

EXAM
DRILL

Electrochemistry

ANSWERS

1. (i) (a) : For the given concentration cell,



$$E_{\text{cell}} = \frac{0.0591}{1} \log \frac{C_2}{C_1} = 0.0591 \log \frac{10^{-3}}{10^{-6}} = 0.0591 \times 3 = 0.1773 \text{ V}$$

(ii) (d) : H_2 has been oxidized and $\text{AgCl}(\text{Ag}^+)$ has been reduced. Hydrogen electrode on left has to be $\text{Pt}/\text{H}_2/\text{H}^+$.

(iii) (a) : In the given reaction, I^- has been oxidised to I_2 and $\text{Cr}_2\text{O}_7^{2-}$ ions have been reduced to Cr^{3+} .

$$\therefore E_{\text{cell}}^{\circ} = E_{\text{Cr}_2\text{O}_7^{2-}}^{\circ} - E_{\text{I}^-/\text{I}_2}^{\circ} \Rightarrow 0.79 = 1.33 - E_{\text{I}^-/\text{I}_2}^{\circ}$$

$$\text{or } E_{\text{I}^-/\text{I}_2}^{\circ} = 0.54 \text{ V}$$

(iv) (d) : The cell reaction is : $\text{Zn} + \text{Cu}^{2+} \longrightarrow \text{Zn}^{2+} + \text{Cu}$
When the cell is completely discharged $E_{\text{cell}} = 0$.

$$\text{Hence, } E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\text{i.e., } 1.10 = \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$\text{or, } \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 37.3 \text{ or } \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 10^{37.3}$$

(v) (c) : The cell is $M|M^{2+}(0.1 \text{ M})||\text{H}^+(1 \text{ M})|\text{H}_2(1 \text{ atm})$

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

$$1.50 = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log (0.1) = E_{\text{cell}}^{\circ} + 0.02955$$

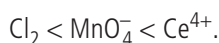
$$E_{\text{cell}}^{\circ} = 1.50 - 0.02955 = 1.4704 \text{ V}$$

$$\text{But } E_{\text{cell}}^{\circ} = E_{\text{H}^+/\text{H}_2}^{\circ} - E_{M^{2+}/M}^{\circ} \Rightarrow 1.47 = 0 - E_{M^{2+}/M}^{\circ}$$

$$E_{M^{2+}/M}^{\circ} = -1.47 \text{ V}$$

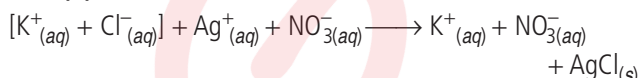
- Hg_2Cl_2
- Copper
- Concentration
- Hydrated ferric oxide

OR



$$\begin{aligned} 6. \text{ (d) : } E_{\text{cell}} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \Rightarrow 0.344 = E_{\text{calomel}} - E_x^{\circ} \\ E_x^{\circ} &= 0.244 - 0.344 \\ E_x^{\circ} &= -0.100 \text{ V} \end{aligned}$$

7. (b) : For the reaction,



Initially the conductance is due to K^+ and Cl^- ions. On adding AgNO_3 , precipitate of AgCl is formed. Thus some Cl^- ions are replaced by NO_3^- ions. As both have nearly the same conductance the conductance remains almost constant. After the end point, addition of AgNO_3 will give Ag^+ and NO_3^- ions in the solution. Hence, conductance will increase rapidly.

$$\begin{aligned} 8. \text{ (a) : } \Delta G^{\circ} &= -nFE_{\text{cell}}^{\circ} \quad \dots(i) \\ \Delta G^{\circ} &= -RT \ln K_{\text{eq}} \quad \dots(ii) \end{aligned}$$

In eq. (i) if E_{cell}° is negative, ΔG° will be positive

In eq. (ii) ΔG° can be positive only if $K_{\text{eq}} < 1$

$$9. \text{ (c) : Degree of dissociation, } \alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}}$$

$$\begin{aligned} \therefore \Lambda_m &= \alpha \times \Lambda_m^{\circ} = (1.9 \times 10^{-9}) \times (200 + 350) \text{ S cm}^2 \text{ mol}^{-1} \\ &= 1.9 \times 550 \times 10^{-9} = 1.045 \times 10^{-6} \text{ S cm}^2 \text{ mol}^{-1} \end{aligned}$$

10. (b) : $\text{KCl}/\text{NaCl}/\text{NH}_4\text{Cl}$ etc. cannot be used as salt bridge in a cell containing silver as one of the electrodes because they react to form a precipitate of AgCl .

11. (b) : I^- ions have much higher oxidation potential than that of water while F^- ions have much lower oxidation potential than that of water.

12. (c) : Specific conductivity is the conductance of 1 cm^3 of the solution whereas molar conductivity is the conductance of a solution containing 1 mole of electrolyte.

13. (d) : The cell constant of a conductivity cell depends upon the distance between the electrodes and the their cross section areas and not on the material of the electrodes.

14. (c) : Standard electrode potential of an electrode should be greater than zero for a stable reduced form as compared to hydrogen gas.

15. ΔG is positive for an electrolytic cell because electrical energy is supplied so that redox reaction occurs which was non-spontaneous.

$$16. \Lambda_m = \frac{\kappa \times 1000(\text{cm}^3/\text{L})}{\text{Molarity}}$$

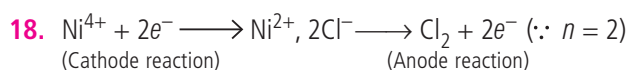
$$\Lambda_m = \frac{0.0248 \times 1000}{0.2} = 124 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

$$17. \Lambda_m^0 [\text{Al}_2(\text{SO}_4)_3] = 2\lambda_m^0(\text{Al}^{3+}) + 3\lambda_m^0(\text{SO}_4^{2-})$$

$$858 \text{ S cm}^2 \text{mol}^{-1} = 2\lambda_m^0(\text{Al}^{3+}) + 3 \times 160 \text{ S cm}^2 \text{mol}^{-1}$$

$$2\lambda_m^0(\text{Al}^{3+}) = 378 \text{ S cm}^2 \text{mol}^{-1}$$

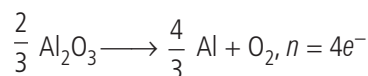
$$\lambda_m^0(\text{Al}^{3+}) = 189 \text{ S cm}^2 \text{mol}^{-1}$$



$$E_{\text{cell}}^0 = \frac{0.0591}{n} \log K_c; 0.32 = \frac{0.0591}{2} \log K_c$$

$$\log K_c = 10.8291 \text{ or } K_c = 6.7468 \times 10^{10}$$

OR



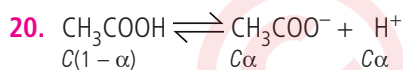
$\Delta G = -nFE$, putting value of $\Delta G = +960 \text{ kJ}$, $n = 4$

$$960,000 = -4 \times 96500 \times E$$

$$\text{or } E = -2.487 \text{ V}$$

Minimum potential difference needed to reduce Al_2O_3 is 2.487 V.

19. The reduction potential of silver electrode is +ve while that of NHE is zero. EMF of the cell will be +ve only if reduction takes place at the silver electrode *i.e.*, it will act as cathode.



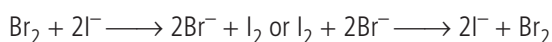
$$K_{\text{eq}} = C\alpha^2 \text{ or } \alpha = \sqrt{\frac{K_{\text{eq}}}{C}} = \frac{\Lambda_m}{\Lambda_m^0}$$

$$\frac{\Lambda_m}{390.7} = \sqrt{\frac{1.8 \times 10^{-5}}{0.01}} = \sqrt{18 \times 10^{-4}} = 4.243 \times 10^{-2}$$

$$\Lambda_m = 16.57 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

OR

The reaction can be either



$$1^{\text{st}} \text{ reaction, EMF} = E_{\text{Br}_2/\text{Br}^-}^0 - E_{\text{I}_2/\text{I}^-}^0 = 1.08 - 0.54 = 0.54 \text{ V}$$

$$2^{\text{nd}} \text{ reaction, EMF} = E_{\text{I}_2/\text{I}^-}^0 - E_{\text{Br}_2/\text{Br}^-}^0 = 0.54 - 1.08 = -0.54 \text{ V}$$

The reaction that will take place is :



$$21. \text{(a) Specific conductance } (\kappa) = \frac{1}{R} \times \text{Cell Constant}$$

$$= \frac{1}{100 \Omega} \times 1.25 \text{ cm}^{-1} = 0.0125 \Omega \text{ cm}^{-1}$$

$$\text{(b) Molar conductance } (\Lambda_m) = \frac{\kappa \times 1000(\text{cm}^3/\text{L})}{\text{molarity}}$$

$$= \frac{0.0125 \Omega \text{ cm}^{-1} \times 1000(\text{cm}^3/\text{L})}{7.5 \times 10^{-3} \text{ mol L}^{-1}} = 1.66 \text{ S cm}^2 \text{mol}^{-1}$$

22. For the reaction,



$$E_{\text{cell}}^0 = E_{\text{Fe}^{2+}/\text{Fe}}^0 - E_{\text{Cd}^{2+}/\text{Cd}}^0 = 0.441 - 0.403 = 0.038 \text{ V}$$

Applying Nernst equation

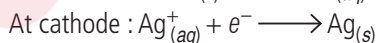
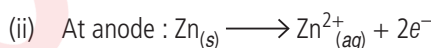
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Cd}^{2+}]}{[\text{Fe}^{2+}]}$$

$$E_{\text{cell}} = 0.038 - \frac{0.0591}{n} \log \frac{10^{-3}}{0.6} (\because n = 2)$$

$$= 0.038 + 0.0821 = 0.1201 \text{ V}$$

23. The cell is represented as : $\text{Zn}_{(\text{s})} | \text{Zn}^{2+}_{(\text{aq})} || \text{Ag}^{+}_{(\text{aq})} | \text{Ag}_{(\text{s})}$

(i) Anode



(iii) The current is carried by the cations and the anions through the salt bridge internally and current flows from silver to zinc electrode externally.

24. The cell reaction is : $\text{Cd} + \text{Ni}^{2+} \longrightarrow \text{Cd}^{2+} + \text{Ni}$

$$E_{\text{cell}}^0 = -0.25 - (-0.40) = 0.15 \text{ V}$$

Applying Nernst equation,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{2} \log \frac{[\text{Cd}^{2+}]}{[\text{Ni}^{2+}]}$$

$$0.20 = 0.15 - \frac{0.0591}{2} \log \frac{[\text{Cd}^{2+}]}{2}$$

$$-\log \frac{[\text{Cd}^{2+}]}{2} = 1.690$$

$$\log [\text{Cd}^{2+}] = -1.690 + 0.3010 = -1.389$$

$$[\text{Cd}^{2+}] = \text{antilog}(-1.389) = 0.0408 \text{ M}$$

25. Applying Nernst equation

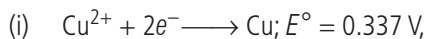
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}$$

$$= 1.33 - \frac{0.0591}{6} \log \frac{(0.20)^2}{(0.10)(10^{-4})^{14}}$$

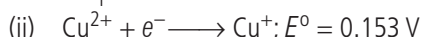
$$= 1.33 - \frac{0.0591}{6} \log(4 \times 10^{55})$$

$$= 1.33 - \frac{0.0591}{6} (55 + 0.6021) = 0.78 \text{ V}$$

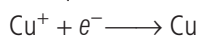
OR



$$\Delta G_1^\circ = -2 \times F \times 0.337 \text{ J}$$



$$\Delta G_2^\circ = -1 \times F \times 0.153 \text{ J}$$

Subtract eqⁿ (ii) from (i) we get

$$\Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ = [-0.674 - (-0.153)] F$$

$$= -0.521 F$$

$$\therefore -nFE_{\text{Cu}^+/\text{Cu}}^\circ = -0.521 F$$

$$E_{\text{Cu}^+/\text{Cu}}^\circ = +0.521 \text{ V}$$

26. (a) *A* is a strong electrolyte whereas *B* is a weak electrolyte

(b) In case of weak electrolyte molar conductivity increases but never reaches a limiting value. In case of strong electrolyte, interionic forces of attraction decreases on dilution. As result ions are more free to move about. Hence, molar conductivity increases and reaches a limiting value at infinite dilution.

27. Reaction at anode of fuel cell

$$67.2 \text{ L of H}_2 \text{ correspond to } = \frac{2 \times 96500}{22.4} \times 67.2 \text{ Coulomb}$$

$$\text{Time} = 15 \times 60 \text{ second}$$

$$\text{Average current} = \frac{2 \times 96500 \times 67.2}{22.4 \times 15 \times 60} = 643.3 \text{ A}$$

$$\text{Mass of copper deposited by } \frac{2 \times 96500 \times 67.2}{22.4} \text{ C}$$

$$= \frac{63.5}{2 \times 96500} \times \frac{2 \times 96500 \times 67.2}{22.4} = 190.5 \text{ g}$$

28. (i) We know, $\Delta G^\circ = -nFE^\circ$ Also for Daniel cell $n = 2$

$$\therefore \Delta G^\circ = -2 \times 96500 \times 1.1 \text{ J}$$

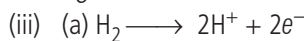
$$= -212300 \text{ J or } -212.30 \text{ kJ}$$

(ii) $E_{\text{cell}}^\circ = \frac{0.059}{1} \log K_C \quad [n = 1]$

or $E_{\text{cell}}^\circ = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^\circ - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = 1.44 - 0.68 = 0.76 \text{ V}$

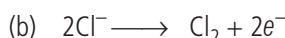
$$0.76 = 0.059 \log K_C$$

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



$$\therefore E_{OP} = E_{OP}^\circ - \frac{0.059}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}} = 0 - \frac{0.059}{2} \log \frac{[0.02]^2}{2}$$

$$E_{OP(\text{H}_2/\text{H}^+)} = +0.118 \text{ V}$$



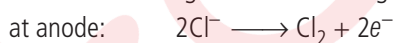
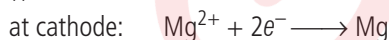
$$\therefore E_{OP} = E_{OP}^\circ - \frac{0.059}{2} \log_{10} \frac{P_{\text{Cl}_2}}{[\text{Cl}^-]^2}$$

$$= -1.36 - \frac{0.059}{2} \log \frac{10}{[0.1]^2}$$

$$\therefore E_{OP(\text{Cl}^-/\text{Cl}_2)} = -1.4485 \text{ V}$$

OR

(i) Reactions are:

We know that, eq. of Mg formed = Eq. of Cl_2 formed

$$\therefore \frac{6.5}{24.3/2} = \frac{W_{\text{Cl}_2}}{35.5} \quad \therefore W_{\text{Cl}_2} = 18.99 \text{ g}$$

at NTP, $PV = \frac{W}{M} RT$

$$1 \times V = \frac{18.99}{71} \times 0.0821 \times 298 = 6.54 \text{ L}$$

$$\therefore \text{Volume of Cl}_2 = 6.54 \text{ litre}$$

(ii) According to Nernst equation, electrode potential of Zn electrode is:

$$E_{\text{Zn}} = E^\circ + \frac{0.0591}{2} \log [\text{Zn}^{2+}] = -0.763 + 0.0295 \log 10^{-2}$$

$$= -0.763 - 2 \times 0.0295 = -0.822 \text{ V}$$

Given $E_{\text{calomel}}(\text{satd.}) = 0.242 \text{ V}$

$$E_{\text{cell}} = E_{\text{calomel}} - E_{\text{Zn}} = 0.242 - (-0.822)$$

$$\therefore E_{\text{cell}} = 1.064 \text{ V}$$

29. (i) **Faraday's first law of electrolysis** : The amount of chemical reaction and hence the mass of any substance deposited or liberated at any electrode is directly proportional to the quantity of electricity passed through the electrolyte.Thus, if *W* grams of the substance is deposited on passing *Q* coulombs of electricity.

$$W = ZQ$$

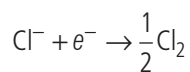
Where *Z* is the constant of proportionality and is called electrochemical equivalent.**Faraday's second Law of Electrolysis** : When the same amount of electricity is passed through solution of different electrolytes connected in series, the masses of the substances

produced at the electrodes are directly proportional to their equivalent weights.

For example AgNO_3 solution and CuSO_4 solution connected in series, if the same quantity of electricity is passed

$$\frac{\text{Mass of Ag deposited}}{\text{Mass of Cu deposited}} = \frac{\text{Eq wt. of Ag}}{\text{Eq wt. of Cu}}$$

(ii) Quantity of charge passed $Q = I \times t$
 $= 1\text{A} \times 15 \times 60 \text{ sec} = 900 \text{ C}$



Thus, 1F, $1 \times 96500 \text{ C}$ deposit = 35.5 g of chlorine

$$900 \text{ C will deposit} = \frac{35.5 \times 900}{96500} = 0.331 \text{ g}$$

(iii) Given, $\kappa = 0.002765 \text{ mho cm}^{-1}$, $R = 400 \text{ ohm}$

$$\kappa = \frac{1}{R} \times \frac{l}{A} \quad \left(\frac{l}{A} = \text{cell constant} \right)$$

$$0.002765 = \frac{1}{400} \times \text{cell constant}$$

$$\therefore \text{Cell constant} = 1.106 \text{ cm}^{-1}$$

30. (i) Tarnish will be removed if the following reaction takes place



EMF of this cell reaction $E_{\text{Ag}_2\text{S}/2\text{Ag}/\text{S}^{2-}}^{\circ} - E_{\text{Al}^{3+}/\text{Al}}^{\circ}$

$$E_{\text{cell}} = -0.71 - (-1.66) = 0.95 \text{ V}$$

As EMF is positive, the reaction will take place and tarnish will be removed.

(ii) Given, R of solution = 384 ohm

$$\text{Conductance} = \frac{1}{R} = \frac{1}{384} \text{ ohm}^{-1}; G = 2.604 \times 10^{-3} \text{ ohm}^{-1}$$

Given, cell constant = 0.5 cm^{-1}

$$\text{Specific conductance, } \kappa = G \times \frac{l}{A}$$

$$\therefore \kappa = 2.604 \times 10^{-3} \times 0.5 = 1.302 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$$

Also, we know, eq. conductance,

$$\Lambda = \frac{\kappa \times 1000}{C} = \frac{1.302 \times 10^{-3} \times 1000}{0.01} \text{ ohm}^{-1} \text{ cm}^2 (\text{g. eq.})^{-1}$$

$$\therefore \Lambda = 130.2 \text{ ohm}^{-1} \text{ cm}^2 (\text{g. eq.})^{-1}$$

OR

(i) The half-cell reaction is



According to Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{1} \log \frac{[\text{NO}_2][\text{H}_2\text{O}]}{[\text{NO}_3^-][\text{H}^+]^2} \quad [n = 1]$$

$$= 0.78 - 0.059 \log 1/(8)^2 = 0.78 - (-0.106) = 0.886 \text{ V}$$

(ii) In neutral solution $[\text{H}^+] = 10^{-7}$

$$\therefore E = 0.78 - \frac{0.059}{1} \log \frac{1}{(10^{-7})^2} = 0.78 - 0.059 \times 14$$

$$= 0.78 - 0.826 = -0.046 \text{ V}$$

