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CHEMISTRY

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Electro-Chemistry

REVISION MODULE



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REVISION MODULE

POINTS TO

REMEMBER

- Electrochemistry:** Electrochemistry is the study of production of electricity from the energy released during a spontaneous chemical reaction and the use of electrical energy to bring about non-spontaneous chemical transformations.
- Ohm's Law:** It states that the potential difference (V) across the conductor is directly proportional to the current (I) flowing through it. Mathematically,

$$V \propto I \text{ or } V = IR$$

where R is a constant called resistance of the conductor. Ohm's law is obeyed by both the metallic, as well as electrolytic conductors.

- Resistance (R):** It is the property of a substance by which it obstructs the flow of electric current through it. The electrical resistance (R) of any object is directly proportional to its length (l) and inversely proportional to its area of cross-section (A).

Thus, $R \propto \frac{l}{A}$ or $R = \rho \frac{l}{A}$

where ρ (rho) is a constant of proportionality called specific resistance or resistivity.

$$\rho = R \frac{A}{l}$$

If $l = 1 \text{ cm}$ and $A = 1 \text{ cm}^2$ then $R = \rho$.

Thus, resistivity may be defined as the resistance offered by a conductor of 1 cm length with area of cross-section equal to 1 cm^2 , i.e., it is the resistance of 1 cm^3 of the conductor.

Units: $\rho = R \frac{A}{l} = \text{ohm} \frac{\text{cm}^2}{\text{cm}} = \text{ohm cm}$

Its SI unit is ohm metre ($\Omega \text{ m}$).

- Conductance (G):** It is the reciprocal of resistance and may be defined as the ease with which the electric current flows through a conductor.

$$G = \frac{1}{R}$$

Its SI unit is Siemen (S).

$$1 \text{ S} = \text{ohm}^{-1} (\text{mho})$$

- Conductivity (κ):** It is the reciprocal of resistivity (ρ).

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} = G \times \frac{l}{A}$$

If $l = 1 \text{ cm}$ and $A = 1 \text{ cm}^2$, then $\kappa = G$.

Hence, conductivity of an electrolytic solution may be defined as the conductance of a solution of 1 cm length with area of cross-section equal to 1 cm^2 .

Alternatively, it may be defined as the conductance of 1 cm^3 of the solution of an electrolyte.

Units: $\kappa = \frac{1}{\rho} = \frac{1}{\text{ohm cm}} = \text{ohm}^{-1} \text{cm}^{-1} (\text{S cm}^{-1})$

The SI unit of conductivity is S m^{-1} .

6. Factors Affecting Metallic Conductance

Electrical conductance through metal is called metallic or electronic conductance and is due to the movement of electrons. It depends on:

- The nature and structure of metal.
- The number of valence electrons per atom.
- Temperature (it decreases with increase in temperature).

7. Factors Affecting Electrolytic Conductance

Electrolyte: An electrolyte is a substance that dissociates in solution to produce ions and hence conduct electricity in dissolved or molten state.

Examples: HCl, NaOH, KCl (Strong electrolytes).

CH_3COOH , NH_4OH (Weak electrolytes).

The conductance of electricity by ions present in the solution is called electrolytic or ionic conductance. The following factors govern the flow of electricity through a solution of electrolyte.

- Nature of electrolyte or interionic attractions:** Lesser the solute-solute interactions, greater will be the freedom of movement of ions and higher will be the conductance.
- Solvation of ions:** Larger the magnitude of solute-solvent interactions, greater is the extent of solvation and lower will be the electrical conductance.
- The nature of solvent and its viscosity:** Larger the solvent-solvent interactions, larger will be the viscosity and more will be the resistance offered by the solvent to flow of ions and hence lesser will be the electrical conductance.
- Temperature:** As the temperature of electrolytic solution rises solute-solute, solute-solvent and solvent-solvent interactions decrease, which results in the increase of electrolytic conductance.

8. Difference between Metallic and Electrolytic Conductance

S.No.	Metallic Conductance	Electrolytic Conductance
(i)	Movement of electrons is responsible for conduction.	Movement of ions is responsible for conduction.
(ii)	Does not involve transfer of matter.	Matter moves in the form of ions.
(iii)	Decreases with increase in temperature as kernels start vibrating which produce hindrance in the flow of electrons.	Increases with increase in temperature due to decrease in interionic attraction or increase in dissociation.

9. Measurement of Conductance:

As we know, $\kappa = \frac{1}{R} \times \frac{l}{A}$

The value of κ could be known, if we measure l , A and R . The value of the resistance of the solution between two parallel electrodes is determined by using 'Wheatstone' bridge method (Fig. 2.1).

It consists of two fixed resistance R_3 and R_4 , a variable resistance R_1 and the conductivity cell having the unknown resistance R_2 . The bridge is balanced when no current passes through the detector. Under these conditions,

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} \quad \text{or} \quad R_2 = \frac{R_1 R_4}{R_3}$$

Knowing the values of R_1 , R_3 and R_4 the resistance of the solution, R_2 is determined. The reciprocal of R_2 gives the conductance of the solution.

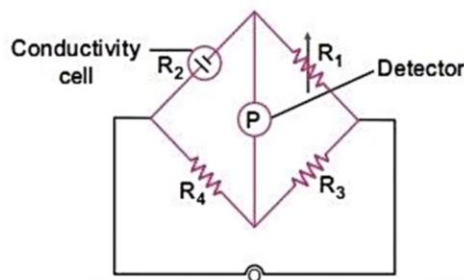


Fig. 2.1: Wheatstone Bridge

10. **Molar Conductivity (Λ_m):** It may be defined as the conducting power of all the ions produced by dissolving one gram mole of an electrolyte placed between two large electrodes at one centimetre apart. Mathematically,

$$\Lambda_m = \kappa \times V, \quad \Lambda_m = \frac{\kappa \times 1000}{c}$$

where, V is the volume of solution in cm^3 containing 1 gram mole of electrolyte and c is the molar concentration.

$$\text{Units: } \Lambda_m = \frac{\kappa \times 1000}{c} = \frac{\text{S cm}^{-1}}{\text{mol cm}^{-3}} \\ = \text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \text{ or } \text{S cm}^2 \text{ mol}^{-1}$$

11. **Variation of Conductivity and Molar Conductivity with Concentration:**

Conductivity decreases with the decrease in concentration, this is because the number of ions per unit volume that carry the current in the solution decreases on dilution.

Molar conductivity ($\Lambda_m = \kappa \times V$) increases with the decrease in concentration or increase in dilution. This is because the total volume V of solution containing one mole of electrolyte increases with increase in dilution. It has been found that the decrease in κ on dilution of a solution is more than compensated by increase in its volume.

Graphical representation of the variation of Λ_m vs \sqrt{c}

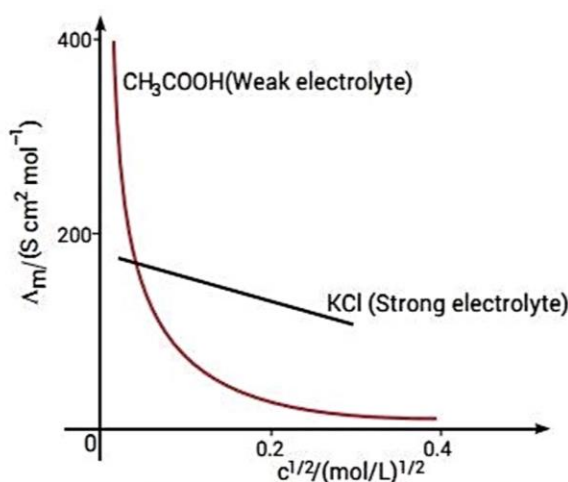


Fig. 2.2: Λ_m vs \sqrt{c} for weak and strong electrolytes

Limiting Molar Conductivity (Λ_m°): The limiting value of molar conductivity when the concentration approaches zero is known as limiting molar conductivity or molar conductivity at infinite dilution.

It is possible to determine the molar conductivity at infinite dilution (Λ_m°) in case of strong electrolyte by extrapolation of curve of Λ_m vs \sqrt{c} (Fig. 2.2). On contrary, the value of molar conductivity of weak electrolyte at infinite dilution cannot be determined by extrapolation of the curve as the curve becomes almost parallel to y-axis when concentration approaches to zero.

The mathematical relationship between Λ_m and Λ_m° for strong electrolyte was developed by Debye, Huckel and Onsager. In simplified form, the equation can be given as

$$\Lambda_m = \Lambda_m^\circ - bc^{1/2}$$

where Λ_m° is the molar conductivity at infinite dilution and b is a constant which depends on the nature of the solvent and temperature.

- 12. Kohlrausch's Law:** It states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

In general, if an electrolyte on dissociation gives v_+ cations and v_- anions then its limiting molar conductivity is given by

$$\Lambda_m^{\circ} = v_+ \lambda_+^{\circ} + v_- \lambda_-^{\circ}$$

Here, λ_+° and λ_-° are the limiting molar conductivities of cations and anions, respectively.

Applications of Kohlrausch's Law:

- (a) **Calculation of molar conductivities of weak electrolyte at infinite dilution:** For example, molar conductivity of acetic acid (weak acid) at infinite dilution can be obtained from the knowledge of molar conductivities at infinite dilution of strong electrolytes like HCl, CH_3COONa and NaCl as illustrated below:

$$\begin{aligned}\Lambda_{m(\text{CH}_3\text{COOH})}^{\circ} &= \lambda_{\text{CH}_3\text{COO}^-}^{\circ} + \lambda_{\text{H}^+}^{\circ} \\ &= [\lambda_{\text{CH}_3\text{COO}^-}^{\circ} + \lambda_{\text{Na}^+}^{\circ}] + [\lambda_{\text{H}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}] - [\lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}]\end{aligned}$$

$$\text{i.e., } \Lambda_{m(\text{CH}_3\text{COOH})}^{\circ} = \Lambda_{m(\text{CH}_3\text{COONa})}^{\circ} + \Lambda_{m(\text{HCl})}^{\circ} - \Lambda_{m(\text{NaCl})}^{\circ}$$

- (b) **Determination of degree of dissociation of weak electrolytes:**

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m^c}{\Lambda_m^{\circ}}$$

- (c) **Determination of dissociation constant (K) of weak electrolytes:**

$$K = \frac{c\alpha^2}{1-\alpha}$$

$$\text{Also, } \alpha = \frac{\Lambda_m^c}{\Lambda_m^{\circ}}$$

$$\therefore K = \frac{c(\Lambda_m^c/\Lambda_m^{\circ})^2}{1 - \Lambda_m^c/\Lambda_m^{\circ}} = \frac{c(\Lambda_m^c)^2}{\Lambda_m^{\circ}(\Lambda_m^{\circ} - \Lambda_m^c)}$$

- (d) **Determination of solubility of sparingly soluble salts:**

$$\Lambda_m^{\circ} = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{\kappa \times 1000}{\text{Solubility}} \quad \text{or, Solubility} = \frac{\kappa \times 1000}{\Lambda_m^{\circ}}$$

- 13. Electrochemical Cells:** An electrochemical cell is a device in which chemical energy of the redox reaction is converted into electrical energy. The redox reaction is carried out in an indirect manner and the decrease in free energy during chemical reaction appears as electrical energy.

The simplest electrochemical cell is Daniel cell or Galvanic cell in which a zinc rod is placed in a solution of Zn^{2+} ions (say, ZnSO_4) in the left container and a bar of copper metal is immersed in a solution of Cu^{2+} ions (say, CuSO_4) in the right container. The two metals which act as electrodes are connected by a metallic wire through a voltmeter. The two solutions are joined by an inverted U-tube containing semi-solid paste of either KCl, KNO_3 or NH_4Cl in gelatin or agar-agar jelly. This arrangement of U-tube is called salt bridge (Fig. 2.3).

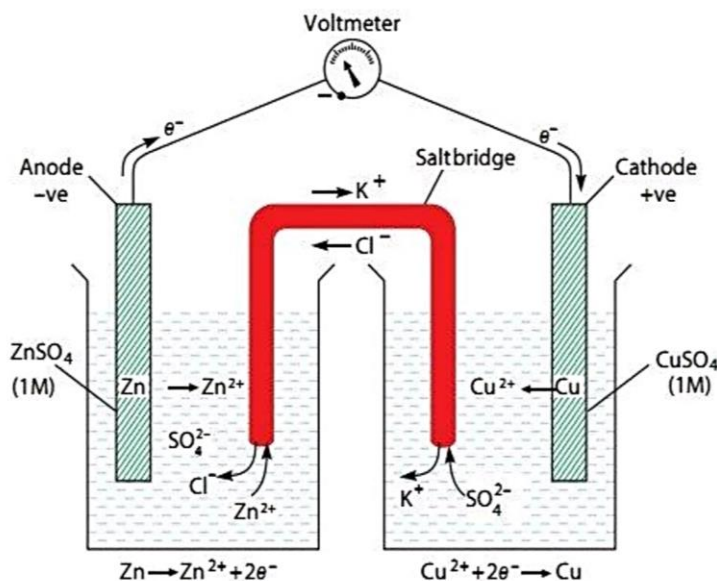


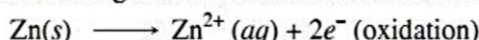
Fig. 2.3: A simple voltaic cell

The overall cell reaction,



can be split into two half cells. The deflection in the voltmeter indicates the flow of current through the external circuit. The conventional current flows through the outer circuit from copper metal to zinc metal, which implies flow of electrons from zinc to copper bar.

- (a) At zinc electrode, the metal undergoes oxidation and releases two electrons.



Because oxidation is taking place, the electrode behaves as anode. These electrons travel through wire and reach the copper metal.

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

The above reaction occurs at the copper electrode. Electronation takes place which is a reduction process and that is why it acts as cathode.

As a result of the two half cell reactions, zinc metal dissolves in anode solution to form Zn^{2+} ions, while the Cu^{2+} ions are discharged at the cathode by accepting two electrons and are deposited at cathode. The electrical neutrality is maintained in two half cells using a salt bridge. The anions of the inert electrolyte in the salt bridge migrate to the anodic chamber and cations to the cathodic chamber. As a result, as the reaction progresses, copper bar gains weight whereas zinc rod loses weight. As a consequence, the cell continues to function till either zinc metal or copper ions in solution are consumed fully.

Since electrons are released at anode, it acquires negative polarity and cathode becomes positive because it needs electrons for the reduction of +ve ions. This observation is against the usual electrolytic cell where anode is +ve and cathode is -ve.

Salt Bridge and Its Functions

A commonly used form of salt bridge consists of a glass U-tube containing semi-solid paste of either KCl, KNO_3 or NH_4Cl in gelatin or agar-agar jelly.

The electrolytes that are often used in salt bridge are called inert electrolytes which are supposed:

- not to interact chemically with either of the solutions present in anodic or cathodic chamber.
 - not to interfere with overall cell reaction.
 - only those electrolytes can be used in a salt bridge in which mobility of ions is almost the same.
- Example, KCl, K_2SO_4 , etc.

A salt bridge carries out two important functions:

- It allows only flow of ions through it. Thus, the circuit is completed.
- It also maintains the electrical neutrality.

- 14. Cell Diagram or Representation of an Electrochemical Cell:** The following conventions or notations are applied for writing the cell diagram in accordance with IUPAC recommendations: The Daniel cell is represented as follows:



(a) Anode half cell is written on the left hand side while cathode half cell on right hand side.

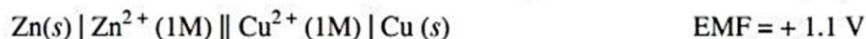
(b) A single vertical line separates the metal from aqueous solution of its own ions.



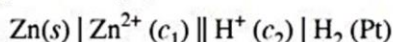
(c) A double vertical line represents salt bridge which allows the passage of ions through it but prevents the mixing of two solutions.

(d) The molar concentration (c) is placed in brackets after the formula of the corresponding ion.

(e) The value of EMF of the cell is written on the extreme right of the cell. For example,



(f) If an inert electrode like platinum is involved in the construction of the cell, it may be written along with the working electrode in bracket, say for example, when a zinc anode is connected to a hydrogen electrode.



15. Reversibility of Daniel Cell:

- (a) When external voltage is less than 1.10 V, electrons flow from Zn to Cu but current flows from Cu to Zn, i.e., in opposite direction. Zinc dissolves at anode and copper deposits at cathode [see Fig. 2.4(a)]
- (b) When external voltage applied is less than 1.10 V and is increased slowly, it is observed that the reaction continues to take place till the external voltage attains the value 1.10 V. When this is so, reaction stops altogether and no current flows [see Fig. 2.4(b)].
- (c) If the value of external voltage exceeds the voltage of Daniel cell (1.10 V), the reaction takes place in opposite direction, i.e., the cell functions like an electrolytic cell [see Fig. 2.4(c)].

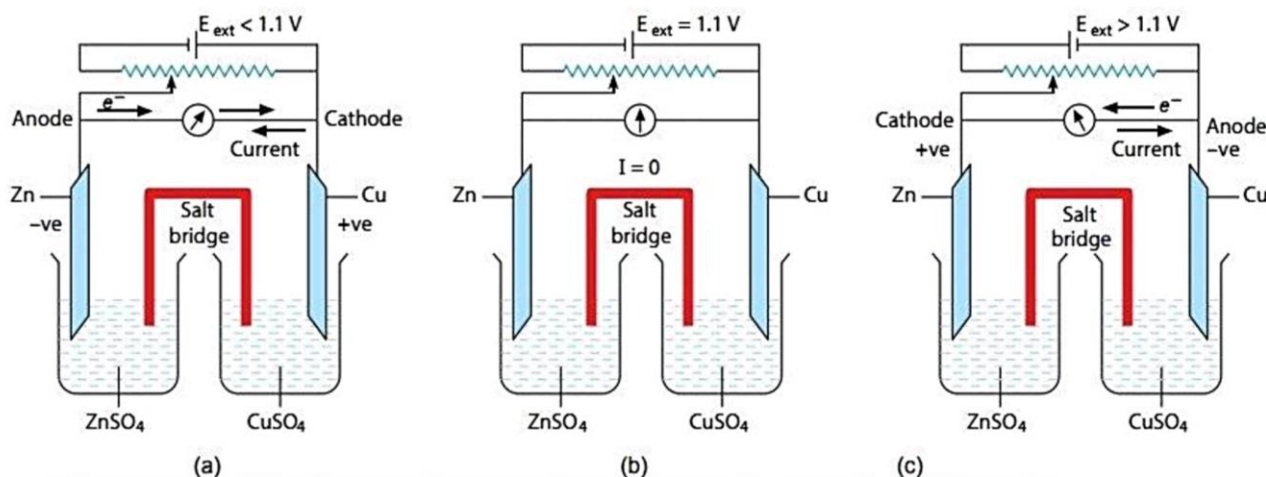
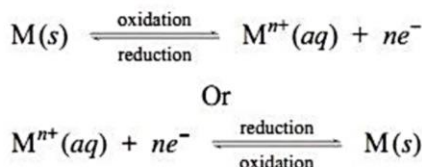


Fig. 2.4: Functioning of Daniel cell when external voltage E_{ext} opposing the cell potential is applied

- 16. Electrode Potential:** It may be defined as the tendency of a metal, when it is placed in contact with its own ions to either lose or gain electrons and in turn become positively or negatively charged. The electrode potential will be named as oxidation or reduction potential depending upon whether oxidation or reduction has taken place.



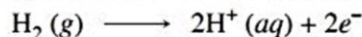
Characteristics:

- Both oxidation and reduction potentials are equal in magnitude but opposite in sign.
- The reduction potential shows an increase with increasing concentration and decrease with decreasing concentration of ions in a solution.
- It is not a thermodynamic property, so values of E are not additive.

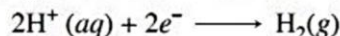
- 17. Standard Hydrogen Electrode (SHE):** It is a reference electrode and its reduction potential is arbitrarily assigned as zero volt at all temperature. The standard hydrogen electrode consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution having 1M concentration of H^+ ions. Pure hydrogen gas at 1 bar pressure is continuously bubbled through the solution at a temperature of 298 K (Fig. 2.5).

The hydrogen electrode can act both ways—as an anode or as a cathode.

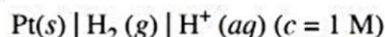
Acting as anode — oxidation takes place,



Acting as cathode — reduction takes place,



Representation of SHE



- 18. Standard Electrode Potential (E^0):** It may be defined as the electrode potential of an electrode determined relative to standard hydrogen electrode under standard conditions. The standard conditions taken are:

- 1 M concentration of each ion in the solution.
- A temperature of 298 K.
- 1 bar pressure for each gas.

- 19. Cell Potential or EMF of a Cell:** The difference between the electrode potentials of two half cells is called cell potential. It is known as electromotive force (EMF) of the cell if no current is drawn from the cell.

$$E_{\text{cell}} = E_{\text{reduction}} - E_{\text{oxidation}} = E_{\text{cathode}} - E_{\text{anode}}$$

Since anode is put on left and cathode on right, therefore it follows

$$E_{\text{cell}} = E_R - E_L$$

For a Daniel cell,

$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{Cu}^{2+}/\text{Cu}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0 \\ &= 0.34V - (-0.76V) \\ &= 1.10V \end{aligned}$$

- 20. Nernst Equation:** It relates electrode potential with the concentration of ions.

For an electrode reaction, $M^{n+}(aq) + ne^- \longrightarrow M(s)$

Nernst equation can be written as

$$\begin{aligned} E_{M^{n+}/M} &= E_{M^{n+}/M}^0 - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]} \\ E_{M^{n+}/M} &= E_{M^{n+}/M}^0 - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]} \end{aligned}$$

where, $E_{M^{n+}/M}$ = Electrode potential

$E_{M^{n+}/M}^0$ = Standard electrode potential

$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

T = Temperature in kelvin

n = No. of electrons gained

F = Faraday constant (96500 C mol^{-1})

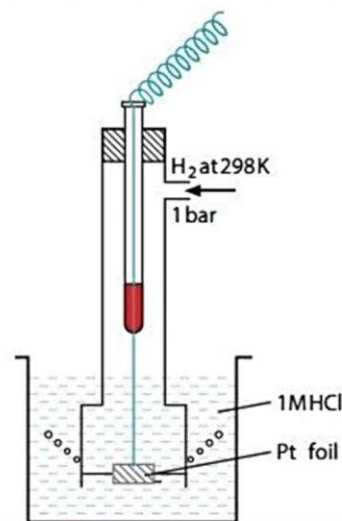


Fig. 2.5: Standard or Normal Hydrogen Electrode

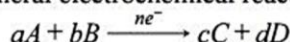
Substituting the value of R and F , we get

$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}, \text{ at } 298 \text{ K}$$

or
$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} + \frac{0.0591}{n} \log [M^{n+}], \text{ at } 298 \text{ K}$$

Thus, the reduction potential increases with the increase in the concentration of ions.

For a general electrochemical reaction of the type:



Nernst equation can be given as

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303}{nF} RT \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Substituting the values of R and F we get

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ at } 298 \text{ K}$$

- 21. Equilibrium Constant from Nernst Equation:** For a Daniel cell, at equilibrium

$$E_{\text{cell}} = 0 = E_{\text{cell}}^{\circ} - \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

or
$$E_{\text{cell}}^{\circ} = \frac{2.303RT}{2F} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

But at equilibrium, $\frac{[Zn^{2+}]}{[Cu^{2+}]} = K_c$

$$\therefore E_{\text{cell}}^{\circ} = \frac{2.303RT}{2F} \log K_c$$

$$E_{\text{cell}}^{\circ} = \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log K_c = \frac{0.0591}{2} \log K_c$$

In general, $E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c$ or, $\log K_c = \frac{n}{0.0591} E_{\text{cell}}^{\circ}$

- 22. EMF and Gibbs Free Energy:** The work done by a reversible galvanic cell is equal to decrease in its free energy.

Mathematically, $\Delta_r G = -nFE_{\text{cell}}^{\circ}$

If concentration of all the reacting species is unity, then,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} \text{ and we get, } \Delta_r G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

From $\Delta_r G^{\circ}$, we can calculate the equilibrium constant of a reaction,

$$\Delta_r G^{\circ} = -RT \ln K_c \text{ or } \Delta_r G^{\circ} = -2.303 RT \log K_c$$

- 23. Concentration Cells:** If two electrodes of the same metal are dipped separately into two solutions of the same electrolyte having different concentrations and the solutions are connected through salt bridge, such cells are known as **concentration cells**. In these cells, oxidation takes place on the electrode with lower concentration (c_1) while reduction takes place on the electrode with higher concentration (c_2). For example, $H_2 | H^+(c_1) || H^+(c_2) | H_2$; $Cu | Cu^{2+}(c_1) || Cu^{2+}(c_2) | Cu$; $Zn | Zn^{2+}(c_1) || Zn^{2+}(c_2) | Zn$

The EMF of concentration cell at 298 K is given by

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{c_2}{c_1}, \text{ where } c_2 > c_1$$

24. **Electrochemical Series:** The arrangement of various standard half-cells in the order of their decreasing standard reduction potential values is known as electrochemical series

Table 2.1: Standard Electrode Potentials at 298 K

Note: Ions are present as aqueous species and H₂O as liquid; gases and solids are shown by g and s.

Reaction (Oxidised form + $ne^- \rightarrow$ Reduced form)			E°/V	
<div style="writing-mode: vertical-rl; transform: rotate(180deg);">Increasing strength of oxidising agent</div>	$F_2(g) + 2e^-$	$\rightarrow 2F^-$		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
	$Fe^{2+} + 2e^-$	$\rightarrow Fe(s)$		-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
			<div style="writing-mode: vertical-rl; transform: rotate(180deg);">Increasing strength of reducing agent</div>	

- A negative value of E° means that the redox couple is stronger reducing agent than H^+/H_2 . e.g., Mg (-2.36).
- A positive value of E° means that the redox couple is weaker reducing agent than H^+/H_2 . e.g., Br₂ (1.09).

25. **Electrolysis:** The process of decomposition of an electrolyte when electric current is passed through its aqueous solution or fused state is called electrolysis.

The process of electrolysis of a substance is governed by Faraday's laws of electrolysis.

(a) **Faraday's first law of electrolysis**

"The amount of any substance deposited or liberated at the electrode is directly proportional to the quantity of electricity passing through the electrolyte."

If w grams of the substance deposited on passing Q coulombs of electricity, then

$$w \propto Q \text{ or } w \propto I \times t \quad [\because Q = I \times t]$$

or

$$w = Z \times I \times t$$

where, Z is a constant of proportionality known as electrochemical equivalent of the substance deposited.

- **Electrochemical equivalent (Z):** If $I = 1$ ampere and $t = 1$ second, then

$$w = Z$$

Thus, the electrochemical equivalence may be defined as the amount of the substance deposited by passing one ampere of current for one second or by passing one coulomb of charge through the electrolyte.

- 1 Faraday = Quantity of electricity carried by 1 mole of electrons.
($6.023 \times 10^{23} \text{ mol}^{-1} \times 1.6 \times 10^{-19} \text{ C} = 96472 \text{ C mol}^{-1} \approx 96500 \text{ C mol}^{-1}$)

- If n mol of electrons are involved in an electrode reaction, then

$n \times 96500 \text{ C}$ of charge will deposit = M g of the element

$$1 \text{ C of charge will deposit} = \frac{M}{n \times 96500} \text{ g of element}$$

But 1 C of charge deposit mass of element = Z g

$$\therefore Z = \frac{M}{n \times 96500} \text{ g} = \frac{E}{96500} \text{ g}$$

where E is the equivalent mass of the element and is equal to $\frac{\text{Atomic mass}}{\text{Valency}}$ of the element.
or $E = 96500 \times Z$

- **Equivalent mass:** The mass of an element deposited by passing 96500 C of charge.

(b) **Faraday's second law of electrolysis**

"When same quantity of electricity is passed through different electrolytes, the amount of different substances deposited at the electrodes is directly proportional to their equivalent masses."

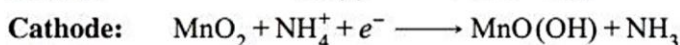
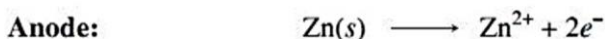
Mathematically,
$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

26. **Commercial Cells (Batteries):** Batteries are the electrochemical cells used commercially to generate electricity. "Any battery consists of two or more than two galvanic cells connected in series where the chemical energy of the redox reactions is converted into electrical energy." There are mainly two types of batteries:

- (a) **Primary cells (Batteries):** These cells are not chargeable because the electrode reaction occurs only once and after the use over a period of time the cells become dead and cannot be reused.

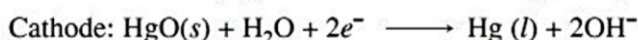
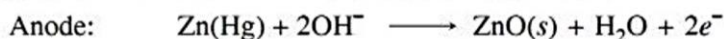
The most familiar example of this type of cell is the **Dry cell** (known as **Leclanche cell** after its discoverer) which is used commonly in watches, radios, calculators, etc. It consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by a moist paste of NH_4Cl and ZnCl_2 (Fig. 2.6).

The electrode reactions are:



The cell has a potential of nearly 1.5 V.

Another type of primary cell is the **Mercury cell**, consisting of zinc-mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO . The electrode reactions are:



The cell potential is approximately 1.35 V and remains constant as the ionic concentration of the solution is not changed during its life.

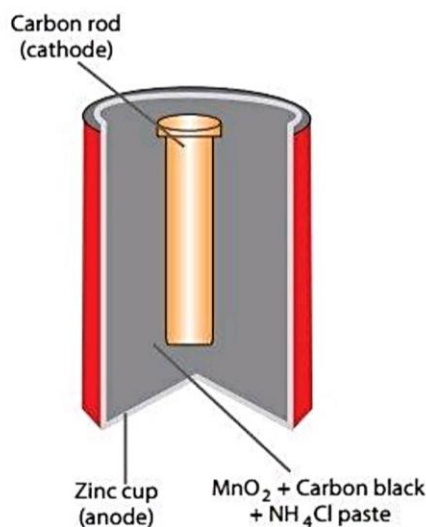


Fig. 2.6: The dry cell

(b) Secondary cells (Batteries)

A secondary battery is rechargeable and can be used again and again. It is recharged by passing current through it from an external source. Most familiar example of secondary cell is the **Lead storage battery** commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode.

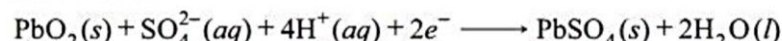
A 38% solution of H_2SO_4 is used as an electrolyte (Fig. 2.7).

The cell reactions when the battery is in use, are:

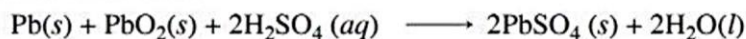
At anode:



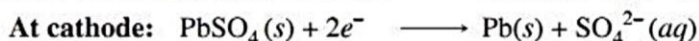
At cathode:



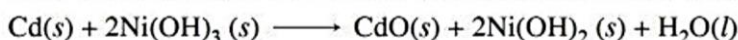
The overall reaction is:



On recharging the cell, operated like an electrolytic cell; the reaction is reversed and $\text{PbSO}_4(\text{s})$ on anode and cathode is converted into Pb and PbO_2 , respectively.



Another important secondary cell is the **Nickel-cadmium cell** which has longer life than the lead storage cell but is costly. Here, the overall reaction during discharge of the battery is



- 27. Fuel Cells:** Fuel cells are those cells which produce electrical energy directly from the combustion of fuels such as hydrogen, carbon monoxide or methane. The most successful fuel cell, $\text{H}_2\text{-O}_2$ cell utilises the reaction between hydrogen and oxygen to produce water. Hydrogen and oxygen are bubbled through a porous carbon electrode in the cell into concentrated aqueous sodium hydroxide. Catalysts are incorporated into the electrode (Fig. 2.8). The electrode reactions are

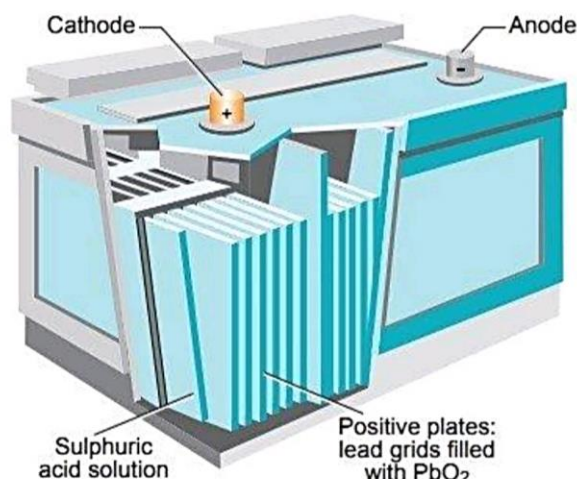
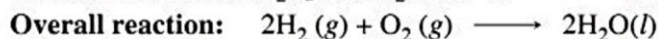
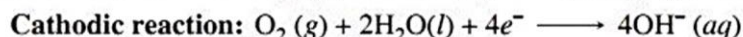
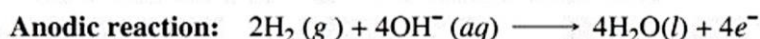


Fig. 2.7: The lead storage battery

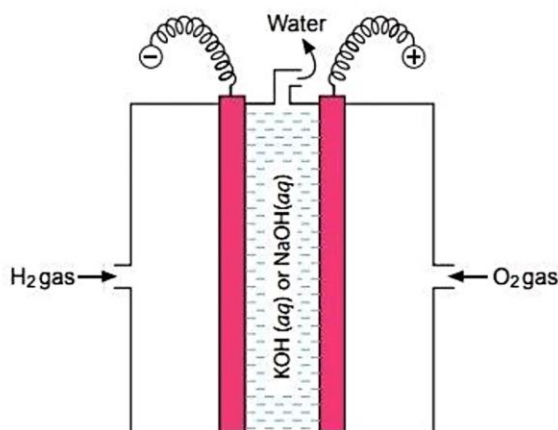


Fig. 2.8: A simple H_2 - O_2 fuel cell

Advantages of Fuel Cells:

- It is a pollution-free device since no harmful products are formed.
- Its efficiency is about 75% which is considerably higher than conventional cells.
- These cells are light in weight as compared to electrical generators to produce corresponding quantity of power.
- It is a continuous source of energy if the supply of gases is maintained.

28. **Corrosion:** The process of slow eating up of metals by gases and water vapours present in atmosphere due to the formation of certain compounds like oxides, sulphides, carbonates, etc. is called corrosion. Corrosion of iron is known as rusting. Chemically, rust is hydrated ferric oxide, $Fe_2O_3 \cdot xH_2O$. Corrosion may be considered as an electrochemical phenomenon. According to electrochemical theory of rusting, the impure iron surface behaves like a small electrochemical cell in the presence of moisture containing oxygen or carbon dioxide. Such a cell is called corrosion cell or corrosion couple. In these miniature corrosion cells, pure iron acts as anode, impure surface area acts as cathode and moisture having dissolved carbon dioxide or oxygen acts as electrolyte.

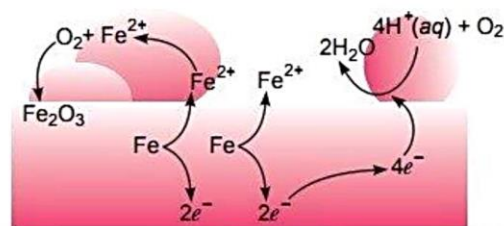
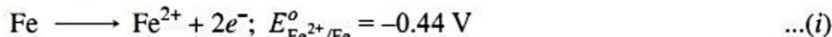
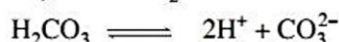


Fig. 2.9: Corrosion

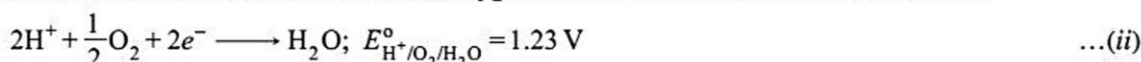
At anode, oxidation of iron takes place. Thus, Fe enters into the solution as Fe^{2+} ions leaving behind electrons which are pushed into cathodic area.



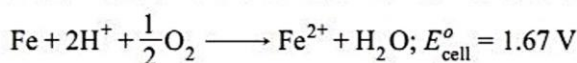
At cathode, the electrons are picked up by the H^+ ions which are produced from H_2CO_3 (formed due to dissolution of CO_2 in moisture) or from H_2O .



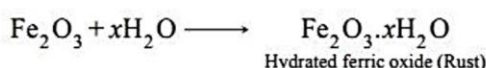
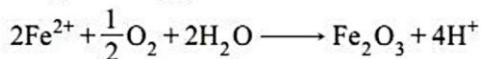
H^+ ions, thus formed, reduces the dissolved oxygen as the net reaction at the cathodic area is



The overall reaction of the corrosion cell can be obtained by adding equations (i) and (ii)



The ferrous ions so formed move through water and come at the surface where these are further oxidised by atmospheric oxygen to ferric ions and form rust which is hydrated ferric oxide (Fig. 2.9).



29. Prevention of Corrosion: The metal surface can be protected against corrosion by the following methods:

(a) **Barrier protection:** A thin film is introduced between iron and atmospheric oxygen, carbon dioxide and moisture. The following methods are adopted for depositing thin film on metal surface:

- (i) By covering the surface with paint or a thin film of grease.
- (ii) By electroplating iron with some non-corrosive metals such as nickel, chromium, copper, etc.

(b) **Sacrificial protection:** In this method, iron surface is covered with a more electropositive metal than iron which gets oxidised in preference to iron. In such a situation the more electropositive metal loses electrons instead of iron and thus this metal is sacrificed at the cost of iron, hence the name sacrificial protection. Iron is generally coated with zinc and this process is called galvanization.

(c) **Electrical protection:** This is also a case of sacrificial protection. This method is used for the protection of underground water pipes or iron tanks. In this method, the exposed surface of iron is protected by connecting it to a block of some active metal such as magnesium, aluminium or zinc (Fig. 2.10). This more electropositive metal acts as anode and lose electrons in preference to iron. The iron surface acts as cathode. This method, therefore, is also called cathodic protection. The electrons released at the anode are accepted by H^+ ions of water at the surface of iron. More electropositive metal is consumed gradually in the process and needs periodical replacement.

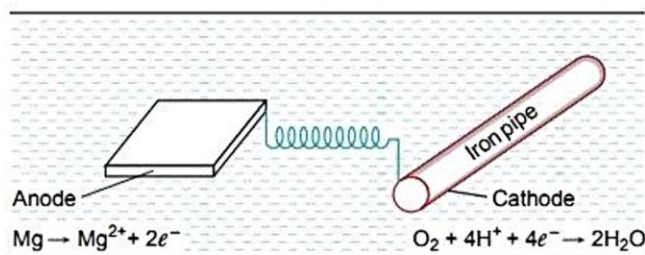


Fig. 2.10: Electric Protection

30. Products of Electrolysis: Under the influence of electric current through molten electrolytes or their aqueous solutions, ions move towards oppositely charged electrodes. Many times the electrode products differ. For example, the electrolysis of molten sodium chloride yields sodium metal at the cathode and chlorine gas is liberated at the anode.

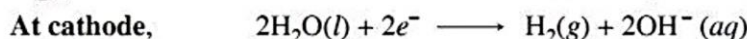


At anode: $\text{Cl}^- \longrightarrow \text{Cl} + e^-$ Oxidation

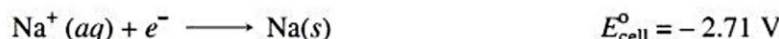


At cathode: $\text{Na}^+ + e^- \longrightarrow \text{Na(s)}$ Reduction

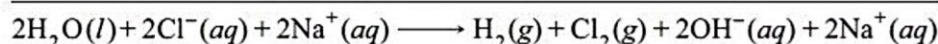
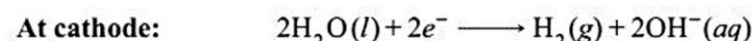
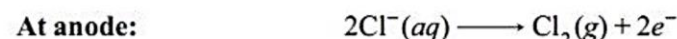
However, when a concentrated aqueous solution of sodium chloride is electrolysed, H_2 gas at cathode and Cl_2 gas at anode are obtained. This is because water is preferably reduced at cathode.



This happens because the standard reduction potential of water is greater than the standard reduction potential of Na^+ ion.

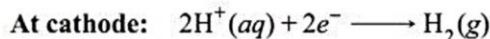
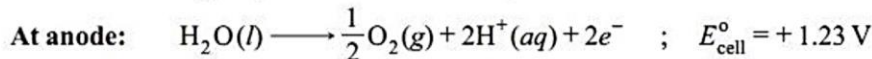
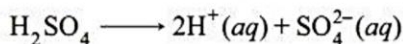


At anode, however, Cl_2 gas is liberated because of over potential of oxygen. In fact, the remaining solution after electrolysis yields solid NaOH on evaporating. Thus,

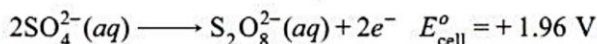


(a) Electrolysis of dilute H_2SO_4

During electrolysis of dilute H_2SO_4 , the products are $H_2(g)$ at cathode and $O_2(g)$ at anode:

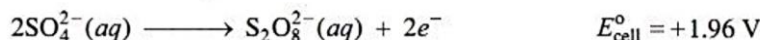
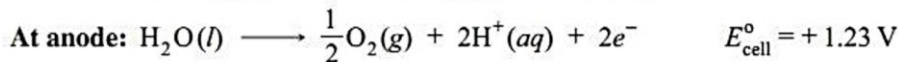
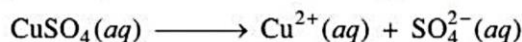


If H_2SO_4 is concentrated then the following reaction occurs at anode



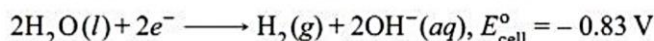
(b) Electrolysis of aqueous copper sulphate using inert electrodes (Pt)

In this, copper is deposited at cathode and oxygen is liberated at anode.

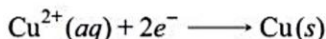


Water, having low E° , would be preferably oxidised at anode instead of SO_4^{2-} ions.

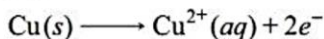
Cu^{2+} ions have greater reduction potential, copper metal is deposited at the cathode.



(c) If $CuSO_4$ is electrolysed between two copper electrodes (active electrodes), the Cu^{2+} ions discharge at the cathode (negatively charged) and the following reaction occurs



Thus, copper metal is deposited at cathode. At the anode, copper is converted into Cu^{2+} ions with the following change:



Thus, copper is dissolved (oxidised) at anode and deposited (reduced) at cathode. This forms the basis of an industrial process in which impure copper is converted into copper of high purity. The impure copper is made as anode that dissolves on passing current and pure copper is deposited at cathode.

(d) Electrolysis of aqueous sodium bromide: Like aqueous $NaCl$, the electrode products are $Br_2(l)$ at anode and $H_2(g)$ at cathode.

Conclusions: 1. Cathodic reaction will be one which has higher $E_{reduction}^{\circ}$ value.

2. Anodic reaction will be one which has higher $E_{oxidation}^{\circ}$ value or lower $E_{reduction}^{\circ}$ value.

Important Formulae

1. $R = \rho \left(\frac{l}{A} \right) = \rho \times \text{Cell constant}$

where, R = Resistance

A = Area of cross-section of the electrodes

ρ = Resistivity

2. $\kappa = \frac{1}{R} \times \text{cell constant}$

where, κ = Conductivity or specific conductance

3. $\Lambda_m = \frac{\kappa \times 1000}{M}$

where, Λ_m = Molar conductivity

M = Molarity of the solution.

- $\Lambda_m^{\circ}(A_xB_y) = x\Lambda_m^{\circ}(A^{y+}) + y\Lambda_m^{\circ}(B^{x-})$
 where, Λ_m° = Molar conductivity at infinite dilution, x and y are the number of cations and anions produced by one formula unit of the electrolyte on complete dissociation.
- $\alpha = \frac{\Lambda_m^c}{\Lambda_m^{\circ}}$
 where, α = Degree of dissociation
 Λ_m^c = Molar conductivity at a given concentration
- For a weak binary electrolyte AB

$$K = \frac{c\alpha^2}{1-\alpha} = \frac{c(\Lambda_m^c)^2}{\Lambda_m^{\circ}(\Lambda_m^{\circ} - \Lambda_m^c)}$$

 where, K = Dissociation constant

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$= E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ}$$
- Nernst equations for a general electrode reaction:

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

$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} - \frac{2.303 RT}{nF} \log \frac{1}{[M^{n+}]}$$

$$E_{M^{n+}/M} = E_{M^{n+}/M}^{\circ} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]} \text{ at } 298 \text{ K}$$
- Nernst equation for a general electrochemical reaction:

$$aA + bB \xrightarrow{ne^{-}} cC + dD$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

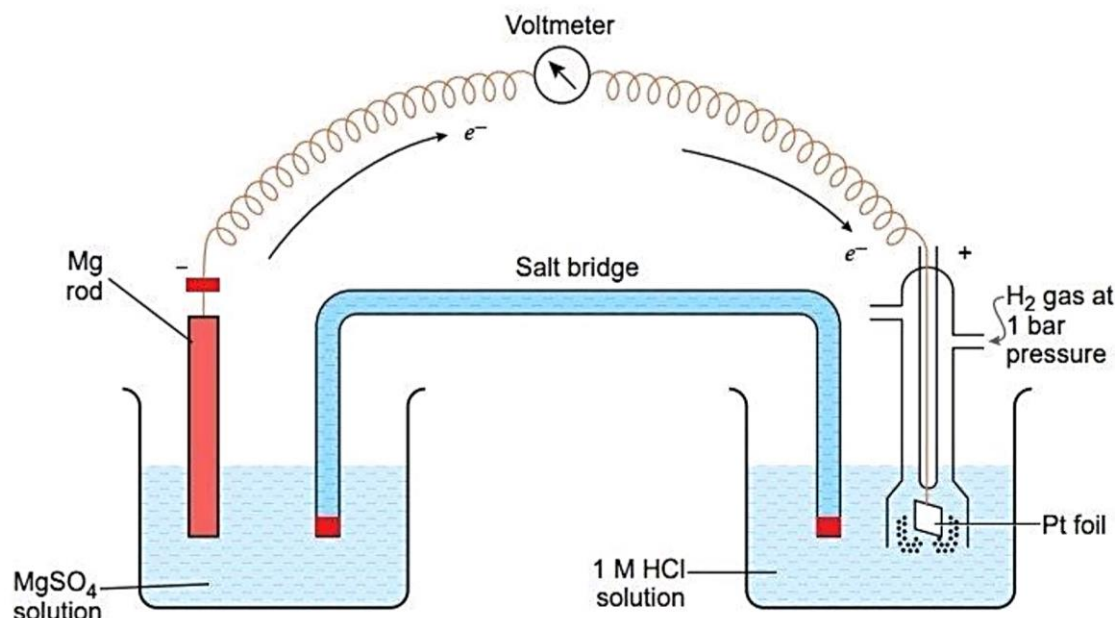
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303 RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ at } 298 \text{ K}$$
- $\log K_c = \frac{n}{0.0591} E_{\text{cell}}^{\circ}$
 where, K_c = Equilibrium constant
- $\Delta_r G^{\circ} = -nFE_{\text{cell}}^{\circ}$
 $\Delta_r G^{\circ} = -2.303 RT \log K_c$
 where, $\Delta_r G^{\circ}$ = Standard Gibbs energy of the reaction
- $Q = I \times t$
 where Q = Quantity of charge in coulombs
 I = Current in amperes
 t = Time in seconds
- $m = Z \times I \times t$
 where m = Mass of the substance deposited at the electrodes
 Z = Electrochemical equivalent

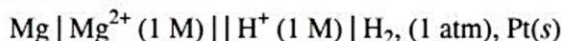
NCERT Intext Questions

Q. 1. How would you determine the standard electrode potential of the system $\text{Mg}^{2+} | \text{Mg}$?

Ans. Set up an electrochemical cell consisting of $\text{Mg} | \text{MgSO}_4 (1 \text{ M})$ as one electrode by dipping a magnesium rod in 1 M MgSO_4 solution and standard hydrogen electrode $\text{Pt}, \text{H}_2 (1 \text{ atm}) | \text{H}^+ (1 \text{ M})$ as the second electrode as shown in given figure.



Measure the EMF of the cell and also note the direction of deflection in the voltmeter. The direction of deflection shows that electrons flow from magnesium electrode to hydrogen electrode. Thus, the cell may be represented as follows:



$$E_{\text{cell}}^{\circ} = E_{\text{H}^+ / \frac{1}{2} \text{H}_2}^{\circ} - E_{\text{Mg}^{2+} / \text{Mg}}^{\circ}$$

But

$$E_{\text{H}^+ / \frac{1}{2} \text{H}_2}^{\circ} = 0$$

Hence,

$$E_{\text{Mg}^{2+} / \text{Mg}}^{\circ} = - E_{\text{cell}}^{\circ}$$

Q. 2. Can you store copper sulphate solutions in a zinc pot?

[HOTS]

Ans. For this we have to check whether the following reaction will take place or not.

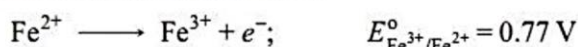


$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+} / \text{Cu}}^{\circ} - E_{\text{Zn}^{2+} / \text{Zn}}^{\circ} = 0.34 - (-0.76) = 1.10 \text{ V}$$

As E_{cell}° is positive, the reaction will take place. Therefore, we cannot store copper sulphate in zinc pot.

Q. 3. Consult the table of the standard electrode potential and suggest three substances that can oxidise ferrous ions under suitable conditions.

Ans. Oxidation of ferrous ions means

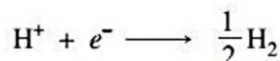


Only those substances can oxidise Fe^{2+} to Fe^{3+} which are stronger oxidising agents and have positive reduction potentials greater than 0.77 V so that E_{cell} of the cell reaction is positive. This is for elements lying below $\text{Fe}^{3+} / \text{Fe}^{2+}$ in the electrochemical series, for example, Br_2 , Cl_2 and F_2 .

Q. 4. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

[HOTS]

Ans. For hydrogen electrode



$$E_{H^+/\frac{1}{2}H_2} = E_{H^+/\frac{1}{2}H_2}^{\circ} - \frac{0.0591}{n} \log \frac{1}{[H^+]}$$

Here, $n = 1$,

$$\log \frac{1}{[H^+]} = \text{pH} = 10, E_{H^+/\frac{1}{2}H_2}^{\circ} = 0$$

$$\therefore E_{H^+/\frac{1}{2}H_2} = 0 - 0.0591 \times 10 = -0.591 \text{ V}$$

Q. 5. Calculate the emf of the cell in which the following reaction takes place:



Given that $E_{\text{cell}}^{\circ} = 1.05 \text{ V}$

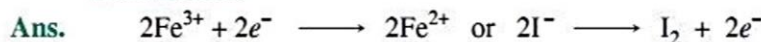
Ans. From Nernst equation to the given cell reaction

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2} \\ &= 1.05 \text{ V} - \frac{0.0591}{2} \log \frac{0.160}{(0.002)^2} = 1.05 - \frac{0.0591}{2} \log (4 \times 10^4) \\ &= 1.05 - \frac{0.0591}{2} (4.6021) \\ &= 1.05 - 0.14 \text{ V} = 0.91 \text{ V} \end{aligned}$$

Q. 6. The cell in which the following reaction occurs:



has $E_{\text{cell}}^{\circ} = 0.236 \text{ V}$ at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.



Thus, for the given cell reaction, $n = 2$.

$$\Delta_r G^{\circ} = -nFE_{\text{cell}}^{\circ} = -2 \times 96500 \times 0.236 \text{ J mol}^{-1} = -45548 \text{ J mol}^{-1} = -45.55 \text{ kJ mol}^{-1}$$

$$\Delta_r G^{\circ} = -2.303 RT \log K_c$$

$$\begin{aligned} -\log K_c &= \frac{\Delta_r G^{\circ}}{2.303 RT} = \frac{-45.55 \text{ kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} \\ &= -7.983 \end{aligned}$$

$$\therefore K_c = \text{Antilog}(7.983) = 9.616 \times 10^7$$

Q. 7. Why does the conductivity of a solution decrease with dilution?

Ans. Conductivity of a solution is the conductance of ions present in a unit volume of the solution. On dilution, the number of ions per unit volume decreases. So, the conductivity also decreases.

Q. 8. Suggest a way to determine the Λ_m° value of water.

[HOTS]

Ans. $\Lambda_{m(\text{H}_2\text{O})}^{\circ} = \lambda_{(\text{H}^+)}^{\circ} + \lambda_{(\text{OH}^-)}^{\circ}$
 $= \lambda_{(\text{H}^+)}^{\circ} + \lambda_{(\text{OH}^-)}^{\circ} + \lambda_{(\text{Cl}^-)}^{\circ} - \lambda_{(\text{Cl}^-)}^{\circ} + \lambda_{(\text{Na}^+)}^{\circ} - \lambda_{(\text{Na}^+)}^{\circ}$

Rearranging we get

$$\Lambda_{m(\text{H}_2\text{O})}^{\circ} = [\lambda_{(\text{H}^+)}^{\circ} + \lambda_{(\text{Cl}^-)}^{\circ}] + [\lambda_{(\text{Na}^+)}^{\circ} + \lambda_{(\text{OH}^-)}^{\circ}] - [\lambda_{(\text{Na}^+)}^{\circ} + \lambda_{(\text{Cl}^-)}^{\circ}]$$

$$\Lambda_{m(\text{H}_2\text{O})}^{\circ} = \Lambda_{m(\text{HCl})}^{\circ} + \Lambda_{m(\text{NaOH})}^{\circ} - \Lambda_{m(\text{NaCl})}^{\circ}$$

Thus, the molar conductivity of water at infinite dilution can be determined from the knowledge of $\Lambda_{m(\text{HCl})}^{\circ}$, $\Lambda_{m(\text{NaOH})}^{\circ}$ and $\Lambda_{m(\text{NaCl})}^{\circ}$.

- Q. 9.** The molar conductivity of 0.025 mol L^{-1} methanoic acid is $46.1 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate its degree of dissociation and dissociation constant.

[Given $\lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda^\circ(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}$.]

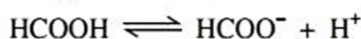
[HOTS]

Ans. $\Lambda_m^\circ(\text{HCOOH}) = \lambda_{\text{H}^+}^\circ + \lambda_{\text{HCOO}^-}^\circ = 349.6 \text{ S cm}^2 \text{ mol}^{-1} + 54.6 \text{ S cm}^2 \text{ mol}^{-1}$

$$\Lambda_m^\circ = 404.2 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^c = 46.1 \text{ S cm}^2 \text{ mol}^{-1} \text{ (Given)}$$

$$\therefore \alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{46.1}{404.2} = 0.114$$



Initial conc.	$c \text{ mol L}^{-1}$	0	0
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Conc. at equilibrium	$c(1 - \alpha)$	$c\alpha$	$c\alpha$
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$$K = \frac{c\alpha \cdot c\alpha}{c(1 - \alpha)} = \frac{c\alpha^2}{1 - \alpha} = \frac{0.025 \times (0.114)^2}{1 - 0.114}$$

$$= 3.67 \times 10^{-4} \text{ mol/L}$$

- Q. 10.** If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire? [HOTS]

Ans. $Q \text{ (coulomb)} = I \text{ (ampere)} \times t \text{ (s)} = (0.5 \text{ ampere}) (2 \times 60 \times 60 \text{ s}) = 3600 \text{ C}$

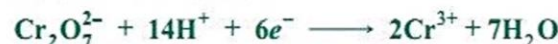
A flow of 96500 C is equivalent to the flow of 1 mole of electrons, i.e., 6.02×10^{23} electrons

$$\therefore 3600 \text{ C is equivalent to flow of electrons} = \frac{6.02 \times 10^{23}}{96500} \times 3600 = 2.246 \times 10^{22} \text{ electrons}$$

- Q. 11.** Suggest a list of metals that are extracted electrolytically.

Ans. Na, Ca, Mg and Al.

- Q. 12.** Consider the reaction:



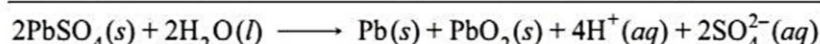
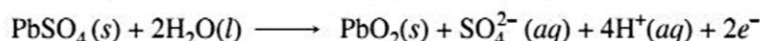
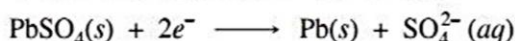
What is the quantity of electricity in coulombs needed to reduce 1 mol of $\text{Cr}_2\text{O}_7^{2-}$?

Ans. From the given reaction, 1 mole of $\text{Cr}_2\text{O}_7^{2-}$ ions require

$$6F = 6 \times 96500 \text{ C} = 579000 \text{ C of electricity for reduction to } \text{Cr}^{3+} \text{ ion.}$$

- Q. 13.** Write the chemistry of recharging the lead storage battery, highlighting all the materials that are involved during recharging.

Ans. During recharging, electrical energy is supplied to the cell from an external source. The reactions are reverse of those that takes place during discharge.

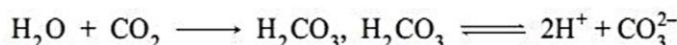


- Q. 14.** Suggest two materials other than hydrogen that can be used as fuels in fuel cells.

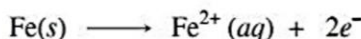
Ans. Methyl alcohol and methane.

- Q. 15.** Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

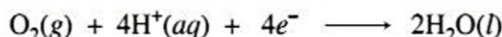
Ans. The water layer present on the surface of iron dissolves acidic oxides of air like CO_2 to form acids which dissociate to give H^+ ions.



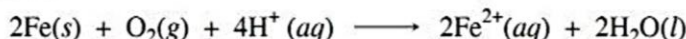
In the presence of H^+ ions, iron starts losing electrons at some spot to form ferrous ions. Hence, this spot acts as the anode:



The electrons thus released move through the metal to reach another spot where H^+ ions and the dissolved oxygen gain these electrons and reduction reaction takes place. Hence, this spot acts as the cathode:



The overall reaction is given as:



Therefore, an electrochemical cell is set up on the surface.

Ferrous ions are further oxidised by the atmospheric oxygen to ferric ions which combine with water molecules to form hydrated ferric oxide, $Fe_2O_3 \cdot xH_2O$, which is rust.

NCERT Exercises

- Q. 1.** Arrange the following metals in the order in which they displace each other from the solution of their salts.

Al, Cu, Fe, Mg and Zn

Ans. Mg, Al, Zn, Fe, Cu.

- Q. 2.** Given the standard electrode potentials

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

Arrange these metals in their increasing order of reducing power.

[CBSE (AI) 2010]

Ans. Lower the reduction potential, more easily it is oxidised and hence greater is the reducing power. Therefore, the increasing order of reducing power is $Ag < Hg < Cr < Mg < K$.

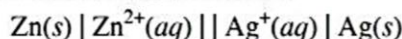
- Q. 3.** Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. Further show:

(i) Which of the electrode is negatively charged?

(ii) The carriers of the current in the cell.

(iii) Individual reaction at each electrode.

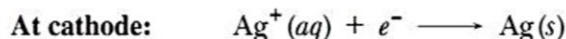
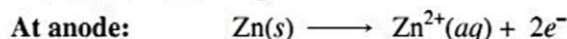
Ans. The cell will be represented as:



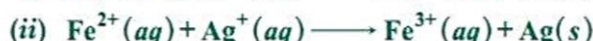
(i) Anode (zinc electrode) will be negatively charged.

(ii) Electrons and ions.

(iii) The reaction occurring



- Q. 4.** Calculate the standard cell potentials of galvanic cell in which the following reactions take place:



[Given: $E_{Cr^{3+}/Cr}^{\circ} = -0.74 \text{ V}$, $E_{Cd^{2+}/Cd}^{\circ} = -0.40 \text{ V}$, $E_{Ag^+/Ag}^{\circ} = 0.80 \text{ V}$, $E_{Fe^{3+}/Fe^{2+}}^{\circ} = 0.77 \text{ V}$]

Calculate $\Delta_r G^{\circ}$ and equilibrium constant of the reactions.

Ans. (i) $E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = -0.40 \text{ V} - (-0.74 \text{ V}) = +0.34 \text{ V}$

$$\begin{aligned} \Delta_r G^{\circ} &= -nFE_{cell}^{\circ} = -6 \text{ mol} \times 96500 \text{ C mol}^{-1} \times 0.34 \text{ V} \\ &= -196860 \text{ CV mol}^{-1} = -196860 \text{ J mol}^{-1} = -196.86 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta_r G^{\circ} = -2.303 RT \log K_c$$

$$-196860 = -2.303 \times 8.314 \times 298 \log K_c \quad \text{or} \quad \log K_c = 34.5014$$

$$K_c = \text{Antilog } 34.5014 = 3.172 \times 10^{34}$$

$$\begin{aligned}
 (ii) \quad E_{\text{cell}}^{\circ} &= +0.80 \text{ V} - 0.77 \text{ V} = +0.03 \text{ V} \\
 \Delta_r G^{\circ} &= -nFE_{\text{cell}}^{\circ} = -(1 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.03 \text{ V}) \\
 &= -2895 \text{ CV mol}^{-1} = -2895 \text{ J mol}^{-1} = -2.895 \text{ kJ mol}^{-1} \\
 \Delta_r G^{\circ} &= -2.303 RT \log K_c \\
 -2895 &= -2.303 \times 8.314 \times 298 \times \log K_c \\
 \text{or} \quad \log K_c &= 0.5074 \\
 \text{or} \quad K_c &= \text{Antilog}(0.5074) = 3.22
 \end{aligned}$$

Q. 5. Write the Nernst equation and emf of the following cells at 298 K:

- (i) $\text{Mg}(s) | \text{Mg}^{2+} (0.001 \text{ M}) || \text{Cu}^{2+} (0.0001 \text{ M}) | \text{Cu}(s)$
 (ii) $\text{Fe}(s) | \text{Fe}^{2+} (0.001 \text{ M}) || \text{H}^+ (1 \text{ M}) | \text{H}_2(g) (1 \text{ bar}) | \text{Pt}(s)$
 (iii) $\text{Sn}(s) | \text{Sn}^{2+} (0.050 \text{ M}) || \text{H}^+ (0.020 \text{ M}) | \text{H}_2(g) (1 \text{ bar}) | \text{Pt}(s)$
 (iv) $\text{Pt}(s) | \text{Br}^- (0.010 \text{ M}) | \text{Br}_2(l) || \text{H}^+ (0.030 \text{ M}) | \text{H}_2(g) (1 \text{ bar}) | \text{Pt}(s)$
 [Given, $E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} = -2.37 \text{ V}$, $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = +0.34 \text{ V}$, $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V}$,
 $E_{\text{Sn}^{2+}/\text{Sn}}^{\circ} = -0.14 \text{ V}$, $E_{1/2\text{Br}_2/\text{Br}^-}^{\circ} = +1.08 \text{ V}$.]

Ans. (i) Cell reaction: $\text{Mg} + \text{Cu}^{2+} \longrightarrow \text{Mg}^{2+} + \text{Cu}; n = 2$

Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$

$$\therefore E_{\text{cell}} = 0.34 - (-2.37) - \frac{0.0591}{2} \log \frac{10^{-3}}{10^{-4}} = 2.71 - 0.02955 = 2.68 \text{ V}$$

(ii) Cell reaction: $\text{Fe} + 2\text{H}^+ \longrightarrow \text{Fe}^{2+} + \text{H}_2; n = 2$

Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}$

$$\begin{aligned}
 \therefore E_{\text{cell}} &= 0 - (-0.44) - \frac{0.0591}{2} \log \frac{10^{-3}}{(1)^2} \\
 &= 0.44 - \frac{0.0591}{2} \times (-3) = 0.44 + 0.0887 = 0.529 \text{ V}
 \end{aligned}$$

(iii) Cell reaction: $\text{Sn} + 2\text{H}^+ \longrightarrow \text{Sn}^{2+} + \text{H}_2; n = 2$

Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2} = 0 - (-0.14) - \frac{0.0591}{2} \log \frac{0.05}{(0.02)^2}$

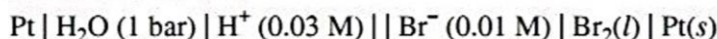
$$= 0.14 - \frac{0.0591}{2} \log 125 = 0.14 - \frac{0.0591}{2} (2.0969) = 0.078 \text{ V}$$

(iv) Cell reaction: $2\text{Br}^- + 2\text{H}^+ \longrightarrow \text{Br}_2 + \text{H}_2; n = 2$

Nernst equation: $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{1}{[\text{Br}^-]^2 [\text{H}^+]^2}$

$$\begin{aligned}
 \therefore E_{\text{cell}} &= (0 - 1.08) - \frac{0.0591}{2} \log \frac{1}{(0.01)^2 (0.03)^2} \\
 &= -1.08 - \frac{0.0591}{2} \log (1.111 \times 10^7) = -1.08 - \frac{0.0591}{2} (7.0457) \\
 &= -1.08 - 0.208 = -1.288 \text{ V}
 \end{aligned}$$

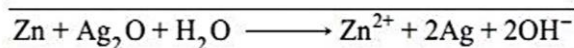
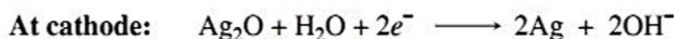
As E_{cell} is negative, therefore cell reaction will not take place. For the cell to show positive emf cell, representation should be



Q. 6. In the button cells widely used in watches and other devices, the following reaction takes place:



Determine $\Delta_r G^\circ$ and E° for the reaction.



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ$$

$$E_{\text{cell}}^\circ = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$$

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ, n = 2$$

$$\Delta G^\circ = -2 \times 96500 \times 1.10$$

$$\Delta G^\circ = -2.123 \times 10^5 \text{ J/mol}$$

Q. 7. Define conductivity and molar conductivity for the solution of an electrolyte. Discuss their variation with concentration.

Ans. Refer to Points to remember 5 and 10 for definition.

Variation of Conductivity and Molar Conductivity with Concentration: Conductivity always decreases with the decrease in concentration both, for weak and strong electrolytes. This is because the number of ions per unit volume that carry the current in a solution decreases on dilution. The conductivity of a solution at any given concentration is the conductance of one unit volume of solution kept between two platinum electrodes with unit area of cross section and at a distance of unit length. This is clear from the equation:

$$G = \frac{\kappa A}{l} = \kappa \quad (\text{both } A \text{ and } l \text{ are unity in their appropriate units in m or cm}).$$

Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with the area of cross section A and distance of unit length. Therefore,

$$\Lambda_m = \frac{\kappa A}{l} = \kappa$$

Since $l = 1$ and $A = V$ (volume containing 1 mole of electrolyte)

$$\Lambda_m = \kappa V$$

Molar conductivity increases with the decrease in concentration. This is because the total volume, V , of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume.

Q. 8. The conductivity of 0.20 M solution of KCl at 298 K is 0.0248 S cm^{-1} . Calculate its molar conductivity.

Ans. $\Lambda_m = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{0.0248 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.20 \text{ mol L}^{-1}} = 124 \text{ S cm}^2 \text{ mol}^{-1}$

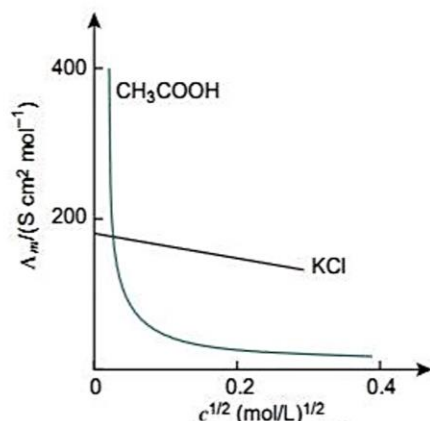
Q. 9. The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500Ω . What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is $0.146 \times 10^{-3} \text{ S cm}^{-1}$?

Ans. Conductivity (κ) = $\frac{1}{\text{Resistance (R)}} \times \text{Cell constant}$

$$\kappa = 0.146 \times 10^{-3} \text{ S cm}^{-1}, R = 1500 \Omega$$

$$0.146 \times 10^{-3} \text{ S cm}^{-1} = \frac{1}{1500 \Omega} \times \text{Cell constant}$$

$$\therefore \text{Cell constant} = 0.146 \times 10^{-3} \text{ S cm}^{-1} \times 1500 \Omega = 219 \times 10^{-3} \text{ cm}^{-1} = 0.219 \text{ cm}^{-1}$$



Molar conductivity versus $c^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.

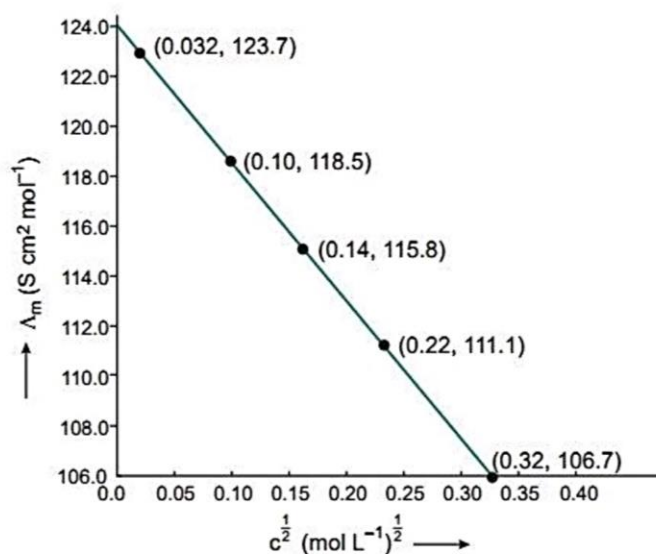
- Q. 10. The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

Concentration/M	0.001	0.010	0.020	0.050	0.100
$10^2 \times \kappa / \text{S m}^{-1}$	1.237	11.85	23.15	55.53	106.74

Calculate Λ_m for all concentrations and draw a plot between Λ_m and $c^{1/2}$. Find the value of Λ_m° .

Ans. $\frac{1 \text{ S cm}^{-1}}{100 \text{ S m}^{-1}} = 1$ (unit conversion factor)

Conc. (M)	κ (S m^{-1})	κ (S cm^{-1})	$\Lambda_m = \frac{1000 \times \kappa}{\text{Molarity}} (\text{S cm}^2 \text{ mol}^{-1})$	$c^{1/2} (\text{M}^{1/2})$
10^{-3}	1.237×10^{-2}	1.237×10^{-4}	$\frac{1000 \times 1.237 \times 10^{-4}}{10^{-3}} = 123.7$	0.0316
10^{-2}	11.85×10^{-2}	11.85×10^{-4}	$\frac{1000 \times 11.85 \times 10^{-4}}{10^{-2}} = 118.5$	0.100
2×10^{-2}	23.15×10^{-2}	23.15×10^{-4}	$\frac{1000 \times 23.15 \times 10^{-4}}{2 \times 10^{-2}} = 115.8$	0.141
5×10^{-2}	55.53×10^{-2}	55.53×10^{-4}	$\frac{1000 \times 55.53 \times 10^{-4}}{5 \times 10^{-2}} = 111.1$	0.224
10^{-1}	106.74×10^{-2}	106.74×10^{-4}	$\frac{1000 \times 106.74 \times 10^{-4}}{10^{-1}} = 106.7$	0.316



Plot between Λ_m and $c^{1/2}$

Λ_m° = Intercept on the Λ_m axis = $124.0 \text{ S cm}^2 \text{ mol}^{-1}$

- Q. 11. Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity. If Λ_m° for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant?

Ans. $c = 0.00241 \text{ M}$, $\kappa = 7.896 \times 10^{-5} \text{ S cm}^{-1}$, $\Lambda_m^\circ = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

Substituting the values, we get

$$\begin{aligned} \Lambda_m &= \frac{7.896 \times 10^{-5} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.00241 \text{ mol L}^{-1}} \\ &= 32.76 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{32.76}{390.5} = 0.084$$

$$\alpha = 0.084\%$$

	$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$		
Initial concentration	c	0	0
Concentration at equilibrium	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$K = \frac{0.00241(0.084)^2}{(1-0.084)} = 1.86 \times 10^{-5}$$

Q. 12. How much charge is required for the following reduction:

(i) 1 mol of Al^{3+} to Al ?

(ii) 1 mol of Cu^{2+} to Cu ?

(iii) 1 mol of MnO_4^- to Mn^{2+} ?

[CBSE 2020 (56/5/1)]

Ans. (i) $\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$

\therefore Quantity of charge required for reduction of 1 mol of $\text{Al}^{3+} = 3F$
 $= 3 \times 96500 \text{ C} = 289500 \text{ C}$

(ii) $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$

\therefore Quantity of charge required for reduction of 1 mol of $\text{Cu}^{2+} = 2F = 2 \times 96500 \text{ C}$
 $= 193000 \text{ C}$

(iii) $\text{MnO}_4^- \longrightarrow \text{Mn}^{2+}$

Oxidation number of Mn changes from +7 to +2.

\therefore Quantity of charge required $= 5F = 5 \times 96500 \text{ C} = 482500 \text{ C}$

Q. 13. 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 ?

Ans. (i) $\text{Ca}^{2+} + 2e^- \longrightarrow \text{Ca}$

As, 40 g of Ca, require electricity $= 2F$

\therefore 20 g of Ca will require electricity $= \frac{20}{40} \times 2 = 1F$

(ii) $\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$

As, 1 mol of Al, i.e., 27 g of Al require electricity $= 3F$

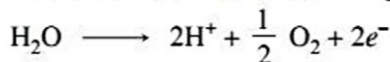
\therefore 40 g of Al will require electricity $= \frac{3}{27} \times 40 = 4.44F$

Q. 14. How much electricity is required in coulomb for the oxidation of

(i) 1 mol of H_2O to O_2

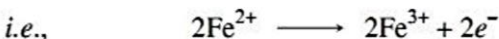
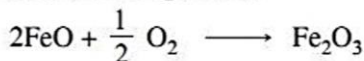
(ii) 1 mol of FeO to Fe_2O_3 ?

Ans. (i) The electrode reaction for 1 mol of H_2O is given as



\therefore Quantity of electricity required $= 2F = 2 \times 96500 \text{ C} = 193000 \text{ C}$

(ii) The electrode reaction is given as



For the oxidation of 2 moles of FeO , required charge $= 2F$

\therefore For the oxidation of 1 mole of FeO , required charge $= 1F = 96500 \text{ C}$

- Q. 15.** A solution of $\text{Ni}(\text{NO}_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode? [CBSE (F) 2014]

Ans. Quantity of electricity passed = $I \times t = (5 \text{ A}) \times (20 \times 60 \text{ s}) = 6000 \text{ C}$

The electrode reaction is: $\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}$

$2 \times 96500 \text{ C}$ deposit Ni = 58.7 g

$$\therefore 6000 \text{ C will deposit Ni} = \frac{58.7}{2 \times 96500} \times 6000 \text{ g} = 1.825 \text{ g}$$

- Q. 16.** Three electrolytic cells A, B and C containing solutions of ZnSO_4 , AgNO_3 and CuSO_4 , respectively were 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?

Ans. $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$

108 g of Ag is deposited by 96500 C

$$\therefore 1.45 \text{ g of Ag will be deposited by } \frac{96500}{108} \times 1.45 \text{ C} = 1295.6 \text{ C}$$

$$t = \frac{Q}{I} = \frac{1295.6}{1.50} = 863.7 \text{ s}$$

$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$

$2 \times 96500 \text{ C}$ deposit Cu = 63.5 g

$$\therefore \text{Cu deposited by } 1295.6 \text{ C} = \frac{63.5}{2 \times 96500} \times 1295.6 = 0.426 \text{ g}$$

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

$2 \times 96500 \text{ C}$ deposit Zn = 65.3 g

$$\therefore \text{Zn deposited by } 1295.6 \text{ C} = \frac{65.3}{2 \times 96500} \times 1295.6 = 0.438 \text{ g}$$

- Q. 17.** Using the standard electrode potentials given below, predict if the reaction between the following is feasible:

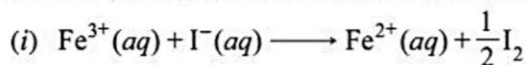
- $\text{Fe}^{3+}(\text{aq})$ and $\text{I}^-(\text{aq})$
- $\text{Ag}^+(\text{aq})$ and $\text{Cu}(\text{s})$
- $\text{Fe}^{3+}(\text{aq})$ and $\text{Br}^-(\text{aq})$
- $\text{Ag}(\text{s})$ and $\text{Fe}^{3+}(\text{aq})$
- $\text{Br}_2(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$

Given standard electrode potentials:

$$E_{\text{I}_2/\text{I}^-}^\circ = 0.541 \text{ V}, \quad E_{\text{Cu}^{2+}/\text{Cu}}^\circ = +0.34 \text{ V}, \quad E_{\text{Br}_2/\text{Br}^-}^\circ = +1.090 \text{ V},$$

$$E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}, \quad E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = +0.77 \text{ V}.$$

Ans. A reaction is feasible if e.m.f. of the cell reaction is positive.



$$\therefore E_{\text{cell}}^\circ = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ - E_{\text{I}_2/\text{I}^-}^\circ = 0.77 \text{ V} - 0.54 \text{ V} = 0.23 \text{ V (feasible)}.$$



$$E_{\text{cell}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Cu}^{2+}/\text{Cu}}^\circ = 0.80 \text{ V} - 0.34 \text{ V} = 0.46 \text{ V (feasible)}.$$

- (iii) $\text{Fe}^{3+}(\text{aq}) + \text{Br}^{-}(\text{aq}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + \frac{1}{2}\text{Br}_2$
 $E_{\text{cell}}^{\circ} = 0.77 \text{ V} - 1.09 \text{ V} = -0.32 \text{ V}$ (not feasible).
- (iv) $\text{Ag}(\text{s}) + \text{Fe}^{3+}(\text{aq}) \longrightarrow \text{Ag}^{+}(\text{aq}) + \text{Fe}^{2+}(\text{aq})$,
 $E_{\text{cell}}^{\circ} = 0.77 \text{ V} - 0.80 \text{ V} = -0.03 \text{ V}$ (not feasible).
- (v) $\frac{1}{2}\text{Br}_2(\text{aq}) + \text{Fe}^{2+}(\text{aq}) \longrightarrow \text{Br}^{-}(\text{aq}) + \text{Fe}^{3+}(\text{aq})$,
 $E_{\text{cell}}^{\circ} = 1.09 \text{ V} - 0.77 \text{ V} = 0.32 \text{ V}$ (feasible).

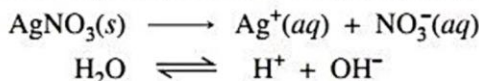
Q. 18. Predict the products of electrolysis in each of the following

- (i) An aqueous solution of AgNO_3 with silver electrodes.
 (ii) An aqueous solution of AgNO_3 with platinum electrodes.
 (iii) A dilute solution of H_2SO_4 with platinum electrodes.
 (iv) An aqueous solution of CuCl_2 with platinum electrodes.

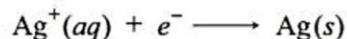
[CBSE 2019 (56/3/2)]

[CBSE 2020 (56/4/3)]

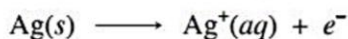
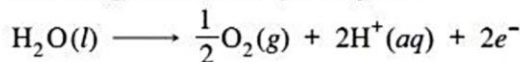
Ans. (i) Electrolysis of aqueous solution of AgNO_3 with silver electrodes:



At cathode: Since, the reduction potential of Ag^{+} (+0.80 V) is greater than that of water, (−0.83 V), Ag^{+} will get reduced preferentially and silver metal will get deposited at the cathode. will be deposited as Ag in preference to H^{+} ions.



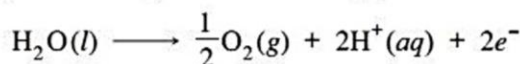
At anode: Following reactions may take place



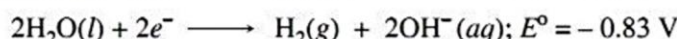
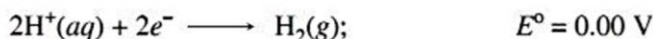
Among these reactions, the reduction potential of silver is minimum. Therefore, the silver anode will itself undergo oxidation to form Ag^{+} ions which will pass into the solution.

(ii) **At cathode:** As given in part (i).

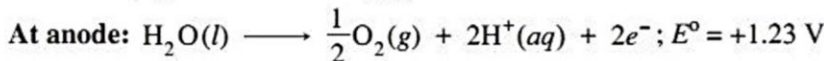
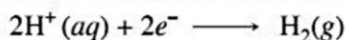
At anode: Since the reduction potential of water is less than that of NO_3^{-} ions, water will get preferentially oxidised and oxygen will be evolved.



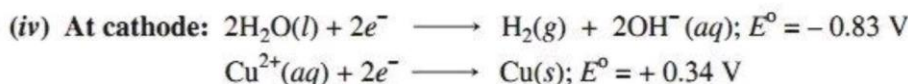
(iii) **At cathode:**



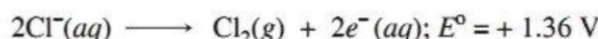
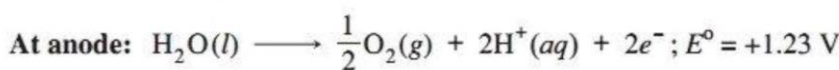
Since, H^{+} ions possess a higher reduction potential as compared to that of water, H^{+} will get preferentially reduced and H_2 gas is obtained at the cathode.



Since, the reduction potential of H_2O is less than that of SO_4^{2-} ions, water will get preferentially oxidised and oxygen will be evolved at the anode.



As E° for Cu^{2+} is greater than H_2O . So, copper metal is deposited at the anode.



Since E° value of H_2O is less than Cl^- , water will get preferentially oxidised at anode and O_2 gas will be evolved.



Multiple Choice Questions

Choose and write the correct option(s) in the following questions.

- An electrochemical cell can behave like an electrolytic cell when _____.
 [NCERT Exemplar; CBSE 2020 (56/4/2)]
 (a) $E_{\text{cell}} = 0$ (b) $E_{\text{cell}} > E_{\text{ext}}$ (c) $E_{\text{ext}} > E_{\text{cell}}$ (d) $E_{\text{cell}} = E_{\text{ext}}$
- The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called _____.
 [NCERT Exemplar]
 (a) cell potential (b) cell emf (c) potential difference (d) cell voltage
- The correct cell to represent the following reaction is
 $\text{Zn} + 2\text{Ag}^+ \longrightarrow \text{Zn}^{2+} + 2\text{Ag}$ [CBSE 2023 (56/1/1)]
 (a) $2\text{Ag} | \text{Ag}^+ || \text{Zn} | \text{Zn}^{2+}$ (b) $\text{Ag}^+ | \text{Ag} || \text{Zn}^{2+} | \text{Zn}$
 (c) $\text{Ag} | \text{Ag}^+ || \text{Zn} | \text{Zn}^{2+}$ (d) $\text{Zn} | \text{Zn}^{2+} || \text{Ag}^+ | \text{Ag}$
- Which cell will measure standard electrode potential of copper electrode? [NCERT Exemplar]
 (a) $\text{Pt}(s) | \text{H}_2(g, 0.1 \text{ bar}) | \text{H}^+(aq., 1 \text{ M}) || \text{Cu}^{2+}(aq., 1 \text{ M}) | \text{Cu}$
 (b) $\text{Pt}(s) | \text{H}_2(g, 1 \text{ bar}) | \text{H}^+(aq., 1 \text{ M}) || \text{Cu}^{2+}(aq., 2 \text{ M}) | \text{Cu}$
 (c) $\text{Pt}(s) | \text{H}_2(g, 1 \text{ bar}) | \text{H}^+(aq., 1 \text{ M}) || \text{Cu}^{2+}(aq., 1 \text{ M}) | \text{Cu}$
 (d) $\text{Pt}(s) | \text{H}_2(g, 1 \text{ bar}) | \text{H}^+(aq., 0.1 \text{ M}) || \text{Cu}^{2+}(aq., 1 \text{ M}) | \text{Cu}$
- The positive value of the standard electrode potential of Cu^{2+}/Cu indicates that _____.
 [NCERT Exemplar]
 (a) this redox couple is a stronger reducing agent than the H^+/H_2 couple.
 (b) this redox couple is a stronger oxidising agent than H^+/H_2 .
 (c) Cu can displace H_2 from acid.
 (d) It can act as anode.
- Standard electrode potential for $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple is +0.15 V and that for the Cr^{3+}/Cr couple is -0.74 V. The two couple in their standard states are connected to make cell. The cell potential will be
 (a) +1.19 V (b) 0.89 V (c) +0.18 V (d) +1.83 V
- Which of the following statement is not correct about an inert electrode in a cell? [NCERT Exemplar]
 (a) It does not participate in the cell reaction.
 (b) It provides surface either for oxidation or for reduction reaction.
 (c) It provides surface for conduction of electrons.
 (d) It provides surface for redox reaction.
- Using the data given below find out the strongest reducing agent. [NCERT Exemplar]
 $E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}$, $E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$, $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$, $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$
 (a) Cl^- (b) Cr (c) Cr^{3+} (d) Mn^{2+}

9. Using the data given in Q. 8 find out in which option the order of reducing power is correct.

[NCERT Exemplar]

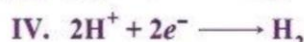
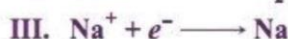
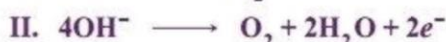
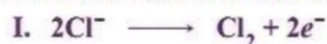
- (a) $\text{Cr}^{3+} < \text{Cl}^- < \text{Mn}^{2+} < \text{Cr}$ (b) $\text{Mn}^{2+} < \text{Cl}^- < \text{Cr}^{3+} < \text{Cr}$
(c) $\text{Cr}^{3+} < \text{Cl}^- < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$ (d) $\text{Mn}^{2+} < \text{Cr}^{3+} < \text{Cl}^- < \text{Cr}$

10. Use the data given in Q. 8 find out the most stable oxidised species.

[NCERT Exemplar]

- (a) Cr^{3+} (b) MnO_4^-
(c) $\text{Cr}_2\text{O}_7^{2-}$ (d) Mn^{2+}

11. Four half reactions I to IV are shown below:



Which two of these reactions are most likely to occur when concentrated brine is electrolysed?

[CBSE 2023 (56/5/2)]

- (a) I and III (b) I and IV
(c) II and III (d) II and IV

12. Zinc is coated over iron to prevent rusting of iron because

[CBSE 2020 (56/5/3)]

- (a) $E_{\text{Zn}^{2+}/\text{Zn}}^\circ = E_{\text{Fe}^{2+}/\text{Fe}}^\circ$ (b) $E_{\text{Zn}^{2+}/\text{Zn}}^\circ < E_{\text{Fe}^{2+}/\text{Fe}}^\circ$
(c) $E_{\text{Zn}^{2+}/\text{Zn}}^\circ > E_{\text{Fe}^{2+}/\text{Fe}}^\circ$ (d) None of these

13. ΔG and E_{cell}° for a spontaneous reaction will be

[CBSE 2023 (56/1/1)]

- (a) positive, negative (b) negative, negative (c) negative, positive (d) positive, positive

14. The standard emf of a galvanic cell involving 3 moles of electrons in a redox reaction is 0.59 V. The equilibrium constant for the reaction of the cell is

- (a) 10^{10} (b) 10^{20}
(c) 10^{30} (d) 10^{15}

15. Which of the following solutions of KCl will have the highest value of specific conductance?

[CBSE 2020 (56/3/2)]

- (a) 0.5 M (b) 0.01 M
(c) 0.1 M (d) 1.0 M

16. Which of the statements about solutions of electrolytes is not correct?

[NCERT Exemplar]

- (a) Conductivity of solution depends upon size of ions.
(b) Conductivity depends upon viscosity of solution.
(c) Conductivity does not depend upon solvation of ions present in solution.
(d) Conductivity of solution increases with temperature.

17. Kohlrausch given the following relation for strong electrolytes:

$$\Lambda = \Lambda_0 - A\sqrt{C}$$

Which of the following equality holds?

[CBSE 2020 (56/5/2)]

- (a) $\Lambda = \Lambda_0$ as $C \rightarrow \sqrt{A}$ (b) $\Lambda = \Lambda_0$ as $C \rightarrow \infty$
(c) $\Lambda = \Lambda_0$ as $C \rightarrow 0$ (d) $\Lambda = \Lambda_0$ as $C \rightarrow 1$

18. $\Lambda_{m(\text{NH}_4\text{OH})}^\circ$ is equal to _____.

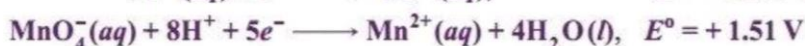
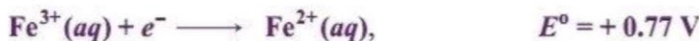
[NCERT Exemplar]

- (a) $\Lambda_{m(\text{NH}_4\text{OH})}^\circ + \Lambda_{m(\text{NH}_4\text{Cl})}^\circ - \Lambda_{m(\text{HCl})}^\circ$ (b) $\Lambda_{m(\text{NH}_4\text{Cl})}^\circ + \Lambda_{m(\text{NaOH})}^\circ - \Lambda_{m(\text{NaCl})}^\circ$
(c) $\Lambda_{m(\text{NH}_4\text{Cl})}^\circ + \Lambda_{m(\text{NaCl})}^\circ - \Lambda_{m(\text{NaOH})}^\circ$ (d) $\Lambda_{m(\text{NaOH})}^\circ + \Lambda_{m(\text{NaCl})}^\circ - \Lambda_{m(\text{NH}_4\text{Cl})}^\circ$

19. Which of the following option will be the limiting molar conductivity of CH_3COOH if the limiting molar conductivity of CH_3COONa is $91 \text{ S cm}^2 \text{ mol}^{-1}$? Limiting molar conductivity for individual ions are given in the following table. [CBSE Sample Paper 2021]

S. No.	Ions	Limiting molar conductivity/ $\text{S cm}^2 \text{ mol}^{-1}$
1.	H^+	349.6
2.	Na^+	50.1
3.	K^+	73.5
4.	OH^-	199.1

- (a) $350 \text{ S cm}^2 \text{ mol}^{-1}$ (b) $375.3 \text{ S cm}^2 \text{ mol}^{-1}$
(c) $390.5 \text{ S cm}^2 \text{ mol}^{-1}$ (d) $340.4 \text{ S cm}^2 \text{ mol}^{-1}$
20. Charge carried by 1 mole of electrons is
(a) 6.023×10^{23} coulomb (b) 9.65×10^4 coulomb
(c) 1.6×10^{-19} coulomb (d) 6.28×10^{19} coulomb
21. The quantity of charge required to obtain one mole of aluminium from Al_2O_3 is _____. [NCERT Exemplar]
(a) 1F (b) 6F (c) 3F (d) 2F
22. If the standard electrode potential of an electrode is greater than zero, then we can infer that its [CBSE 2020 (56/2/1)]
(a) reduced form is more stable compared to hydrogen gas.
(b) oxidised form is more stable compared to hydrogen gas.
(c) reduced and oxidised forms are equally stable.
(d) reduced form is less stable than the hydrogen gas.
23. Consider the following standard electrode potential values: [CBSE 2023 (56/5/2)]



What is the cell potential for the redox reaction?

- (a) -2.28 V (b) -0.74 V (c) $+0.74 \text{ V}$ (d) $+2.28 \text{ V}$
24. E°_{cell} for some half cell reactions are given below. On the basis of these mark the correct answer.
- (i) $\text{H}^+(\text{aq}) + e^- \longrightarrow \frac{1}{2}\text{H}_2(\text{g}) \quad E^\circ_{\text{cell}} = 0.00 \text{ V}$
(ii) $2\text{H}_2\text{O}(\text{l}) \longrightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e^- \quad E^\circ_{\text{cell}} = 1.23 \text{ V}$
(iii) $2\text{SO}_4^{2-}(\text{aq}) \longrightarrow \text{S}_2\text{O}_8^{2-}(\text{aq}) + 2e^- \quad E^\circ_{\text{cell}} = 1.96 \text{ V}$
- (a) In dilute sulphuric acid solution, hydrogen will be reduced at anode.
(b) In concentrated sulphuric acid solution, water will be oxidised at anode.
(c) In dilute sulphuric acid solution, water will be oxidised at anode.
(d) In dilute sulphuric acid solution, SO_4^{2-} ion will be oxidised to tetrathionate at anode.
25. In a Leclanche dry cell, the cathode is [CBSE 2020 (56/3/3)]
(a) Zn container (b) MnO_2
(c) Graphite rod (d) NH_4Cl
26. In a lead storage battery [CBSE 2020 (56/4/1)]
(a) PbO_2 is reduced to PbSO_4 at the cathode.
(b) Pb is oxidised to PbSO_4 at the anode.
(c) Both electrodes are immersed in the same aqueous solution of H_2SO_4 .
(d) All the above are true.

27. In fuel cell

[CBSE 2020 (56/3/3)]

- (a) chemical energy is converted to electrical energy.
- (b) energy of combustion of fuel is converted to chemical energy.
- (c) energy of combustion of fuel is converted to electrical energy.
- (d) electrical energy is converted to chemical energy.

28. Which of the following analogy is correct?

- (a) Resistance : ohm :: Resistivity : ohm m
- (b) Λ_m^∞ : Molarity :: Λ_{eq}^∞ : Normality
- (c) Metallic conductance : Electrons :: Electrolytic conductance : ions
- (d) All of these

29. Which of the following solutions of KCl will have the highest value of molar conductivity?

[CBSE 2023 (56/2/1)]

- (a) 0.01 M (b) 1 M (c) 0.5 M (d) 0.1 M

30. Match the following Columns:

Column-I	Column-II
(i) Conductivity	A. Λ/A
(ii) Cell constant	B. κ
(iii) Anode	C. negative electrode in electrolytic cell
(iv) Cathode	D. positive electrode in electrolytic cell

- (a) (i) — A, (ii) — C, (iii) — B, (iv) — D (b) (i) — B, (ii) — A, (iii) — D, (iv) — C
- (c) (i) — D, (ii) — A, (iii) — B, (iv) — C (d) (i) — B, (ii) — D, (iii) — A, (iv) — C

Answers

- 1. (c) 2. (b) 3. (d) 4. (c) 5. (b) 6. (b) 7. (d) 8. (b) 9. (b) 10. (a)
- 11. (b) 12. (b) 13. (c) 14. (c) 15. (c) 16. (c) 17. (c) 18. (b) 19. (c) 20. (b)
- 21. (c) 22. (a) 23. (c) 24. (c) 25. (c) 26. (d) 27. (c) 28. (d) 29. (a) 30. (b)



Assertion-Reason Questions

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

- (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
- (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
- (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
- (d) Assertion (A) is incorrect, but Reason (R) is correct statement.

1. Assertion (A) : E_{cell} should have a positive value for the cell to function.

Reason (R) : $E_{\text{cathode}} < E_{\text{anode}}$

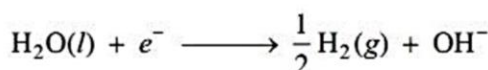
2. Assertion (A) : Mercury cell does not give steady potential.

Reason (R) : In the cell reaction, ions are not involved in solution.

3. Assertion (A) : Cu is less reactive than hydrogen.

Reason (R) : $E_{\text{Cu}^{2+}/\text{Cu}}^\circ$ is negative.

4. Assertion (A) : Copper sulphate cannot be stored in zinc vessel.
Reason (R) : Zinc is less reactive than copper.
5. Assertion (A) : $E_{Ag^+/Ag}$ increases with increase in concentration of Ag^+ ions.
Reason (R) : $E_{Ag^+/Ag}$ has a positive value.
6. Assertion (A) : Current stops flowing when $E_{cell} = 0$.
Reason (R) : Equilibrium of the cell reaction is attained.
7. Assertion (A) : For measuring resistance of an ionic solution an AC source is used.
Reason (R) : Concentration of ionic solution will change if DC source is used.
8. Assertion (A) : Conductivity decreases with decrease in concentration of electrolyte.
Reason (R) : Number of ions per unit volume that carry the current in a solution decreases on dilution.
[CBSE 2023 (56/2/1)]
9. Assertion (A) : Conductivity decreases for weak electrolyte and increases for strong electrolyte with decrease in concentration.
Reason (R) : On dilution, the number of ions per unit volume that carry the current decreases.
10. Assertion (A) : Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.
Reason (R) : For weak electrolytes, degree of dissociation decreases with dilution of solution.
[CBSE 2023 (56/4/2)]
11. Assertion (A) : Electrolysis of NaCl solution gives chlorine at anode instead of O_2 .
Reason (R) : Formation of oxygen at anode requires overvoltage.
12. Assertion (A) : The following reaction takes place at cathode during the electrolysis of aqueous sodium chloride:



Reason (R) : The reaction with lower value of E° is preferred at cathode.

Answers

1. (c) 2. (d) 3. (c) 4. (c) 5. (b) 6. (a) 7. (a) 8. (a) 9. (d) 10. (c)
11. (a) 12. (c)



Passage-based/Case-based/ Source-based Questions

Read the given passages and answer the questions that follow.

PASSAGE-1

Rahul set-up an experiment to find resistance of aqueous KCl solution for different concentrations at 298 K using a conductivity cell connected to a Wheatstone bridge. He fed the Wheatstone bridge with a.c. power in the audio frequency range 550 to 5000 cycles per second. Once the resistance was calculated from null point he also calculated the conductivity κ and molar conductivity Λ_m and recorded his readings in tabular form.

[CBSE 2023 (56/5/2)]

S. No.	Conc. (M)	$\kappa \text{ S cm}^{-1}$	$\Lambda_m \text{ S cm}^2 \text{ mol}^{-1}$
1.	1.00	111.3×10^{-3}	111.3
2.	0.10	12.9×10^{-3}	129.0
3.	0.01	1.41×10^{-3}	141.0

Answer the following questions:

1. Why does conductivity decrease with dilution?
2. If Λ_m° of KCl is $150.0 \text{ S cm}^2 \text{ mol}^{-1}$, calculate the degree of dissociation of 0.01 M KCl.

3. If Rahul had used HCl instead to KCl then would you expect the Λ_m values to be more or less than those per KCl for a given concentration. Justify.

OR

Amit a classmate of Rahul repeated the same experiment with CH_3COOH solution instead of KCl solution. Give one point that would be similar and one that would be different in his observations as compared to Rahul.

Answers

1. This is due to the fact that the number of ions per unit volume that carry the current in the solution decreases with dilution.

2. Degree of dissociation,

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^o}$$

$$= \frac{141 \text{ S cm}^2 \text{ mol}^{-1}}{150 \text{ S cm}^2 \text{ mol}^{-1}} = 0.94$$

$$\alpha = 94\%$$

3. Smaller the ion higher is the mobility of the ion and hence higher is the molar conductivity of ions therefore HCl will have greater molar conductivity (Λ_m) than KCl for a given concentration.

OR

Similarity : Conductivity decreases with increase in dilution both for HCl and CH_3COOH solutions.

Dissimilarity: With increase in dilution there is very small increase in Λ_m for HCl and very large increase in Λ_m for CH_3COOH (especially near infinite dilution).

PASSAGE-2

A Lead storage battery is the most important type of secondary cell having a lead anode and a grid of lead packed with PbO_2 as cathode. A 38% solution of sulphuric acid is used as electrolyte. (Density = 1.294 g mL^{-1}). The battery holds 3.5 L of the acid. During the discharge of the battery, the density of H_2SO_4 falls to 1.139 g mL^{-1} . (20% H_2SO_4 by mass) [CBSE Sample Paper 2020]

- Write the reaction taking place at the cathode when the battery is in use.
- How much electricity in terms of Faraday is required to carry out the reduction of one mole of PbO_2 ?
- What is the molarity of sulphuric acid before discharge?

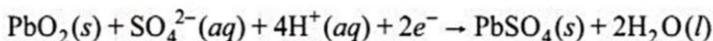
OR

(i) Lead storage battery is considered a secondary cell. Why?

(ii) Write the products of electrolysis when dilute sulphuric acid is electrolysed using Platinum electrodes.

Answers

1. Reaction taking place at cathode when the battery is in use:



2. From above reaction

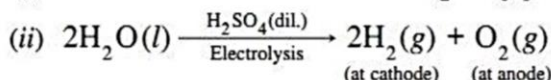
1 mole of PbO_2 require 2F of electricity for reduction to PbSO_4 .

3. Molarity = $\frac{\% \times \text{density} \times 10}{\text{Molar mass of } \text{H}_2\text{SO}_4} = \frac{38 \times 1.294 \times 10}{98} = 5.017 \text{ mol L}^{-1}$

Molarity = 5.02 mol L^{-1}

OR

(i) Because after use it can be recharged by passing current through it in the opposite direction.



CONCEPTUAL QUESTIONS

Q. 1. What would happen if no salt bridge were used in an electrochemical cell (like Zn-Cu cell)?

Ans. The metal ions (Zn^{2+}) formed by the loss of electrons will accumulate in one electrode and the negative ions (SO_4^{2-}) will accumulate in the other. Thus, the solutions will develop charges and the current will stop flowing. Moreover, the inner circuit will not be completed.

Q. 2. Why does a galvanic cell become dead after some time?

Ans. As the reaction proceeds, concentration of ions in anodic half keeps on increasing while in the cathodic half it keeps on decreasing. Hence, their electrode potentials also keeps on changing until they become equal and then e.m.f. of the cell becomes zero.

Q. 3. Consider a cell given below:

[NCERT Exemplar]



Write the reactions that occur at anode and cathode.

Ans. Anode: $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2e^-$

Cathode: $\text{Cl}_2 + 2e^- \longrightarrow 2\text{Cl}^-$

Q. 4. Depict the galvanic cell in which the cell reaction is $\text{Cu} + 2\text{Ag}^+ \longrightarrow 2\text{Ag} + \text{Cu}^{2+}$.

[NCERT Exemplar] [HOTS]

Ans. $\text{Cu} | \text{Cu}^{2+}(\text{conc.}) || \text{Ag}^+(\text{conc.}) | \text{Ag}$

Q. 5. What is the reference electrode in determining the standard electrode potential?

Ans. Normal hydrogen electrode (NHE).

Q. 6. Why is it not possible to measure the single electrode potential?

Ans. Oxidation or reduction cannot take place alone. Moreover, electrode potential is a relative tendency and can be measured with respect to a reference electrode only.

Q. 7. Define electrochemical series.

Ans. The arrangement of elements in the increasing or decreasing order of their standard reduction potential is called electrochemical series.

Q. 8. Write Nernst equation for single electrode potential.

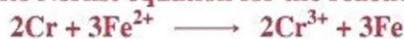
Ans. For the electrode reaction $\text{M}^{n+} + ne^- \longrightarrow \text{M}$

$$E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^{\circ} - \frac{2.303RT}{nF} \log \frac{[\text{M}]}{[\text{M}^{n+}]} = E_{\text{M}^{n+}/\text{M}}^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[\text{M}^{n+}]}$$

Q. 9. Write Nernst equation for the general cell reaction $a\text{A} + b\text{B} \xrightarrow{ne^-} x\text{X} + y\text{Y}$.

Ans. If n moles of electrons are transferred, Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{[\text{X}]^x [\text{Y}]^y}{[\text{A}]^a [\text{B}]^b}$.

Q. 10. Write Nernst equation for the reaction



Ans. $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{6F} \ln \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$ ($\because n = 6$)

Q. 11. How can the reduction potential of an electrode be increased?

Ans. $\text{M}^{n+} + ne^- \longrightarrow \text{M}$,

$$E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^{\circ} - \frac{RT}{nF} \ln \frac{1}{[\text{M}^{n+}]} = E_{\text{M}^{n+}/\text{M}}^{\circ} + \frac{RT}{nF} \ln [\text{M}^{n+}]$$

Thus, electrode potential can be increased by increasing the metal ion concentration.

Q. 12. What flows in the internal circuit of a galvanic cell?

Ans. Ions

Q. 13. What does the negative value of E_{cell}° indicate?

Ans. Negative E_{cell}° value means $\Delta_r G^{\circ}$ will be +ve, and the cell will not work.

Q. 14. Out of zinc and tin, whose coating is better to protect iron objects?

[CBSE 2020 (56/1/1)]

Ans. Zinc

Q. 15. Why is alternating current used for measuring resistance of an electrolytic solution? [NCERT Exemplar]

Ans. Alternating current is used to prevent electrolysis so that concentration of ions in the solution remains constant.

Q. 16. What is meant by cell constant?

Ans. Cell constant is the ratio of distance (l) between electrodes and area of cross-section (A). It is denoted by $\frac{l}{A}$. Its unit is cm^{-1} .

Q. 17. Define specific conductance or conductivity.

Ans. Specific conductance is defined as conductance of electrolyte when distance between electrodes is 1 cm and area of cross section is 1 cm^2 .

Q. 18. What is the effect of temperature on ionic conductance?

[CBSE 2019 (56/3/2)]

Ans. The ionic conductance increases with increase in temperature because the degree of dissociation increases with increase in temperature.

Q. 19. Write the mathematical expression for Kohlrausch's law.

Ans. $\Lambda_m^{\circ} = \nu_c \Lambda_c^{\circ} + \nu_a \Lambda_a^{\circ}$, where ν_c and ν_a are the number of cations and anions respectively in one formula unit of the compound.

Q. 20. Why on dilution the Λ_m of CH_3COOH increases drastically while that of CH_3COONa increases gradually? [NCERT Exemplar]

Ans. In the case of CH_3COOH , which is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation.



Q. 21. How much charge is required for the reduction of 1 mol of Zn^{2+} to Zn?

[CBSE Patna 2015]

Ans. $\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$

Quantity of charge required for the reduction of one mole of $\text{Zn}^{2+} = 2F = 2 \times 96500 \text{ C} = 193000 \text{ C}$ 1

[CBSE Marking Scheme 2015]

Q. 22. How will the pH of brine (aq. NaCl solution) be affected when it is electrolysed?

[NCERT Exemplar] [HOTS]

Ans. The pH of the solution will increase as NaOH is formed in the electrolytic cell.

Q. 23. Value of standard electrode potential for the oxidation of Cl^- ions is more positive than that of water, even then in the electrolysis of aqueous sodium chloride, why is Cl^- oxidised at anode instead of water? [NCERT Exemplar]

Ans. On electrolysis of aqueous sodium chloride, oxidation of water at anode requires over potential hence Cl^- is oxidised instead of water.

Q. 24. What is primary cell? Give an example.

Ans. A primary cell is one in which the redox reaction occurs only once and the cell becomes dead after some time and cannot be used again, e.g., dry cell.

Q. 25. Why does a dry cell become dead after a long time even if it has not been used?

Ans. Even though not in use, a dry cell becomes dead after some time because the acidic NH_4Cl corrodes the zinc container.

Q. 26. What is the role of ZnCl_2 in a dry cell?

Ans. ZnCl_2 combines with the NH_3 produced to form the complex salt $[\text{Zn}(\text{NH}_3)_2 \text{Cl}_2]$ otherwise the pressure developed due to NH_3 would crack the seal of the cell.

Q. 27. Unlike dry cell, the mercury cell has a constant cell potential throughout its useful life. Why?

[NCERT Exemplar]

Ans. Ions are not involved in the overall cell reaction of mercury cells.

Q. 28. Write the name of the electrolyte used in (i) fuel cell (ii) mercury cell.

Ans. (i) Concentrated aqueous KOH solution.
(ii) Moist mercuric oxide (HgO) mixed with KOH.

Q. 29. What is the overall electrochemical reaction taking place in rusting?

Ans. $2\text{Fe}(s) + \text{O}_2(g) + 4\text{H}^+(aq) \longrightarrow 2\text{Fe}^{2+}(aq) + 2\text{H}_2\text{O}(l)$

Q. 30. Write the chemical formula of rust.

Ans. $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

Q. 31. What is galvanization?

Ans. The process of coating zinc over iron is called galvanization.

Q. 32. What is cathodic protection?

Ans. A process in which a metal is connected with a more reactive metal which acts as anode and the metal to be protected acts as a cathode is known as cathodic protection.

Q. 33. Which type of a metal can be used in cathodic protection of iron against rusting?

Ans. A metal which is more electropositive than iron such as Al, Zn, Mg can be used in cathodic protection of iron against rusting.

Q. 34. Using the E° values of X and Y, predict which is better for coating the surface of iron to prevent rust and why?

Given: $[E^\circ(\text{Fe}^{2+}/\text{Fe}) = -0.44 \text{ V}]$, $[E^\circ(\text{X}^{2+}/\text{X}) = -2.36 \text{ V}]$, $[E^\circ(\text{Y}^{2+}/\text{Y}) = -0.14 \text{ V}]$

[CBSE 2019 (56/4/3)]

Ans. X, as its standard reduction potential is less than Y. Therefore, it will undergo oxidation more easily than Y.

Q. 35. Three iron sheets have been coated separately with three metals A, B and C whose standard electrode potentials are given below.

Metal	A	B	C	Iron
E°	-0.46 V	-0.66 V	-0.20 V	-0.44 V

Identify in which case rusting will take place faster when coating is damaged.

[HOTS]

Ans. As iron (-0.44 V) has lower standard reduction potential than C (-0.20 V) only and therefore when coating is broken, rusting will take place faster.



Short Answer Questions-I

Each of the following questions are of 2 marks.

Q. 1. At what pH of HCl solution will hydrogen gas electrode show electrode potential of -0.118 V? H_2 gas is passed at 298 K and 1 atm pressure.

Ans. $\text{H}^+ + e^- \longrightarrow \frac{1}{2}\text{H}_2$

Applying Nernst equation,

$$E_{\text{H}^+/\frac{1}{2}\text{H}_2} = E_{\text{H}^+/\frac{1}{2}\text{H}_2}^\circ - \frac{0.059}{n} \log \frac{1}{[\text{H}^+]}$$

$$-0.118 = 0 - \frac{0.059}{1} \log \frac{1}{[\text{H}^+]}$$

$$\begin{aligned} -0.118 &= 0.059 \log [H^+] \\ \text{or} \quad -0.118 &= -0.059 \text{ pH} \\ \text{pH} &= 2 \end{aligned}$$

Q. 2. Give reasons:

[CBSE 2023 (56/2/1)]

- Mercury cell delivers a constant potential during its life time.
- In the experimental determination of electrolytic conductance, Direct Current (DC) is not used.

Ans. (i) Overall reaction does not involve any ion whose concentration may change. Hence, it delivers a constant potential during its life time.
(ii) Direct current (DC) causes electrolysis of the solution consequently. The concentration of the electrolyte near the electrodes changes and this results in the change in the resistance (and hence the conductance) of the solution. Therefore direct current is not used.

Q. 3. The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm^{-1} . Calculate its molar conductivity. [CBSE Delhi 2013]

Ans.

$$\begin{aligned} \Lambda_m &= \frac{\kappa \times 1000}{C} \\ &= \frac{0.025 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.2 \text{ mol L}^{-1}} \\ &= 125 \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

Q. 4. The molar conductivity of a 1.5 M solution of an electrolyte is found to be $138.9 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate the conductivity of this solution. [CBSE (AI) 2012]

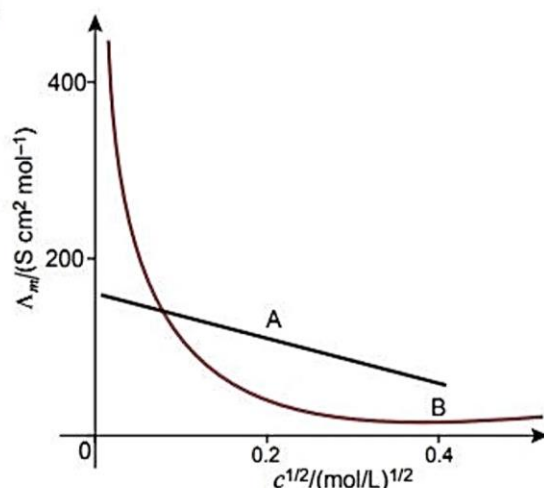
Ans.

$$\begin{aligned} \Lambda_m &= \frac{\kappa \times 1000}{M} \\ \kappa &= \frac{\Lambda_m \times M}{1000} \\ \kappa &= \frac{138.95 \text{ S cm}^2 \text{ mol}^{-1} \times 1.5 \text{ mol L}^{-1}}{1000 \text{ cm}^3 \text{ L}^{-1}} \\ &= 0.208425 \text{ cm}^{-1} \end{aligned}$$

Q. 5. The following curve is obtained when molar conductivity (Λ_m) is plotted against the square root of concentration, $c^{1/2}$ for two electrolytes A and B.

- How do you account for the increase in the molar conductivity of the electrolyte A on dilution?
- As seen from the graph, the value of limiting molar conductivity (Λ_m°) for electrolyte B cannot be obtained graphically. How can this value be obtained? [CBSE Sample Paper 2016]

Ans. (i) As seen from the graph, electrolyte 'A' is a strong electrolyte which is ionised almost completely in solutions. For strong electrolyte 'A', the number of ions does not increase appreciably on dilution and only mobility of ions increases due to decrease in interionic attraction. Therefore, molar conductivity increases a little as shown in graph by a straight line.
(ii) Limiting molar conductivity (Λ_m°) for weak electrolyte 'B' can be obtained by using Kohlrausch law of independent migration of ions which says that limiting molar conductivity of an electrolyte is equal to the sum of the individual contribution of the cation and anion of the electrolyte.



- Q. 6. State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? [CBSE (AI) 2014]

Ans.

(11) Ans:-
Kohlrausch's law of independent migration of ion states, at infinite dilution when dissociation is complete each ion makes a definite contribution to molar conductivity of the electrolyte irrespective of other ion with which it is associated.
i.e. each ion contributes to the molar conductivity of the electrolyte and their sum is finite.
e.g. $\Lambda_{HCl}^{\infty} = \Lambda_{Cl^-}^{\infty} + \Lambda_{H^+}^{\infty}$
Conductivity of a solution is the conductance of ions present in unit volume of solution. As with dilution, number of ions present in unit volume of solution decreases, conductivity also decreases.
[Topper's Answer (AI) 2014]

- Q. 7. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is $39.05 \text{ S cm}^2 \text{ mol}^{-1}$. [Given $\lambda_{(H^+)}^{\infty} = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda_{(CH_3COO^-)}^{\infty} = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$] [CBSE Delhi 2017]

Ans. $\Lambda_{(CH_3COOH)}^{\infty} = \lambda_{(CH_3COO^-)}^{\infty} + \lambda_{(H^+)}^{\infty}$
 $= (40.9 + 349.6) \text{ S cm}^2 \text{ mol}^{-1} = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$
 $\alpha = \frac{\Lambda_m^c}{\Lambda_m^{\infty}} = \frac{39.05 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.1$
 $\Rightarrow \alpha = 10\%$

- Q. 8. Calculate the time to deposit 1.27 g of copper at cathode when a current of 2 A was passed through the solution of CuSO_4 . (Molar mass of Cu = 63.5 g mol^{-1} , $1 \text{ F} = 96500 \text{ C mol}^{-1}$) [CBSE Allahabad 2015]

Ans. $\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$
63.5 g of copper is deposited by $2 \times 96500 \text{ C}$.
 $\therefore 1.27 \text{ g of copper will be deposited by } \frac{2 \times 96500 \times 1.27}{63.5} \text{ C} = 3860 \text{ C}$
 $I = 2 \text{ A}, Q = 3860 \text{ C}$
 $\therefore t = \frac{Q}{I} = \frac{3860}{2} = 1930 \text{ s}$

- Q. 9. How many moles of mercury will be produced by electrolysis of $1.0 \text{ M Hg(NO}_3)_2$ solution with a current of 2.00 A for 3 hours? [CBSE (AI) 2011]

Ans. Mass of mercury produced at the cathode,

$$m = Z \times I \times t = \frac{M \times I \times t}{n \times F}$$

$$m = \frac{M \text{ g mol}^{-1} \times 2 \text{ A} \times 3 \times 60 \times 60 \text{ s}}{2 \times 96500 \text{ C mol}^{-1}}$$

$$= 0.1119 \times M \text{ g}$$

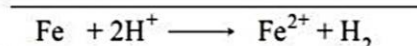
$$\text{No. of moles of mercury produced} = \frac{0.1119 \times M \text{ g}}{M \text{ g mol}^{-1}} = 0.1119 \text{ moles}$$

- Q. 10. Calculate the emf of the following cell at 298 K:
 $\text{Fe(s)} | \text{Fe}^{2+}(0.01\text{M}) || \text{H}^+(1\text{M}) | \text{H}_2(\text{g}) (1 \text{ bar}), \text{Pt(s)}$
Given: $E_{\text{Cell}}^{\circ} = 0.44 \text{ V}$.

[CBSE 2023 (56/5/2)]

Ans. At anode : $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2e^-$

At cathode: $2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$



Substituting the values $n = 2$, $E_{\text{cell}}^{\circ} = 0.44 \text{ V}$, $[\text{Fe}^{2+}] = 1 \times 10^{-2} \text{ M}$, $[\text{H}^+] = 1 \text{ M}$, in Nernst equation for above cell reaction

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}, \text{ we get}$$

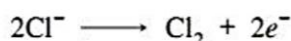
$$E_{\text{cell}} = 0.44 - \frac{0.059}{2} \log \frac{10^{-2}}{(1)^2} = 0.44 + \frac{0.059}{2} \times 2 \times \log 10$$

$$E_{\text{cell}}^{\circ} = 0.499 \text{ V}$$

Q. 11. How many molecules of chlorine should be deposited from molten sodium chloride in one minute by a current of 300 milliampere?

Ans. $Q = I \times t$

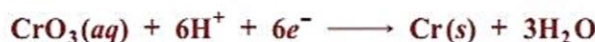
Here, $I = \frac{300}{1000} = 0.3 \text{ A}$; $t = 60 \text{ s}$; $Q = 0.3 \text{ A} \times 60 \text{ s} = 18 \text{ C}$



$$2 \times 96500 \text{ C deposit } \text{Cl}_2 = 1 \text{ mol}$$

$$\therefore 18 \text{ C will deposit } \text{Cl}_2 = \frac{1 \text{ mol} \times 18 \text{ C} \times 6.022 \times 10^{23}}{2 \times 96500 \text{ C}} \text{ molecules} = 5.616 \times 10^{19} \text{ molecules}$$

Q. 12 Chromium metal is electroplated using an acidic solution containing CrO_3 according to the following equation:



Calculate how many grams of chromium will be electroplated by 24,000 coulombs. How long will it take to electroplate 1.5 g chromium using 12.5 A current?

[Atomic mass of $\text{Cr} = 52 \text{ g mol}^{-1}$, $1 \text{ F} = 96500 \text{ C mol}^{-1}$]

Ans. $6 \times 96500 \text{ C deposit } \text{Cr} = 52 \text{ g}$

$$\therefore 24,000 \text{ C will deposit } \text{Cr} = \frac{52 \text{ g}}{6 \times 96500 \text{ C}} \times 24,000 \text{ C} = 2.155 \text{ g}$$

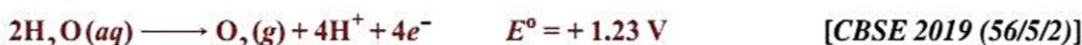
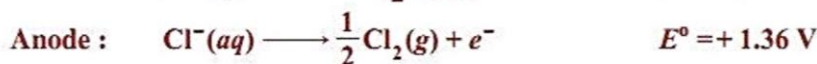
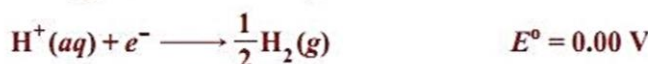
$$52 \text{ g of Cr is deposited by } 6 \times 96500 \text{ C.}$$

$$\therefore 1.5 \text{ g of Cr require} = \frac{6 \times 96500 \text{ C}}{52 \text{ g}} \times 1.5 \text{ g} = 16701.9 \text{ C}$$

$$Q = I \times t \Rightarrow t = \frac{Q}{I}$$

$$\therefore \text{Time for which the current is passed} = \frac{16701.9 \text{ C}}{12.5 \text{ A}} = 1336.15 \text{ s}$$

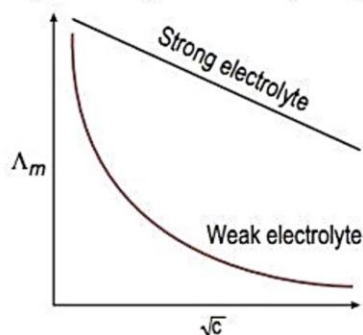
Q. 13. Following reactions may occur at cathode and anode during electrolysis of aqueous sodium chloride. What products will be held at anode and cathode? Use given E° values to justify your answer.



Ans. $\text{H}_2(\text{g})$ is produced at cathode due to greater E° value of H^+ ion and $\text{Cl}_2(\text{g})$ is produced at anode due to over-potential of oxygen.

- Q. 14.** Solutions of two electrolytes 'A' and 'B' are diluted. The Λ_m of 'B' increases 1.5 times while that of A increases 25 times. Which of the two is a strong electrolyte? Justify your answer. Graphically show the behaviour of 'A' and 'B'. [CBSE 2022]

Ans. B is a strong electrolyte. The molar conductivity increases slowly with dilution as there is no increase in number of ions on dilution as strong electrolytes are completely dissociated.



- Q. 15.** Name the cell which:

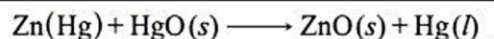
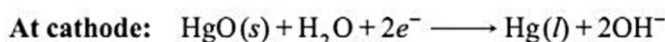
[CBSE 2023 (56/4/2)]

- was used in Apollo Space programme.
- is used in automobiles and inverters.
- is suitable for hearing aids and watches.
- does not give a steady potential and is used in transistors.

Ans. (i) Fuel cells (ii) Lead storage battery/cell
(iii) Mercury cell (iv) Dry cell

- Q. 16.** Write the name of the cell which is generally used in hearing aids. Write the reactions taking place at the anode and the cathode of this cell. [CBSE (AI) 2017]

Ans. Mercury cell

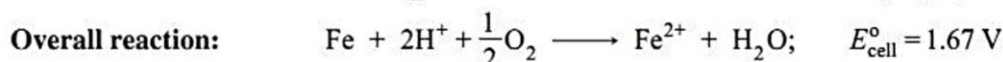
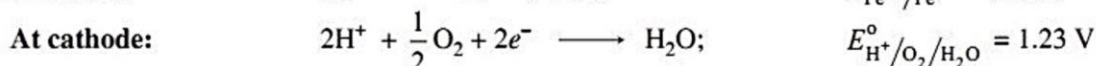
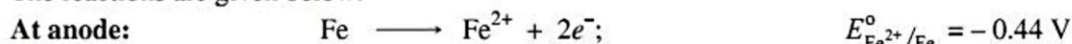


- Q. 17.** Write electrode reactions taking place in (i) Ni-Cd cell, (ii) Lead Acid Accumulator.

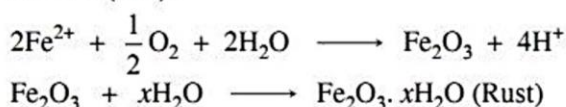
Ans. (i) $\text{Cd(s)} + 2\text{OH}^-(\text{aq}) \longrightarrow \text{Cd(OH)}_2(\text{s}) + 2e^-$ (at anode)
 $\text{NiO}_2(\text{s}) + 2\text{H}_2\text{O} + 2e^- \longrightarrow \text{Ni(OH)}_2(\text{s}) + 2\text{OH}^-(\text{aq})$ (at cathode)
 (ii) $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \longrightarrow \text{PbSO}_4(\text{s}) + 2e^-$ (at anode)
 $\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2e^- \longrightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$ (at cathode)

- Q. 18.** The chemistry of corrosion of iron is essentially an electrochemical phenomenon. Explain the reactions occurring during the corrosion of iron in the atmosphere. [CBSE Delhi 2011]

Ans. According to electrochemical theory of rusting, the impure iron surface behaves like small electrochemical cell in the presence of water containing dissolved oxygen or carbon dioxide. In this cell pure iron acts as anode and impure iron surface acts as cathode. Moisture having dissolved CO_2 or O_2 acts as an electrolyte. The reactions are given below:



The Fe^{2+} ions are further oxidised by atmospheric oxygen to Fe^{3+} ions, which comes out in the form of hydrated ferric oxide (rust).





Short Answer Questions-II

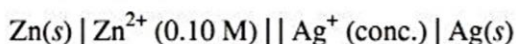
Each of the following questions are of 3 marks.

- Q. 1.** One half-cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. The other half-cell consists of a zinc electrode in a 0.10 M solution of $\text{Zn}(\text{NO}_3)_2$. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver ions in the solution.

[Given: $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.763 \text{ V}$, $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$]

[CBSE (F) 2010]

Ans. Electrochemical cell



$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{R}} - E^\circ_{\text{L}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} \\ &= 0.80 \text{ V} - (-0.763 \text{ V}) = 1.563 \text{ V} \end{aligned}$$

We know that,

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \\ 1.48 &= 1.563 - \frac{0.0591}{2} \log \frac{[0.10]}{[\text{Ag}^+]^2} \end{aligned}$$

$$\log \frac{[0.10]}{[\text{Ag}^+]^2} = \frac{0.083}{0.02955} = 2.8088$$

Or $\frac{[0.10]}{[\text{Ag}^+]^2} = \text{antilog } 2.8088 = 643.87$

$$[\text{Ag}^+]^2 = \frac{0.10}{643.87} = 1.553 \times 10^{-4}$$

$$[\text{Ag}^+] = 1.246 \times 10^{-2} \text{ M}$$

- Q. 2.** A zinc rod is dipped in 0.1 M solution of ZnSO_4 . The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential ($E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$).

Ans. The electrode reaction written as reduction reaction is



Applying Nernst equation, we get

$$E_{\text{Zn}^{2+}/\text{Zn}} = E^\circ_{\text{Zn}^{2+}/\text{Zn}} - \frac{0.0591}{2} \log \frac{1}{[\text{Zn}^{2+}]}$$

As 0.1 M ZnSO_4 solution is 95% dissociated, this means that in the solution,

$$[\text{Zn}^{2+}] = \frac{95}{100} \times 0.1 \text{ M} = 0.095 \text{ M}$$

$$\begin{aligned} E_{\text{Zn}^{2+}/\text{Zn}} &= -0.76 - \frac{0.0591}{2} \log \frac{1}{0.095} \\ &= -0.76 - 0.02955 (\log 1000 - \log 95) = -0.76 - 0.02955 (3 - 1.9777) \\ &= -0.76 - 0.03021 = -0.79021 \text{ V} \end{aligned}$$

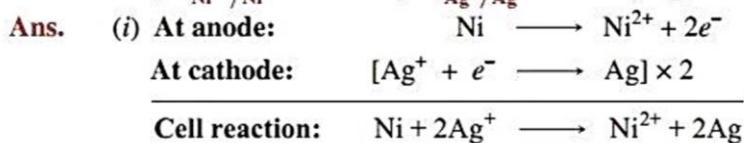
- Q. 3.** A strip of nickel metal is placed in a 1 molar solution of $\text{Ni}(\text{NO}_3)_2$ and a strip of silver metal is placed in a 1 molar solution of AgNO_3 . An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter.

(i) Write the balanced equation for the overall reaction occurring in the cell and calculate the cell potential.

- (ii) Calculate the cell potential, E , at 25°C for the cell if the initial concentration of $\text{Ni}(\text{NO}_3)_2$ is 0.100 molar and the initial concentration of AgNO_3 is 1.00 molar.

$$[E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.25 \text{ V}; E_{\text{Ag}^+/\text{Ag}}^\circ = 0.80 \text{ V}, \log 10^{-1} = -1]$$

[CBSE (F) 2012]



$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

$$= E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Ni}^{2+}/\text{Ni}}^\circ = 0.80 \text{ V} - (-0.25 \text{ V})$$

$$E_{\text{cell}}^\circ = 1.05 \text{ V}$$

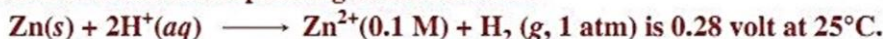
$$(ii) E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

$$\text{Here, } n = 2, E_{\text{cell}}^\circ = 1.05 \text{ V}, [\text{Ni}^{2+}] = 0.1 \text{ M}, [\text{Ag}^+] = 1.0 \text{ M}$$

$$E_{\text{cell}} = 1.05 \text{ V} - \frac{0.059}{2} \log \frac{(0.1)}{(1)^2}$$

$$E_{\text{cell}} = 1.05 \text{ V} - 0.0295 \log 10^{-1} = 1.05 + 0.0295 \text{ V} = 1.0795 \text{ V}$$

- Q. 4. The emf of a cell corresponding to the reaction.

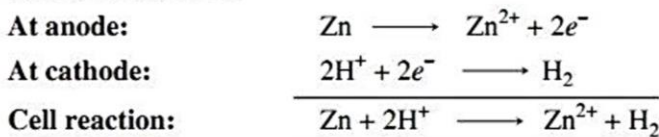


Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.

$$[E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76 \text{ V}, E_{\text{H}^+/\text{H}_2}^\circ = 0 \text{ V}]$$

[HOTS]

Ans. Half-cell reactions:



$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2}$$

$$= (E_{\text{H}^+/\text{H}_2}^\circ - E_{\text{Zn}^{2+}/\text{Zn}}^\circ) - \frac{0.0591}{2} \log \frac{0.1}{[\text{H}^+]^2}$$

$$= [0 - (-0.76)] - 0.02955 [\log 10^{-1} - 2 \log (\text{H}^+)]$$

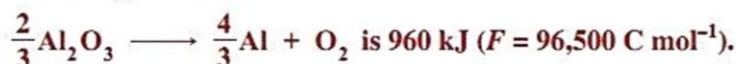
$$0.28 = 0.76 - 0.02955 (-1 + 2 \text{ pH})$$

$$2 \text{ pH} - 1 = 16.244$$

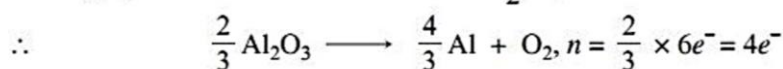
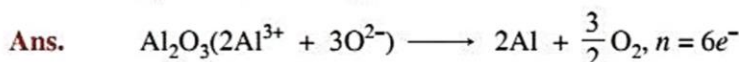
$$\text{pH} = 8.62$$

$$[\because \text{pH} = -\log (\text{H}^+)]$$

- Q. 5. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C . The free energy change for the decomposition reaction



[HOTS]



$$\Delta_r G = 960 \times 1000 = 960000 \text{ J}$$

$$\Delta_r G = -nFE_{\text{cell}}^\circ$$

$$\Rightarrow E_{\text{cell}} = -\frac{\Delta_r G}{nF} = \frac{-960000}{4 \times 96500} = -2.487 \text{ V}$$

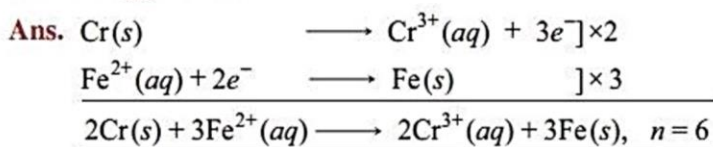
\therefore Minimum potential difference needed to reduce Al_2O_3 is -2.487 V .

Q. 6. Calculate $\Delta_r G^\circ$ and $\log K_c$ for the following reaction at 298 K:



Given: $E^\circ_{\text{cell}} = 0.30 \text{ V}$

[CBSE (F) 2016]



Here, $n = 6$, $E^\circ_{\text{cell}} = 0.30 \text{ V}$

Substituting the values in the expression, $\log K_c = \frac{n}{0.059} E^\circ_{\text{cell}}$, we get

$$\log K_c = \frac{6}{0.059} \times 0.30$$

or $\log K_c = 30.5085$

$$K_c = \text{Antilog}(30.5085)$$

or $K_c = 3.224 \times 10^{30}$

$$\begin{aligned}\Delta G^\circ &= -nFE^\circ_{\text{cell}} \\ &= -6 \times 96500 \times 0.30 = -173700 \text{ J mol}^{-1} \\ \Delta G^\circ &= -173.7 \text{ kJ mol}^{-1}\end{aligned}$$

Q. 7. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is $5.55 \times 10^3 \text{ ohm}$. Calculate its resistivity, conductivity and molar conductivity. [CBSE (AI) 2012]

Ans. $A = \pi r^2 = 3.14 \times \left(\frac{1}{2} \text{ cm}\right)^2 = 0.785 \text{ cm}^2$; $l = 50 \text{ cm}$

$$\text{Resistivity, } \rho = \frac{R \times A}{l} = \frac{5.55 \times 10^3 \text{ ohm} \times 0.785 \text{ cm}^2}{50 \text{ cm}} = 87.135 \text{ ohm cm}$$

$$\text{Conductivity, } \kappa = \frac{1}{\rho} = \frac{1}{87.135 \text{ ohm cm}} = 0.01148 \text{ S cm}^{-1}$$

$$\begin{aligned}\text{Molar Conductivity, } \Lambda_m &= \frac{\kappa \times 1000}{M} \\ &= \frac{0.01148 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.05 \text{ mol L}^{-1}} = 229.6 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

Q. 8. From the following molar conductivities at infinite dilution, calculate Λ_m° for NH_4OH .

$$\Lambda_m^\circ \text{ for } \text{Ba}(\text{OH})_2 = 457.6 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ \text{ for } \text{BaCl}_2 = 240.6 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ \text{ for } \text{NH}_4\text{Cl} = 129.8 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Ans. $\Lambda_{m(\text{NH}_4\text{OH})}^\circ = \lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{OH}^-}^\circ$

$$\begin{aligned}&= (\lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{Cl}^-}^\circ) + \frac{1}{2}(\lambda_{\text{Ba}^{2+}}^\circ + 2\lambda_{\text{OH}^-}^\circ) - \frac{1}{2}(\lambda_{\text{Ba}^{2+}}^\circ + 2\lambda_{\text{Cl}^-}^\circ) \\ &= \Lambda_{m(\text{NH}_4\text{Cl})}^\circ + \frac{1}{2}[\Lambda_{m(\text{Ba}(\text{OH})_2)}^\circ] - \frac{1}{2}[\Lambda_{m(\text{BaCl}_2)}^\circ] \\ &= 129.8 + \frac{1}{2} \times 457.6 - \frac{1}{2} \times 240.6 \\ &= 238.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\end{aligned}$$

Q. 9. Conductivity of $2.5 \times 10^{-4} \text{ M}$ methanoic acid is $5.25 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociation.

[Given: $\lambda^\circ(\text{H}^+) = 349.5 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda^\circ(\text{HCOO}^-) = 50.5 \text{ S cm}^2 \text{ mol}^{-1}$.] [CBSE Allahabad 2015]

Ans.

$$\Lambda_m^c = \frac{\kappa \times 1000}{M}$$

$$\Lambda_m^c = \frac{5.25 \times 10^{-5} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{2.5 \times 10^{-4} \text{ mol L}^{-1}} = 210 \text{ S cm}^2 \text{ mol}^{-1}$$

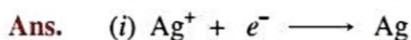
$$\begin{aligned}\Lambda_m^0(\text{HCOOH}) &= \Lambda_{\text{HCOO}^-}^0 + \Lambda_{\text{H}^+}^0 \\ &= 50.5 \text{ S cm}^2 \text{ mol}^{-1} + 349.5 \text{ S cm}^2 \text{ mol}^{-1} = 400 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_m^c}{\Lambda_m^0} = \frac{210 \text{ S cm}^2 \text{ mol}^{-1}}{400 \text{ S cm}^2 \text{ mol}^{-1}} = 0.525$$

or

$$\alpha = 52.5\%$$

- Q. 10.** (i) A current of 1.50 A was passed through an electrolytic cell containing AgNO_3 solution with inert electrodes. The weight of Ag deposited was 1.50 g. How long did the current flow?
(ii) Write the reactions taking place at the anode and cathode in the above cell.
(iii) Give reactions taking place at the two electrodes if these are made up of Ag.



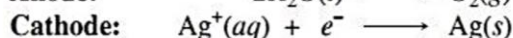
Quantity of charge required to deposit 108 g of silver = 96500 C

$$\therefore \text{Quantity of charge required to deposit 1.50 g of silver} = \frac{96500}{108} \times 1.50 = 1340.28 \text{ C}$$

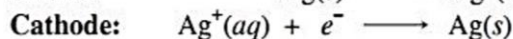
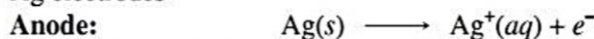
$$t = \frac{Q}{I}$$

$$\therefore \text{Time taken} = \frac{1340.28}{1.50} = 893.52 \text{ s}$$

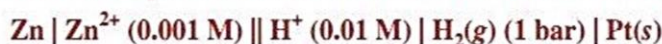
(ii) Inert electrodes



(iii) Ag electrodes

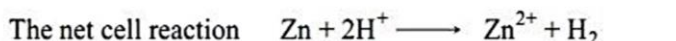
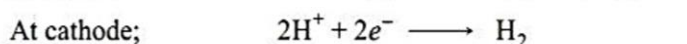
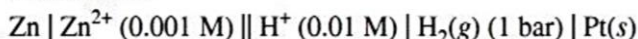


- Q. 11.** Write the Nernst equation and calculate the emf of the following cell at 298 K. [CBSE 2022 (56/4/2)]



$$\text{Given: } E_{\text{Zn}^{2+}/\text{Zn}}^0 = -0.76 \text{ V}, E_{\text{H}^+/\text{H}_2}^0 = 0.00 \text{ V}, [\log 10 = 1]$$

Ans. Given cell is



Nernst equation for the given cell is

$$\begin{aligned}E_{\text{cell}} &= E_{\text{cell}}^0 - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{H}^+]^2} \\ &= (0.00 + 0.76) - \frac{0.0591}{2} \log \frac{0.001}{0.01 \times 0.01} \\ &= \frac{.76}{1} - \frac{.0591}{2} = \frac{1.52 - .059}{2} = \frac{1.461}{2} = 0.7305 \text{ V}\end{aligned}$$

- Q. 12.** (i) The cell in which the following reaction occurs:



has $E_{\text{cell}}^0 = 0.236 \text{ V}$ at 298 K. Calculate the standard Gibbs energy of the cell reaction.

(Given : 1 F = 96500 C mol⁻¹)

(ii) How many electrons flow through a metallic wire if a current of 0.5A is passed for 2 hours?

(Given : 1 F = 96500 C mol⁻¹)

[CBSE (AI) 2017]

Ans.

Ans. (b) Given reaction is:-
 $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^{-}(\text{aq}) \longrightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{s})$

∴ n-factor, $n=2$
 $E^{\circ}_{\text{cell}} = 0.236 \text{ V}$ (given)

$\Delta G^{\circ} = ?$
 We know,
 $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$
 $= -(2)(96500)(0.236) = -45548 \text{ J mol}^{-1}$
 $\Delta G^{\circ} = -45.548 \text{ KJ mol}^{-1}$

(b) Given:- Current, $I = 0.5 \text{ A}$ & time, $t = 2 \text{ hrs}$
 Let 'n' electrons pass through it.
 We know
 charge, $Q = It = ne$
 'e' is charge on one electron. ($e = 1.6 \times 10^{-19} \text{ C}$)
 Substituting, we get,
 $0.5 \times 2 \times 3600 = x \times 1.6 \times 10^{-19}$
 $x = \frac{0.5 \times 2 \times 3600}{1.6 \times 10^{-19}}$
 $x = 2.25 \times 10^{22} \text{ electrons}$

Ann [Topper's Answer (AI) 2017]



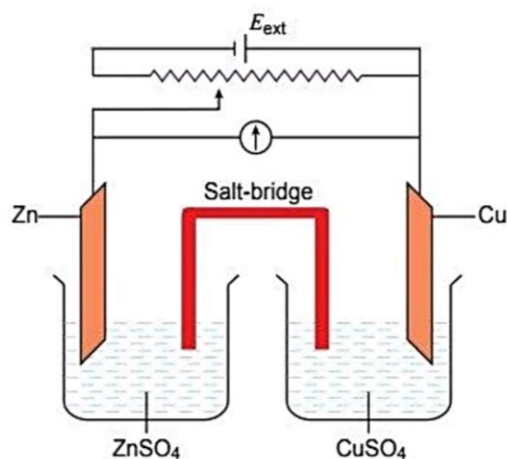
Long Answer Questions

Each of the following questions are of 5 marks.

- Q. 1. The electrochemical cell given alongside converts the chemical energy released during the redox reaction
 $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$
 to electrical energy. It gives an electrical potential of 1.1 V when concentration Zn^{2+} and Cu^{2+} ions is unity. State the direction of flow of current and also specify whether zinc and copper are deposited or dissolved at their respective electrodes when:
- an external opposite potential of less than 1.1 V is applied.
 - an external potential of 1.1 V is applied.
 - an external potential of greater than 1.1 V is applied.
- [HOTS]

Ans. (i) Reaction continues to take place.

Electrons flow from Zn electrode to copper electrode, hence current flows from Cu to Zn. Zn dissolves and copper deposits at their respective electrodes.



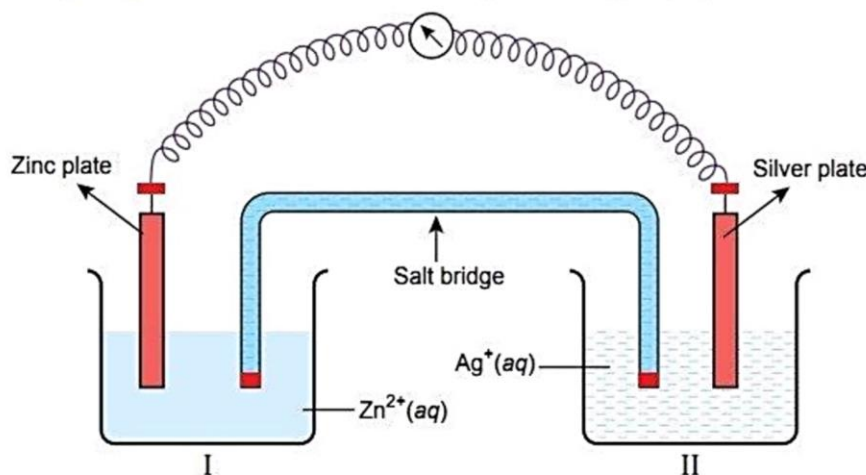
(ii) The reaction stops and no current flows.

A state of equilibrium is achieved and no change is observed at zinc and copper electrodes.

(iii) Reaction takes place in opposite directions.

Electrons flow from copper electrode to zinc electrode and hence current flows from Zn to Cu. Zinc deposits and copper dissolves at their respective electrodes. The cell functions as an electrolytic cell.

Q. 2. Consider the figure given below and answer the questions (i) to (vi):



(i) Write the direction of electron flow.

(ii) Is silver plate the anode or cathode?

(iii) What will happen if salt bridge is removed?

(iv) When will the cell stop functioning?

(v) How will concentration of Zn^{2+} ions and Ag^+ ions be affected when the cell functions?

(vi) How will the concentration of Zn^{2+} ions and Ag^+ ions be affected after the cell becomes 'dead'?

[NCERT Exemplar] [HOTS]

Ans. (i) Electrons move from Zn to Ag.

(ii) Ag is the cathode.

(iii) Cell will stop functioning.

(iv) When $E_{\text{cell}} = 0$.

(v) Concentration of Zn^{2+} ions will increase and concentration of Ag^+ ions will decrease.

(vi) When $E_{\text{cell}} = 0$, equilibrium is reached and concentration of Zn^{2+} ions and Ag^+ ions will not change.

Q. 3. Calculate e.m.f and ΔG for the following cell at 298 K:



[Given: $E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} = -2.37 \text{ V}$, $E_{\text{Ag}^+/\text{Ag}}^{\circ} = +0.80 \text{ V}$]

[CBSE Guwahati 2015]

Ans. At anode: $\text{Mg} \longrightarrow \text{Mg}^{2+} + 2e^-$

At cathode: $[\text{Ag}^+ + e^- \longrightarrow \text{Ag}] \times 2$



$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ &= E_{\text{Ag}^+/\text{Ag}}^{\circ} - E_{\text{Mg}^{2+}/\text{Mg}}^{\circ} \\ &= 0.80 \text{ V} - (-2.37 \text{ V}) = 3.17 \text{ V} \end{aligned}$$

Substituting $E_{\text{cell}}^{\circ} = 3.17 \text{ V}$, $n = 2$, $[\text{Mg}^{2+}] = 1 \times 10^{-2} \text{ M}$, $[\text{Ag}^+] = 1 \times 10^{-4} \text{ M}$ in Nernst equation for above cell reaction,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}, \text{ we get}$$

$$E_{\text{cell}} = 3.17 - \frac{0.059}{2} \log \frac{10^{-2}}{(10^{-4})^2}$$

$$E_{\text{cell}} = 3.17 - 0.0295 \log 10^6$$

$$E_{\text{cell}} = 3.17 - 0.177 \text{ V}$$

$$E_{\text{cell}} = 2.993 \text{ V} = \mathbf{2.993 \text{ V}}$$

Substituting $n = 2$, $F = 96500 \text{ C mol}^{-1}$, $E_{\text{cell}} = 2.993 \text{ V}$ in the expression, $\Delta G = -nFE_{\text{cell}}$ we get

$$\Delta G = -2 \times 96500 \text{ C mol}^{-1} \times 2.993 \text{ V}$$

$$\Delta G = -577649 \text{ J mol}^{-1} = \mathbf{-577.649 \text{ kJ mol}^{-1}}$$

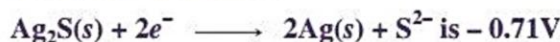
- Q. 4. (i) Calculate the standard free energy change for the following reaction at 25°C .



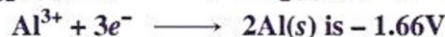
$$E_{\text{Au}^{3+}/\text{Au}}^\circ = +1.50 \text{ V}, \quad E_{\text{Ca}^{2+}/\text{Ca}}^\circ = -2.87 \text{ V}$$

Predict whether the reaction will be spontaneous or not at 25°C . Which of the above two half cells will act as an oxidising agent and which one will be a reducing agent?

- (ii) Tarnished silver contains Ag_2S . Can this tarnish be removed by placing tarnished silver ware in an aluminium pan containing an inert electrolytic solution such as NaCl ? The standard electrode potential for half reaction: [HOTS]



and for



Ans.

(i)

$$E_{\text{cell}}^\circ = E_{\text{Ca}^{2+}/\text{Ca}}^\circ - E_{\text{Au}^{3+}/\text{Au}}^\circ$$

$$= (-2.87 \text{ V}) - (1.50 \text{ V}) = -4.37 \text{ V}$$

$$\Delta_r G_{\text{cell}}^\circ = -nFE_{\text{cell}}^\circ$$

$$= -6 \times 96500 \times (-4.37 \text{ V}) = \mathbf{+2530.230 \text{ kJ/mol}}$$

Since $\Delta_r G^\circ$ is positive, therefore, reaction is non-spontaneous.

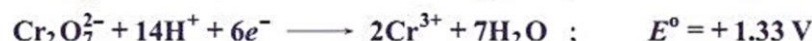
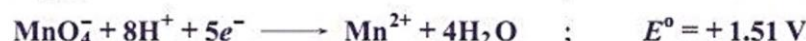
Au^{3+}/Au half cell will be an oxidising agent while Ca^{2+}/Ca half cell will be a reducing agent.

- (ii) E_{cell}° for reaction of tarnished silver ware with aluminium pan is

$$(-0.71 \text{ V}) - (-1.66 \text{ V}) \text{ i.e., } \mathbf{+0.95 \text{ V}}$$

Tarnished silver ware, therefore, can be cleaned by placing it in an aluminium pan as E_{cell}° is positive.

- Q. 5. (i) On the basis of E° values identify which amongst the following is the strongest oxidising agent



- (ii) The following figure 2, represents variation of (Λ_m) vs \sqrt{c} for an electrolyte. Here Λ_m is the molar conductivity and c is the concentration of the electrolyte.

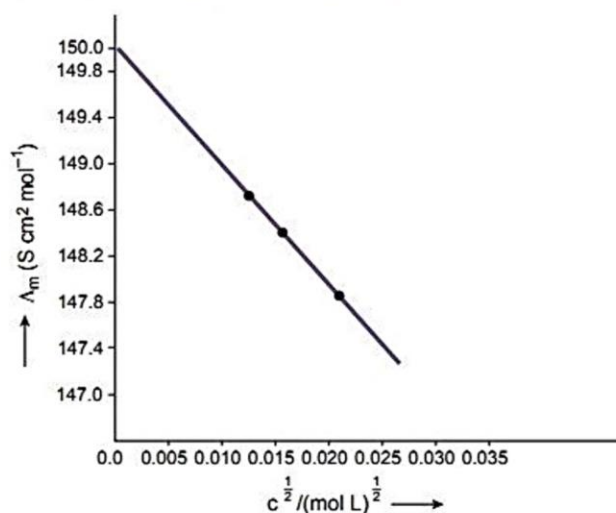


Figure 2

- (a) Define molar conductivity.
(b) Identify the nature of electrolyte on the basis of the above plot. Justify your answer.
(c) Determine the value of Λ_m° for the electrolyte.
(d) Show how to calculate the value of A for the electrolyte using the above graph.

[CBSE Sample Paper 2021]

Ans. (i) MnO_4^-

(ii) (a) Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross-section A and distance of unit length.

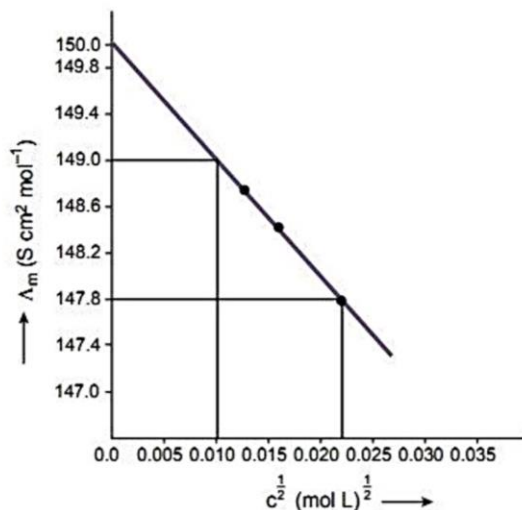
(b) The given plot shows that molar conductivity (Λ_m) increases slowly with dilution so the electrolyte must be strong.

(c) $\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$

From the given plot we find that

$\Lambda_m^\circ = 150 \text{ S cm}^2 \text{ mol}^{-1}$

(d)



$$A = -\text{slope} = -\frac{149 - 147.8}{0.010 - 0.022}$$

$$A = 100 \text{ S cm}^2 \text{ mol}^{-1} / (\text{mol/L}^{-1})^{1/2}$$

Q. 6. (i) Represent the cell in which the following reaction takes place:



Calculate the emf if $E_{\text{cell}}^\circ = 1.41 \text{ V}$.

(ii) How does molar conductivity vary with increase in concentration for strong electrolyte and weak electrolyte? How can you obtain limiting molar conductivity (Λ_m°) for weak electrolyte?

[CBSE 2019 (56/2/2)]

Ans. (i) $\text{Al}(s) | \text{Al}^{3+}(0.01 \text{ M}) || \text{Ni}^{2+}(0.1 \text{ M}) | \text{Ni}(s)$

1

$$E_{\text{(cell)}} = E_{\text{cell}}^\circ - \frac{0.059}{6} \log \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3}, \quad \frac{1}{2}$$

$$E_{\text{(cell)}} = 1.41 \text{ V} - \frac{0.059}{6} \log \frac{(0.01)^2}{(0.1)^3} \quad 1$$

$$E_{\text{(cell)}} = 1.4198 \text{ V}$$

or $E_{\text{cell}} = 1.42 \text{ V} \quad \frac{1}{2}$

(ii) Λ_m decreases with increase in concentration for both strong and weak electrolyte

Λ_m° can be obtained for weak electrolyte by applying Kohlrausch law / $\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ \quad 1 + 1$

[CBSE Marking Scheme 2019 (56/2/2)]

- Q. 7. At 291 K, the molar conductivities at infinite dilution of NH_4Cl , NaOH and NaCl are 129.8, 217.4 and $108.9 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. If the molar conductivity of a centinormal solution of NH_4OH is $9.33 \text{ S cm}^2 \text{ mol}^{-1}$, what is the percentage dissociation of NH_4OH at this dilution? Also calculate the dissociation constant of NH_4OH . [HOTS]

Ans. Here, we are given:

$$\Lambda_m^\circ \text{ for } \text{NH}_4\text{Cl} = 129.8 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ \text{ for } \text{NaOH} = 217.4 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ \text{ for } \text{NaCl} = 108.9 \text{ S cm}^2 \text{ mol}^{-1}$$

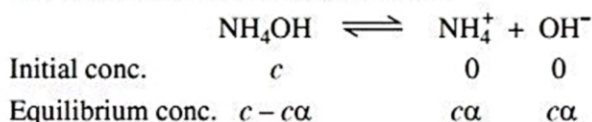
By Kohlrausch's law,

$$\begin{aligned}\Lambda_m^\circ \text{ for } \text{NH}_4\text{OH} &= \lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{OH}^-}^\circ \\ &= \Lambda_m^\circ (\text{NH}_4\text{Cl}) + \Lambda_m^\circ (\text{NaOH}) - \Lambda_m^\circ (\text{NaCl}) \\ &= [129.8 + 217.4 - 108.9] \text{ S cm}^2 \text{ mol}^{-1} = 238.3 \text{ S cm}^2 \text{ mol}^{-1} \\ \Lambda_m^c &= 9.33 \text{ S cm}^2 \text{ mol}^{-1} \text{ (Given)}\end{aligned}$$

$$\therefore \text{Degree of dissociation } (\alpha) = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{9.33}{238.3} = 0.0392$$

or Percentage dissociation = $0.0392 \times 100 = 3.92$

Calculation of dissociation constant



$$K = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

Substituting, $c = 0.01 \text{ N} = 0.01 \text{ M}$, and $\alpha = 0.0392$, we get

$$\text{We get, } K = \frac{(0.01)(0.0392)^2}{1 - 0.0392} = \frac{10^{-2} \times (3.92 \times 10^{-2})^2}{0.9608} = 1.599 \times 10^{-5}$$

- Q. 8. (i) State Kohlrausch law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch law.

(ii) Calculate Λ_m° for acetic acid.

$$\text{Given that } \Lambda_m^\circ (\text{HCl}) = 426 \text{ S cm}^2 \text{ mol}^{-1}, \Lambda_m^\circ (\text{NaCl}) = 126 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_m^\circ (\text{CH}_3\text{COONa}) = 91 \text{ S cm}^2 \text{ mol}^{-1}$$

[CBSE Delhi 2010]

Ans. (i) For definition refer to Basic Concepts Point 12.

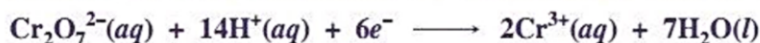
$$\text{Expression for the molar conductivity of acetic acid: } \Lambda_m^\circ (\text{CH}_3\text{COOH}) = \Lambda_{\text{CH}_3\text{COO}^-}^\circ + \Lambda_{\text{H}^+}^\circ$$

$$\begin{aligned}\Lambda_m^\circ (\text{CH}_3\text{COOH}) &= \Lambda_{\text{CH}_3\text{COO}^-}^\circ + \Lambda_{\text{H}^+}^\circ \\ &= \Lambda_{\text{CH}_3\text{COO}^-}^\circ + \Lambda_{\text{Na}^+}^\circ + \Lambda_{\text{H}^+}^\circ + \Lambda_{\text{Cl}^-}^\circ - (\Lambda_{\text{Na}^+}^\circ + \Lambda_{\text{Cl}^-}^\circ) \\ &= \Lambda_{\text{m}(\text{CH}_3\text{COONa})}^\circ + \Lambda_{\text{m}(\text{HCl})}^\circ - \Lambda_{\text{m}(\text{NaCl})}^\circ \\ &= (91 + 426 - 126) \text{ S cm}^2 \text{ mol}^{-1} = 391 \text{ S cm}^2 \text{ mol}^{-1}\end{aligned}$$

- Q. 9. (i) What type of a battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery.

(ii) Calculate the potential for half-cell containing

$0.10 \text{ M K}_2\text{Cr}_2\text{O}_7(aq)$, $0.20 \text{ M Cr}^{3+}(aq)$ and $1.0 \times 10^{-4} \text{ M H}^+(aq)$. The half cell reaction is

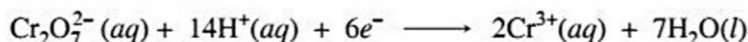


and the standard electrode potential is given as $E^\circ = 1.33 \text{ V}$.

[CBSE (AI) 2011]

Ans. (i) Refer to Points to remember 26(b).

(ii) For half cell reaction



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}$$

Here, $E^{\circ} = 1.33 \text{ V}$, $n = 6$, $[\text{Cr}^{3+}] = 0.2 \text{ M}$, $[\text{Cr}_2\text{O}_7^{2-}] = 0.1 \text{ M}$, $[\text{H}^+] = 1 \times 10^{-4} \text{ M}$

Substituting these values in the given expression, we get

$$\begin{aligned} E_{\text{cell}} &= 1.33 \text{ V} - \frac{0.0591}{6} \log \frac{(0.20)^2}{(0.1)(10^{-4})^{14}} \\ &= 1.33 \text{ V} - \frac{0.0591}{6} \log (4 \times 10^{55}) \\ &= 1.33 \text{ V} - \frac{0.0591}{6} [\log 4 + \log 10^{55}] \\ &= 1.33 \text{ V} - \frac{0.0591}{6} [2 \log 2 + 55 \log 10] \\ &= 1.33 \text{ V} - \frac{0.0591}{6} [2 \times 0.3010 + 55] \\ &= 1.33 \text{ V} - 0.548 \text{ V} = 0.782 \text{ V} \end{aligned}$$

Q. 10. (i) Define the following terms:

(a) Limiting molar conductivity

(b) Fuel cell

[CBSE (AI) 2014]

(ii) Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100Ω . If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520Ω , calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 mol L^{-1} KCl solution is $1.29 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$.

Ans. (i) (a) The limiting value of molar conductivity when concentration approaches to zero is called limiting molar conductivity.

(b) A fuel cell is a device which converts energy produced during the combustion of fuels like hydrogen, methane, methyl alcohol etc. directly into electrical energy. One such successful fuel cell is hydrogen-oxygen fuel cell.

(ii) For 0.1 mol L^{-1} KCl solution,

Conductivity, $\kappa = 1.29 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$, Resistance, $R = 100 \Omega$

Cell constant = Conductivity \times resistance

$$= 1.29 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1} \times 100 \Omega = 1.29 \text{ cm}^{-1}$$

For 0.02 mol L^{-1} solution,

Resistance = 520Ω , Cell constant = 1.29 cm^{-1}

$$\begin{aligned} \text{Conductivity, } \kappa &= \frac{\text{Cell constant}}{\text{Resistance}} \\ &= \frac{1.29 \text{ cm}^{-1}}{520 \Omega} \\ &= 0.00248 \Omega^{-1} \text{ cm}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Molar conductivity, } \Lambda_m &= \frac{\text{Conductivity } (\kappa) \times 1000 \text{ cm}^3 \text{ L}^{-1}}{\text{Molarity}} \\ &= \frac{0.00248 \Omega^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.02 \text{ mol L}^{-1}} \\ &= 124 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

- Q. 11. (i) Conductivity of 2×10^{-3} M methanoic acid is $8 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociation if Λ_m° for methanoic acid is $404 \text{ S cm}^2 \text{ mol}^{-1}$. [CBSE 2023 (56/2/1)]
(ii) Calculate the $\Delta_r G^\circ$ and $\log K_c$ for the given reaction at 298 K:



[Given: $E_{\text{Ni}^{2+}/\text{Ni}}^\circ = -0.25 \text{ V}$, $E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}$

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

- Ans. (i) Given: Conc. of $\text{HCOOH} = 2 \times 10^{-3} \text{ M}$, $\kappa = 8 \times 10^{-5} \text{ S cm}^{-1}$

Substituting the values in the expression $\Lambda_m^c = \frac{\kappa \times 1000}{M}$

$$\Lambda_{m(\text{HCOOH})}^c = \frac{8 \times 10^{-5} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{2 \times 10^{-3} \text{ mol L}^{-1}} = 40 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{m(\text{HCOOH})}^c = 40 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Lambda_{m(\text{HCOOH})}^\circ = 404 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_m^c}{\Lambda_m^\circ} = \frac{40}{404} = 0.09$$

- (ii) For the reaction $\text{Ni(s)} + 2\text{Ag}^+(\text{aq}) \rightleftharpoons \text{Ni}^{2+}(\text{aq}) + 2\text{Ag(s)}$; $n = 2$

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Ni}^{2+}/\text{Ni}}^\circ = 0.80 \text{ V} - (-0.25 \text{ V}) = 1.05 \text{ V}$$

$$\log K_c = \frac{n}{0.059} \times E_{\text{cell}}^\circ = \frac{2}{0.059} \times 1.05 = 35.5932$$

$$\Delta_r G^\circ = -nFE_{\text{cell}}^\circ = -2 \times 96500 \times 1.05$$

$$\Delta_r G^\circ = -202650 \text{ J mol}^{-1} \text{ or } \Delta_r G^\circ = -202.65 \text{ KJ mol}^{-1}$$

- Q. 12. (i) Calculate E_{cell}° for the following reaction at 298 K:



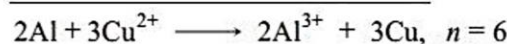
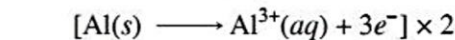
Given: $E_{\text{cell}}^\circ = 1.98 \text{ V}$

- (ii) Using the E° values of A and B, predict which is better for coating the surface of iron [$E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44 \text{ V}$] to prevent corrosion and why?

[Given: $E_{\text{A}^{2+}/\text{A}}^\circ = -2.37 \text{ V}$, $E_{\text{B}^{2+}/\text{B}}^\circ = -0.14 \text{ V}$]

[CBSE Central 2016]

- Ans. (i)



Here, $n = 6$, $E_{\text{cell}}^\circ = 1.98 \text{ V}$, $[\text{Al}^{3+}] = 1 \times 10^{-2} \text{ M}$, $[\text{Cu}^{2+}] = 1 \times 10^{-2} \text{ M}$

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.059}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Cu}^{2+}]^3}$$

Substituting these values in the Nernst equation for above electrochemical change, we get

$$1.98 = E_{\text{cell}}^\circ - \frac{0.059}{6} \log \frac{(10^{-2})^2}{(10^{-2})^3}$$

$$1.98 = E_{\text{cell}}^\circ - \frac{0.059}{6} \log 10^2$$

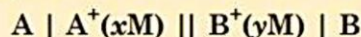
$$E_{\text{cell}}^\circ = 1.98 + \frac{0.059}{6} \times 2 \log 10 = 1.98 + 0.0197 = 1.9997 \text{ V}$$

- (ii) A, as its standard reduction potential is less than B, therefore, it will undergo oxidation more easily than B.

Questions for Practice

Choose and write the correct answer for each of the following.

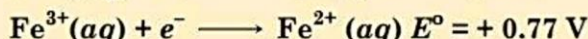
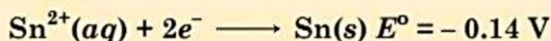
1. A hypothetical electrochemical cell is shown below:



The emf measured is +0.20 V. The cell reaction is

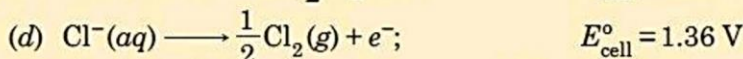
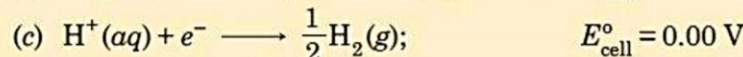
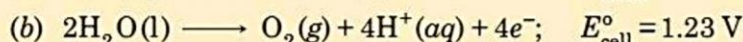
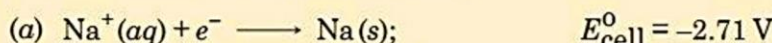
- (a) $A + B^+ \longrightarrow A^+ + B$
 (b) The cell reaction cannot be predicted.
 (c) $A^+ + e^- \longrightarrow A, B^+ + e^- \longrightarrow B$
 (d) $A^+ + B \longrightarrow A + B^+$
2. When 0.1 mole of MnO_4^{2-} is oxidised, the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is
- (a) 96500 C (b) 9650 C
 (c) 96.50 C (d) 2×96500 C

3. A voltaic cell is made by connecting two half cells represented by half equations below: [CBSE 2023 (56/5/2)]



Which statement is correct about this voltaic cell?

- (a) Fe^{2+} is oxidised and the voltage of the cell is -0.91 V.
 (b) Sn is oxidised and the voltage of the cell is 0.91 V.
 (c) Fe^{2+} is oxidised and the voltage of the cell is 0.91 V.
 (d) Sn is oxidised and the voltage of the cell is 0.63 V.
4. In the electrolysis of aqueous sodium chloride solution, which of the following half cell reaction will occur at anode? [NCERT Exemplar]



5. Which of the following cell was used in Apollo space programme?

[CBSE 2023 (56/5/2)]

- (a) Mercury cell (b) Daniel cell
 (c) H_2-O_2 Fuel cell (d) Dry cell

In the following questions, two statements are given—one labeled Assertion (A) and the other labeled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below:

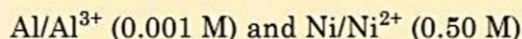
- (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
 (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
 (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
 (d) Assertion (A) is incorrect, but Reason (R) is correct statement.

6. **Assertion (A)** : Conductivity of an electrolyte decreases with decrease in concentration.
Reason (R) : Number of ions per unit volume increase on dilution. [CBSE 2023 (56/2/1)]
7. **Assertion (A)** : Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.
Reason (R) : For weak electrolytes, degree of dissociation increases with dilution of solution. [CBSE 2023 (56/4/2)]
8. **Assertion (A)** : Rusting of iron is quicker in saline water than in ordinary water.
Reason (R) : Salt water helps in flow of current in the miniature cell developed on the iron surface.
9. **Assertion (A)** : An electrochemical cell can be set up only if the redox reaction is spontaneous.
Reason (R) : A reaction is spontaneous if free energy change is negative.
10. **Assertion (A)** : If $\lambda_{Na^+}^{\circ}$ and $\lambda_{Cl^-}^{\circ}$ are molar limiting conductivity of sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation: $\lambda_{NaCl}^{\circ} = \lambda_{Na^+}^{\circ} + \lambda_{Cl^-}^{\circ}$
Reason (R) : This is according to Kohlrausch law of independent migration of ions.

Answer the following questions:

11. In a plot of Λ_m against the square root of concentration ($C^{1/2}$) for strong and weak electrolyte, the value of limiting molar conductivity of a weak electrolyte cannot be obtained graphically. Suggest a way to obtain this value. Also state the related law, if any. [CBSE 2023 (56/4/2)]
12. (i) (a) What should be the signs (positive/negative) for E_{Cell}° and ΔG° for a spontaneous redox reaction occurring under standard conditions?
(b) State Faraday's first law of electrolysis.
(ii) Calculate the emf of the following cell at 298 K:
 $Fe(s) | Fe^{2+}(0.01M) || H^+(1M) | H_2(g) (1 \text{ bar}), Pt(s)$
Given: $E_{Cell}^{\circ} = 0.44 \text{ V}$.
13. (i) For a weak electrolyte, molar conductance in dilute solution increases sharply as its concentration in solution is decreased. Give reason.
(ii) Write overall cell reaction for lead storage battery when the battery is being charged.
14. Two half-reactions of an electrochemical cell are given below:
 $MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l); E^{\circ} = +1.51 \text{ V}$
 $Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e^-; E^{\circ} = +0.51 \text{ V}$
Construct the redox equation from the standard potential of the cell and predict if the reaction is reactant favoured or product favoured.
15. Calculate $\Delta_r G^{\circ}$ and $\log K_c$ for the following reaction: [CBSE 2019 (56/4/1)]
 $Cd^{2+}(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Cd(s)$
[Given: $E_{Cd^{2+}/Cd}^{\circ} = -0.403 \text{ V}$, $E_{Zn^{2+}/Zn}^{\circ} = -0.763 \text{ V}$]
16. Account for the following:
(i) Alkaline medium inhibits the rusting of iron.
(ii) Iron does not rust even if the zinc coating is broken in a galvanized iron pipe.

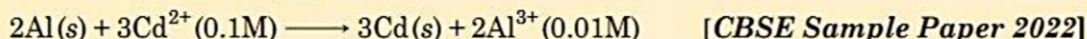
17. A voltaic cell is set up at 25°C with the following half cells:



Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

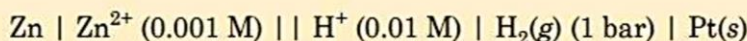
$$E_{\text{Ni}^{2+}/\text{Ni}}^{\circ} = -0.25 \text{ V}; E_{\text{Al}^{3+}/\text{Al}}^{\circ} = -1.66 \text{ V} (\log 8 \times 10^{-6} = -5.097)$$

18. The conductivity of 0.001028 mol L⁻¹ acetic acid is $4.95 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its dissociation constant if Λ_m° for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$.
19. Give three point of differences between electrochemical cell and electrolytic cell.
20. Represent the cell in which the following reaction takes place. The value of E° for the cell is 1.260 V. What is the value of E_{cell} ?



21. Write the Nernst equation and calculate the emf of the following cell at 298 K.

[CBSE 2022 (56/4/2)]



$$\text{Given: } E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}, E_{\text{H}^{+}/\text{H}_2}^{\circ} = 0.00 \text{ V}, [\log 10 = 1]$$

22. (i) The electrical resistance of a column of 0.02 M NaOH solution of diameter 1.40 cm and length 44 cm is $5.00 \times 10^3 \text{ ohm}$. Calculate its resistivity, conductivity and molar conductivity. [CBSE (C) 2021(56/1/1)]

(ii) Depict the galvanic cell in which the reaction take place:



Further show:

- (i) Which of the electrodes is positively charged?
- (ii) The carriers of the current in the outer circuit.
23. (i) State Faraday's first law of electrolysis. How much charge, in terms of Faraday, is required for the reduction of 1 mol Cu^{2+} to Cu?

(ii) Calculate emf of the following cell at 298 K for

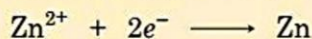


$$[E_{\text{cell}}^{\circ} = +2.71 \text{ V}, 1\text{F} = 96500 \text{ C mol}^{-1}, \log 10 = 1]$$

[CBSE 2023 (56/1/1)]

24. (i) The molar conductivities of NH_4^{+} and Cl^{-} ion are $73.8 \text{ S cm}^2 \text{ mol}^{-1}$ and $76.2 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. The conductivity of 0.1 M NH_4Cl is $1.29 \times 10^{-2} \text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociation.

(ii) Calculate the half-cell potential at 298 K for the reaction



$$\text{if } [\text{Zn}^{2+}] = 0.1 \text{ M and } E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$$

[CBSE 2023 (56/4/2)]

Answers

1. (a) 2. (b) 3. (b) 4. (d) 5. (c) 6. (a) 7. (a) 8. (a) 9. (b) 10. (a)
14. 0.3105 V 15. $\Delta_r G^{\circ} = -69.48 \text{ kJ mol}^{-1}$, $\log K_c = 12.20$
17. 1.4602 V 18. $1.78 \times 10^{-5} \text{ mol L}^{-1}$ 21. 0.7305 V
22. (i) $\rho = 175 \text{ } \Omega \text{ cm}$, $\kappa = 0.0057 \text{ S cm}^{-1}$, $\Lambda_m = 285 \text{ S cm}^2 \text{ mol}^{-1}$ 23. (i) 2F (ii) 2.68 V
24. (i) 149.7 mho $\text{cm}^2 \text{ mol}^{-1}$, 0.86 (ii) -0.789 V



