Electrochemistry

Recap Notes

- **Electrochemistry :** It is the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

Differences between electrochemical cell and electrolytic cell

Electrochemical cell (Galvanic or Voltaic cell)	Electrolytic cell
1. It is a device which converts chemical energy into electrical energy.	1. It is a device which converts electrical energy into chemical energy.
2. It is based upon the redox reaction which is spontaneous. *i.e.,* ΔG = –ve	2. The redox reaction is non-spontaneous and takes place only when electrical energy is supplied. *i.e.*, ΔG = +ve
3. Two electrodes are usually set up in two separate beakers.	3. Both the electrodes are suspended in the solution or melt of the electrolyte in the same beaker.
4. The electrolytes taken in the two beakers are different.	4. Only one electrolyte is taken.
5. The electrodes taken are of different materials.	5. The electrodes taken may be of the same or different materials.
6. The electrode on which oxidation takes place is called the *anode* (or –ve pole) and the electrode on which reduction takes place is called the *cathode* (or +ve pole).	6. The electrode which is connected to the –ve terminal of the battery is called the *cathode*; the cations migrate to it which gain electrons and hence, a reduction takes place, the other electrode is called the *anode*.
7. To set up this cell, a salt bridge/porous pot is used.	7. No salt bridge is used in this case.

- **Nernst equation :** For a reduction reaction,

  $M^{n+}_{(aq)} + ne^- \longrightarrow M_{(s)}$;

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF}\log\frac{1}{[M^{n+}_{(aq)}]}$$

At 298 K,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{1}{[M^{n+}_{(aq)}]}$$

  - ▶ For concentration cell, EMF at 298 K is given by

$$E_{\text{cell}} = \frac{0.0591}{n}\log\frac{C_2}{C_1}$$

where $C_2 > C_1$

- **Applications of Nernst equation :**
  - ▶ **To calculate electrode potential of a cell :**

$$aA + bB \xrightarrow{ne^-} xX + yY$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log\frac{[X]^x[Y]^y}{[A]^a[B]^b} \text{(At 298 K)}$$

- **To calculate equilibrium constant :** At equilibrium, $E_{\text{cell}} = 0$

$$E^\circ_{\text{cell}} = \frac{0.0591}{n}\log K_c \text{ at 298 K}$$

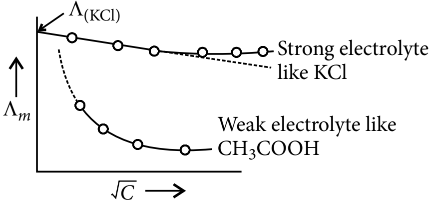
- **Relation between cell potential and Gibbs energy change :**
  $\Delta G = -nFE^\circ_{\text{cell}}$; $\Delta G^\circ = -2.303\, RT \log K_c$

- **Conductance in electrolytic solutions :**

Property	Formula	Units	Effect of dilution
Conductance (G)	$\frac{1}{R} = \frac{a}{\rho l} = \frac{\kappa a}{l}$	Ohm^{-1} (Ω^{-1})/Siemens (S)	Increases as larger number of ions are produced.
Specific conductance (κ) or conductivity	$\frac{1}{\rho}$ or $G\frac{l}{a}$	$\text{Ohm}^{-1}\ \text{cm}^{-1}/\text{S m}^{-1}$	Decreases as number of ions per cm^3 decreases.
Equivalent conductivity (Λ_{eq})	$\kappa \times V$ or $\kappa \times \frac{1000}{N}$	$\Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}/\text{S m}^2\ \text{eq}^{-1}$	Increases with dilution due to large increase in V.
Molar conductivity (Λ_m)	$\kappa \times V$ or $\kappa \times \frac{1000}{M}$	$\Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}/\text{S m}^2\ \text{mol}^{-1}$	Increases with dilution due to large increase in V.

- **Limiting molar conductivity :** When concentration approaches zero *i.e.*, at infinite dilution, the molar conductivity is known as *limiting molar conductivity* (Λ°_m).
- **Variation of molar conductivity with concentration :** For a strong electrolyte it is shown by *Debye–Huckel Onsager equation* as follows :

$$\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$$



Here, Λ°_m = Molar conductivity at infinite dilution (Limiting molar conductivity)

Λ_m = Molar conductivity at V-dilution

A = Constant which depends upon nature of solvent and temperature

C = Concentration

Plot of Λ_m against $C^{1/2}$ is a straight line with intercept equal to Λ°_m and slope equal to '$-A$'. Thus, Λ_m decreases linearly with $\sqrt{C}$, when $C = 0$, $\Lambda_m = \Lambda^\circ_m$ and Λ°_m can be determined experimentally.

  - **For weak electrolytes :** There is a very large increase in conductance with dilution especially near infinite dilution as no. of ions increases. Λ_m increases as C decreases but does not reach a constant value even at infinite dilution. Hence, their Λ°_m cannot be determined experimentally.
  - **For a strong electrolyte :** There is only a small increase in conductance with dilution. This is because a strong electrolyte is completely dissociated in solution and so, the number of ions remain constant and on dilution, interionic attractions decreases as ions move far apart.

- **Kohlrausch's law of independent migration of ions :** It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.
  $\Lambda^\circ_m = \upsilon_+\lambda^\circ_+ + \upsilon_-\lambda^\circ_-$; where λ°_+ and λ°_- are the limiting molar conductivities of the cation and anion respectively and υ_+ and υ_- are stoichiometric number of cations and anions respectively in one formula unit of the electrolyte.

- **Applications of Kohlrausch's law :**
  - **Calculation of molar conductivity of weak electrolytes :**

$$\Lambda^\circ_{m\,(CH_3COOH)} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{H^+}$$

$$= \left(\lambda^\circ_{H^+} + \lambda^\circ_{Cl^-}\right) + \left(\lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+}\right) - \left(\lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}\right)$$

$$= \Lambda^\circ_{m\,(HCl)} + \Lambda^\circ_{m\,(CH_3COONa)} - \Lambda^\circ_{m\,(NaCl)}$$

  - **Calculation of degree of dissociation :**

$$\text{Degree of dissociation } (\alpha) = \frac{\Lambda_m}{\Lambda^\circ_m}$$

$$= \frac{\text{Molar conductivity at concentration } c}{\text{Molar conductivity at infinite dilution}}$$

  - **Calculation of dissociation constant (K_c) of weak electrolyte :**

	$AB \rightleftharpoons$	A^+	$+ B^-$
Initial conc.	c	0	0
Conc. at equil.	$(c - c\alpha)$	$c\alpha$	$c\alpha$

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

- **Electrolytic Cells and Electrolysis**
  - **Electrolysis** is the process of decomposition of an electrolyte by passing electricity through its aqueous solution or molten state.

- **Products of Electrolysis**

Electrolyte	Products		Reactions involved	
	At cathode	At anode	At cathode	At anode
Molten NaCl	Na metal	Cl_2 gas	$Na^+_{(l)} + e^- \rightarrow Na_{(l)}$	$Cl^-_{(l)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^-$
Aqueous NaCl	H_2 gas	Cl_2 gas	$H_2O_{(l)} + e^- \rightarrow \frac{1}{2}H_{2(g)} + OH^-_{(aq)}$	$Cl^-_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^-$
Dil. H_2SO_4	H_2 gas	O_2 gas	$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$	$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$
Conc. H_2SO_4	H_2 gas	$S_2O_8^{2-}$	$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$	$2SO^{2-}_{4(aq)} \rightarrow S_2O^{2-}_{8\,(aq)} + 2e^-$

- **Overvoltage/Over potential :** Oxidation of H_2O is relatively slow process and thus needs extra potential. This extra potential needed to oxidise H_2O is called overvoltage/over potential. Due to overvoltage, the oxidation of chloride ion occurs at anode in preference to H_2O.

- **Discharge potential :** The minimum potential that must be applied across the electrodes to bring about the electrolysis and thus, discharge of the ions on the electrode is known as discharge potential. It is infact the ability of ions to discharge first at electrodes.

Practice Time

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions (MCQs)

1. Given below are the standard electrode potentials of few half-cells. The correct order of these metals in increasing reducing power will be

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

(a) K < Mg < Cr < Ag
(b) Ag < Cr < Mg < K
(c) Mg < K < Cr < Ag
(d) Cr < Ag < Mg < K

2. $\Delta_r G$ for the cell with the cell reaction:

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)}$$

$[E^\circ_{Ag_2O/Ag} = 0.344 \text{ V}, E^\circ_{Zn^{2+}/Zn} = -0.76 \text{ V}]$

(a) 2.13×10^5 J mol^{-1} (b) -2.13×10^5 J mol^{-1}
(c) 1.06×10^5 J mol^{-1} (d) -1.06×10^5 J mol^{-1}

3. For a cell reaction: $M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$, the Nernst equation for electrode potential at any concentration measured with respect to standard hydrogen electrode is represented as

(a) $E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$

(b) $E_{(M/M^{n+})} = E^\circ_{(M/M^{n+})} - \frac{RT}{nF} \ln \frac{[M^{n+}]}{[M]}$

(c) $E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{RT}{nF} \log \frac{1}{[M]}$

(d) $E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{RT}{nF} \ln [M^{n+}]$

4. Limiting molar conductivity for some ions is given below (in S cm^2 mol^{-1}) :

Na^+ - 50.1, Cl^- - 76. 3, H^+ - 349.6, CH_3COO^- - 40.9, Ca^{2+} - 119.0.

What will be the limiting molar conductivities (Λ°_m) of $CaCl_2$, CH_3COONa and NaCl respectively?

(a) 97.65, 111.0 and 242.8 S cm^2 mol^{-1}
(b) 195.3, 182.0 and 26.2 S cm^2 mol^{-1}
(c) 271.6, 91.0 and 126.4 S cm^2 mol^{-1}
(d) 119.0, 1024.5 and 9.2 S cm^2 mol^{-1}

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

(a) the nature and structure of the metal
(b) the number of valence electrons per atom
(c) change in temperature
(d) all of these.

6. A galvanic cell has electrical potential of 1.1 V. If an opposing potential of 1.1 V is applied to this cell, what will happen to the cell reaction and current flowing through the cell?

(a) The reaction stops and no current flows through the cell.
(b) The reaction continuous but current flows in opposite direction.
(c) The concentration of reactants becomes unity and current flows from cathode to anode.
(d) The cell does not function as a galvanic cell and zinc is deposited on zinc plate.

7. In a Daniell cell,

(a) the chemical energy liberated during the redox reaction is converted to electrical energy
(b) the electrical energy of the cell is converted to chemical energy
(c) the energy of the cell is utilised in conduction of the redox reaction
(d) the potential energy of the cell is converted into electrical energy.

8. Mark the correct Nernst equation for the given cell.

$Fe_{(s)}|Fe^{2+}(0.001 \text{ M})||H^+ (1 \text{ M}) | H_{2(g)}(1 \text{ bar})|Pt_{(s)}$

(a) $E_{cell} = E^\circ_{cell} - \frac{0.591}{2} \log \frac{[Fe^{2+}][H^+]^2}{[Fe][H_2]}$

(b) $E_{cell} = E^\circ_{cell} - \frac{0.591}{2} \log \frac{[Fe][H^+]^2}{[Fe^{2+}][H_2]}$

(c) $E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}][H_2]}{[Fe][H^+]^2}$

(d) $E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Fe][H_2]}{[Fe^{2+}][H^+]^2}$

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

(a) silver is deposited at cathode and O_2 is liberated at anode

(b) silver is deposited at cathode and H_2 is liberated at anode

(c) hydrogen is liberated at cathode and O_2 is liberated at anode

(d) silver is deposited at cathode and Pt is dissolved in electrolyte.

10. A standard hydrogen electrode has a zero potential because

(a) hydrogen can be most easily oxidised

(b) hydrogen has only one electron

(c) the electrode potential is assumed to be zero

(d) hydrogen is the lightest element.

11. At 25°C, Nernst equation is

(a) $E_{cell} = E^\circ{}_{cell} - \frac{0.0591}{n}\log\frac{[\text{ion}]_{RHS}}{[\text{ion}]_{LHS}}$

(b) $E_{cell} = E^\circ{}_{cell} - \frac{0.0591}{n}\log\frac{[M]_{RHS}}{[M]_{LHS}}$

(c) $E_{cell} = E^\circ{}_{cell} + \frac{0.0591}{n}\log\frac{[\text{ion}]_{RHS}}{[\text{ion}]_{LHS}}$

(d) $E_{cell} = E^\circ{}_{cell} - \frac{0.0591}{n}\log\frac{[\text{ion}]_{LHS}}{[\text{ion}]_{RHS}}$

12. Electrode potential data of few cells is given below. Based on the data, arrange the ions in increasing order of their reducing power.

$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$; $E^\circ = +0.77$ V

$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$; $E^\circ = -1.66$ V

$Br_{2(aq)} + 2e^- \rightarrow 2Br^-_{(aq)}$; $E^\circ = +1.09$ V

(a) $Br^- < Fe^{2+} < Al$ (b) $Fe^{2+} < Al < Br^-$

(c) $Al < Br^- < Fe^{2+}$ (d) $Al < Fe^{2+} < Br^-$

13. Mark the correct relationship from the following.

(a) Equilibrium constant is related to emf as
$\log K = \frac{nFE}{2.303RT}$

(b) EMF of a cell Zn | $Zn^{2+}{}_{(a_1)}$ || $Cu^{2+}{}_{(a_2)}$ | Cu is
$E = E^\circ - \frac{0.591}{n}\log\frac{[a_2]}{[a_1]}$

(c) Nernst equation is
$E_{cell} = E^\circ{}_{cell} - \frac{0.0591}{n}\log\frac{[\text{Products}]}{[\text{Reactants}]}$

(d) For the electrode M^{n+}/M at 273 K
$E = E^\circ + \frac{0.591}{n}\log[M^{n+}]$

14. The specific conductivity of $N/10$ KCl solution at 20°C is 0.0212 ohm^{-1} cm^{-1} and the resistance of the cell containing this solution at 20°C is 55 ohm. The cell constant is

(a) 3.324 cm^{-1} (b) 1.166 cm^{-1}

(c) 2.372 cm^{-1} (d) 3.682 cm^{-1}

15. Following reactions are taking place in a Galvanic cell,

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

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

(a) $Zn_{(s)} | Zn^{2+}_{(aq)} || Ag^+_{(aq)} | Ag_{(s)}$

(b) $Zn^{2+} | Zn || Ag | Ag^+$

(c) $Zn_{(aq)} | Zn^{2+}_{(s)} || Ag^+_{(s)} | Ag_{(aq)}$

(d) $Zn_{(s)} | Ag^+_{(aq)} || Zn^{2+}_{(aq)} | Ag_{(s)}$

16. What will be the molar conductivity of Al^{3+} ions at infinite dilution if molar conductivity of $Al_2(SO_4)_3$ is 858 S cm^2 mol^{-1} and ionic conductance of SO_4^{2-} is 160 S cm^2 mol^{-1} at infinite dilution?

(a) 189 S cm^2 mol^{-1} (b) 698 S cm^2 mol^{-1}

(c) 1018 S cm^2 mol^{-1} (d) 429 S cm^2 mol^{-1}

17. E° value of Ni^{2+}/Ni is –0.25 V and Ag^+/Ag is +0.80 V. If a cell is made by taking the two electrodes what is the feasibility of the reaction?

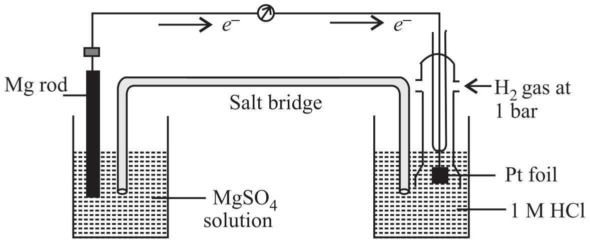
(a) Since E° value for the cell will be positive, redox reaction is feasible.

(b) Since E° value for the cell will be negative, redox reaction is not feasible.

(c) Ni cannot reduce Ag^+ to Ag hence reaction is not feasible.

(d) Ag can reduce Ni^{2+} to Ni hence reaction is feasible.

18. A cell is set up as shown in the figure. It is observed that EMF of the cell comes out to be 2.36 V. Which of the given statements is not correct about the cell?



(a) Reduction takes place at magnesium electrode and oxidation at SHE.

(b) Oxidation takes place at magnesium electrode and reduction at SHE.

(c) Standard electrode potential for $Mg^{2+}|Mg$ will be –2.36 V.

(d) Electrons flow from magnesium electrode to hydrogen electrode.

19. Limiting molar conductivity of NaBr is

(a) $\Lambda_m^\circ NaBr = \Lambda_m^\circ NaCl + \Lambda_m^\circ KBr$

(b) $\Lambda_m^\circ NaBr = \Lambda_m^\circ NaCl + \Lambda_m^\circ KBr - \Lambda_m^\circ KCl$

(c) $\Lambda_m^\circ NaBr = \Lambda_m^\circ NaOH + \Lambda_m^\circ NaBr - \Lambda_m^\circ NaCl$

(d) $\Lambda_m^\circ NaBr = \Lambda_m^\circ NaCl - \Lambda_m^\circ NaBr$

20. Choose the option with correct words to fill in the blanks.

According to preferential discharge theory, out of number of ions the one which requires _____ energy will be liberated ____ at a given electrode.

(a) least, first (b) least, last

(c) highest, first (d) highest, last

21. For the cell reaction :

$2Cu^+_{(aq)} \rightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$, the standard cell potential is 0.36 V. The equilibrium constant for the reaction is

(a) 1.2×10^6 (b) 7.4×10^{12}

(c) 2.4×10^6 (d) 5.5×10^8

22. E° values of three metals are listed below.

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}\,;\, E^\circ = -0.76$ V

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

$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}\,;\, E^\circ = -0.14$ V

Which of the following statements are correct on the basis of the above information?

(i) Zinc will be corroded in preference to iron if zinc coating is broken on the surface.

(ii) If iron is coated with tin and the coating is broken on the surface then iron will be corroded.

(iii) Zinc is more reactive than iron but tin is less reactive than iron.

(a) (i) and (ii) (b) (ii) and (iii)

(c) (i), (ii) and (iii) (d) (i) and (iii)

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

(a) Zn, Al, Mg, Fe, Cu (b) Cu, Fe, Mg, Al, Zn

(c) Mg, Al, Zn, Fe, Cu (d) Al, Mg, Fe, Cu, Zn

24. The reaction which is taking place in nickel - cadmium battery can be represented by which of the following equation?

(a) $Cd + NiO_2 + 2H_2O \rightarrow Cd(OH)_2 + Ni(OH)_2$

(b) $Cd + NiO_2 + 2OH^- \rightarrow Ni + Cd(OH)_2$

(c) $Ni + Cd(OH)_2 \rightarrow Cd + Ni(OH)_2$

(d) $Ni(OH)_2 + Cd(OH)_2 \rightarrow Ni + Cd + 2H_2O$

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

(a) 124 Ω^{-1} cm^2 mol^{-1} (b) 204 Ω^{-1} cm^2 mol^{-1}

(c) 101 Ω^{-1} cm^2 mol^{-1} (d) 300 Ω^{-1} cm^2 mol^{-1}

26. Fluorine is the best oxidising agent because it has

(a) highest electron affinity

(b) highest reduction potential

(c) highest oxidation potential

(d) lowest electron affinity.

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

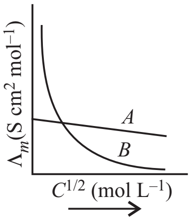
(a) $2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$

(b) $2SO^{2-}_{4(aq)} \rightarrow S_2O^{2-}_{8(aq)} + 2e^-$

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

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

28. Mark the correct choice of electrolytes represented in the graph.



(a) $A \rightarrow NH_4OH$, $B \rightarrow NaCl$

(b) $A \rightarrow NH_4OH$, $B \rightarrow NH_4Cl$

(c) $A \rightarrow CH_3COOH$, $B \rightarrow CH_3COONa$

(d) $A \rightarrow KCl$, $B \rightarrow NH_4OH$

29. Molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm^2 mol^{-1}, the degree of dissociation and dissociation constant will be (Given : $\lambda^\circ_{H^+} = 349.6$ S cm^2 mol^{-1} and $\lambda^\circ_{HCOO^-} = 54.6$ S cm^2 mol^{-1})

(a) 11.4%, 3.67×10^{-4} mol L^{-1}

(b) 22.8%, 1.83×10^{-4} mol L^{-1}

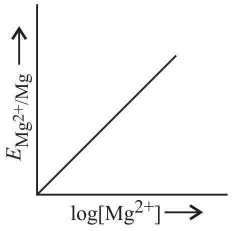
(c) 52.2%, 4.25×10^{-4} mol L^{-1}

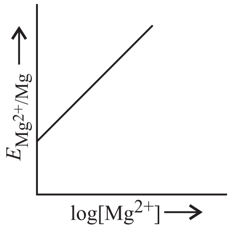
(d) 1.14%, 3.67×10^{-6} mol L^{-1}

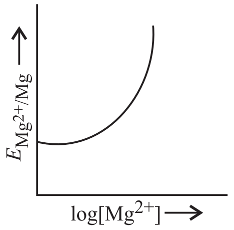
30. Electrode potential for Mg electrode varies according to the equation,

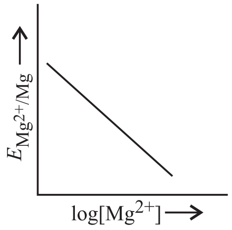
$$E_{Mg^{2+}|Mg} = E^\circ_{Mg^{2+}|Mg} - \frac{0.059}{2}\log\frac{1}{[Mg^{2+}]}.$$

The graph of $E_{Mg^{2+}|Mg}$ *vs* log $[Mg^{2+}]$ is

(a) 

(b) 

(c) 

(d) 

31. E° values for the half cell reactions are given below:

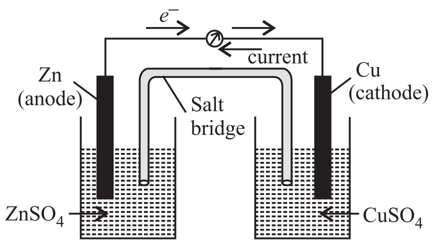
$Cu^{2+} + e^- \rightarrow Cu^+$; $E^\circ = 0.15$ V

$Cu^{2+} + 2e^- \rightarrow Cu$; $E^\circ = 0.34$ V

What will be the E° of the half-cell : $Cu^+ + e^- \rightarrow Cu$?

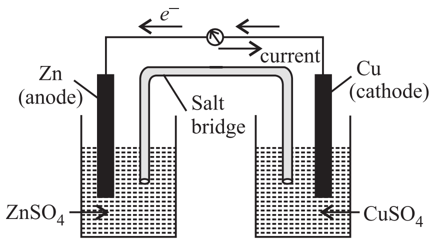
(a) +0.49 V (b) +0.19 V
(c) +0.53 V (d) +0.30 V

32. Given below are two figures of Daniell cell (*X*) and (*Y*). Study the figures and mark the incorrect statement from the following.



$E_{ext} < 1.1$ V

(*X*)



$E_{ext} > 1.1$V

(*Y*)

(a) In fig (*X*), electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn ($E_{ext} < 1.1$ V).
(b) In fig (*Y*), electrons flow from Cu to Zn and current flows from Zn to Cu ($E_{ext} > 1.1$ V).
(c) In fig (*X*), Zn dissolves at anode and Cu deposits at cathode.
(d) In fig (*Y*), Zn is deposited at Cu and Cu is deposited at Zn.

33. Which of the following is/are an application of electrochemical series?

(a) To compare the relative oxidising and reducing power of substances.
(b) To predict evolution of hydrogen gas on reaction of metal with acid.
(c) To predict spontaneity of a redox reaction.
(d) All of these

34. Two solutions of *X* and *Y* electrolytes are taken in two beakers and diluted by adding 500 mL of water. Λ_m of *X* increases by 1.5 times while that of *Y* increases by 20 times, what could be the electrolytes *X* and *Y* ?

(a) $X \rightarrow NaCl$, $Y \rightarrow KCl$
(b) $X \rightarrow NaCl$, $Y \rightarrow CH_3COOH$
(c) $X \rightarrow KOH$, $Y \rightarrow NaOH$
(d) $X \rightarrow CH_3COOH$, $Y \rightarrow NaCl$

35. What would be the equivalent conductivity of a cell in which 0.5 N salt solution offers a resistance of 40 ohm whose electrodes are 2 cm apart and 5 cm^2 in area?

(a) 10 ohm^{-1} cm^2 eq^{-1} (b) 20 ohm^{-1} cm^2 eq^{-1}
(c) 30 ohm^{-1} cm^2 eq^{-1} (d) 25 ohm^{-1} cm^2 eq^{-1}

36. The half-cell reactions with their appropriate standard reduction potentials are

(i) $Pb^{2+} + 2e^- \rightarrow Pb$; $E^\circ = -0.13$ V
(ii) $Ag^+ + e^- \rightarrow Ag$; $E^\circ = +0.80$ V

Based on the above data, which of the following reactions will take place?

(a) $Pb^{2+} + 2Ag \rightarrow 2Ag^+ + Pb$
(b) $2Ag + Pb \rightarrow 2Ag^+ + Pb^{2+}$
(c) $2Ag^+ + Pb \rightarrow Pb^{2+} + 2Ag$
(d) $Pb^{2+} + 2Ag^+ \rightarrow Pb + Ag$

37. Units of the properties measured are given below. Which of the properties has not been matched correctly?

(a) Molar conductance = S m^2 mol^{-1}
(b) Cell constant = m^{-1}
(c) Specific conductance = S m^2
(d) Equivalent conductance = S m^2 $(g\ eq)^{-1}$

38. When water is added to an aqueous solution of an electrolyte, what is the change in specific conductivity of the electrolyte?

(a) Conductivity decreases
(b) Conductivity increases
(c) Conductivity remains same
(d) Conductivity does not depend on number of ions.

39. The specific conductance of a saturated solution of AgCl at 25°C is 1.821×10^{-5} mho cm^{-1}. What is the solubility of AgCl in water (in $g\ L^{-1}$), if limiting molar conductivity of AgCl is 130.26 mho $cm^2\ mol^{-1}$?
(a) $1.89 \times 10^{-3}\ g\ L^{-1}$ (b) $2.78 \times 10^{-2}\ g\ L^{-1}$
(c) $2.004 \times 10^{-2}\ g\ L^{-1}$ (d) $1.43 \times 10^{-3}\ g\ L^{-1}$

40. The standard reduction potential for the half-cell reaction, $Cl_2 + 2e^- \rightarrow 2Cl^-$ will be
($Pt^{2+} + 2Cl^- \rightarrow Pt + Cl_2$, $E^\circ_{cell} = -0.15$ V ;
$Pt^{2+} + 2e^- \rightarrow Pt$, $E^\circ = 1.20$ V)
(a) –1.35 V (b) +1.35 V
(c) –1.05 V (d) +1.05 V

41. Zn gives hydrogen with H_2SO_4 and HCl but not with HNO_3 because
(a) Zn acts as oxidising agent when reacts with HNO_3
(b) HNO_3 is weaker acid than H_2SO_4 and HCl
(c) Zn is above the hydrogen in electrochemical series
(d) NO_3^- is reduced in preference to H^+ ion.

42. Given below are few reactions with some expressions. Mark the expression which is not correctly matched.
(a) For concentration cell,
$Ag|Ag^+(C_1)||Ag^+(C_2)|Ag$; $E_{cell} = -\frac{0.0591}{1}\log\frac{C_1}{C_2}$
(b) For the cell, $2Ag^+ + H_2(1\ atm) \rightarrow 2Ag + 2H^+(1\ M)$;
$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Ag^+]^2}{[H^+]^2}$
(c) For an electrochemical reaction, at equilibrium $aA + bB \xrightleftharpoons{ne^-} cC + dD$;
$E^\circ_{cell} = \frac{0.0591}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b}$
(d) For the cell, $M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$;
$E = E^\circ - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]}$

43. Which of the following is the cell reaction that occurs when the following half-cells are combined?
$I_2 + 2e^- \rightarrow 2I^-$ (1 M) ; $E^\circ = +0.54$ V
$Br_2 + 2e^- \rightarrow 2Br^-$ (1 M) ; $E^\circ = +1.09$ V
(a) $2Br^- + I_2 \rightarrow Br_2 + 2I^-$
(b) $I_2 + Br_2 \rightarrow 2I^- + 2Br^-$
(c) $2I^- + Br_2 \rightarrow I_2 + 2Br^-$
(d) $2I^- + 2Br^- \rightarrow I_2 + Br_2$

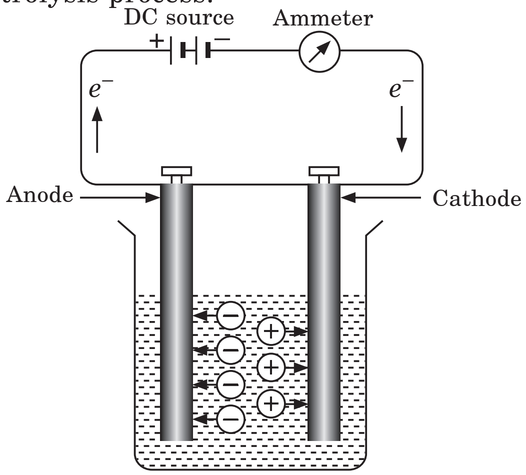
44. In a cell reaction, $Cu_{(s)} + 2Ag^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$
$E^\circ_{cell} = +0.46$ V. If the concentration of Cu^{2+} ions is doubled then E°_{cell} will be
(a) doubled
(b) halved
(c) increased by four times
(d) unchanged.

45. Molar conductivity of NH_4OH can be calculated by the equation,
(a) $\Lambda^\circ_{NH_4OH} = \Lambda^\circ_{Ba(OH)_2} + \Lambda^\circ_{NH_4Cl} - \Lambda^\circ_{BaCl_2}$
(b) $\Lambda^\circ_{NH_4OH} = \Lambda^\circ_{BaCl_2} + \Lambda^\circ_{NH_4Cl} - \Lambda^\circ_{Ba(OH)_2}$
(c) $\Lambda^\circ_{NH_4OH} = \frac{\Lambda^\circ_{Ba(OH)_2} + 2\Lambda^\circ_{NH_4Cl} - \Lambda^\circ_{BaCl_2}}{2}$
(d) $\Lambda^\circ_{NH_4OH} = \frac{\Lambda^\circ_{NH_4Cl} + \Lambda^\circ_{Ba(OH)_2}}{2}$

46. The equivalent conductivity of $N/10$ solution of acetic acid at 25°C is 14.3 $ohm^{-1}\ cm^2\ equiv^{-1}$. What will be the degree of dissociation of acetic acid ($\Lambda^\infty_{CH_3COOH} = 390.71\ ohm^{-1}\ cm^2\ equiv^{-1}$)?
(a) 3.66% (b) 3.9%
(c) 2.12% (d) 0.008%

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

48. The process of chemical decomposition of the electrolyte by the passage of electricity through its melt or aqueous solution is called electrolysis. The following apparatus is used for the electrolysis process:



Nandini, a young scientist, tried different electrolysis experiments using various electrolytes.

The incorrect observation of her experiment is

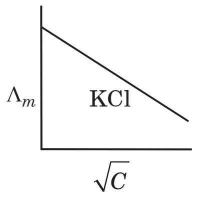
(a) cations which get reduced at cathode preferentially are hydronium ions in electrolysis of aqueous NaCl

(b) cations reaching to cathode are Cu^{2+} ions during electrolysis of $CuSO_4$ solution

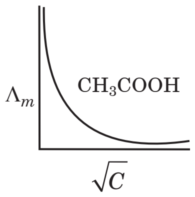
(c) during electrolysis of conc. H_2SO_4, $S_2O_8^{2-}$ is formed at anode

(d) $S_2O_8^{2-}$ is formed at anode during electrolysis of $CuSO_4$ solution.

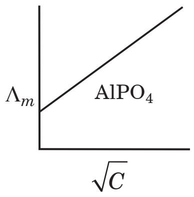
49. Jiya, a class-12 student recorded Λ_m of various electrolytes like acetic acid, sodium chloride and $AlPO_4$, etc., at various concentrations. Then she plotted Λ_m versus $\sqrt{C}$. Graphs obtained by her are shown below:



I



II



III

Which of the given graph(s) is/are correct?

(a) I only (b) I and II only

(c) I and III only (d) I, II and III

50. Which of the given Nernst equation representation(s) is/are not correct for the given cell?

Mg | Mg^{2+}(0.130 M) || Ag^+ (0.0001 M) | Ag

I. $$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{2F} \ln \frac{[Mg^{2+}]}{[Ag^+]^2}$$

II. $$E_{\text{cell}} = \left(E^\circ_{Ag^+/Ag} - E^\circ_{Mg^{2+}/Mg}\right) - \frac{0.059}{2} \ln \frac{[Mg^{2+}]}{[Ag^+]^2}$$

III. $$E_{\text{cell}} = E^\circ_{\text{cell}} + \frac{0.059}{2} \log \frac{[Ag^+]^2}{[Mg^{2+}]}$$

IV. $$E_{\text{cell}} = \left(E^\circ_{Ag^+/Ag} - E^\circ_{Mg^{2+}/Mg}\right) - \frac{0.059}{2} \log \frac{(0.0001)^2}{(0.130)}$$

(a) I only (b) I and III only

(c) II and IV only (d) II, III and IV only

51. Shubh learnt during his electrochemistry class that the standard electrode potentials are very important and we can extract a lot of useful informations from them. If the standard electrode potential of an electrode is greater than zero then its reduced form is more stable compared to hydrogen gas. Similarly, if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of the species.

Based on the given data,

$Fe^{2+}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}$; $E^\circ = -0.44$ V

$Sn^{2+}_{(aq)} + 2e^- \longrightarrow Sn_{(s)}$; $E^\circ = -0.14$ V

$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$; $E^\circ = -0.76$ V

$Cr^{3+}_{(aq)} + 3e^- \longrightarrow Cr_{(s)}$; $E^\circ = -0.74$ V

He made following conclusions:

I. $SnSO_4$ solution can be stored in Fe vessel.

II. $FeSO_4$ solution can be stored in Zn vessel.

III. $Cr_2(SO_4)_3$ solution can be stored in Sn vessel.

IV. $ZnSO_4$ solution cannot be stored in iron vessel.

The correct conclusion(s) is/are

(a) I and II (b) III and IV

(c) III only (d) all of these.

52. Arun, a class-12 student has a good habit of practicing the topic at home whichever taught in the class. After learning Nernst equation in class, he tried writing few Nernst equations for different cells. Next day when he shown the work to his class teacher she said all are correct except one.

The incorrect Nernst equation is

(a) $Pt_{(s)} | H_{2(g)}, (1\text{ bar}) | H^+_{(aq)}, 1\text{ M} || M^{4+}_{(aq)}, M^{2+}_{(aq)} | Pt_{(s)}$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2} \log \frac{[M^{2+}][H^+]^2}{[M^{4+}]}$$

(b) $Pt | M | M^{3+} (0.001\text{ mol L}^{-1}) || Ag^+ (0.01\text{ mol L}^{-1}) | Ag$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{3} \log \frac{[M^{3+}]}{[Ag^+]^3}$$

(c) $Zn_{(s)} | ZnSO_{4(aq)} || CuSO_{4(aq)} | Cu_{(s)}$

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

(d) $Ni_{(s)} | Ni^{2+}_{(aq)} || Ag^+_{(aq)} | Ag_{(s)}$

$$E_{\text{cell}} = (E^\circ_{Ag^+/Ag} - E^\circ_{Ni^{2+}/Ni}) - \frac{0.059}{2} \log \frac{[Ni^{2+}]}{[Ag^+]^2}$$

Case Based MCQs

Case I : Read the passage given below and answer the following questions from 53 to 57.

The study of the conductivity of electrolyte solutions is important for the development of electrochemical devices, for the characterisation of the dissociation equilibrium of weak electrolytes and for the fundamental understanding of charge transport by ions. The conductivity of electrolyte is measured for electrolyte solution with concentrations in the range of 10^{-3} to 10^{-1} mol L^{-1}, as solution in this range of concentrations can be easily prepared. The molar conductivity (Λ_m) of strong electrolyte solutions can be nicely fit by Kohlrausch equation.

$$\Lambda_m = \Lambda_m^\circ - K\sqrt{C} \qquad \text{...(i)}$$

Where, Λ_m° is the molar conductivity at infinite dilution and C is the concentration of the solution. K is an empirical proportionality constant to be obtained from the experiment. The molar conductivity of weak electrolytes, on the other hand, is dependent on the degree of dissociation of the electrolyte. At the limit of very dilute solution, the Ostwald dilution law is expected to be followed,

$$\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^\circ} + \frac{\Lambda_m}{(\Lambda_m^\circ)^2}\frac{C_A}{K_d} \qquad \text{...(ii)}$$

where, C_A is the analytical concentration of the electrolyte and K_d is dissociation constant. The molar conductivity at infinite dilution can be decomposed into the contributions of each ion.

$$\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ \qquad \text{...(iii)}$$

Where, λ_+ and λ_- are the ionic conductivities of positive and negative ions, respectively and ν_+ and ν^- are their stoichiometric coefficients in the salt molecular formula.

53. Which statement about the term infinite dilution is correct?

(a) Infinite dilution refers to hypothetical situation when the ions are infinitely far apart.

(b) The molar conductivity at infinite dilution of NaCl can be measured directly in solution.

(c) Infinite dilution is applicable only to strong electrolytes.

(d) Infinite dilution refers to a real situation when the ions are infinitely far apart.

54. Which of the following is a strong electrolyte in aqueous solution?

(a) HNO_2 (b) HCN

(c) NH_3 (d) HCl

55. Which of the following is a weak electrolyte in aqueous solution?

(a) K_2SO_4 (b) Na_3PO_4

(c) NaOH (d) H_2SO_3

56. If the molar conductivities at infinite dilution for NaI, CH_3COONa and $(CH_3COO)_2Mg$ are 12.69, 9.10 and 18.78 S cm^2 mol^{-1} respectively at 25°C, then the molar conductivity of MgI_2 at infinite dilution is

(a) 25.96 S cm^2, mol^{-1} (b) 390.5 S cm^2 mol^{-1}

(c) 189.0 S cm^2 mol^{-1}

(d) 3.89×10^{-2} S cm^2 mol^{-1}

57. Which of the following is the correct order of molar ionic conductivities of the following ions in aqueous solutions?

(a) $Li^+ < Na^+ < K^+ < Rb^+$

(b) $Li^+ > Na^+ > K^+ > Rb^+$

(c) $Rb^+ < Na^+ < Li^+ < K^+$

(d) $Li^+ < Rb^+ < Na^+ < K^+$

Case II : Read the passage given below and answer the following questions from 58 to 62.

The electrochemical cell shown below is concentration cell.

$M|M^{2+}$ (saturated solution of a sparingly soluble salt, MX_2)$||M^{2+}$ (0.001 mol dm^{-3})$|M$

The emf of the cell depends on the difference in concentrations of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.

58. The solubility product (K_{sp}, mol^3 dm^{-9}) of MX_2 at 298 K based on the information available for the given concentration cell is (take $2.303 \times R \times 298/F = 0.059$)

(a) 2×10^{-15} (b) 4×10^{-15}

(c) 3×10^{-12} (d) 1×10^{-12}

59. The value of ΔG (in kJ mol^{-1}) for the given cell is (take 1 F = 96500 C mol^{-1})

(a) 3.7 (b) –3.7

(c) 10.5 (d) –11.4

60. The equilibrium constant for the following reaction is

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

(Given: $E^\circ_{Ce^{4+}/Ce^{3+}} = 1.44$ V and $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.68$ V)

(a) 7.6×10^{12}
(b) 6.5×10^{10}
(c) 5.2×10^{9}
(d) 3.4×10^{12}

61. The solubility product of a saturated solution of Ag_2CrO_4 in water at 298 K if the emf of the cell $Ag|Ag^+$ (satd. Ag_2CrO_4 soln)$||Ag^+$ (0.1 M)$|Ag$ is 0.164 V at 298 K, is

(a) 3.359×10^{-12} mol^3 L^{-3}
(b) 2.287×10^{-12} mol^3 L^{-3}
(c) 1.158×10^{-12} mol^3 L^{-3}
(d) 4.135×10^{-12} mol^3 L^{-3}

62. To calculate the standard emf of the cell, which of the following options is correct if $E°$ is reduction potential values?

(a) emf = $E°_{\text{cathode}} - E°_{\text{anode}}$
(b) emf = $E°_{\text{anode}} - E°_{\text{cathode}}$
(c) emf = $E°_{\text{anode}} + E°_{\text{cathode}}$
(d) None of these

Case III : Read the passage given below and answer the following questions.

Nernst equation relates the reduction potential of an electrochemical reaction to the standard potential and activities of the chemical species undergoing oxidation and reduction.

Let us consider the reaction, $M^{n+}{}_{(aq)} \longrightarrow nM_{(s)}$

For this reaction, the electrode potential measured with respect to standard hydrogen electrode can be given as

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

In the following questions (Q. No. 63-67), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

63. Assertion : For concentration cell, $Zn_{(s)}|Zn^{2+}{}_{(aq)}||Zn^{2+}{}_{(aq)}|Zn$

$C_1 \quad C_2$

For spontaneous cell reaction, $C_1 < C_2$

Reason : For concentration cell, $E_{\text{cell}} = \frac{RT}{nF}\log\frac{C_2}{C_1}$

For spontaneous reaction, E_{cell} = +ve so, $C_2 > C_1$.

64. Assertion : For the cell reaction,

$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

voltmeter gives zero reading at equilibrium.

Reason : At the equilibrium, there is no change in concentration of Cu^{2+} and Zn^{2+} ions.

65. Assertion : The Nernst equation gives the concentration dependence of emf of the cell.

Reason : In a cell, current flows from cathode to anode.

66. Assertion : Increase in the concentration of copper half cell in a cell, increases the emf of the cell.

Reason : $E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$

67. Assertion : Electrode potential for the electrode Mn^+/Mn with concentration is given by the expression under STP conditions.

$$E = E° + \frac{0.059}{n}\log[Mn^+]$$

Reason : STP conditions require the temperature to be 273 K.

Case IV : Read the passage given below and answer the following questions from 68 to 72.

The concentration of potassium ions inside a biological cell is at least twenty times higher than the outside. The resulting potential difference across the cell is important in several processes such as transmission of nerve impulses and maintaining the ion balance. A simple model for such a concentration cell involving a metal M is

$M_{(s)}|M^+(aq.;\ 0.05\ \text{molar})||M^+(aq;\ 1\ \text{molar})|M_{(s)}$

68. For the above cell,

(a) $E_{\text{cell}} = 0\ ;\ \Delta G > 0$
(b) $E_{\text{cell}} > 0\ ;\ \Delta G < 0$
(c) $E_{\text{cell}} < 0\ ;\ \Delta G > 0$
(d) $E_{\text{cell}} > 0\ ;\ \Delta G = 0$

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

(a) 130 mV
(b) 185 mV
(c) 154 mV
(d) 600 mV

70. The value of equilibrium constant for a feasible cell reaction is

(a) < 1 (b) $= 1$

(c) > 1 (d) zero

71. What is the emf of the cell when the cell reaction attains equilibrium?

(a) 1 (b) 0

(c) > 1 (d) < 1

72. The potential of an electrode change with change in

(a) concentration of ions in solution

(b) position of electrodes

(c) voltage of the cell

(d) all of these.

Case V : Read the passage given below and answer the following questions from 73 to 75.

All chemical reactions involve interaction of atoms and molecules. A large number of atoms/ molecules are present in a few gram of any chemical compound varying with their atomic/ molecular masses. To handle such large number conveniently, the mole concept was introduced. All electrochemical cell reactions are also based on mole concept. For example, a 4.0 molar aqueous solution of NaCl is prepared and 500 mL of this solution is electrolysed. This leads to the evolution of chlorine gas at one of the electrode. The amount of products formed can be calculated by using mole concept.

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

(a) 0.5 (b) 1.0

(c) 1.5 (d) 1.9

74. If cathode is a Hg electrode, then the maximum weight of amalgam formed from this solution is

(Given : Atomic mass of Na = 23u and Hg = 200.59 u)

(a) 300 g (b) 446 g

(c) 396 g (d) 296 g

75. In electrolysis of aqueous NaCl solution when Pt electrode is taken, then which gas is liberated at cathode?

(a) H_2 gas (b) Cl_2 gas

(c) O_2 gas (d) None of these

Assertion & Reasoning Based MCQs

For question numbers 76-90, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

76. Assertion : The conductivity depends on the charge and size of the ions in which they dissociate, the concentration of ions or ease with which the ions move under potential gradient.

Reason : The conductivity of solutions of different electrolytes in the same solvent and at a given temperature is same.

77. Assertion : If standard reduction potential for the reaction,

$Ag^+ + e^- \rightarrow Ag$ is 0.80 volt, then for the reaction, $2Ag^+ + 2e^- \rightarrow 2Ag$, it will be 1.60 volt.

Reason : If concentration of Ag^+ ions is doubled, the standard electrode potential remains same.

78. Assertion : If $\lambda^o_{Na^+}$ and $\lambda^o_{Cl^-}$ are molar limiting conductivities of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation, $\Lambda^\circ_{NaCl} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$.

Reason : This is according to Kohlrausch law of independent migration of ions.

79. Assertion : The conductivity of solution is greater than pure solvent.

Reason : Conductivity depends upon number of the ions present in solution.

80. Assertion : At the end of electrolysis using platinum electrodes, an aqueous solution of copper sulphate turns colourless.

Reason : Copper in $CuSO_4$ is converted to $Cu(OH)_2$ during the electrolysis.

81. Assertion : The electrical resistance of any object decreases with increase in its length.

Reason : The electrical resistance of any object decreases with increase in its area of cross-section.

82. Assertion : Substances like glass, ceramics, etc. having very low conductivity are known as insulators.

Reason : They do not allow the passage of electric current through them.

83. Assertion : Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally.

Reason : Kohlrausch law helps to find the molar conductivity of a weak electrolyte at infinite dilution.

84. Assertion : The observed conductance depends upon the nature of the electrolyte and the concentration of the solution.

Reason : The cell constant of a cell depends upon the nature of the material of the electrodes.

85. Assertion : The molar conductivity of strong electrolyte decreases with increase in concentration.

Reason : At high concentration, migration of ions is slow.

86. Assertion : The molar conductance of weak electrolyte at infinite dilution is equal to the sum of molar conductance of cations and anions.

Reason : Kohlrausch's law is applicable for strong electrolytes.

87. Assertion : Equivalent conductance of all electrolytes decreases with increasing concentration.

Reason : More number of ions are available per gram equivalent at higher concentration.

88. Assertion : Specific conductance decreases with dilution whereas equivalent conductance increases.

Reason : On dilution, number of ions per millilitre decreases but total number of ions increases considerably.

89. Assertion : The ratio of specific conductivity to the observed conductance does not depend upon the concentration of the solution taken in the conductivity cell.

Reason : Specific conductivity decreases with dilution whereas observed conductance increases with dilution.

90. Assertion : Kohlrausch law helps to find the molar conductivity of weak electrolyte at infinite dilution.

Reason : Molar conductivity of a weak electrolyte at infinite dilution cannot be determined experimentally.

SUBJECTIVE TYPE QUESTIONS

Very Short Answer Type Questions (VSA)

1. Express the relation between conductivity and molar conductivity of a solution held in a cell?

2. Limiting molar conductivity of an electrolyte cannot be determined experimentally. Why?

3. Following reactions occur at cathode during the electrolysis of aqueous silver chloride solution :

$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$, $E^\circ = +0.80$ V

$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)}$, $E^\circ = 0.00$ V

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?

4. Give reason :

Molar conductivity of CH_3COOH increases on dilution.

5. Give reason :

On the basis of E° values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl.

6. What is the necessity to use a salt bridge in a Galvanic cell?

7. What is the use of platinum foil in the hydrogen electrode?

8. Out of HCl and NaCl, which do you expect will have greater value for Λ_m and why?

9. State Kohlrausch's law of independent migration of ions. Write its one application.

10. Following reactions occur at cathode during the electrolysis of aqueous copper (II) chloride solution :

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)} \text{ ; } E^\circ = +0.34 \text{ V}$$

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)} \text{ ; } E^\circ = 0.00 \text{ V}$$

On the basis of their standard reduction electrode potential (E°) values, which reaction is feasible at the cathode and why?

Short Answer Type Questions (SA-I)

11. Define the term degree of dissociation. Write an expression that relates the molar conductivity of a weak electrolyte to its degree of dissociation.

12. (i) Explain why fluorine is the strongest oxidising agent?

(ii) Lithium metal is the strongest reducing agent. Why?

13. The standard electrode potential (E°) for Daniell cell is +1.1 V. Calculate the $\Delta_r G^\circ$ for the reaction.

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

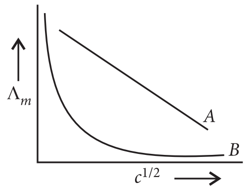
($1 \text{ F} = 96500 \text{ C mol}^{-1}$)

14. What is the difference between electronic and electrolytic conductors?

15. Define electrochemical cell. What happens if external potential applied becomes greater than E°_{cell} of electrochemical cell?

16. Why a galvanic cell stops working after sometime?

17. In the plot of molar conductivity (Λ_m) *vs* square root of concentration ($c^{1/2}$),following curves are obtained for two electrolytes *A* and *B*.



Answer the following :

(i) Predict the nature of electrolytes *A* and *B*.

(ii) What happens on extrapolation of Λ_m to concentration approaching zero for electrolytes *A* and *B*?

18. Two half-reactions of an electrochemical cell are given below :

$MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \rightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$, $E^\circ = + 1.51\text{V}$

$Sn^{2+}_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 2e^-$, $E^\circ = + 0.15$ V

Construct the redox equation from the standard potential of the cell and predict if the reaction is reactant favoured or product favoured.

19. The conductivity of 0.001 M acetic acid is 4×10^{-5} S/cm. Calculate the dissociation constant of acetic acid, if molar conductivity at infinite dilution for acetic acid is 390 S cm^2/mol.

20. Equilibrium constant (K_c) for the given cell reaction is 10. Calculate E°_{cell}.

$$A_{(s)} + B^{2+}_{(aq)} \rightleftharpoons A^{2+}_{(aq)} + B_{(s)}$$

21. Given that the standard electrode potential (E°) of metals are :

$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V,

$Cu^{2+}/Cu = 0.34$ V,

$Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74$ V,

$Fe^{2+}/Fe = -0.44$ V.

Arrange these metals in an increasing order of their reducing power.

Short Answer Type Questions (SA-II)

22. Mention few applications of electrochemical series.

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

Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.50 M)

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

$E^\circ_{Ni^{2+}/Ni} = -0.25$ V and $E^\circ_{Al^{3+}/Al} = -1.66$ V.

($\log 8 \times 10^{-6} = -5.09$)

24. A cell is prepared by dipping copper rod in 1 M copper sulphate solution and zinc rod in 1 M zinc sulphate solution. The standard reduction potential of copper and zinc are 0.34 V and –0.76 V respectively.

(i) What will be the cell reaction?

(ii) What will be the standard electromotive force of the cell?

(iii) Which electrode will be positive?

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

26. Calculate the potential for half-cell containing

0.10 M $K_2Cr_2O_{7(aq)}$, 0.20 M $Cr^{3+}_{(aq)}$ and

1.0×10^{-4} M $H^{+}_{(aq)}$. The half cell reaction is :

$Cr_2O^{2-}_{7(aq)} + 14H^{+}_{(aq)} + 6e^{-} \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$
and the standard electrode potential is given as $E^\circ = 1.33$ V.

27. Estimate the minimum potential difference needed to reduce Al_2O_3 at 500°C. The Gibbs energy change for the decomposition reaction,

$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$ is 960 kJ.

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

28. For the cell reaction,

$Ni_{(s)}|Ni^{2+}_{(aq)}||Ag^{+}_{(aq)}|Ag_{(s)}$

Calculate the equilibrium constant at 25°C. How much maximum work would be obtained by operation of this cell?

$E^\circ_{(Ni^{2+}/Ni)} = -0.25\ V$ and $E^\circ_{Ag^+/Ag} = 0.80$ V

29. Calculate $\Delta_r G$ and $\log K_c$ for the following reaction.

$Cd^{2+}_{(aq)} + Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + Cd_{(s)}$

Given : $E^\circ_{Cd^{2+}/Cd} = -0.403$ V ; $E^\circ_{Zn^{2+}/Zn} = -0.763$ V

30. The equivalent conductivity of 0.05 N solution of a monobasic acid is 15.8 mho $cm^2\ eq^{-1}$. If equivalent conductivity of the acid at infinite dilution is 350 mho $cm^2\ eq^{-1}$, calculate the (a) degree of dissociation of acid (b) dissociation constant of acid.

31. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.5×10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.

32. Depict the galvanic cell in which the reaction $Zn_{(s)} + 2Ag^{+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$ takes place. Further show :

(i) Which of the electrode is negatively charged?

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

(iii) Individual reaction at each electrode.

33. What is the difference between a chemical and a concentration cell?

34. A copper-silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell.

Given : $E^\circ_{Ag^+/Ag} = +0.80\ V$, $E^\circ_{Cu^{2+}/Cu} = +0.34\ V$

35. The resistance of 100 cm^3 aqueous solution of 0.025 M $CuSO_4$ is 520 ohm at 298 K. Calculate the molar conductivity if the cell constant of the conductivity cell is 153.7 m^{-1}.

36. When a certain conductance cell was filled with 0.1 M KCl, it has a resistance of 85 ohms at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductance of the electrolyte at this concentration.

[Specific conductance of 0.1 M KCl
= 1.29×10^{-2} $ohm^{-1}\ cm^{-1}$]

Long Answer Type Questions (LA)

37. E°_{cell} for the given redox reaction is 2.71 V.

$Mg_{(s)} + Cu^{2+}\ (0.01\ M) \longrightarrow Mg^{2+}\ (0.001\ M) + Cu_{(s)}$

Calculate E_{cell} for the reaction. Write the direction of flow of current when an external opposite potential applied is

(i) less than 2.71 V and (ii) greater than 2.71 V

38. (a) Calculate standard emf of the cell in which following reaction takes place at 25°C.

$Cu_{(s)} + Cl_{2(g)} \rightleftharpoons Cu^{2+} + 2Cl^{-}$

$E^\circ_{Cl_2/Cl^-} = +1.36$ V, $E^\circ_{Cu^{2+}/Cu} = +0.34$ V

Also calculate standard free energy change and equilibrium constant of the reaction.

(b) The emf of a galvanic cell composed of two hydrogen electrode is 0.16 volt at 25°C. Calculate pH of the anode solution if the cathode is in a solution with pH = 1.

39. (a) Calculate the cell emf and ΔG° for the cell reaction at 25°C for the cell :

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

E° values at 25°C : $Zn^{2+}/Zn = -0.763$ V;

$Cd^{2+}/Cd = -0.403$ V; $F = 96500$ C mol^{-1};

$R = 8.314$ J K^{-1} mol^{-1}.

(b) If E° for copper electrode is 0.34 V, how will you calculate its emf value when the solution in contact with it is 0.1 M in copper ions? How does emf for copper electrode change when concentration of Cu^{2+} ions in the solution is decreased?

40. (a) Equivalent conductance of a 0.0128 N solution of acetic acid is 1.4 mho cm^2 eq^{-1} and conductance at infinite dilution is 391 mho cm^2 eq^{-1}. Calculate degree of dissociation and dissociation constant of acetic acid.

(b) The equivalent conductances of sodium acetate, sodium chloride and hydrochloric acid are 83, 127 and 426 mho cm^2 eq^{-1} at 250°C respectively. Calculate the equivalent conductance of acetic acid solution.

ANSWERS

OBJECTIVE TYPE QUESTIONS

1. (b) : Higher the oxidation potential, more easily it is oxidised and hence greater is the reducing power. Hence, increasing order of reducing power is Ag < Cr < Mg < K.

2. (b) : $E^\circ_{cell} = E^\circ_{Ag_2O/Ag} - E^\circ_{Zn^{2+}/Zn}$

$= 0.344 - (-0.76) = 1.104$ V

$\Delta G^\circ = -nFE^\circ_{cell} = -2 \times 96500 \times 1.104$

$= -2.13 \times 10^5$ J mol^{-1}

3. (a) : $$E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

Since concentration of solid is taken as unity,

$$E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]}$$

4. (c) : $\Lambda^\circ_{m\ CaCl_2} = \lambda^\circ_{Ca^{2+}} + 2\lambda^\circ_{Cl^-}$

$= 119.0 + 2 \times 76.3 = 271.6$ S cm^2 mol^{-1}

$\Lambda^\circ_{m\ CH_3COONa} = \lambda^\circ_{CH_3COO^-} + \lambda^\circ_{Na^+}$

$= 40.9 + 50.1 = 91$ S cm^2 mol^{-1}

$\Lambda^\circ_{m\ NaCl} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-}$

$= 50.1 + 76.3 = 126.4$ S cm^2 mol^{-1}

5. (d) : The electronic conductance depends on all these factors.

6. (a) : If an external potential of 1.1 V is applied to the cell, the reaction stops and no current flows through the cell. Any further increase in external potential again starts the reaction but in opposite direction and the cell functions as an electrolytic cell.

7. (a) : Daniell cell converts the chemical energy liberated during the redox reaction to electrical energy and has an electrode potential of 1.1 V.

8. (c) : At anode : $Fe \rightarrow Fe^{2+}(0.001\ M) + 2e^-$

At cathode : $2H^+\ (1\ M) + 2e^- \rightarrow H_2\ (1\ bar)$

Net reaction : $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$

Nernst equation for the given cell,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2}\log\frac{[Fe^{2+}][H_2]}{[Fe][H^+]^2}$$

9. (a) : At cathode : $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

At anode : $2OH^-_{(aq)} \rightarrow \frac{1}{2}O_{2(g)} + H_2O_{(l)} + 2e^-$

10. (c) : According to convention, the standard hydrogen electrode is assigned a zero potential at all temperatures.

11. (a) : $$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Ion]_{RHS}}{[Ion]_{LHS}}$$

12. (a) : Lower the reduction potential, more is the reducing power. Thus, the order is

$Br^- < Fe^{2+} < Al$.

13. (c) : (a) $\log K = \dfrac{nFE^\circ_{cell}}{2.303RT}$

(b) $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{2}\log\dfrac{[a_1]}{[a_2]}$

(d) Expression is valid at 298 K, not at 273 K.

14. (b) : $\kappa = G \times \dfrac{l}{A}$

$$\frac{l}{A} = \kappa \times \frac{1}{G} = \kappa \times R = 0.0212 \times 55 = 1.166\ \text{cm}^{-1}$$

15. (a) : $Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$ can be represented as

$Zn_{(s)} \,|\, Zn^{2+}_{(aq)} \,||\, Ag^+_{(aq)} \,|\, Ag_{(s)}$

16. (a) : $\Lambda^\circ_{Al_2(SO_4)_3} = 2\lambda^\circ_{Al^{3+}} + 3\lambda^\circ_{SO_4^{2-}}$

$$\lambda^\circ_{Al^{3+}} = \frac{\Lambda^\circ_{Al_2(SO_4)_3} - 3\lambda^\circ_{SO_4^{2-}}}{2}$$

$$= \frac{858 - (3 \times 160)}{2} = 189\ \text{S cm}^2\ \text{mol}^{-1}$$

17. (a) : The cell reaction will be

$Ni_{(s)} + 2Ag^+_{(aq)} \longrightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$
$= 0.80 - (-0.25) = +1.05\text{ V}$

$\Delta G^\circ = -nFE^\circ_{\text{cell}}$

As $E^\circ_{\text{cell}} = +\text{ve}$,

$\Delta G^\circ = -\text{ve}$, hence reaction is feasible.

18. (a) : $Mg^{2+}_{(aq)} + 2e^- \longrightarrow Mg_{(s)}$; $E^\circ = -2.36\text{ V}$
$2H^+ + 2e^- \longrightarrow H_{2(g)}$; $E^\circ = 0.00\text{ V}$
Thus, oxidation takes place at magnesium electrode and reduction at hydrogen electrode.

19. (b) : $\Lambda^\circ_m\, NaBr = \Lambda^\circ_m\, NaCl + \Lambda^\circ_m\, KBr - \Lambda^\circ_m\, KCl$

20. (a) : The ion which requires less energy is liberated first.

21. (a) : $\log K_c = \dfrac{nE^\circ_{\text{cell}}}{0.0591}$

For the given reaction, $n = 1$

$\log K_c = \dfrac{1 \times 0.36}{0.0591} = 6.09$

$K_c = \text{antilog } 6.09 = 1.2 \times 10^6$

22. (c) : Iron coated with zinc does not get rusted even if cracks appear on the surface because Zn will take part in redox reaction not Fe as Zn is more reactive than Fe. If iron is coated with tin and cracks appear on the surface, Fe will take part in redox reaction because Sn is less reactive than Fe.

23. (c) : In reactivity series,

Mg > Al > Zn > Fe > Cu

$\xrightarrow{\text{Reactivity decreases}}$

Hence, Mg can displace Al, Al can displace Zn and so on.

24. (a) : Nickel-Cadmium battery

Anode - Cd ; Cathode - NiO_2 ; Electrolyte - KOH

At anode : $Cd_{(s)} + 2OH^-_{(aq)} \longrightarrow Cd(OH)_{2(s)} + 2e^-$

At cathode : $NiO_{2(s)} + 2H_2O_{(l)} + 2e^- \longrightarrow Ni(OH)_{2(s)} + 2OH^-_{(aq)}$

$Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(l)} \longrightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(s)}$

25. (c) : $\Lambda_m = \dfrac{\kappa \times 1000}{M} = \dfrac{1.52 \times 10^{-2} \times 1000}{0.15}$

$= 101\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$

26. (b) : Higher the reduction potential, stronger is the oxidising agent.

27. (a) : During the electrolysis of dilute sulphuric acid, the following process is possible at anode:

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

28. (d) : For strong electrolytes, the plot between Λ_m and $C^{1/2}$ is a straight line.
For weak electrolytes, Λ_m increases steeply on dilution, especially near low concentrations.

29. (a) : $\lambda^\circ_{HCOOH} = \lambda^\circ_{H^+} + \lambda^\circ_{HCOO^-}$

$= 349.6 + 54.6 = 404.2\text{ S cm}^2\text{ mol}^{-1}$

$\alpha = \dfrac{\Lambda_m}{\Lambda^\circ_m} = \dfrac{46.1}{404.2} = 0.114 \times 100 = 11.4\%$

$K_a = \dfrac{C\alpha^2}{1-\alpha} = \dfrac{0.025 \times (0.114)^2}{1 - 0.114}$

$= \dfrac{0.025 \times 0.114 \times 0.114}{0.886} = 3.67 \times 10^{-4}\text{ mol L}^{-1}$

30. (b) : $E = E^\circ + \dfrac{0.059}{2}\log[Mg^{2+}]$.

Hence, plot of E *vs* log $[Mg^{2+}]$ will be linear with positive slope and intercept = E°.

31. (c) : $Cu^{2+} + e^- \longrightarrow Cu^+$; $E^\circ_1 = 0.15\text{ V}, \Delta G^\circ_1, n_1 = 1$
$Cu^{2+} + 2e^- \longrightarrow Cu$; $E^\circ_2 = 0.34\text{ V}, \Delta G^\circ_2, n_2 = 2$
$Cu^+ + e^- \longrightarrow Cu$; $E^\circ_3 = ?, \Delta G^\circ_3, n_3 = 1$
$\Delta G^\circ_3 = \Delta G^\circ_2 - \Delta G^\circ_1$
$-n_3 FE^\circ_3 = -n_2 FE^\circ_2 + n_1 FE^\circ_1$
$-E^\circ_3 = -2 \times 0.34 + 1 \times 0.15$
$E^\circ_3 = 0.68 - 0.15 = +0.53\text{ V}$

32. (d) : In fig. (*Y*), zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

33. (d)

34. (b) : Electrolyte *X* is strong electrolyte as on dilution the number of ions remain same, only interionic attraction decreases and hence not much increase in Λ_m as seen. While Λ_m for a weak electrolyte increases significantly.

35. (b) : $\kappa = \dfrac{1}{R} \times \dfrac{l}{A} = \dfrac{1}{40} \times \dfrac{2}{5}$

$$\Lambda_{eq} = \kappa \times \frac{1000}{N} = \frac{1}{40} \times \frac{2}{5} \times \frac{1000}{0.5} = 20\text{ ohm}^{-1}\text{ cm}^2\text{ eq}^{-1}$$

36. (c) : At cathode : $Ag^+ + e^- \longrightarrow Ag$; $E^\circ = +0.80\text{ V}$
At anode : $Pb \longrightarrow Pb^{2+} + 2e^-$; $E^\circ = +0.13\text{ V}$
$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.80 - 0.13 = 0.67\text{ V}$
Hence, the reaction will be
$2Ag^+ + Pb \longrightarrow Pb^{2+} + 2Ag$

37. (c) : Specific conductance = S m^{-1}

38. (a) : Conductivity decreases because number of ions per unit volume decreases.

39. (c) : Solubility $= \dfrac{\kappa \times 1000}{\Lambda^\circ_m}$

$= \dfrac{1.821 \times 10^{-5} \times 1000}{130.26} = 13.97 \times 10^{-5}\ \text{mol L}^{-1}$

$= 13.97 \times 10^{-5} \times 143.5 \qquad (\text{AgCl} = 108 + 35.5 = 143.5)$

$= 2.004 \times 10^{-2}\ \text{g L}^{-1}$

40. (b) : $\text{Pt} + \text{Cl}_2 \rightarrow \text{Pt}^{2+} + 2\text{Cl}^- \ ; E^\circ_{\text{cell}} = 0.15\ \text{V}$

$+ \quad \text{Pt}^{2+} + 2e^- \rightarrow \text{Pt} \ ; E^\circ = 1.20\ \text{V}$

$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^- \ ; E^\circ = 1.35\ \text{V}$

41. (d) : Due to reduction of NO_3^- in preference to H^+ ion. H^+ ion is not reduced to give H_2 gas.

42. (b) : For $2\text{Ag}^+ + \text{H}_2\ (1\ \text{atm}) \rightarrow 2\text{Ag} + 2\text{H}^+(1\ \text{M})$

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

43. (c) : $2\text{I}^- \rightarrow \text{I}_2 + 2e^-$ (Oxidation)

$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$ (Reduction)

$2\text{I}^- + \text{Br}_2 \rightarrow \text{I}_2 + 2\text{Br}^-$ is net cell reaction

44. (d) : $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

It will remain unchanged.

45. (c) : $\Lambda^\circ_{\text{Ba(OH)}_2} = \Lambda^\circ_{\text{Ba}^{2+}} + 2\Lambda^\circ_{\text{OH}^-}$

$\Lambda^\circ_{\text{BaCl}_2} = \Lambda^\circ_{\text{Ba}^{2+}} + 2\Lambda^\circ_{\text{Cl}^-}$

$\Lambda^\circ_{\text{NH}_4\text{Cl}} = \Lambda^\circ_{\text{NH}_4^+} + \Lambda^\circ_{\text{Cl}^-}$

After substituting the above in

$$\Lambda^\circ_{\text{NH}_4\text{OH}} = \frac{\Lambda^\circ_{\text{Ba(OH)}_2} + 2\Lambda^\circ_{\text{NH}_4\text{Cl}} - \Lambda^\circ_{\text{BaCl}_2}}{2}$$

we get, $\Lambda^\circ_{\text{NH}_4\text{OH}} = \Lambda^\circ_{\text{NH}_4^+} + \Lambda^\circ_{\text{OH}^-}$

46. (a) : $\Lambda^\infty_{m\ \text{CH}_3\text{COOH}} = 390.71\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$

$\Lambda^c_{m\ \text{CH}_3\text{COOH}} = 14.3\ \text{ohm}^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$

Degree of dissociation (α)

$$= \frac{\Lambda^c_m}{\Lambda^\infty_m} = \frac{14.3}{390.71} = 0.0366 \ \textit{i.e.}\ 3.66\%$$

47. (c) : E°_{cell} should be positive for a spontaneous reaction as $\Delta G^\circ = -nFE^\circ_{\text{cell}}$.

48. (d) : Possible reactions at the anode during electrolysis of CuSO_4 solution are

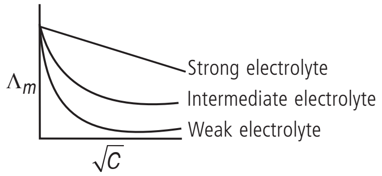
$2\text{SO}^{2-}_{4(aq)} \rightarrow \text{S}_2\text{O}^{2-}_{8(aq)} + 2e^- \ ; E^\circ_{\text{red}} = +2.07\ \text{V}$

$2\text{H}_2\text{O}_{(l)} \rightarrow \text{O}_{2(g)} + 4\text{H}^+_{(aq)} + 4e^- \ ; E^\circ_{\text{red}} = +1.23\ \text{V}$

Comparing reduction potentials values,

H_2O molecules will be oxidised at anode, given oxygen gas.

49. (b) : Salts that have polyvalent cations or anions are intermediate electrolytes (AlPO_4).



50. (c) : At cathode (Reduction) : $2\text{Ag}^+_{(aq)} + 2e^- \rightarrow 2\text{Ag}_{(s)}$

At anode (oxidation) : $\text{Mg}_{(s)} \rightarrow \text{Mg}^{2+}_{(aq)} + 2e^-$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{2F}\ln\frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2} = E^\circ_{\text{cell}} - \frac{0.059}{2}\log\frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Mg}^{2+}/\text{Mg}}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2}\log\frac{(0.130)}{(0.0001)^2}$$

51. (c) : A more negative E° value means that the redox couple is stronger reducing agent than the other one.

52. (c) : For the cell given in option (c),

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

53. (a) **54. (d)**

55. (d) : Weak electrolytes do not dissociate in aqueous solution.

56. (a) : According to Kohlrausch's law

$\Lambda^\circ_{(\text{MgI}_2)} = \Lambda^\circ_{[(\text{CH}_3\text{COO})_2\text{Mg}]} + 2\Lambda^\circ_{(\text{NaI})} - 2\Lambda^\circ_{(\text{CH}_3\text{COONa})}$

$= 18.78 + 2(12.69) - 2(9.10) = 25.96\ \text{S cm}^2\ \text{mol}^{-1}$

57. (a)

58. (b) : $0.059 = \dfrac{+0.059}{2}\log\dfrac{0.001}{[M^{2+}]}$

$\log\dfrac{0.001}{[M^{2+}]} = 2 \quad \text{or} \quad [M^{2+}] = 10^{-5}$

Let solubility of salt be s mol/litre.

$$\text{Thus,}\ \underset{0}{MX_2} \longrightarrow \underset{s}{M^{2+}} + \underset{2s}{2X^-}$$

$\therefore \quad K_{sp} = 4s^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15}$

59. (d) : $\Delta G = -nFE = -2 \times 96500 \times 0.059$

$= -11387\ \text{J mol}^{-1} = -11.4\ \text{kJ mol}^{-1}$

60. (a) : $E^\circ_{\text{cell}} = \dfrac{0.059}{1}\log K_C$

$E^\circ_{\text{cell}} = E^\circ_{\text{Ce}^{4+}/\text{Ce}^{3+}} - E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$

$= 1.44 - 1.68 = 0.76\ \text{V}$

$\log_{10} K_c = \dfrac{0.76}{0.059} = 12.88$

$K_c = 7.6 \times 10^{12}$

61. (b) : $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.059}{1}\log\dfrac{[\text{Ag}^+]}{[\text{Ag}^+]_{\text{Satd. Ag}_2\text{CrO}_4}}$

$$0.164 = \frac{0.059}{1}\log\frac{0.1}{[Ag^+]_{\text{Satd. }Ag_2CrO_4}}$$

$[Ag^+]_{\text{Satd. }Ag_2CrO_4} = 1.66 \times 10^{-4}$ M

So, $[CrO_4^{2-}] = \frac{1.66\times10^{-4}}{2}$

$K_{sp}(Ag_2CrO_4) = [Ag^+]^2\,[CrO_4{}^{2-}]$

$= (1.66\times10^{-4})^2\left(\frac{1.66\times10^{-4}}{2}\right)$

$= 2.287 \times 10^{-12}$ mol^3 L^{-3}

62. (a)

63. (a) : $\log\left(\frac{C_1}{C_2}\right) < 0$ for spontaneity.

$\therefore\ C_1 < C_2$

64. (a)

65. (b)

66. (a)

67. (d) : Nernst equation is measured at 298 K. At STP conditions, temperature to be 273 K.

68. (b) :

$$\begin{array}{l} M_{(s)} \longrightarrow M^+_{(aq)}\ (0.05\text{ M}) + e^- \\ M^+_{(aq)}\ (1.0\text{ M}) + e^- \longrightarrow M_{(s)} \\ \hline M^+_{(aq)}\ (1.0\text{ M}) \longrightarrow M^+_{(aq)}\ (0.05\text{ M}) \\ \hline \end{array}$$

For concentration cell, $E_{\text{cell}} = -\frac{0.059}{1}\log\frac{0.05}{1}$

$E_{\text{cell}} = -\frac{0.059}{1}\log(5\times10^{-2})$

$E_{\text{cell}} = -\frac{0.059}{1}[(-2)+\log 5] = -0.059(-2 + 0.698)$

$= -0.059(-1.302) = 0.0768$

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

If E_{cell} is positive, ΔG is negative.

69. (c) : $\frac{E_1}{E_2} = \frac{\log 0.05}{\log 0.0025}$

$\frac{E_1}{E_2} = \frac{\log 5\times10^{-2}}{\log 25\times10^{-4}}$

$E_1 = 0.0768$

$\frac{0.0168}{E_2} = \frac{-1.3}{-2.6} = \frac{1}{2}$ or $E_2 = 154\text{ mV}$

70. (c) : $K = \text{antilog}\left(\frac{nE^\circ}{0.0591}\right)$

For feasible cell, E° is positive, hence from the above equation, $K > 1$ for a feasible cell reaction.

71. (b)

72. (a)

73. (b) : $n_{\text{NaCl}} = \frac{4\times500}{1000} = 2\text{ mol}$

$\therefore\ n_{Cl_2} = 1$ mol

74. (b) : n_{Na} deposited = 2 mol

$\therefore\ n_{\text{Na – Hg}}$ formed = 2 mol

$\therefore$ Mass of amalgam formed = 2 × 223 = 446 g

75. (a) : H_2 gas at cathode.

76. (c) : The conductivity of solutions of different electrolytes in the same solvent and at a given temperature is different.

Effect of concentration on electrode potential is found by Nernst equation.

77. (d) : Standard reduction potential of an electrode has a fixed value.

78. (a) : According to Kohlrausch law, "limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte."

79. (a) : When electrolytes are dissolved in solvent they furnish their own ions in the solution hence, its conductivity increases.

80. (c) : Cu^{2+} ions are deposited as Cu.

81. (d) : The electrical resistance of any object is directly proportional to its length, l, and inversely proportional to its area of cross-section, A. So, it increases with increase in length of object and decreases with increase in area of cross-section of object.

82. (a) : The substances which do not allow the flow of electric current through them are termed as insulators.

83. (b) : In the plot of molar conductivity versus concentration, the extrapolation to zero concentration is not possible. Since the graph is not linear.

84. (c) : The cell constant depends upon the distance between the electrodes and their area of cross section.

85. (a)

86. (c) : $\Lambda^\infty_{AB} = \lambda^\infty_{A^+} + \lambda^\infty_{B^-}$

Kohlrausch's law is applicable for weak electrolytes.

87. (c) : At higher concentration, mobility of ions decreases. Hence, conductance decreases.

88. (c) : Total number of ions will increase slightly on dilution (not considerably).

89. (b)

90. (a)

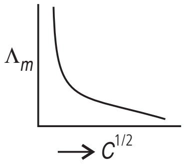
SUBJECTIVE TYPE QUESTIONS

1. $\Lambda_m = \frac{\kappa\times1000}{M}$ in CGS units

$\Lambda_m = \frac{\kappa\times10^{-3}}{M}$ in SI units

where, κ is the conductivity, M is the molar concentration and Λ_m is molar conductivity.

2. In weak electrolyte, the conductivity of the solution increases very slowly with dilution of solution and goes on increasing up to infinity. Therefore, it cannot be measured experimentally.



3. The species that get reduced at cathode is the one having higher value of standard reduction potential. Hence, the reaction that will occur at cathode is

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}.$$

4. Molar conductivity increases with 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 K on dilution of a solution is more than compensated by increase in its volume.

5. The reaction at anode with lower value of $E°$ is preferred *i.e.*, O_2 gas should be liberated but on account of over potential of oxygen reaction at anode, preferred reaction is

$$Cl^-_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^-$$

i.e., Cl_2 gas is liberated at anode in the electrolysis of aq. NaCl.

6. The salt bridge allows the movement of ions from one solution to the other without mixing of the two solutions. Moreover, it helps to maintain the electrical neutrality of the solutions in the two half cells.

7. It is used for the inflow and outflow of electrons.

8. HCl will have greater value of Λ_m because H^+ ions are smaller than Na^+ ions and hence H^+ ions have greater ionic mobility than Na^+ ions.

9. Kohlrausch's law of independent migration of ions : It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

Kohlrausch's law helps in the calculation of degree of dissociation of weak electrolytes like acetic acid.

10. The species that get reduced at cathode is the one which have higher value of standard reduction potential. Hence, the reaction that will occur at cathode is

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

11. The fraction of the total number of molecules present in solution as ions is known as degree of dissociation.

Molar conductivity $(\lambda_m) = \alpha\lambda^\circ_m$

where λ°_m is the molar conductivity at infinite dilution.

12. (i) Because fluorine has highest reduction potential.
(ii) Lithium metal is strongest reducing agent because Li has lowest reduction potential *i.e.*, $E^\circ_{Li^+/Li} = -3.05$ V

13. Here $n = 2$, $E^\circ_{cell} = 1.1$ V, $F = 96500$ C mol^{-1}

$\Delta_r G° = -nFE^\circ_{cell}$

$\Delta_r G° = -2 \times 1.1 \times 96500 = -212300$ J mol^{-1}

$= -212.3$ kJ mol^{-1}

14. The substance which conducts electricity by ions present in solution is called electrolytic conductor *e.g.*, NaCl solution. Substances which conduct electricity in solid state are called electronic conductors. These are made up of metals. *e.g.*, Cu, Zn, Al. (Electrolytes are electrolytic conductors while electrodes are electronic conductors).

15. The device which converts the chemical energy liberated during the chemical reaction to electrical energy is called electrochemical cell.

If external potential applied becomes greater than E°_{cell} of electrochemical cell then the cell behaves as an electrolytic cell and the direction of flow of current is reversed.

16. With time, concentrations of the electrolytic solutions change. Hence, their electrode potentials change when the electrode potentials of the two half-cells become equal, the cell stops working.

17. (i) Electrolyte A is a strong electrolyte while electrolyte B is a weak electrolyte.

(ii) For electrolyte A, the plot becomes linear near high dilution and thus can be extrapolated to zero concentration to get the molar conductivity at infinite dilution.

For weak electrolyte B, Λ_m increases steeply on dilution and extrapolation to zero concentration is not possible. Hence, molar conductivity at infinite dilution cannot be determined.

18. At anode : $Sn^{2+}_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + 2e^-] \times 5$

At cathode : $MnO^-_{4(aq)} + 8H^+_{(aq)} + 5e^- \longrightarrow$
$Mn^{2+}_{(aq)} + 4H_2O_{(l)}] \times 2$

Net cell reaction :

$$2MnO^-_{4(aq)} + 5Sn^{2+}_{(aq)} + 16H^+_{(aq)} \longrightarrow 2Mn^{2+}_{(aq)} + 5Sn^{4+}_{(aq)} + 8H_2O_{(l)}$$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 1.51\text{ V} - 0.15\text{ V} = 1.36$ V

Since, cell potential is positive therefore the reaction is product favoured.

19. $C = 0.001$ M, $\kappa = 4 \times 10^{-5}$ S cm^{-1},

$\Lambda^\infty_m = 390$ S cm^2/mol

$$\Lambda^c_m = \frac{\kappa \times 1000}{C}$$

Substituting the values,

$$\Lambda^c_m = \frac{4 \times 10^{-5} \times 1000}{0.001} = 40 \text{ S cm}^2\text{/mol}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{40}{390} = 0.10256 \approx 0.103$$

$$\begin{array}{ccccc} CH_3COOH & \rightleftharpoons & CH_3COO^- & + & H^+ \\ c & & 0 & & 0 \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

$$K_a = \frac{0.001(0.103)^2}{(1-0.103)} = \frac{1.061\times10^{-5}}{0.897} = 1.18\times10^{-5}$$

20. $A_{(s)} + B^{2+}_{(aq)} \rightleftharpoons A^{2+}_{(aq)} + B_{(s)}$

Here, $n = 2$

using formula,

$$E^\circ_{cell} = \frac{0.059}{n}\log K_c$$

$$E^\circ_{cell} = \frac{0.059}{2}\log 10$$

$E^\circ_{cell} = 0.0295$ V

21. The reducing power increases with decreasing value of electrode potential. Hence, the order is Ag < Cu < Fe < Cr < Mg < K.

22. (i) Ions with higher reduction potentials are strong oxidising agents while lower reduction potentials are strong reducing agents.

(ii) The electrode with higher electrode potential ($E°$) acts as cathode while with lower electrode potential will act as anode.

(iii) Predicting the feasibility of redox reaction.

(iv) Predicting the capability of metal to evolve H_2 gas from acid.

23. At anode : $Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^-] \times 2$

At cathode : $Ni^{2+} + 2e^- \rightarrow Ni_{(s)}] \times 3$

Cell reaction : $2Al_{(s)} + 3Ni^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Ni_{(s)}$

Applying Nernst equation to the above cell reaction,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2\times3}\log\frac{[Al^{3+}]^2}{[Ni^{2+}]^3}$$

Now, $E^\circ_{cell} = E^\circ_{Ni^{2+}/Ni} - E^\circ_{Al^{3+}/Al}$

$$= -0.25 - (-1.66) = 1.41 \text{ V}$$

$$\therefore \quad E_{cell} = 1.41 - \frac{0.0591}{6}\log\frac{(10^{-3})^2}{(0.5)^3}$$

$$= 1.41 - \frac{0.0591}{6}\log(8\times10^{-6})$$

$$= 1.41 - \frac{0.0591}{6}(-5.09)$$

$$= 1.41 + 0.050 = 1.46 \text{ V}$$

24. (i) The cell reactions are :

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$ (Anode)

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ (Cathode)

Net reaction :

$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

(ii) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.34 \text{ V} - (-0.76 \text{ V})$
$= 1.10$ V

(iii) Copper electrode will be positive on which reduction takes place.

25. Resistance of 0.1 M KCl solution $R = 100\ \Omega$

Conductivity $\kappa = 1.29$ S m^{-1}

Cell constant $G^* = \kappa \times R = 1.29 \times 100 = 129$ m^{-1}

Resistance of 0.02 M KCl solution, $R = 520\ \Omega$

$$\text{Conductivity, } \kappa = \frac{\text{cell constant}}{R} = \frac{129 \text{ m}^{-1}}{520\ \Omega} = 0.248 \text{ S m}^{-1}$$

Concentration, $C = 0.02$ mol L^{-1}

$= 1000 \times 0.02$ mol m^{-3} = 20 mol m^{-3}

$$\text{Molar conductivity, } \Lambda_m = \frac{\kappa}{C} = \frac{0.248 \text{ S m}^{-1}}{20 \text{ mol m}^{-3}}$$

$$= 0.0124 \text{ S m}^2 \text{ mol}^{-1}$$

26. For half cell reaction,

$Cr_2O^{2-}_{7(aq)} + 14H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}][H^+]^{14}}$$

Given, $E^\circ_{cell} = 1.33$ V, $n = 6$, $[Cr^{3+}] = 0.2$ M

$[Cr_2O_7^{2-}] = 0.1$ M, $[H^+] = 1 \times 10^{-4}$ M

$$E_{cell} = 1.33 - \frac{0.0591}{6}\log\frac{(0.20)^2}{(0.1)(10^{-4})^{14}}$$

$$= 1.33 - \frac{0.0591}{6}\log(4\times10^{55})$$

$$= 1.33 - \frac{0.0591}{6}[\log 4 + \log 10^{55}]$$

$$= 1.33 - \frac{0.0591}{6}[\log 4 + 55 \log 10]$$

$$= 1.33 - \frac{0.0591}{6}[0.602 + 55]$$

$$= 1.33 - 0.548 = 0.782 \text{ V}$$

27. $Al_2O_3\ (2Al^{3+} + 3O^{2-}) \longrightarrow 2Al + \frac{3}{2}O_2,\ n = 6e^-$

$$\therefore \quad \frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2,\ n = \frac{2}{3} \times 6e^- = 4e^-$$

$\Delta G = 960 \times 1000 = 960000$ J

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

$$E_{cell} = -\frac{\Delta G}{nF} = \frac{-960000}{4\times96500} = -2.487 \text{ V}$$

Minimum potential difference needed to reduce Al_2O_3 is –2.487 V.

28. At anode : $Ni \longrightarrow Ni^{2+} + 2e^-$

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

Cell reaction : $Ni + 2Ag^+ \longrightarrow Ni^{2+} + 2Ag$

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

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

$E^\circ_{cell} = 1.05\text{ V}$

$$E^\circ_{cell} = \frac{0.0591}{n}\log K_c$$

$$\log K_c = \frac{E^\circ_{cell} \times n}{0.0591} = \frac{1.05 \times 2}{0.0591}$$

$\log K_c = 35.53$

$K_c = \text{antilog } 35.53 = 3.38 \times 10^{35}$

29. $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.403 - (-0.763) = 0.36\text{ V}$

$\Delta_r G^\circ = -nFE^\circ_{cell} = -2 \times 96500 \times 0.36$

$= -69480\text{ J} = -69.48\text{ kJ}$

Using formula, $\log K_c = \dfrac{nE^\circ_{cell}}{0.059} = \dfrac{2 \times 0.36}{0.059} = 12.20$

$K_c = \text{antilog } 12.20 = 1.58 \times 10^{12}$

30. (a) Degree of dissociation, $\alpha = \dfrac{\Lambda_{eq}}{\Lambda^\infty_{eq}}$

$\therefore \quad \alpha = \dfrac{15.8}{350} = 0.04514$

(b) For monobasic acid, $HA \rightleftharpoons H^+ + A^-$

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

As $\alpha <<< 1$ hence $(1 - \alpha) \approx 1$

$\therefore \quad K = 0.05 \times (0.04514)^2 \Rightarrow K = 1.019 \times 10^{-4}$

31. Given : Diameter = 1 cm, length = 50 cm

$R = 5.5 \times 10^3$ ohm, $M = 0.05$ M

$\rho = ? \quad \kappa = ? \quad \Lambda_m = ?$

Area of the column,

$$a = \pi r^2 = 3.14 \times \left(\frac{1}{2}\text{ cm}\right)^2 = \frac{3.14}{4}\text{ cm}^2$$

Resistivity,

$$\rho = R \cdot \frac{a}{l} = 5.5 \times 10^3\text{ ohm} \times \frac{3.14\text{ cm}^2}{4 \times 50\text{ cm}} = 86.35\text{ ohm cm}$$

Again, conductivity, $\kappa = \dfrac{1}{\rho}$

$$= \frac{1}{86.35} = 1.158 \times 10^{-2}\text{ ohm}^{-1}\text{ cm}^{-1}$$

and molar conductivity, $\Lambda_m = \kappa \cdot \dfrac{10^3}{M}$

$$= 1.158 \times 10^{-2}\text{ ohm}^{-1}\text{ cm}^{-1} \times \frac{10^3}{5 \times 10^{-2}}$$

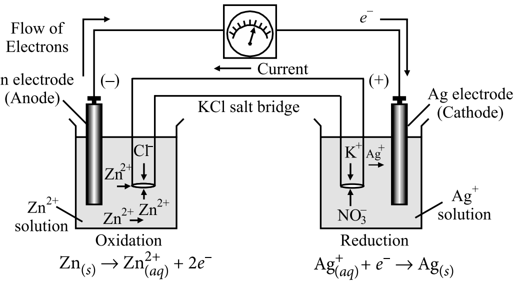
$= 231.6\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$

32. The reaction is

$Zn_{(s)} + 2Ag^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$

Cell can be represented as

$Zn \,|\, Zn^{2+}_{(aq)} \,||\, Ag^+_{(aq)} \,|\, Ag$



(i) The zinc electrode is negatively charged (anode) as it pushes the electrons into the external circuit.

(ii) Ions are the current carriers within the cell.

(iii) The reactions occurring at two electrodes are :

At zinc electrode (anode) : $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

At silver electrode (cathode) : $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$

33. A chemical cell is a galvanic cell in which electrical energy produced is due to chemical changes occurring within the cell and no transfer of matter takes place. It involves the use of two different electrode dipped in solutions of different electrolytes.

A concentration cell is a galvanic cell in which electrical energy is produced due to physical change involving transfer of matter from one part of the cell to the other. It involves the use of the same electrodes dipped in solutions of the same electrolyte with different concentrations (or electrodes of different concentration dipped in the same solution of the electrolyte).

34. The given cell may be represented as

$Cu_{(s)} \,|Cu^{2+}\,(0.10\text{ M})||\, Ag^+\,(C)|\, Ag_{(s)}$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.80\text{ V} - 0.34\text{ V} = 0.46\text{ V}$

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

or $\quad 0.422\text{ V} = 0.46\text{ V} - \dfrac{0.0591}{2}\log\dfrac{0.1}{[Ag^+]^2}$

$\quad -0.038\text{ V} = -0.0295\log\dfrac{0.1}{[Ag^+]^2}$

or $\quad \log\dfrac{0.1}{[Ag^+]^2} = \dfrac{-0.038}{-0.0295} = 1.288$

or $\quad \dfrac{0.1}{[Ag^+]^2} = \text{antilog } 1.288 = 19.41$

$\therefore \quad [Ag^+]^2 = \dfrac{0.1}{19.41} = 5.1519 \times 10^{-3}$

$[Ag^+] = 7.1 \times 10^{-2}$ M

35. Given : $V = 100\text{ cm}^3$, $M = 0.025$ M, $R = 520$ ohm

$G = 153.7\text{ m}^{-1} = 1.537\text{ cm}^{-1}$, $\Lambda_m = ?$

$$\kappa = G \times \frac{1}{R} = 1.537\ \text{cm}^{-1} \times \frac{1}{520\ \text{ohm}}$$

$$= 2.95 \times 10^{-3}\ \text{ohm}^{-1}\text{cm}^{-1}$$

Again, $\Lambda_m = \dfrac{\kappa \times 10^3}{M}$

$$= \frac{2.95 \times 10^{-3}\ \text{ohm}^{-1}\ \text{cm}^{-1} \times 10^3}{0.025\ \text{mol cm}^{-3}}$$

$$\Lambda_m = 118.0\ \text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

36. $\kappa = 1.29 \times 10^{-2}\ \text{ohm}^{-1}\ \text{cm}^{-1}$

$\kappa = \dfrac{1}{R} \times$ Cell constant

$\Rightarrow$ Cell constant $= \kappa \times R$

$$= 1.29\ \text{S m}^{-1} \times 85\ \Omega = 109.65\ \text{m}^{-1}$$

For second solution,

$$\kappa = \frac{1}{R} \times \text{Cell constant} = \frac{1}{96\ \Omega} \times 109.65\ \text{m}^{-1}$$

$$= 1.142\ \Omega^{-1}\text{m}^{-1}$$

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.142\ \Omega^{-1}\text{m}^{-1} \times 1000\ \text{cm}^3}{0.052}$$

$$\Lambda_m = \frac{1.142\ \Omega^{-1}\text{cm}^{-1} \times 10^{-2} \times 1000\ \text{cm}^3}{0.052\ \text{mol}}$$

$$= 219.62\ \text{S cm}^2\ \text{mol}^{-1}$$

37. $E_{\text{cell}} = E^\circ{}_{\text{cell}} - \dfrac{0.0591}{n} \log \dfrac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]}$

$$= 2.71 - \frac{0.0591}{2} \log \frac{0.001}{0.01} = 2.73955\ \text{V}$$

(i) If external opposing potential is less than 2.71 V then current will flow from Cu to Mg.

(ii) If external opposing potential is greater than 2.71 V then current will flow in opposite direction *i.e.* from Mg to Cu.

38. (a) The given cell may be represented as

$\text{Cu}_{(s)} | \text{Cu}^{2+} || \text{Cl}_2 | \text{Cl}^-$

(i) $E^\circ_{\text{cell}} = E^\circ_c - E^\circ_a = (+1.36\ \text{V}) - (+0.34\ \text{V}) = 1.02\ \text{V}$

(ii) $\Delta_r G^\circ = -nFE^\circ = -2 \times 96500\ \text{C} \times 1.02\ \text{V} = 196.86\ \text{kJ}$

(iii) $E^\circ{}_{\text{Cell}} = \dfrac{0.0591}{n} \log K$

$$K = \text{antilog}\ \frac{2 \times 1.02}{0.0591} = \text{antilog}\ (34.51)$$

$$K = 3.236 \times 10^{34}$$

(b) The given cell may be represented as

Pt, H_2 (1 atm) | H^+ (pH = ?) || H^+ (pH = 1) | H_2 (1 atm)

Using formula, $E_{\text{cell}} = \dfrac{0.0591}{1} \log \dfrac{[\text{H}^+]_c}{[\text{H}^+]_a}$

or $0.16 = 0.0591\ [\log [\text{H}^+]_c - \log [\text{H}^+]_a]$

or $0.16 = 0.0591\ [\text{pH}_a - \text{pH}_c]$

$0.16 = 0.0591\ [\text{pH}_a - 1]$

or $\text{pH}_a - 1 = \dfrac{0.16}{0.0591} = 2.70$

or $\text{pH}_a = 2.70 + 1 = 3.70$

39. (a) $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = -0.403 - (-0.763)$

$$= 0.36\ \text{V}$$

The net cell reaction is

$\text{Zn}_{(s)} + \text{Cd}^{2+}_{(aq)} \longrightarrow \text{Zn}^{2+}_{(aq)} + \text{Cd}_{(s)}$

Here, value of $n = 2$

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

$$= 0.36 - \frac{0.0591}{2} \log \frac{0.0004}{0.2}$$

$$= 0.36 - \frac{0.0591}{2}(-2.69) = 0.36 + 0.08 = 0.44\ \text{V}$$

$\therefore\ \Delta G = -nFE_{\text{cell}} = -2 \times 96500 \times 0.44$

$$= -84920\ \text{J/mol}$$

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

$$E_{\text{Cu}^{2+}/\text{Cu}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - \frac{0.059}{2} \log \frac{[\text{Cu}]}{[\text{Cu}^{2+}]}$$

$$= 0.34 - \frac{0.059}{2} \log \frac{1}{0.1} = 0.34 - \frac{0.059}{2} \log 10$$

$$= 0.34 - \frac{0.059}{2} \times (1) = 0.34 - 0.0295 = 0.3105\ \text{V}$$

When the concentration of Cu^{2+} ions is decreased, the electrode potential for copper decreases.

40. (a) Given : $\Lambda_{eq} = 1.4$ mho cm^2 eq^{-1},

$\Lambda^\infty{}_{eq} = 391$ mho cm^2 eq^{-1}, $\alpha = ?$, $K_a = ?$

Using formula, $\alpha = \dfrac{\Lambda_{eq}}{\Lambda^\infty_{eq}} = \dfrac{1.4\ \text{mho cm}^2\ \text{eq}^{-1}}{391\ \text{mho cm}^2\ \text{eq}^{-1}}$

$$= 0.00358$$

$$K_a = \frac{\alpha^2 C}{1 - \alpha} = \frac{(0.00358)^2 \times 0.0128}{1 - 0.00358}$$

$$= \frac{1.64 \times 10^{-7}}{0.99642} = 1.64 \times 10^{-7}$$

(b) Given : Λ°_{eq} (CH_3COONa) = 83 mho cm^2 eq^{-1}

Λ°_{eq} (NaCl) = 127 mho cm^2 eq^{-1}

Λ°_{eq} (HCl) = 426 mho cm^2 eq^{-1}

Λ°_{eq} (CH_3COOH) = ?

Using Kohlrausch law of independent migration of ions

$\Lambda^\circ_{eq}(\text{CH}_3\text{COOH}) = \Lambda^\circ_{eq}(\text{CH}_3\text{COONa}) + \Lambda^\circ_{eq}(\text{HCl}) - \Lambda^\circ_{eq}(\text{NaCl})$

or $\Lambda^\circ_{eq}(\text{CH}_3\text{COOH}) = 83 + 426 - 127$

$$= 382\ \text{mho cm}^2\ \text{eq}^{-1}$$

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