.154$V, n = 2

$\Delta G_2 = -nF E^\circ = -2 \times F \times (-0.154) = 0.308\ F$

For, $3Sn^{2+} \rightarrow 3Sn^{4+} + 6e^-$,

$\Delta G_2 = 3\Delta G'_2 = 0.924\ F$

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

$E^o = 1.33$ V, n = 6

$\Delta G'_3 = -nFE^\circ = -6F(1.33) = -7.98\ F$

For, $2Cr_2O_7^{2-} + 28H^+ + 12e^- \rightarrow HCr^{3+}\ 14H_2O$

$\Delta G_3 = 2\Delta G'_3$

$\Delta G_3 = -15.96\ F$

Now, (i) + (ii) + (iii) gives

$3Sn(s) + 2Cr_2O_7^{8-} + 28H^+ \rightarrow 3Sn^{4+} + 4Cr^{+3} + 14H_2O$

$\Delta G = -RT \ln k = \Delta G_1 + \Delta G_2 + \Delta G_3$

$-RT \ln k = -0.816\ F + 0.924\ F - 15.96F$

$\ln k = \frac{F}{RT} \times 15.852$

$\log k = \frac{15.852}{0.0591}$

$\log k = 268$

$k = 10^{268}$

Sol 26: $Ti^+ \rightarrow Ti^{3+} + 2e^-$; $E^o = -1.25$ V

$Co^{3+} + e^- \rightarrow Co^{2+}$

$2Co^{3+} + 2e^- \rightarrow 2Co^{2+}$ $E^o = 1.84$ V

Adding,

$Ti^+ + 2Co^{3+} \rightarrow Ti^{3+} + 2Co^{2+}$

$E^\circ = 0.59$ V

$\Delta G = -nF E^\circ = -RT \ln k$, n = 2

$\log k = \frac{2F}{2.303\ RT} E^\circ = \frac{0.59}{0.0295} = 20$

$k = 10^{20}$

Now, if $Ti^+ = 0.1 \times 2.5 = 25$

Initial milimoles of Co^{3+} = 25 × 0. 2 = 5

	Ti^{+} +	$2Co^{3+} \rightarrow$	Ti^{3+} +	$2Co^{2+}$
t = 0	2. 5	5	0	0
t = t	2. 5 – x	5–2x	x	2x

$$k = \frac{[Ti^{3+}][Co^{2+}]^2}{[Co^{3+}]^2[Ti^+]} = 10^{20}$$

V_{final} = 50 ml

$$\frac{x.4x^2.(50)^2.(50)}{(50).(50)^2(2.5-x)(5-2x)^2} = 10^{20}$$

$$\frac{x^3}{(2.5-x)(2.5-x)^2} = 10^{20}$$

$$\frac{x^3}{(2.5-x)^3} = 10^{20}$$

$x \approx 2.5$ as k >>>1

Putting x = 2. 5

$$(2.5-x)^3 = \frac{(2.5)^3}{10^{20}} = 1.5625 \times 10^{-3}$$

$2.5 - x = 2.5 \times 10^{-7}$

$$[Ti^+] = \frac{2.5.x}{50} = 5 \times 10^{-9}$$

$$[Co^{3+}] = \frac{2(2.5-x)}{50} = 10^{-8}$$

Sol 27: For thiosulphate ($S_2O_3^{2-}$), n = 2

Number of equivalent = n. V. M.

$= 46.3 \times 0.124 \times 2 \times 10^{-9} = 11.4824$ m. eq.

Equivalents of x = eq. of I^-

$$= 1 \times \frac{eq.}{2} \text{ of } I_2 = \frac{1}{2} \times \text{eq. of } S_2O_3^{2-}$$

$$\text{Eq. of x} = \frac{11.4824 \times 10^{-3}}{2}$$

$$\frac{0.617}{M} = \frac{11.4824 \times 10^{-3}}{2}$$

M = 107. 3 gm

Sol 28: At anode,

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

$$\text{Moles of } H_2 \text{ reacted} = \frac{67.2}{22.4} = 3$$

Charge produced by 1 mole H_2=2F

Charge produced by 3 mole H_2=6F

$$\text{Current, } I = \frac{6F}{t} = \frac{6 \times 96500}{15 \times 60}$$

I = 643. 33 A

$Cu^{2+} + 2e \rightarrow Cu$

number of moles of Cu produced = 3

wt. = 3 × 63. 5 g

wt. = 190. 5 g

Sol 29: At cathode, only reduction of water takes place

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

$$\text{Moles of } H_2 \text{ produced} = \frac{9.722}{22.4} = 0.434$$

Charge needed, Q = 2 × 0. 434 = 0. 868

At anode, for oxidation of water

$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$

$$\text{Moles of } O_2 \text{ produced, } n_{O_2} = \frac{2.35}{22.4} = 0.105$$

Charge needed, $q = 4 \times n_{O_2} = 0.420$

Charge utilised for production of $H_2S_2O_8$

= Q. q = 0. 998

$$\text{Moles of } H_2S_2O_8 = \frac{\text{charge utilised}}{2} = 0.224$$

Weight of $H_2S_2O_8$ = 0. 224 × 194 = 43. 456 gm

Sol 30: Initially, mass of H_2SO_4 solution

= 1. 294 × 3. 5 × 1000 gm = 4. 529 kg

$$\text{Wt. of } H_2SO_4 = \frac{39}{100} \times 4.529 = 1.76631 \text{ kg}$$

Moles of H_2SO_4 = 18. 02

$[H_2SO_4]$ = 5. 15 M

Finally, Mass H_2SO_4 solution = 1. 139 × 3. 5 kg

= 3. 9865 kg

$$\text{Mass of } H_2SO_4 = \frac{20}{100} \times 3.9865 \text{ kg} = 0.7973 \text{ kg}$$

Moles of H_2SO_4 = 8. 136

$[H_2SO_4]$ = 2. 324 M

$\therefore \Delta n_{SO_4^{2-}} = 9.884$

2F charge consumes 2 moles of $[SO_4^{2-}]$

According to net reaction

Charge required = 9. 884 F

Ampere hours = $\frac{9.884 \times 96500}{3600}$ = 265 Amp. hr.

Sol 31: $Cu^{2+} + 2e^- \rightarrow Cu$

Moles of Cu deposited = $\frac{3}{63.5}$ = 0. 047

Charge utilised = 2 × 0. 047 × F = 0. 094 F = 9071 C

Charge supplied = 3 × 2 × 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,

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

Moles of Cu deposited = $\frac{0.4}{63.5} = 6.3 \times 10^{-3}$

Charge supplied = $2 \times 6.3 \times 10^{-3}$ F = 1215. 74 C

After deposition of copper,

$H^+ + e \rightarrow \frac{1}{2}H^+$ (as solution is acidic)

Extra charge supplied = 1. 2 × 7 × 60

= 504 C = 5.22×10^{-3} F

Moles of H_2 evolved = $\frac{5.22 \times 10^{-3}}{2} = 2.61 \times 10^{-3}$

Volume of H_2 evolved = $2.61 \times 10^{-3} \times 22400$ = 58. 46 mL

At anode,

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

Total charge,

$Q = 2 \times 6.3 \times 10^{-3} \times F + 5.22 \times 10^{-2} F = 1.78 \times 10^{-2} F$

Moles of O_2 evolved = $\frac{Q}{4} = 4.45 \times 10^{-3}$

Volume of O_2 evolved = $4.45 \times 10^{-3} \times 22400$ = 99. 68 mL

Total volume = 158. 14 mL

Sol 33: $Ag \rightarrow Ag^+ + e^-$

Total charge supplied = $\frac{5 \times 2 \times 3600}{96500}$ = 0. 373 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 × 108 = 42. 41 g

Mass of electrode = 100 – 42. 41 = 57. 58 g

Sol 34: Charge supplied per second

= $\frac{1.5 \times 10^6}{96500}$ = 15. 54 F

Electrolysis:

$2H_2O \rightarrow 2H_2 + O_2$

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

4 F charges electrolysed 2 moles of H_2O.

$\therefore$ 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 = $\frac{8.2 \times 10^{15}}{18 \times 7.77}$ × 86400 × 365

= 1. 9 million years

Sol 35: Initial mass of electrolyte

= 1. 261 × 1000 = 1261 g

Wt. of H_2SO_4 = $\frac{34.6}{100}$ × 1261 = 436. 306

Moles of H_2SO_4 = $\frac{436.306}{98}$ = 4. 45

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

t=0 4. 45

t=t 4. 45–x x

we have, wt. of H_2SO_4 = 27

$$\therefore \frac{(4.45 - x)98}{12.61 \times 436.606 + (4.45 - x)98 + x.18} = 0.27$$

$\Rightarrow$ 436. 608 – 98x = 0. 27(1261 – 80x)

463. 608 – 98x = 340. 47 –21. 6x

76. 4x = 96. 138

x = 1. 258

Change in moles of SO_4^{2-} = x = 1. 258

$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e$

Charge produced by 1 mole SO_4^{2-} = 2F

Charge produced by 1. 258 moles SO_4^{2-}

= 2 × 1. 258 F = 2.4×10^5 C

Sol 36: At anode,

$2H_2O \rightarrow O_2 + 4H^+ + 4e$

pH = 1

$\log[H^+] = 1$

$[H^+] = 0.1$

$n_{H^+} = [H^+] \times v = 0.1 \times 10^{-1} = 10^{-2}$

$[H^+]_i = 10^{-7}$

$n_{H^+} = 10^{-7} \times 10^{-1} = 10^{-8}$

Moles of H^+ produced $= 10^{-2} - 10^{-8}$

$\approx 10^{-2}$

Charge needed $= 10^{-2}$ F = 965 C

Theoretical time $= \dfrac{Q}{I} = \dfrac{96.5 \times 10}{0.965} = 1000$ s

Current efficiency = 80%

Therefore, actual time $= \dfrac{1000 \times 5}{4}$ s = 1250 s

Now, at cathode

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

Current passed $= 10^{-2}$ F

$\therefore$ Moles of copper reduced $= \dfrac{10^{-2}}{2} = 5 \times 10^{-3}$

After passing of current,

Equivalents of copper = equivalents of I_2

= 2 equivalents of $S_2O_3^-$

Equivalents of copper

$= 2 \times 0.04 \times 35 \times 10^{-3}$

Moles of copper $= 31.4 \times 10^{-3}$

($\because$ n = 2 for Cu^{2+})

$\therefore$ Total moles of $Cu^{2+} = 6.4 \times 10^{-3}$

Molarity $= \dfrac{64 \times 10^{-3}}{100 \times 10^{-3}} = 0.064$ M

Sol 37: Current passed $= \dfrac{5 \times 10 \times 3600}{96500}$ F = 1.861 F

At anode

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

Moles of Zn^{2+} reduced $= \dfrac{Q}{2} = 0.9326$

Final, $[Zn^{2+}] = 1 - 0.9326 = 0.067$

At cathode,

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

Final, $[Cu^{2+}] = 1 + 0.9326 = 1.9326$

Now, cell reaction,

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

E° = 1.1 V, n = 2

$$E = E^\circ - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = 1.1 - 0.0295 \log\left(\frac{0.067}{1.9326}\right)$$

$= 1.1 - (0.0295)(-1.45)$

E = 1.143 V

Sol 38: At anode, for quinhydrone electrode,

$QH_2 \rightarrow Q + 2H^+ + 2e^-$

$E = E^\circ - \dfrac{0.0591}{2}\log[H^+]^2$

$E^o + 0.0591\text{ pH} = -0.699 + 0.0591\text{ pH}$

$(\because E^o_{OP} = -E^o_{RP})$

At cathode,

$E = E^\circ = 0.28$

$\therefore E_{cell} = 0.28 - 0.699 + 0.0591\text{ pH}$

$E_{cell} = -0.419 + 0.0591\text{ pH}$

(a) At pH = 5.0,

$E_{cell} = -0.419 + (0.0591) \times (5) = -0.124$ V

(b) When $E_{cell} = 0$,

$\text{pH} = \dfrac{0.419}{0.0591} = 7.1$

(c) At pH = 7.5

$E_{cell} = 0.0235$ V

Since, E_{cell} is positive, reaction takes place in the given direction and cathode (Calomel electrode) is positive electrode.

Sol 39: We have, at anode

$\frac{1}{2}H_2 \rightarrow H^+ + e^-$

$2H_2 \rightarrow 4H^+ + 4e^-$

E° = 0

$E = -0.0591 \log [H^+]$

At cathode

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

Overall cell reaction

$2H_2 + O_2 + 2H_2O \rightarrow 4H^+ + 4OH^-$

we have, $\frac{1}{2}H_2 + H_2O_2 \rightarrow H_2O; \Delta H = -56.7\ kJ$

$2H_2 + O_2 \rightarrow 2H_2O; \Delta H = -2 \times 56.7\ kJ = -113.4\ kJ$

$H_2O \rightarrow H^+ + OH^-; \Delta H = 19.05\ kJ$

$4H_2O \rightarrow 4H^+ + 4OH^-$

$\Delta H = 4 \times 19.05\ kJ = 76.2\ kJ$

Adding,

$2H_2 + O_2 + 2H_2O \rightarrow 4H^+ + 4OH^-$

$\Delta H = -37.2\ kJ$

$\Delta S = nF\left(\frac{\Delta E}{\Delta T}\right)_P = 4 \times 96500 \times 0.001058$

$\Delta S = 408.38$

$\Delta G = -nFE^o = \Delta H - T\Delta S$

$E^\circ = T\left(\frac{\Delta E}{\Delta T}\right)_P - \frac{\Delta H}{\Delta F}$

$E^\circ = 0.4414\ V$

Sol 40: $Ag_2S + 2e^- \rightarrow 2Ag + S^{2-}$

$Ag_2S \rightleftharpoons 2Ag^2 + S^{2-}$

$\Delta G_1 = -RT\ lnk_{sp}$

$Ag^+ \times e^- \rightarrow Ag; \Delta G_2 = -FE^o, n = 1$

$2Ag^+ + 2e^- \rightarrow 2Ag$

$\Delta G_2 = -2FE^o$

$Ag_2S + 2e^- \rightarrow 2Ag + S^{2-}$

$\Delta G = \Delta G_1 + \Delta G_2 = -2FE^o - RT\ ln\ k_{sp}$

$-nFE^o = -2FE^o - RT\ ln\ k_{sp}$

$E'^\circ = E^\circ + \frac{2.303\ RT}{nF}\log k_{sp}$

$E'^\circ = -0.64\ V$

$E = -0.64 - \frac{0.0591}{2}\log[S^{2-}]$

We have,

$H_2S \rightleftharpoons H^+ + HS^-$

$\frac{[H^+].[HS^-]}{[H_2S]} = k_1$

$k_1 = 10^{-8}, [H^+] = 10^{-3}, [H_2S] = 0.1$

$\therefore [HS^-] = 10^{-6}M$

$HS^- \rightleftharpoons H^+ + S^{2-}$

$10^{-6} \qquad 10^{-3}$

$\frac{[S^{2-}].[H]^+}{[HS^-]} = k_2$

$[H^+] = 10^{-3}, [HS^-] = 10^{-6}, k_2 = 1.1 \times 10^{-13}$

$\frac{[S^{2-}].10^{-3}}{10^{-6}} = 1.1 \times 10^{-13}$

$[S^{2-}] = 1.1 \times 10^{-16}\ M$

$E = -0.64 - 0.0295 \log(1.1 \times 10^{-16})$

$= -0.64 - 0.0295(-15.95)$

$E = -0.167\ V$

Sol 41: $\wedge_{eq} = k \times \frac{1000}{N}$

$k = \frac{97.1 \times 0.1}{1000} = 9.71 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$

and, $k = \frac{1}{R}\frac{\ell}{a}$

$R = \frac{\ell}{ka} = \frac{0.5}{9.71 \times 10^{-3} \times 1.5}$

$R = 34.32\ \Omega$

$I = \frac{V}{R} = \frac{5}{34.32}Z$

$I = 0.1456\ A$

Sol 42: $E = \frac{V}{L} = \frac{6}{10/100} = 60\ V/m = 0.6\ V/cm$

Ionic mobility (drift speed) $= \frac{\wedge_\infty^0}{F} \times E$

$= \frac{73.52}{96500} \times 0.6\ cm/s = 4.57 \times 10^{-4}\ cm/s$

Distance in 2 hours $= 4.57 \times 10^{-4} \times 2 \times 3600 = 3.29\ cm$

Sol 43: $R = \frac{1}{k}\frac{\ell}{a}$

$\ell = k\ R\ a = 1.342 \times 170.5 \times 1.86 \times 10^{-4} = 0.0425\ m$

$\ell = 4.25\ cm$

Sol 44: $\wedge_m^0 SrSO_4 = \wedge_m^0 Sr^{2+} + \wedge_m^0 SO_4^{2-}$

$= 59.\ 46 + 79.\ 8 = 139.\ 26\ ohm^{-1}\ cm^2\ mole^{-1}$

$\wedge_m^0 SrSO_4 = 1000 \times \frac{k_{SrSO_4}}{C}$

$C = \frac{1000 \times 1.482 \times 10^{-4}}{139.26}$

$C = 1.\ 064 \times 10^{-3}$

$C = S = 1.\ 064 \times 10^{-3}$ mole/L

$= 1.064 \times 10^{-3} \times 183.\ 6$ gm/L

$S = 0.\ 1953$ gm/L

Sol 45: $\wedge_m^0 (Co_2[Fe(CN)_6]\ )$

$= 2 \wedge_m^0 (Co^{2+}) + \wedge_m^0 ([Fe(CN)_6]\ ^{+})$

$= 2 \times 86 + 444 = 616\ \Omega^{-1}\ cm^{-1}\ mol^{-1}$

$k_{Co_2}\ [Fe(CN)_6] = k_{solution} - k_{water}$

$= 2.\ 06 \times 10^{-6} - 0.\ 41 \times 10^{-6}$

$= 1.\ 65 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$

$= 1.\ 65 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$

$\wedge_m^0 = k \times \frac{1000}{C}$

$C = \frac{k \times 1000}{\wedge_m^0} = \frac{1.65 \times 10^{-6} \times 1000}{616}$

$C = 2.\ 59 \times 10^{-6}$ mol/L

$S = C = 2.\ 59 \times 10^{-6}$ mol/L

$Co_2[Fe(CN)_6] \rightleftharpoons 2Co^{2+} + [Fe(CN)_6]\ ^{4-}$

$k_{sp} = (2s)^2.\ S = 4S^3$

$k_{sp} = 7.\ 682 \times 10^{-17}$

Sol 46: For KCl, $\wedge_m^0 = 138\ \Omega^{-1}\ cm^2\ mol^{-1}$

$\therefore\ \wedge_m = k \times \frac{1000}{C}$

$k = \frac{138 \times 0.02}{1000} = 2.\ 76 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$

$G^* = Rk$

$= 2.\ 76 \times 10^{-3} \times 85 = 0.\ 2346\ cm^{-1}$

$k_{water} = \frac{G^*}{R} = \frac{0.2346}{9200}$

$k_{water} = 2.\ 55 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$

$n_{NaCl} = \frac{500}{58.5} = 8.\ 547$

$k_{NaCl+H_2O} = \frac{0.2346}{7600} = 3.\ 08 \times 10^{-5}$

$k_{NaCl} = k_{NaCl+H_2O}\ \cdot\ k_{H_2O}$

$= (3.\ 08 - 2.\ 55) \times 10^{-5}$

$= 5.\ 3 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$

$C_{NaCl} = \frac{k_{NaCl} \times 1000}{\wedge_m}$

$= \frac{5.3 \times 10^{-6} \times 1000}{126.5} = 4.\ 190 \times 10^{-5}$ mole/L

$C = \frac{n}{V}$

$V = \frac{n}{C} = \frac{8.547}{4.19 \times 10^{-5}}$ (1 L = 1 dm^3)

$V \approx 2 \times 10^5\ dm^3$.

Exercise 2

Single Correct Choice Type

Sol 1: (C) As $E^\circ_{Ag^+/Ag} > E^\circ_{Hg_2/Hg} > E^\circ_{Cu^{2+}/Cu}$

Sol 2: (C) $Mn_3O_4 + 16OH^- \rightarrow 3MnO_4^{2-} + 8H_2O + 10e^-$

$\therefore$ Charge required = 10 F

Sol 3: (A) Only water will be oxidised and reduced at anode and cathode respectively because SRP of SO_4^{2-} is very high (magnitude).

Sol 4: (C) At X

$pH = pk_a + \log \frac{[A^+]}{[H_A]} = pk_a + \log \frac{a}{b}$

$H^+ + e^- + \frac{1}{2}H_2$

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

$\frac{E_1}{0.0591} = -pk_a - \log \frac{a}{b}$

At Y

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

$E_2 = -0.\ 0591\ pH$

$\frac{E_2}{0.0591} = -pk_a - \log \frac{b}{a} = -pk_a + \log \frac{a}{b}$

$$\frac{E_1 + E_2}{0.0591} = -2pk_a$$

$$pk_a = -\frac{E_1 + E_2}{0.118}$$

Sol 5: (A) $\wedge_{eq} = \frac{k \times t}{C}$

$$C = \frac{9 \times 10^{-6}}{1.5 \times 10^{-4}} \times 10^{-3} = 6 \times 10^{-5}\ M$$

$$Ag_3PO_4 \rightleftharpoons 3Ag^+ + PO_4^{3-}$$

$[Ag^+] = 3C = 1.8 \times 10^{-4}$ M

$[PO_4^{3-}] = 6 \times 10^{-5}$ M

$k_{sp} = [Ag^+]^3\ [PO_4^{3-}]$

$k_{sp} = 4.32 \times 10^{-18}$

Sol 6: (B) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

$$[CH_3COONa] = \frac{0.015}{2} = 0.0075$$

$$\wedge_m = k \times \frac{1000}{C}$$

$$= \frac{6.3 \times 10^{-4} \times 1000}{0.0075} = 84\ S\ cm^2\ mol^{-1}$$

Multiple Correct Choice Type

Sol 7: (B, C) $E^\circ_{S_2O_2/SO_4^{2-}} > E^\circ_{Cl_2/Cl^-} > E^\circ_{Br_2/Br^-} > E^\circ_{I_2/I_1}$

species with higher E° can oxidise a species with lower E°.

Sol 8: (B, C, D) In all case H_2O will oxidise at anode to give O_2.

Sol 9: (A, B) $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

$$n_{H_2O} = \frac{270}{18} = 15$$

$V_{H_2} = 15 \times 22.1 = 33.6$ L

$V_{O_2} = 168$ L, evolved at anode

$V_T = 504$ L

Sol 10: (C, D) Refer text

Sol 11: (D, C) $Ag + Cl^- \rightarrow AgCl + e$

Cell reaction

$$\frac{1}{2}H_2 + Ag + Cl^- \rightarrow AgCl = H^+$$

$$E = E^o - 0.0591 \log \frac{[H^+]}{[Cl^-][P_{H_2}]^{1/2}}$$

on increasing $[H^+]$ or decreasing $[Cl^-]$, E will decrease.

Assertion Reasoning Type

Sol 12: (A) Cell Reaction:

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

Sol 13: (D) $E^\circ = E^\circ_{left} - E^\circ_{right}$

E° is intensive.

Sol 14: (A) These are facts.

Comprehension Type

Paragraph 1

Sol 15: (B) $R = \rho G^*$

for KCl, $\wedge_m = 200\ S\ cm^2\ mol^{-1}$

$$k = \frac{C \wedge_m}{1000} = \frac{0.02 \times 200}{1000}$$

$k = 4 \times 10^{-3}$

$G^* = Rk = 100 \times 4 \times 10^{-3}$

$G^* = 0.4$

Sol 16: (C) $k_{water} = \frac{G^*}{R} = \frac{0.4}{10^4} = 4 \times 10^{-5}$

Sol 17: (A) $n_{NaCl} = \frac{585}{58.8} = 10$

$$k_{NaCl+H_2O} = \frac{G^*}{R} = \frac{0.4}{8000} = 5 \times 10^{-5}$$

$$k_{NaCl} = k_{NaCl+H_2O} - k_{H_2O} = 10^{-5}$$

$$\therefore C_{NaCl} = \frac{k_{NaCl} \times 1000}{\wedge_m}$$

$$= \frac{10^{-5} \times 1000}{125} = 8 \times 10^{-5}$$

$$C_{NaCl} = \frac{10}{V}$$

$$V = \frac{10}{8 \times 10^{-5}} = 1.25 \times 10^5\ L$$

Paragraph 2

Sol 18: (B) $NO_3^- + 4H^+ \rightarrow NO + 2H_2O + 3e$(a)

$NO_3^- + 2H^+ + e \rightarrow NO_2 + H_2O$ (b)

For (a),

$$E = -\frac{0.06}{3}\log\frac{P_{NO}}{[H^+]^4[NO_3^-]}$$

For (b),

$$E = E^\circ - \frac{0.06}{1}\log\frac{P_{NO_2}}{[H^+]^2[NO_3^-]}$$

For (a), $[NO_3^-] = [H^+] = 1M$, $P_{NO} = 10^{-3}$

$$E_R = 0.96 - \frac{0.06}{3}\log 10^{-3} = 1.02$$

$Cu \rightarrow Cu^{2+} + 2e$

$$E_L = -0.34 - \frac{0.06}{2}\log[Cu^{2+}]$$

$= -0.34 - 0.03\log[Cu^{2+}]$

$E_L = -0.34 + 0.03\log 10^{-1}$

$= -0.31$

$E = E_R + E_L \approx 0.71$ V

E for $NO_3 \rightarrow NO$,

$$E_1 = 0.65 - 0.02\log\frac{10^{-3}}{[H^+][NO_3^-]}$$

$$E_2 = 0.48 - 0.06\log\frac{10^{-3}}{[H^+]^2[NO_3^-]}$$

Sol 19: (C) $E_1 = E_2$

$0.65 - 0.02(-3 - 5\log[HNO_3])$

$= 0.48 - 0.06(-3 - 3\log[HNO_3])$

$0.65 + 0.06 + 0.1\log[HNO_3]$

$= 0.48 + 0.18 + 0.18\log[HNO_3]$

$0.08\log[HNO_3] = 0.71 - 0.66 = 0.05$

$$\log[HNO_3] = \frac{5}{8}$$

$[HNO_3] = 10^{0.625} \approx 10^{0.66}$

Match the Columns

Sol 20 (A) → p, q

Cl^- will not oxidise at low concentration.

$$\frac{1}{2}Cl^- \rightarrow Cl_2 + e^-$$

$$E = E^\circ - 0.06\log\frac{P_{Cl_2}}{[Cl^-]^{1/2}}$$

(B) → p, q

SEP of Na^+ < SEP of H_2O

∴ Water will get reduced to H_2 at cathode

(C) → q, r

Cl^- will be oxidised as concentrated solution

(D) → p, s

SEP of Ag^+ < SEP of H_2O

∴ 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 : $M^{n+} + ne \rightarrow M$ (electron gone in solution)

At anode : $X^{n-} \rightarrow X + ne^-$ (electron supplied to anode)

Therefore, electron is moving from cathode to anode via internal circuit.

Sol 2: (B) The cell reaction is :

$n + Fe^{2+} \longrightarrow Zn^+ + Fe$; $E_{cell} = 0.2905$ V

$$\Rightarrow E = E^\circ - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Fe^{2+}]}$$

$$\Rightarrow E^\circ = 0.2905 + \frac{0.059}{2}\log\frac{0.1}{0.01} = 0.32 \text{ V}$$

$$\text{Also, } E^\circ = \frac{0.059}{n}\log K$$

$$\Rightarrow \log K = \frac{2E^\circ}{0.059} = \frac{0.32}{0.0295}$$

$\Rightarrow K = (10)^{0.32/0.0295}$

Sol 3: (B) The net reaction is

$$2H^+ + \frac{1}{2}O_2 + Fe \rightarrow H_2O + Fe^{2+} + E^\circ = 1.67 \text{ V}$$

$\Delta G^\circ = -nE^\circ F$

$$= \frac{2\times 1.67\times 96500}{1000} \text{ kJ}$$

$= -322.31$ kJ

Sol 4: (B) 0.01 mol H_2 = 0.02 g equivalent

$\Rightarrow$ Coulombs required = 0.02 × 96500 = 1930 C

$\Rightarrow$ Q = It = 1930 C

$$\Rightarrow t = \frac{1930}{10\times10^{-3}} = 19.3\times10^{4}\text{s}$$

Sol 5: (D) As $AgNO_3$ is added to solution, KCl will be displaced according to following reaction

$AgNO_3(aq) + KCl\,(aq) \rightarrow AgCl(s) + KNO_3(aq)$

For every mole of KCl displaced from solution, one mole of KNO_3 comes in solution resulting in almost constant conductivity. As the end point is reached, added $AgNO_3$ remain in solution increasing ionic concentration, hence conductivity increases.

Sol 6: (D) The half reactions are

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

$O_2(g) + 4H^+ \rightarrow 2Fe^{2+}\,(aq) + 2H_2O(l)$

$$E = E^\circ - \frac{0.059}{4}\log\frac{(10^{-3})^2}{(10^{-3})^4(0.1)} = 1.57\text{ V}$$

Sol 7: (A, B, D) Metals with E° value less than 0.96 V will able to reduce NO_3^- in aqueous solution. Therefore, metals V (E°= –1.19 V),

Fe(E° =–0.04 V), Hg(E° = 0.86 V) will all reduce NO_3^- but Au (E° = 1.40V) cannot reduce NO_3^- in aqueous solution.

Paragraph 1

Sol 8: (B) E° for $2Ag^+ + C_6H_{12}O_6 + H_2O \longrightarrow 2Ag(s) + C_6H_{12}O_7 + 2H^+$ is 0.75V

$$\text{Also, } E^\circ = \frac{0.0592}{2}\log K$$

$$\Rightarrow \log K = \frac{2E^\circ}{0.0592} = 25.33$$

$\Rightarrow$ ln K = 2.303 log K = 58.35

Sol 9: (C) On increasing concentration of NH_3, the concentration of H^+ ion decreases, therefore,

$$E_{red} = E^\circ_{red} - \frac{0.0592}{2}\log[H^+]^2$$

$$= 0 - \frac{0.0592}{2}\times 2\log\,10^{-11} = 0.65\text{ V}$$

i.e. E_{red} increases by 0.65 V.

Sol 10: (D) NH_3 has no effect on the E° of glucose/gluconic acid electrode.

Paragraph 2

Sol 11: (B) Moles of NaCl electrolysed = $4 \times \frac{500}{1000} = 2.0$

$\Rightarrow$ Moles of Cl_2 produced = 1.0

$2Cl^- \rightarrow + 2e^-$

Sol 12: (D) At cathode : $Na^+ + e^- \xrightarrow{Hg} \underset{\text{amalgam}}{Na(Hg)}$

Two moles of Na formed during electrolysis would produce two moles of Na(Hg) amalgam.

$\Rightarrow$ Mass of amalgam =2 × (23 + 200) = 446g

Sol 13: (D) Two Faraday of electric charge would be required for electrolysis of 2.0 moles of NaCl.

$\Rightarrow$ total coulombs = 2 × 96500 = 193000 C

Paragraph 3

Sol 14: (C) For spontaneous redox reaction: $E^\circ_{cell} > 0$

For $2I^- + Cl_2 \rightarrow 2Cl^- + I_2$

E° = 1.36 – 0.54 = 0.82 V > 0

i.e. Cl_2 will spontaneously oxidize I^-.

Sol 15: (D) In other cases $E^\circ_{cell} < 0$, they are non-spontaneous.

For the reaction:

(i) $4Fe^{3+} + 2H_2O \rightarrow 4Fe^{2+} + 4H^+ + O_2$;

$E^\circ = -0.46$ V

(ii) $4Mn^{3+} + 2H_2O \rightarrow 4Mn^{2+} + 4H^+ + O_2$;

E° = + 0.27 V

Sol 16: (A) As evidenced above, reaction (i) is non-spontaneous, therefore, Fe^{3+} is stable in acid solution. However, reaction (ii) is spontaneous Mn^{3+} oxidises H_2O to O_2 and itself reduced to Mn^{2+} in acidic medium.

Sodium fusion extract from aniline produces NaCN which reacts with Fe^{2+} to form $[Fe(CN)_6]^{4-}$. The complex ion then reacts with Fe^{3+} give blue precipitate of Prussian blue.

$$Fe^{3+} + [Fe(CN)_6]^{4-} \rightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3}$$

Paragraph 4

Sol 17: (B) M(s) + M^+ (aq, 1 M) → M^+ (aq, 0.05M) + M(s)

$$E_{cell} = 0 - \frac{2.303\ RT}{F}\log\frac{0.05}{1} > 0$$

Hence, $|E_{cell}| = E_{cell} = 0.70$ V and $\Delta G < 0$ for spontaneity of reaction.

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

= 139 V

Sol 19: $X \longrightarrow Y.\ \Delta_r G^0 = -193\ \text{kJ mol}^{-1}$

$M^+ \longrightarrow M^{3+} + 2e^- \qquad E^0 = -0.25V$

ΔG^0 for the this reaction is

$\Delta G^0 = -nFE^0 = -2 \times (-0.25) \times 96500 = 48250\ J/mol$

48.25 kJ / mole

So the number of moles of M+ oxidized using X⟶ Y will be

$$= \frac{193}{48.25} = 4\,\text{moles}$$

Sol 20: $HK \rightleftharpoons H^+ + X^-$

$$Ka = \frac{[H^+][X^-]}{[HX]}$$

$HY \rightleftharpoons H^+ + Y^-$

$$Ka = \frac{[H^+][X^-]}{[HX]}$$

Λ_m for HX = Λ_{m_1}

Λ_m for HX = Λ_{m_2}

$$\Lambda_{m_1} = \frac{1}{10}\Lambda_{m_2}$$

$$Ka = C \propto^2$$

$$Ka_1 = C_1 \times \left(\frac{\Lambda_{m_1}}{\Lambda^0_{m_1}}\right)^2$$

$$Ka_2 = C_2 \times \left(\frac{\Lambda_{m_2}}{\Lambda^0_{m_2}}\right)^2$$

$$\frac{Ka_1}{Ka_2} = \frac{C_1}{C_2} \times \left(\frac{\Lambda_{m_2}}{\Lambda^0_{m_2}}\right)^2 = \frac{0.01}{0.1} \times \left(\frac{1}{10}\right)^2 = 0.001$$

$$pKa_1 - pKa_2 = 3$$

Sol 21: (D) Anode: $H_2(s) \longrightarrow 2H^+ + 2e^-$

Cathode: $\dfrac{Mn^{+4} + 2e^- \longrightarrow Mn^{+2}}{Mn^{+4} + H^2 \longrightarrow Mn^{+2} + 2H^+}$

$$E = E^\circ - \frac{0.059}{2}\log 10\left(\frac{[Mn^{+2}][H^+]^2}{[Mn^{+4}]P_{H_2}}\right)$$

$$0.092 = 0.151 - \frac{0.059}{2}\log 10(10^X)$$

$$0.092 = 0.151 - \frac{0.059}{2}X$$

$\Rightarrow \quad X = 2$

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