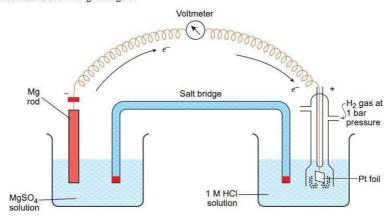
# **Electrochemistry**

## **NCERT Intext Questions**

### Q. 1. How would you determine the standard electrode potential of the system Mg2+ Mg?

Ans. Set up an electrochemical cell consisting of Mg | MgSO<sub>4</sub> (1 M) as one electrode by dipping a magnesium rod in 1 M MgSO<sub>4</sub> solution and standard hydrogen electrode Pt, H<sub>2</sub> (1 atm) | H<sup>+</sup> (1 M) as the second electrode as shown in given figure.



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

$$\begin{split} \text{Mg} \mid \text{Mg}^{2+} \left( 1 \text{ M} \right) \mid \mid \text{H}^{+} \left( 1 \text{ M} \right) \mid \text{H}_{2}, \left( 1 \text{ atm} \right), \text{Pt}(s) \\ E^{o}_{\text{cell}} &= E^{o}_{\text{H}^{+}} / \frac{1}{2} \text{H}_{2} - E^{o}_{\text{Mg}^{2+}} / \text{Mg} \end{split}$$
 But 
$$E^{o}_{\text{H}^{+}} / \frac{1}{2} \text{H}_{2} &= 0 \\ \text{Hence,} \qquad E^{o}_{\text{Mg}^{2+}} / \text{Mg} &= -E^{o}_{\text{cell}} \end{split}$$

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

[HOTS]

Ans. For this we have to check whether the following reaction will take place or not. 
$$Zn(s) + CuSO_4(aq) \longrightarrow ZnSO_4(aq) + Cu(s)$$

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

As  $E_{\rm cell}^{\rm o}$  is positive, the reaction will take place. Therefore, we cannot store copper sulphate in zinc pot.

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

Ans. Oxidation of ferrous ions means

$$Fe^{2+} \longrightarrow Fe^{3+} + e^{-};$$
  $E_{Fe^{3+}/Fe^{2+}}^{o} = 0.77 \text{ V}$ 

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

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

Ans. For hydrogen electrode

$$H^+ + e^- \longrightarrow \frac{1}{2}H_2$$

$$E_{\text{H}^+/\frac{1}{2}\text{H}_2} = E_{\text{H}^+/\frac{1}{2}\text{H}_2}^{\text{o}} - \frac{0.0591}{n} \log \frac{1}{[\text{H}^+]}$$
Here,  $n = 1$ , 
$$\log \frac{1}{[\text{H}^+]} = \text{pH} = 10, \ E_{\text{H}^+/\frac{1}{2}\text{H}_2}^{\text{o}} = 0$$

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

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

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

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

Ans. From Nernst equation to the given cell reaction

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

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

$$2Fe^{3+}(aq) + 2I^{-}(aq) \longrightarrow 2Fe^{2+}(aq) + I_{2}(s)$$

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

Ans.

$$2Fe^{3+} + 2e^{-} \longrightarrow 2Fe^{2+} \text{ or } 2I^{-} \longrightarrow I_2 + 2e^{-}$$

Thus, for the given cell reaction, n = 2.  $\Delta_r G^{\circ} = -nF E_{\text{cell}}^{\circ} = -2 \times 96500 \times 0.236 \text{ J mol}^{-1} = -45548 \text{ J mol}^{-1} = -45.55 \text{ kJ mol}^{-1}$ 

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

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

$$= -7.983$$

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

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

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

# Q. 8. Suggest a way to determine the $\Lambda_m^0$ value of water.

[HOTS]

Ans.

$$\begin{split} & \Lambda_{m(H_2O)}^{\circ} = \lambda_{(H^{+})}^{\circ} + \lambda_{(OH^{-})}^{\circ} \\ & = \lambda_{(H^{+})}^{\circ} + \lambda_{(OH^{-})}^{\circ} + \lambda_{(CI^{-})}^{\circ} - \lambda_{(CI^{-})}^{\circ} + \lambda_{(Na^{+})}^{\circ} - \lambda_{(Na^{+})}^{\circ} \end{split}$$

Rearranging we get

$$\Lambda_{m(\mathsf{H}_{\mathsf{a}}\mathsf{O})}^{\mathsf{o}} = \left[\lambda_{(\mathsf{H}^{\mathsf{h}})}^{\mathsf{o}} + \lambda_{(\mathsf{C}\mathsf{I}^{\mathsf{h}})}^{\mathsf{o}}\right] + \left[\lambda_{(\mathsf{N}\mathsf{a}^{\mathsf{h}})}^{\mathsf{o}} + \lambda_{(\mathsf{O}\mathsf{H}^{\mathsf{h}})}^{\mathsf{o}}\right] - \left[\lambda_{(\mathsf{N}\mathsf{a}^{\mathsf{h}})}^{\mathsf{o}} + \lambda_{(\mathsf{C}\mathsf{I}^{\mathsf{h}})}^{\mathsf{o}}\right]$$

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

Thus, the molar conductivity of water at infinite dilution can be determined from the knowledge of  $\Lambda^o_{m(HCI)}$ ,  $\Lambda^o_{m(NaOI)}$  and  $\Lambda^o_{m(NaCI)}$ .

Q. 9. The molar conductivity of 0.025 mol L<sup>-1</sup> methanoic acid is 46.1 S cm<sup>2</sup> mol<sup>-1</sup>. Calculate its degree of dissociation and dissociation constant.

dissociation and dissociation constant. [Given  $\lambda^0(H^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1} \text{ and } \lambda^0(\text{HCOO}^-) = 54.6 \text{ S cm}^2 \text{ mol}^{-1}.$ ]

[HOTS]

Ans.

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

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

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

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

Initial conc.

$$c \mod L^{-1}$$
 0

Conc. at equilibrium

$$c(1-\alpha)$$
  $c\alpha$   $c\alpha$ 

$$K = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} = \frac{0.025 \times (0.114)^2}{1-0.114}$$

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

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

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

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

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

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

Ans. Na, Ca, Mg and Al.

O. 12. Consider the reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

What is the quantity of electricity in coulombs needed to reduce 1 mol of  $Cr_2O_7^{2-2}$ ?

Ans. From the given reaction, 1 mole of  $Cr_2O_7^{2-}$  ions require

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

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

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

$$\begin{split} & \operatorname{PbSO}_4(s) + 2e^{-} \longrightarrow \operatorname{Pb}(s) + \operatorname{SO}_4^{2-}(aq) \\ & \underbrace{\operatorname{PbSO}_4(s) + 2\operatorname{H}_2\operatorname{O}(l) \longrightarrow \operatorname{PbO}_2(s) + \operatorname{SO}_4^{2-}(aq) + 4\operatorname{H}^+(aq) + 2e^{-}}_{2\operatorname{PbSO}_4(s) + 2\operatorname{H}_2\operatorname{O}(l) \longrightarrow \operatorname{Pb}(s) + \operatorname{PbO}_2(s) + 4\operatorname{H}^+(aq) + 2\operatorname{SO}_4^{2-}(aq) \end{split}$$

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

Ans. Methyl alcohol and methane.

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

Ans. The water layer present on the surface of iron dissolves acidic oxides of air like CO<sub>2</sub> to form acids which dissociate to give H<sup>+</sup> ions.

$$H_2O + CO_2 \longrightarrow H_2CO_3$$
,  $H_2CO_3 \Longrightarrow 2H^+ + CO_3^{2-}$ 

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

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

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

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

The overall reaction is given as:

$$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$$

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

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

## **NCERT Exercises**

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

Al, Cu, Fe, Mg and Zn

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

Q. 2. Given the standard electrode potentials

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

Arrange these metals in their increasing order of reducing power. [CBSE (AI) 2010]

- Ans. Lower the reduction potential, more easily it is oxidised and hence greater is the reducing power. Therefore, the increasing order of reducing power is Ag < Hg < Cr < Mg < K.
- Q. 3. Depict the galvanic cell in which the reaction  $\text{Zn}(s) + 2\text{Ag}^+(aq) \longrightarrow \text{Zn}^{2+}(aq) + 2\text{Ag}(s)$  takes place. Further show:
  - (i) Which of the electrode is negatively charged?
  - (ii) The carriers of the current in the cell.
  - (iii) Individual reaction at each electrode.

Ans. The cell will be represented as:

$$Zn(s) | Zn^{2+}(aq) | | Ag^{+}(aq) | Ag(s)$$

- (i) Anode (zinc electrode) will be negatively charged.
- (ii) Electrons and ions.
- (iii) The reaction occurring

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

At cathode: 
$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$

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

(i) 
$$2\operatorname{Cr}(s) + 3\operatorname{Cd}^{2+}(aq) \longrightarrow 2\operatorname{Cr}^{3+}(aq) + 3\operatorname{Cd}(s)$$

(ii) 
$$\operatorname{Fe}^{2+}(aq) + \operatorname{Ag}^{+}(aq) \longrightarrow \operatorname{Fe}^{3+}(aq) + \operatorname{Ag}(s)$$

[Given: 
$$E_{\text{Cr}^{3+}/\text{Cr}}^{0} = -0.74 \text{ V}, \ E_{\text{Cd}^{2+}/\text{Cd}}^{0} = -0.40 \text{ V}, \ E_{\text{Ag}^{+}/\text{Ag}}^{0} = 0.80 \text{ V}, \ E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{0} = 0.77 \text{ V}]$$

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

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

$$\Delta_r G^\circ = -nFE_{\text{cell}}^\circ = -6 \text{ mol} \times 96500 \text{ C mol}^{-1} \times 0.34 \text{ V}$$
  
= -196860 CV mol<sup>-1</sup> = -196860 J mol<sup>-1</sup> = **-196.86 kJ mol**<sup>-1</sup>

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

$$-196860 = -2.303 \times 8.314 \times 298 \log K_C$$
 or  $\log K_c = 34.5014$ 

$$K_c$$
 = Antilog 34.5014 = 3.172 × 10<sup>34</sup>

(ii) 
$$E_{cell}^6 = +0.80 \text{ V} - 0.77 \text{ V} = + 0.03 \text{ V}$$

$$\Delta_{i}G^{\circ} = -nFE_{cell}^{\circ} = -(1 \text{ mol}) \times (96500 \text{ C mol}^{-1}) \times (0.03 \text{ V})$$

$$= -2895 \text{ CV mol}^{-1} = -2895 \text{ J mol}^{-1} = -2.895 \text{ kJ mol}^{-1}$$

$$\Delta_{i}G^{\circ} = -2.303 \text{ K log } K_{c}$$

$$-2895 = -2.303 \text{ K log } K_{c}$$
or 
$$\log K_{c} = 0.5074$$
or 
$$K_{c} = \text{Antilog } (0.5074) = 3.22$$
Q. 5. Write the Nernst equation and emf of the following cells at 298 K:
(i)  $Mg(s) \mid Mg^{g^{2+}}(0.001 \text{ M}) \mid 100^{g^{2+}}(0.0001 \text{ M}) \mid Cu(s)$ 
(ii)  $S(s) \mid Sn^{2+}(0.050 \text{ M}) \mid H^{+}(1 \text{ M}) \mid H_{2}(g) \text{ (I bar)} \mid Pt(s)$ 
(iii)  $S(s) \mid Sn^{2+}(0.050 \text{ M}) \mid H^{+}(0.020 \text{ M}) \mid H_{2}(g) \text{ (I bar)} \mid Pt(s)$ 
(iii)  $S(s) \mid Sn^{2+}(0.050 \text{ M}) \mid H^{+}(0.020 \text{ M}) \mid H_{2}(g) \text{ (I bar)} \mid Pt(s)$ 
(iii)  $S(s) \mid Sn^{2+}(0.050 \text{ M}) \mid H^{+}(0.020 \text{ M}) \mid H_{2}(g) \text{ (I bar)} \mid Pt(s)$ 
(iii)  $S(s) \mid Sn^{2+}(0.050 \text{ M}) \mid H^{+}(0.020 \text{ M}) \mid H_{2}(g) \text{ (I bar)} \mid Pt(s)$ 
(iii)  $S(s) \mid Sn^{2+}(0.050 \text{ M}) \mid H^{+}(0.020 \text{ M}) \mid H_{2}(g) \text{ (I bar)} \mid Pt(s)$ 
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(iii)  $S(s) \mid Sn^{2+}(0.050 \text{ M}) \mid H^{+}(0.020 \text{ M}) \mid H_{2}(g) \text{ (I bar)} \mid Pt(s)$ 
(iii)  $S(s) \mid Sn^{2+}(s) \mid Sn^{$ 

$$= -1.08 - 0.208 = -1.288 \text{ V}$$

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

 $Pt \mid H_2O (1 \text{ bar}) \mid H^+ (0.03 \text{ M}) \mid Br^- (0.01 \text{ M}) \mid Br_2(l) \mid Pt(s)$ 

Ans.

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

$$\operatorname{Zn}(s) + \operatorname{Ag}_2\operatorname{O}(s) + \operatorname{H}_2\operatorname{O}(l) \longrightarrow \operatorname{Zn}^{2+}(aq) + 2\operatorname{Ag}(s) + 2\operatorname{OH}^-(aq)$$

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

 $Zn \longrightarrow Zn^{2+} + 2e^{-}$ Ans. At anode:  $Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^-$ At cathode:

e: 
$$Ag_2O + H_2O + 2e \longrightarrow 2Ag + 2OH$$

$$Zn + Ag_2O + H_2O \longrightarrow Zn^{2+} + 2Ag + 2OH^-$$

$$E_{cell}^o = E_{cathode}^o - E_{anode}^o = E_{Ag^+/Ag}^o - E_{Zn^{2+}/Zn}^o$$

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

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

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

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

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

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

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

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

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

0.2

c1/2 (mol/L)1/2

Molar conductivity versus  $c^{1/2}$  for acetic acid (weak electrolyte) and potassium

0.4

400

CH<sub>3</sub>COOH

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

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

$$\Lambda_m = \kappa V$$

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

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

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

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

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

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

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

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

• 
$$CH_3$$
— $CHO + 2Cu^{2+} + 5OH$   $\longrightarrow$   $CH_3COO^- + Cu_2O + 3H_2O$ 
Red brown ppt

- Q. 2. (i) A ketone A which undergoes haloform reaction gives compound B on reduction. B on heating with sulphuric acid gives compound C, which forms mono-ozonide D. The compound D on hydrolysis in presence of zinc dust gives only acetaldehyde. Write the structures and IUPAC names of A, B and C. Write down the reactions involved.
  - (ii) Predict the products formed when cyclohexanecarbaldehyde reacts with following reagents.
    - (a) PhMgBr and then H<sub>3</sub>O<sup>+</sup>
    - (b) Tollens' reagent.

[CBSE Sample Paper 2017]

The reactions are as follows:

$$\begin{array}{c} \text{OH} \\ \text{CH}_3\text{--}\text{C}\text{--}\text{CH}_2\text{--}\text{CH}_3 & \xrightarrow{\text{LiAlH}_4}\text{--}\text{CH}_3\text{--}\text{CH}\text{--}\text{CH}_2\text{--}\text{CH}_3 & \xrightarrow{\text{H}_2\text{SO}_4(\text{conc.})}\text{--}\text{CH}\text{--}\text{CH}_3\text{--}\text{CH}\text{--}\text{CH}_3\\ \text{(A)} & \text{(B)} & \text{(C)} \\ & & & & & & & & & & & & & & \\ & & & & & & & & & & & & \\ & & & & & & & & & & & & \\ & & & & & & & & & & & \\ & & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$$

$$(ii) \ (a) \\ \begin{array}{c} O \\ O \\ O \\ Cyclohexane carbaldehyde \end{array} \xrightarrow{Ph-MgBr} \begin{array}{c} O \\ Ph-MgBr \\ Dry \ ether \end{array} \xrightarrow{Ph-MgBr} \begin{array}{c} O \\ C \\ Ph \end{array} \xrightarrow{H_3O^+} \begin{array}{c} O \\ Ph \\ Ph \end{array}$$

Q. 3. Write the structures of A, B, C, D and E in the following reactions:

[CBSE Delhi 2016]

$$C_{6}H_{6} \xrightarrow{CH_{3}COCl} A_{\text{Anhyd. AlCl}_{3}} \xrightarrow{A} \xrightarrow{Zn\text{-Hg/conc. HCl}} B \xrightarrow{(i) \text{ KMnO}_{4}\text{-KOH, }\Delta} C$$

$$\downarrow NaOl$$

$$D + E$$

Ans. 
$$A = \bigcup_{Acetophenone}^{O}$$
;  $B = \bigcup_{Ethyl}^{C}$ ;  $C = \bigcup_{Benzoic}^{O}$ ;  $D \text{ or } E = CHI_3$ ;  $E \text{ or } D = \bigcup_{Benzoic}^{O}$  Sodium benzoate

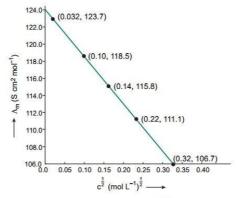
## Q. 10. The conductivity of sodium chloride at 298 K has been determined at different concentrations and the results are given below:

Concentration/M	0.001	0.010	0.020	0.050	0.100
10 <sup>2</sup> × κ/S m <sup>-1</sup>	1.237	11.85	23.15	55.53	106.74

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

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

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



Plot between  $\Lambda_m$  and  $c^{1/2}$ 

 $\Lambda_m^0$  = Intercept on the  $\Lambda_m$  axis = 124.0 S cm<sup>2</sup> mol<sup>-1</sup>

# Q. 11. Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5}$ S cm<sup>-1</sup> Calculate its molar conductivity. If $\Lambda_m^o$ for acetic acid is 390.5 S cm<sup>2</sup> mol<sup>-1</sup>, what is its dissociation constant? Ans. $c = 0.00241 \text{ M}, \kappa = 7.896 \times 10^{-5} \text{ S cm}^{-1}, \Lambda_m^o = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$

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

Substituting the values, we get

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

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

 $\alpha = 0.084\%$ 

Initial concentration

 $c(1-\alpha)$ Concentration at equilibrium ca

$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{c\alpha \cdot c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$
$$K = \frac{0.00241(0.084)^2}{(1-0.084)} = 1.86 \times 10^{-5}$$

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

(i) 1 mol of Al3+ to Al? (ii) 1 mol of Cu2+ to Cu?

(iii) 1 mol of MnO<sub>4</sub> to Mn<sup>2+</sup>?

 $Al^{3+} + 3e^{-} \longrightarrow Al$ Ans.

:. Quantity of charge required for reduction of 1 mol of Al3+ = 3F

 $= 3 \times 96500 \text{ C} = 289500 \text{ C}$ 

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

> $\therefore$  Quantity of charge required for reduction of 1 mol of Cu<sup>2+</sup> = 2F = 2 × 96500 C = 193000 C

[CBSE 2020 (56/5/1)]

 $MnO_4^- \longrightarrow Mn^{2+}$ (iii)

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

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

Q. 13. How much electricity in terms of Faraday is required to produce

(i) 20.0 g of Ca from molten CaCl<sub>9</sub>? (ii) 40.0 g of Al from molten Al<sub>2</sub>O<sub>3</sub>?

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

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

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

(ii) Al<sup>3+</sup> + 3e<sup>-</sup>  $\longrightarrow$  Al

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

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

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

(i) 1 mol of H<sub>2</sub>O to O<sub>2</sub> (ii) 1 mol of FeO to Fe<sub>9</sub>O<sub>9</sub>?

(i) The electrode reaction for 1 mol of H<sub>2</sub>O is given as Ans.

$$H_2O \longrightarrow 2H^+ + \frac{1}{2} O_2 + 2e^-$$

(ii) The electrode reaction is given as

$$2\text{FeO} + \frac{1}{2} \text{ O}_2 \longrightarrow \text{Fe}_2\text{O}_3$$

 $2Fe^{2+} \longrightarrow 2Fe^{3+} + 2e^{-}$ i.e.,

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

:. For the oxidation of 1 mole of FeO, required charge = 1 F = 96500 C

Q. 15. A solution of Ni(NO<sub>3</sub>)<sub>2</sub> is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode? [CBSE (F) 2014]

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

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

ne electrode reaction is: 
$$Ni^{2r} + 2e^{-} \longrightarrow N$$

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

Q. 16. Three electrolytic cells A, B and C containing solutions of ZnSO4, AgNO3 and CuSO4, respectively were connected in series. A steady current of 1.5 amperes was passed through them until 1.45 g of silver deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

Ans. 
$$Ag^+ + e^- \longrightarrow Ag$$

108 g of Ag is deposited by 96500 C

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

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

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

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

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

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

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

Zn deposited by 1295.6 C = 
$$\frac{65.3}{2 \times 96500} \times 1295.6$$

$$= 0.438 g$$

- Q. 17. Using the standard electrode potentials given below, predict if the reaction between the following is feasible:
  - (i)  $Fe^{3+}$  (aq) and  $I^-$  (aq)
  - (ii) Ag+ (aq) and Cu (s)

  - (iii) Fe3+ (aq) and Br (aq) (iv) Ag(s) and Fe3+ (aq)
  - (v)  $Br_2(aq)$  and  $Fe^{2+}(aq)$
  - Given standard electrode potentials:

 $E_{1/2L/l^{-}}^{0} = 0.541 \text{ V}, \qquad E_{Cu^{2+}/Cu}^{0} = +0.34 \text{ V}, \qquad E_{1/2 \text{ Br./Br.}}^{0} = +1.090 \text{ V},$ 

$$E_{\text{Ag}^+/\text{Ag}}^0 = +0.80 \text{ V}, \qquad E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = +0.77 \text{ V}.$$

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

(i) 
$$Fe^{3+}(aq) + I^{-}(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}I_2$$

$$E_{\text{cell}}^{\circ} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - E_{1/2}^{\circ} I_{1/2}/I^{-}$$
= 0.77 V - 0.54 V = **0.23** V (feasible).

(ii) 
$$Ag^{+}(aq) + Cu \longrightarrow Ag(s) + Cu^{2+}(aq)$$
  
 $E^{0}_{cell} = E^{0}_{Ag^{+}/Ag} - E^{0}_{Cu^{2+}/Cu} = 0.80 \text{ V} - 0.34 \text{ V} = 0.46 \text{ V} \text{ (feasible)}.$ 

(iii) 
$$Fe^{3+}(aq) + Br^{-}(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}Br_2$$
  
 $E_{call}^0 = 0.77 \text{ V} - 1.09 \text{ V} = -0.32 \text{ V (not feasible)}.$ 

(iv) 
$$Ag(s) + Fe^{3+}(aq) \longrightarrow Ag^{+}(aq) + Fe^{2+}(aq)$$
,

$$E_{\text{cell}}^{\text{o}} = 0.77 \text{ V} - 0.80 \text{ V} = -0.03 \text{ V}$$
 (not feasible).

$$(v) \quad \frac{1}{2}\operatorname{Br}_{2}(aq) + \operatorname{Fe}^{2+}(aq) \longrightarrow \operatorname{Br}^{-}(aq) + \operatorname{Fe}^{3+}(aq),$$

- $E_{\text{call}}^{\text{o}} = 1.09 \text{ V} 0.77 \text{ V} = 0.32 \text{ V}$  (feasible).
- Q. 18. Predict the products of electrolysis in each of the following (i) An aqueous solution of AgNO3 with silver electrodes.
  - (ii) An aqueous solution of AgNO3 with platinum electrodes.
  - (iii) A dilute solution of H2SO4 with platinum electrodes.
  - [CBSE 2019 (56/3/2)] (iv) An aqueous solution of CuCl2 with platinum electrodes. [CBSE 2020 (56/4/3)]
- (i) Electrolysis of aqueous solution of AgNO3 with silver electrodes: Ans.

extrolysis of aqueous solution of AgNO<sub>3</sub> with silver electrodes  

$$AgNO_3(s) \longrightarrow Ag^+(aq) + NO_3^-(aq)$$

At cathode: Since, the reduction potential of Ag<sup>+</sup> (+0.80 V) is greater than that of water, (-0.83 V),

Ag+ will get reduced preferentially and silver metal will get deposited at the cathode. will be deposited as Ag in preference to H+ ions.

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

At anode: Following reactions may take place

$$H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$$

$$NO_3^-(aq) \longrightarrow NO_3 + e^-$$

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

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

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

At anode: Since the reduction potential of water is less than that of NO<sub>3</sub> ions, water will get preferentially oxidised and oxygen will be evolved.

$$H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$$

(iii) At cathode:

$$2H^{+}(aq) + 2e^{-} \longrightarrow H_{2}(g);$$
  $E^{0} = 0.00 \text{ V}$ 

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq); E^o = -0.83 \text{ V}$$

Since, H+ ions possess a higher reduction potential as compared to that of water, H+ will get preferentially reduced and H2 gas is obtained at the cathode.

$$2H^+(aq) + 2e^- \longrightarrow H_2(g)$$

At anode: 
$$H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-$$
;  $E^0 = +1.23 \text{ V}$ 

$$SO_4^{2-}(aq) \longrightarrow SO_4 + 2e^-; E^0 = 2.0 \text{ V}$$

Since, the reduction potential of H<sub>2</sub>O is less than that of SO<sub>4</sub><sup>2</sup>-ions, water will get preferentially oxidised and oxygen will be evolved at the anode.

[NCERT Exemplar]

(d)  $Mn^{2+}$ 

8. Using the data given below find out the strongest reducing agent.

 $E^{\rm o}_{{\rm Cr}_2{\rm O}_2^{2-}/{\rm Cr}^{3+}} = 1.33~{\rm V}, \quad E^{\rm o}_{{\rm Cl}_2/{\rm Cl}^-} = 1.36~{\rm V}, \quad E^{\rm o}_{{\rm MnO}_4^-/{\rm Mn}^{2+}} = 1.51~{\rm V}, \quad E^{\rm o}_{{\rm Cr}^{3+}/{\rm Cr}} = -0.74~{\rm V}$ 

9.	Using the data given in Q. 8 find out in which	h option the order of reducing p	oower is correct. [NCERT Exemplar]
	(a) $Cr^{3+} < Cl^{-} < Mn^{2+} < Cr$	(b) $Mn^{2+} < Cl^{-} < Cr^{3+} < Cr^{-}$	[NCERT Exemplair]
	(c) $\operatorname{Cr}^{3+} < \operatorname{Cl}^- < \operatorname{Cr}_2 \operatorname{O}_7^{2-} < \operatorname{MnO}_4^-$	(d) $Mn^{2+} < Cr^{3+} < Cl^{-} < Cr$	
10.	Use the data given in Q. 8 find out the most s	stable oxidised species.	[NCERT Exemplar]
	(a) $Cr^{3+}$	(b) MnO <sub>A</sub>	
	(c) $Cr_2O_7^{2-}$	$(d)  \mathrm{Mn}^{2+}$	
11.	Four half reactions I to IV are shown below:		
	I. $2Cl^- \longrightarrow Cl_2 + 2e^-$		
	II. $4OH^- \longrightarrow O_2 + 2H_2O + 2e^-$		
	III. $Na^+ + e^- \longrightarrow Na$		
	IV. $2H^+ + 2e^- \longrightarrow H_2$		
	Which two of these reactions are most likely	to occur when concentrated br	ine is electrolysed?
			[CBSE 2023 (56/5/2)]
	(a) I and III	(b) I and IV	
100100	(c) II and III	(d) II and IV	
12.	Zinc is coated over iron to prevent rusting of		[CBSE 2020 (56/5/3)]
	(a) $E_{Zn^{2+}/Zn}^0 = E_{Fe^{2+}/Fe}^0$	(b) $E_{\text{Zn}^{2+}/\text{Zn}}^{\text{o}} < E_{\text{Fe}^{2+}/\text{Fe}}^{\text{o}}$	
	(c) $E_{Zn^{2+}/Zn}^{o} > E_{Fe^{2+}/Fe}^{o}$	(d) None of these	
13.	$\Delta G$ and $E_{\text{cell}}^0$ for a spontaneous reaction will		[CBSE 2023 (56/1/1)]
1.4	(a) positive, negative (b) negative, negative		ositive, positive
14.	The standard emf of a galvanic cell involving equilibrium constant for the reaction of the		x reaction is 0.59 v. The
	(a) 10 <sup>10</sup>	(b) $10^{20}$	
	$(c)\ 10^{30}$	$(d) 10^{15}$	
15.	Which of the following solutions of KCl will	have the highest value of specifi	c conductance?
			[CBSE 2020 (56/3/2)]
	(a) 0.5 M	(b) 0.01 M	
	(c) 0.1 M	(d) 1.0 M	
16.	Which of the statements about solutions of e		[NCERT Exemplar]
	(a) Conductivity of solution depends upon size		
	<ul><li>(b) Conductivity depends upon viscosity of sol</li><li>(c) Conductivity does not depend upon solvation</li></ul>		
	(d) Conductivity does not depend upon solvano (d) Conductivity of solution increases with tem	the title of the statement of the statement	
17	Kohlrausch given the following relation for s	SWI COLOR OF SWITTER	
17.	$\Lambda = \Lambda_0 - A\sqrt{C}$	strong electrolytes.	
	Marie Say Co. Marie Say Co.		
	Which of the following equality holds? (a) $\Lambda = \Lambda_0$ as $C \longrightarrow \sqrt{A}$	(b) $\Lambda = \Lambda_0$ as $C \longrightarrow \infty$	[CBSE 2020 (56/5/2)]
	(c) $\Lambda = \Lambda_0$ as $C \rightarrow 0$	(d) $\Lambda = \Lambda_0$ as $C \longrightarrow 1$	
18.	$\Lambda^{\circ}_{m(\mathrm{NH_4OH})}$ is equal to	.,	[NCERT Exemplar]
	(a) $\Lambda_{m(NH,OH)}^{0} + \Lambda_{m(NH,CI)}^{0} - \Lambda_{m(HCI)}^{0}$	(b) $\Lambda_{m(NH,Cl)}^0 + \Lambda_{m(NaOH)}^0 - \Lambda$	0 m(NaCl)
	(c) $\Lambda_{m(\text{NH}_4\text{Cl})}^0 + \Lambda_{m(\text{NaCl})}^0 - \Lambda_{m(\text{NaOH})}^0$	(d) $\Lambda_{m(\text{NaOH})}^0 + \Lambda_{m(\text{NaCl})}^0 - \Lambda_m^0$	(NH <sub>4</sub> Cl)

19. Which of the following option will be the limiting molar conductivity of CH<sub>3</sub>COOH if the limiting molar conductivity of CH<sub>3</sub>COONa is 91 S cm<sup>2</sup> mol<sup>-1</sup>? Limiting molar conductivity for individual ions are given in the following table. [CBSE Sample Paper 2021]

S. No. Ions		Limiting molar conductivity/S cm <sup>2</sup> mol <sup>-1</sup>		
1.	H*	349.6		
2.	Na <sup>+</sup>	50.1		
3.	K <sup>+</sup>	73.5		
4.	OH-	199.1		

- (a) 350 S cm<sup>2</sup> mol<sup>-1</sup> (b) 375.3 S cm2 mol-1 (c) 390.5 S cm<sup>2</sup> mol<sup>-1</sup> (d) 340.4 S cm<sup>2</sup> mol<sup>-1</sup>
- 20. Charge carried by 1 mole of electrons is
  - (a)  $6.023 \times 10^{23}$  coulomb (b)  $9.65 \times 10^4$  coulomb
  - (c)  $1.6 \times 10^{-19}$  coulomb (d)  $6.28 \times 10^{19}$  coulomb
- 21. The quantity of charge required to obtain one mole of aluminium from Al<sub>2</sub>O<sub>3</sub> is \_\_\_\_\_\_ [NCERT Exemplar]
  - (a) 1F (b) 6F (c) 3F (d) 2F
- 22. If the standard electrode potential of an electrode is greater than zero, then we can infer that its [CBSE 2020 (56/2/1)]
  - (a) reduced form is more stable compared to hydrogen gas.
  - (b) oxidised form is more stable compared to hydrogen gas.
  - (c) reduced and oxidised forms are equally stable.
  - (d) reduced form is less stable than the hydrogen gas.
- 23. Consider the following standard electrode potential values:

[CBSE 2023 (56/5/2)]

Fe<sup>3+</sup>(aq) + e<sup>-</sup> 
$$\longrightarrow$$
 Fe<sup>2+</sup>(aq),  $E^0 = + 0.77 \text{ V}$   
MnO<sub>4</sub>(aq) + 8H<sup>+</sup> + 5e<sup>-</sup>  $\longrightarrow$  Mn<sup>2+</sup>(aq) + 4H, O(*l*),  $E^0 = + 1.51 \text{ V}$ 

What is the cell potential for the redox reaction?

(a) 
$$-2.28 \text{ V}$$
 (b)  $-0.74 \text{ V}$  (c)  $+0.74 \text{ V}$  (d)  $+2.28 \text{ V}$ 

24. 
$$E_{\text{cell}}^0$$
 for some half cell reactions are given below. On the basis of these mark the correct answer.  
(i)  $H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(q)$   $E_{\text{cell}}^0 = 0.00 \text{ V}$ 

(ii) 
$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^ E_{cell}^0 = 1.23 \text{ V}$$

(iii) 
$$2SO_8^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^ E_{\text{cell}}^0 = 1.96 \text{ V}$$
  
(a) In dilute sulphuric acid solution, hydrogen will be reduced at anode.

- (b) In concentrated sulphuric acid solution, water will be oxidised at anode. (c) In dilute sulphuric acid solution, water will be oxidised at anode.
- (d) In dilute sulphuric acid solution,  $SO_4^{2-}$  ion will be oxidised to tetrathionate at anode.
- 25. In a Leclanche dry cell, the cathode is [CBSE 2020 (56/3/3)]

- (a) Zn container (b) MnO2 (c) Graphite rod (d) NH<sub>4</sub>Cl
- 26. In a lead storage battery [CBSE 2020 (56/4/1)]
  - (a) PbO2 is reduced to PbSO4 at the cathode.
  - (b) Pb is oxidised to PbSO<sub>4</sub> at the anode.
  - (c) Both electrodes are immersed in the same aqueous solution of H2SO4.
  - (d) All the above are true.

27. In fuel cell [CBSE 2020 (56/3/3)]

- (a) chemical energy is converted to electrical energy.
- (b) energy of combustion of fuel is converted to chemical energy.
- (c) energy of combustion of fuel is converted to electrical energy.
- (d) electrical energy is converted to chemical energy.
- 28. Which of the following analogy is correct?
  - (a) Resistance : ohm :: Resistivity : ohm m
  - (b)  $\Lambda_m^{\infty}$ : Molarity ::  $\Lambda_{eq}^{\infty}$ : Normality
  - (c) Metallic conductance: Electrons:: Electrolytic conductance: ions
  - (d) All of these
- 29. Which of the following solutions of KCl will have the highest value of molar conductivity?

(a) 0.01 M

(b) 1 M (c) 0.5 M

[CBSE 2023 (56/2/1)] (d) 0.1 M

30. Match the following Columns:

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

$$\begin{array}{lll} (a) \ (i) - A, \ (ii) - C, \ (iii) - B, \ (iv) - D & (b) \ (i) - B, \ (ii) - A, \ (iii) - D, \ (iv) - C \\ (c) \ (i) - D, \ (ii) - A, \ (iii) - B, \ (iv) - C & (d) \ (i) - B, \ (ii) - D, \ (iii) - A, \ (iv) - C \\ \end{array}$$

#### **Answers**

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

## **Assertion-Reason Questions**

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

- (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
- (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
- (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
- (d) Assertion (A) is incorrect, but Reason (R) is correct statement.
- 1. Assertion (A):  $E_{cell}$  should have a positive value for the cell to function.
  - Reason (R):  $E_{cathode} < E_{anode}$
- 2. Assertion (A): Mercury cell does not give steady potential.
  - **Reason** (R): In the cell reaction, ions are not involved in solution.
- 3. Assertion (A): Cu is less reactive than hydrogen.
  - Reason (R):  $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ}$  is negative.

4. Assertion (A): Copper sulphate cannot be stored in zinc vessel.

**Reason** (R): Zinc is less reactive than copper.

Assertion (A): E<sub>Ag<sup>+</sup>/Ag</sub> increases with increase in concentration of Ag<sup>+</sup> ions.

**Reason** (R):  $E_{Ag^+/Ag}$  has a positive value.

6. Assertion (A): Current stops flowing when  $E_{cell} = 0$ .

Reason (R): Equilibrium of the cell reaction is attained.

7. Assertion (A): For measuring resistance of an ionic solution an AC source is used.

Reason (R): Concentration of ionic solution will change if DC source is used.

8. Assertion (A): Conductivity decreases with decrease in concentration of electrolyte.

Reason (R): Number of ions per unit volume that carry the current in a solution decreases on dilution.

[CBSE 2023 (56/2/1)]

9. Assertion (A): Conductivity decreases for weak electrolyte and increases for strong electrolyte with decrease in concentration.

**Reason** (R): On dilution, the number of ions per unit volume that carry the current decreases.

10. Assertion (A):  $\land_m$  for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.

Reason (R): For weak electrolytes, degree of dissociation decreases with dilution of solution.

[CBSE 2023 (56/4/2)]

11. Assertion (A): Electrolysis of NaCl solution gives chlorine at anode instead of O2.

n (R): Formation of oxygen at anode requires overvoltage.

12. Assertion (A): The following reaction takes place at cathode during the electrolysis of aqueous sodium

$$H_2O(l) + e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-$$

**Reason** (R): The reaction with lower value of  $E^{\circ}$  is preferred at cathode.

### **Answers**

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

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

Read the given passages and answer the questions that follow.

## PASSAGE-1

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

[CBSE 2023 (56/5/2)]

S. No. Conc. (M)		к S cm <sup>-1</sup>	∧ <sub>m</sub> S cm <sup>-2</sup> mol <sup>-1</sup>		
1.	1.00	$111.3 \times 10^{-3}$	111.3		
2.	0.10	$12.9 \times 10^{-3}$	129.0		
3.	0.01	$1.41 \times 10^{-3}$	141.0		

#### Answer the following questions:

- 1. Why does conductivity decrease with dilution?
- 2. If  $\wedge_m^0$  of KCl is 150.0 S cm<sup>2</sup> mol<sup>-1</sup>, calculate the degree of dissociation of 0.01 M KCl.

If Rahul had used HCl instead to KCl then would you expect the ∧<sub>m</sub> values to be more or less than
those per KCl for a given concentration. Justify.

OR

Amit a classmate of Rahul repeated the same experiment with CH<sub>3</sub>COOH solution instead of KCl solution. Give one point that would be similar and one that would be different in his observations as compared to Rahul.

#### **Answers**

- This is due to the fact that the number of ions per unit volume that carry the current in the solution decreases with dilution
- 2. Degree of dissociation,

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

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

OR

Similarity: Conductivity decreases with increase in dilution both for HCl and CH<sub>3</sub>COOH solutions. **Dissimilarity:** With increase in dilution there is very small increase in  $\land_m$  for HCl and very large increase in  $\land_m$  for CH<sub>3</sub>COOH (especially near infinite dilution).

### **PASSAGE-2**

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

- 1. Write the reaction taking place at the cathode when the battery is in use.
- 2. How much electricity in terms of Faraday is required to carry out the reduction of one mole of PbO<sub>2</sub>?
- 3. What is the molarity of sulphuric acid before discharge?

OR

- (i) Lead storage battery is considered a secondary cell. Why?
- (ii) Write the products of electrolysis when dilute sulphuric acid is electrolysed using Platinum electrodes.

#### **Answers**

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

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

2. From above reaction

1 mole of PbO2 require 2F of electricity for reduction to PbSO4.

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

Molarity =  $5.02 \text{ mol L}^{-1}$ 

OR

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

(ii) 
$$2H_2O(l) \xrightarrow{H_2SO_4(dil.)} 2H_2(g) + O_2(g)$$
  
(at cathode) (at anode)

# CONCEPTUAL OUESTIONS

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

Ans. The metal ions (Zn2+) formed by the loss of electrons will accumulate in one electrode and the negative ions (SO<sub>2</sub>) will accumulate in the other. Thus, the solutions will develop charges and the current will stop flowing. Moreover, the inner circuit will not be completed.

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

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

Q. 3. Consider a cell given below:

[NCERT Exemplar]

Write the reactions that occur at anode and cathode.

- $Cu \longrightarrow Cu^{2+} + 2e^{-}$ Ans. Anode:  $Cl_2 + 2e^- \longrightarrow 2Cl^-$
- Cathode:

Q. 4. Depict the galvanic cell in which the cell reaction is  $Cu + 2Ag^+ \longrightarrow 2Ag + Cu^{2+}$ . [NCERT Exemplar] [HOTS]

- Ans. Cu | Cu<sup>2+</sup>(conc.) | Ag<sup>+</sup>(conc.) | Ag
- Q. 5. What is the reference electrode in determining the standard electrode potential?

Ans. Normal hydrogen electrode (NHE).

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

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

Q. 7. Define electrochemical series.

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

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

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

$$E_{\mathbf{M}^{n+},\mathbf{M}} = E_{\mathbf{M}^{n+},\mathbf{M}}^{o} - \frac{2.303RT}{nF} \log \frac{[\mathbf{M}]}{[\mathbf{M}^{n+}]} = E_{\mathbf{M}^{n+},\mathbf{M}}^{o} - \frac{2.303RT}{nF} \log \frac{1}{[\mathbf{M}^{n+}]}$$

Q. 9. Write Nernst equation for the general cell reaction  $aA + bB \xrightarrow{ne^-} xX + vY$ .

Ans. If n moles of electrons are transferred, Nernst equation is  $E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln \frac{[X]^2[Y]^2}{[A]^a[P]^b}$ .

Q. 10. Write Nernst equation for the reaction

$$2Cr + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe$$

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

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

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

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

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

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

Ans. Ions

- Q. 13. What does the negative value of  $E_{cell}^{o}$  indicate?
  - Ans. Negative  $E_{cell}^o$  value means  $\Delta_r G^o$  will be +ve, and the cell will not work.
- Q. 14. Out of zinc and tin, whose coating is better to protect iron objects? [CBSE 2020 (56/1/1)]

ns. Zinc

- Q. 15. Why is alternating current used for measuring resistance of an electrolytic solution? [NCERT Exemplar]
  - Ans. Alternating current is used to prevent electrolysis so that concentration of ions in the solution remains constant.
- Q. 16. What is meant by cell constant?
  - Ans. Cell constant is the ratio of distance (*l*) between electrodes and area of cross-section (*A*). It is denoted by  $\frac{l}{4}$ . Its unit is cm<sup>-1</sup>.
- Q. 17. Define specific conductance or conductivity.

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

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

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

- Q. 19. Write the mathematical expression for Kohlrausch's law.
  - Ans.  $\Lambda_m^o = v_c \Lambda_c^o + v_a \Lambda_a^o$ , where  $v_c$  and  $v_a$  are the number of cations and anions respectively in one formula unit of the compound.
- Q. 20. Why on dilution the Λ<sub>m</sub> of CH<sub>3</sub>COOH increases drastically while that of CH<sub>3</sub>COONa increases gradually?
  [NCERT Exemplar]
- Ans. In the case of CH<sub>3</sub>COOH, which is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation.

 $CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+$ 

- Q. 21. How much charge is required for the reduction of 1 mol of Zn<sup>2+</sup> to Zn? [CBSE Patna 2015]
  - Ans.  $Zn^{2+} + 2e^{-} \longrightarrow Zn$

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

[CBSE Marking Scheme 2015]

[CBSE 2019 (56/3/2)]

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

[NCERT Exemplar] [HOTS]

- Ans. The pH of the solution will increase as NaOH is formed in the electrolytic cell.
- Q. 23. Value of standard electrode potential for the oxidation of Cl<sup>-</sup> ions is more positive than that of water, even then in the electrolysis of aqueous sodium chloride, why is Cl<sup>-</sup> oxidised at anode instead of water?
  [NCERT Exemplar]
  - Ans. On electrolysis of aqueous sodium chloride, oxidation of water at anode requires over potential hence Cl<sup>-</sup> is oxidised instead of water.
- Q. 24. What is primary cell? Give an example.

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

- Q. 25. Why does a dry cell become dead after a long time even if it has not been used?
  - Ans. Even though not in use, a dry cell becomes dead after some time because the acidic NH<sub>4</sub>Cl corrodes the zinc container.
- Q. 26. What is the role of ZnCl<sub>2</sub> in a dry cell?
  - Ans. ZnCl<sub>2</sub> combines with the NH<sub>3</sub> produced to form the complex salt [Zn(NH<sub>3</sub>)<sub>2</sub> Cl<sub>2</sub>] otherwise the pressure developed due to NH<sub>3</sub> would crack the seal of the cell.

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

[NCERT Exemplar]

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

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

Ans. (i) Concentrated aqueous KOH solution.

(ii) Moist mercuric oxide (HgO) mixed with KOH.

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

11S.  $2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$ 

O. 30. Write the chemical formula of rust.

Ans. Fe<sub>2</sub>O<sub>3</sub>. xH<sub>2</sub>O

Q. 31. What is galvanization?

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

Q. 32. What is cathodic protection?

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

- Q. 33. Which type of a metal can be used in cathodic protection of iron against rusting?
- Ans. A metal which is more electropositive than iron such as Al, Zn, Mg can be used in cathodic protection of iron against rusting.
- Q. 34. Using the  $E^0$  values of X and Y, predict which is better for coating the surface of iron to prevent rust and why?

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

[CBSE 2019 (56/4/3)]

- Ans. X, as its standard reduction potential is less than Y. Therefore, it will undergo oxidation more easily than Y.
- Q. 35. Three iron sheets have been coated separately with three metals A, B and C whose standard electrode potentials are given below.

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

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

## **Short Answer Questions-I**

Each of the following questions are of 2 marks.

Q. 1. At what pH of HCl solution will hydrogen gas electrode show electrode potential of -0.118 V? H<sub>2</sub> gas is passed at 298 K and 1 atm pressure.

Ans. 
$$H^+ + e^- \longrightarrow \frac{1}{2}H_2$$

Applying Nernst equation,

$$\begin{split} E_{\text{H}^{+}/\frac{1}{2}\text{H}_{2}} &= E_{\text{H}^{+}/\frac{1}{2}\text{H}_{2}}^{\text{o}} - \frac{0.059}{n} \log \frac{1}{[\text{H}^{+}]} \\ &- 0.118 = 0 - \frac{0.059}{1} \log \frac{1}{[\text{H}^{+}]} \end{split}$$

$$-0.118 = 0.059 \log [H^+]$$
  
 $-0.118 = -0.059 \text{ pH}$   
 $pH = 2$ 

O. 2. Give reasons:

or

[CBSE 2023 (56/2/1)]

- (i) Mercury cell delivers a constant potential during its life time.
- (ii) In the experimental determination of electrolytic conductance, Direct Current (DC) is not used .
- Ans. (i) Overall reaction does not involve any ion whose concentration may change. Hence, it delivers a constant potential during its life time.
  - (ii) Direct current (DC) causes electrolysis of the solution consequently. The concentration of the electrolyte near the electrodes changes and this results in the change in the resistance (and hence the conductance) of the solution. Therefore direct current is not used.
- Q. 3. The conductivity of 0.20 M solution of KCl at 298 K is 0.025 S cm<sup>-1</sup>. Calculate its molar conductivity. [CBSE Delhi 2013]

Ans.

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

$$= \frac{0.025 \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.2 \text{ mol L}^{-1}}$$

$$= 125 \text{ S cm}^2 \text{ mol}^{-1}$$

Q. 4. The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm<sup>2</sup> mol<sup>-1</sup>. Calculate the conductivity of this solution. [CBSE (AI) 2012]

Ans.

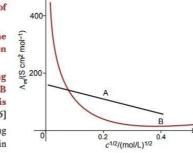
$$\Lambda_{m} = \frac{\kappa \times 1000}{M}$$

$$\kappa = \frac{\Lambda_{m} \times M}{1000}$$

$$\kappa = \frac{138.95 \text{ S cm}^{2} \text{mol}^{-1} \times 1.5 \text{ mol L}^{-1}}{1000 \text{ cm}^{3} \text{ L}^{-1}}$$

- Q. 5. The following curve is obtained when molar conductivity  $(\Lambda_m)$  is plotted against the square root of concentration,  $c^{1/2}$  for two electrolytes A and B.
  - (i) How do you account for the increase in the molar conductivity of the electrolyte A on dilution?
  - (ii) As seen from the graph, the value of limiting molar conductivity (Λ<sup>o</sup><sub>m</sub>) for electrolyte B cannot be obtained graphically. How can this value be obtained? [CBSE Sample Paper 2016]

Ans. (i) As seen from the graph, electrolyte 'A' is a strong electrolyte which is ionised almost completely in solutions. For strong electrolyte 'A', the number of



- solutions. For strong electrolyte 'A', the number of ions does not increase appreciably on dilution and only mobility of ions increases due to decrease in interionic attraction. Therefore, molar conductivity increases a little as shown in graph by a straight line.
- (ii) Limiting molar conductivity (Λ<sup>0</sup><sub>m</sub>) for weak electrolyte 'B' can be obtained by using Kohlrausch law of independent migration of ions which says that limiting molar conductivity of an electrolyte is equal to the sum of the individual contribution of the cation and anion of the electrolyte.

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

Ans.

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	[Topper's Answer (AI) 2014]

Q. 7. Calculate the degree of dissociation ( $\alpha$ ) of acetic acid if its molar conductivity ( $\Lambda_m$ ) is 39.05 S cm<sup>2</sup> mol<sup>-1</sup>. [Given  $\lambda_{(H^+)}^0 = 349.6$  S cm<sup>2</sup> mol<sup>-1</sup> and  $\lambda_{(CH,COO^-)}^0 = 40.9$  S cm<sup>2</sup> mol<sup>-1</sup>] [CBSE Delhi 2017]

Q. 8. Calculate the time to deposit 1.27 g of copper at cathode when a current of 2 A was passed through the solution of CuSO<sub>4</sub>.

(Molar mass of Cu = 63.5 g mol<sup>-1</sup>, 1 F = 96500 C mol<sup>-1</sup>) Ans.  $Cu^{2+} + 2e^- \longrightarrow Cu$ 

[CBSE Allahabad 2015]

[CBSE 2023 (56/5/2)]

63.5 g of copper is deposited by  $2 \times 96500$  C.

$$\therefore$$
 1.27 g of copper will be deposited by  $\frac{2 \times 96500 \times 1.27}{63.5}$  C = 3860 C

$$I = 2 \text{ A}, Q = 3860 \text{ C}$$
  

$$\therefore t = \frac{Q}{L} = \frac{3860}{2} = 1930 \text{ s}$$

Q. 9. How many moles of mercury will be produced by electrolysing 1.0 M Hg(NO<sub>3</sub>)<sub>2</sub> solution with a current of 2.00 A for 3 hours? [CBSE (AI) 2011]

Ans. Mass of mercury produced at the cathode,

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

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

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

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

Q. 10. Calculate the emf of the following cell at 298 K: Fe(s) | Fe<sup>2+</sup>(0.01M) || H<sup>+</sup>(1M) | H<sub>2</sub>(g) (1 bar), Pt(s)

ar), Pt(s)

Fe(s) | Fe<sup>-0</sup> (0.01M) || H<sup>-1</sup> (1M) | H<sub>2</sub>(g) (1 bar), Pt(s) Given:  $E_{\text{cell}}^0 = 0.44 \text{ V}$ .

Ans. At anode : Fe 
$$\longrightarrow$$
 Fe<sup>2+</sup> + 2e<sup>-</sup>

At cathode:  $2H^+ + 2e^- \longrightarrow H_2$ 

Fe  $+2H^+ \longrightarrow Fe^{2+} + H_2$ 

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

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^{+}]^{2}}$$
, we get 
$$E_{\text{cell}} = 0.44 - \frac{0.059}{2} \log \frac{10^{-2}}{(1)^{2}} = 0.44 + \frac{0.059}{2} \times 2 \times \log 10$$

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

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

Ans. 
$$Q = I \times t$$

Ans.

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

 $2Cl^{-} \longrightarrow Cl_{2} + 2e^{-}$ 

2 × 96500 C deposit Cl<sub>2</sub> = 1 mol  
∴ 18 C will deposit Cl<sub>2</sub> = 
$$\frac{1 \text{ mol} \times 18 \text{ C} \times 6.022 \times 10^{23}}{2 \times 96500 \text{ C}}$$
 molecules = 5.616 × 10<sup>19</sup> molecules

Q. 12 Chromium metal is electroplated using an acidic solution containing CrO<sub>3</sub> according to the following equation:

$$CrO_3(aq) + 6H^+ + 6e^- \longrightarrow Cr(s) + 3H_2O$$

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

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

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

52 g of Cr is deposited by 6 × 96500 C.

Cathode:  $Na^+(aq) + e^- \longrightarrow Na(s)$ 

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

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

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

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

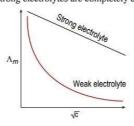
$$H^{+}(aq) + e^{-} \longrightarrow \frac{1}{2}H_{2}(g) \qquad E^{0} = 0.00 \text{ V}$$
Anode: 
$$Cl^{-}(aq) \longrightarrow \frac{1}{2}Cl_{2}(g) + e^{-} \qquad E^{0} = +1.36 \text{ V}$$

 $2H_2O(aq) \longrightarrow O_2(g) + 4H^+ + 4e^- \qquad E^0 = +1.23 \text{ V} \qquad [CBSE 2019 (56/5/2)]$ 

Ans. H<sub>2</sub>(g) is produced at cathode due to greater E<sup>o</sup> value of H<sup>+</sup> ion and Cl<sub>2</sub>(g) is produced at anode due to overpotential of oxygen.

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

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



Q. 15. Name the cell which:

[CBSE 2023 (56/4/2)]

- (i) was used in Apollo Space programme.
- (ii) is used in automobiles and inverters.
- (iii) is suitable for hearing aids and watches.
- (iv) does not give a steady potential and is used in transistors.
- Ans. (i) Fuel cells (iii) Mercury cell

(ii) Lead storage battery/cell

(at anode)

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

Ans. Mercury cell

At anode:  $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$ 

At cathode:  $HgO(s) + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$ 

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

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

Ans. (i)  $Cd(s) + 2OH(aq) \longrightarrow Cd(OH)_2(s) + 2e^{-s}$ 

$$NiO_2(s) + 2H_2O + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$$
 (at cathode)

(ii) 
$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^{-}$$
 (at anode)

 $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$  (at cathode)

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

Ans. According to electrochemical theory of rusting, the impure iron surface behaves like small electrochemical cell in the presence of water containing dissolved oxygen or carbon dioxide. In this cell pure iron acts as anode and impure iron surface acts as cathode. Moisture having dissolved CO<sub>2</sub> or O<sub>2</sub> acts as an electrolyte. The reactions are given below:

At anode: Fe  $\longrightarrow$  Fe<sup>2+</sup> + 2e<sup>-</sup>;  $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V}$ At cathode:  $2\text{H}^{+} + \frac{1}{2}\text{O}_{2} + 2e^{-} \longrightarrow \text{H}_{2}\text{O};$   $E_{\text{H}^{+}/\text{O}_{2}/\text{H}_{2}\text{O}}^{\circ} = 1.23 \text{ V}$ Overall reaction: Fe + 2H<sup>+</sup> +  $\frac{1}{2}\text{O}_{2} \longrightarrow \text{Fe}^{2+} + \text{H}_{2}\text{O};$   $E_{\text{cell}}^{\circ} = 1.67 \text{ V}$ 

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

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O \longrightarrow Fe_2O_3 + 4H^+$$
  
 $Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3, xH_2O \text{ (Rust)}$ 

# **Short Answer Questions-II**

Each of the following questions are of 3 marks.

Q. 1. One half-cell in a voltaic cell is constructed from a silver wire dipped in silver nitrate solution of unknown concentration. The other half-cell consists of a zinc electrode in a 0.10 M solution of Zn(NO<sub>3</sub>)<sub>2</sub>. A voltage of 1.48 V is measured for this cell. Use this information to calculate the concentration of silver ions in the solution.

[Given: 
$$E_{Z_n^{2+}/Z_n}^0 = -0.763 \text{ V}, E_{A\sigma^+/A\sigma}^0 = +0.80 \text{ V}]$$
 [CBSE (F) 2010]

Ans. Electrochemical cell

$$Zn(s) | Zn^{2+} (0.10 \text{ M}) | | Ag^{+} (conc.) | Ag(s)$$
  
 $E_{cell}^{o} = E_{R}^{o} - E_{L}^{o} = E_{Ag^{+}/Ag}^{o} - E_{Zn^{2+}/Zn}^{o}$   
 $= 0.80 \text{ V} - (-0.763) \text{ V} = 1.563 \text{ V}$ 

We know that,

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

$$1.48 = 1.563 - \frac{0.0591}{2} \log \frac{[0.10]}{[\text{Ag}^{+}]^{2}}$$

$$\log \frac{[0.10]}{[\text{Ag}^{+}]^{2}} = \frac{0.083}{0.02955} = 2.8088$$
Or
$$\frac{[0.10]}{[\text{Ag}^{+}]^{2}} = \text{antilog } 2.8088 = 643.87$$

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

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

Q. 2. A zinc rod is dipped in 0.1 M solution of ZnSO<sub>4</sub>. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential ( $E_{2n^{2+}/Z_n}^0 = -0.76 \text{ V}$ ).

Ans. The electrode reaction written as reduction reaction is

$$Zn^{2+} + 2e^{-} \longrightarrow Zn (n = 2)$$

Applying Nernst equation, we get

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

As 0.1 M ZnSO<sub>4</sub> solution is 95% dissociated, this means that in the solution,

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

$$E_{Zn^{2+}/Zn} = -0.76 - \frac{0.0591}{2} \log \frac{1}{0.095}$$

$$= -0.76 - 0.02955 (\log 1000 - \log 95) = -0.76 - 0.02955 (3 - 1.9777)$$

$$= -0.76 - 0.03021 = -0.79021 \text{ V}$$

- Q. 3. A strip of nickel metal is placed in a 1 molar solution of Ni(NO<sub>3</sub>)<sub>2</sub> and a strip of silver metal is placed in a 1 molar solution of AgNO<sub>3</sub>. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter.
  - Write the balanced equation for the overall reaction occurring in the cell and calculate the cell potential.

(ii) Calculate the cell potential, E, at 25°C for the cell if the initial concentration of Ni(NO<sub>3</sub>)<sub>2</sub> is 0.100 molar and the initial concentration of AgNO3 is 1.00 molar.

 $[E_{\text{Ni}^{2+}/\text{Ni}}^{0} = -0.25 \text{ V}; E_{\text{Ag}^{+}/\text{Ag}}^{0} = 0.80 \text{ V}, \log 10^{-1} = -1]$ At anode: Ni  $\longrightarrow$  Ni<sup>2+</sup> + 2e<sup>-</sup> [CBSE (F) 2012]

Ans.  $[Ag^+ + e^- \longrightarrow Ag] \times 2$ 

At cathode:

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

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

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

 $E_{coll}^{o} = 1.05 \text{ V}$ 

(ii)

 $E_{\text{cell}} = E_{\text{cell}}^{0} - \frac{0.059}{n} \log \frac{[\text{Ni}^{2+}]}{[\Delta \alpha^{+}]^{2}}$ 

Here, n = 2,  $E_{\text{cell}}^{0} = 1.05 \text{ V}$ ,  $[\text{Ni}^{2+}] = 0.1 \text{ M}$ ,  $[\text{Ag}^{+}] = 1.0 \text{ M}$ 

$$E_{\text{cell}} = 1.05 \text{ V} - \frac{0.059}{2} \log \frac{(0.1)}{(1)^2}$$
  
 $E_{\text{cell}} = 1.05 \text{ V} - 0.0295 \log 10^{-1} = 1.05 + 0.0295 \text{ V} = 1.0795 \text{ V}$ 

[HOTS]

 $[:] pH = -\log(H^+)$ 

[HOTS]

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

 $Zn(s) + 2H^{+}(aq) \longrightarrow Zn^{2+}(0.1 \text{ M}) + H_{2}(g, 1 \text{ atm}) \text{ is } 0.28 \text{ volt at } 25^{\circ}\text{C}.$ 

Write the half-cell reactions and calculate the pH of the solution at the hydrogen electrode.  $[E_{Zn^{2+}/Zn}^{o} = -0.76 \text{ V}, E_{H^{+}/H_{2}}^{o} = 0 \text{ V}]$ 

Ans. Half-cell reactions:

 $Zn \longrightarrow Zn^{2+} + 2e^{-}$ At anode:

At cathode:

 $2H^{+} + 2e^{-} \longrightarrow H_{2}$   $Zn + 2H^{+} \longrightarrow Zn^{2+} + H_{2}$ 

Cell reaction:

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

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

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

pH = 8.62

Q. 5. Estimate the minimum potential difference needed to reduce Al<sub>2</sub>O<sub>3</sub> at 500°C. The free energy change for the decomposition reaction

$$\frac{2}{3}$$
Al<sub>2</sub>O<sub>3</sub>  $\longrightarrow \frac{4}{3}$ Al + O<sub>2</sub> is 960 kJ ( $F = 96,500 \text{ C mol}^{-1}$ ).

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

Ans.  $\frac{2}{3}$  Al<sub>2</sub>O<sub>3</sub>  $\longrightarrow \frac{4}{3}$  Al + O<sub>2</sub>,  $n = \frac{2}{3} \times 6e^{-} = 4e^{-}$ 

$$\therefore \qquad \frac{1}{3} \text{Al}_2 \text{O}_3 \longrightarrow \frac{1}{3} \text{Al} + \text{O}_2, n = \frac{1}{3}$$

 $\Delta_r G = 960 \times 1000 = 960000 \text{ J}$  $\Delta_r G = -nFE_{cell}^0$ Now.

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

Minimum potential difference needed to reduce Al<sub>2</sub>O<sub>3</sub> is - 2.487 V.

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

$$2\operatorname{Cr}(s) + 3\operatorname{Fe}^{2+}(aq) \longrightarrow 2\operatorname{Cr}^{3+}(aq) + 3\operatorname{Fe}(s)$$

Given:  $E_{\text{cell}}^{\text{o}} = 0.30 \text{ V}$ 

[CBSE (F) 2016]

Ans. 
$$Cr(s)$$

$$Cr(s)$$
  $\longrightarrow Cr^{3+}(aq) + 3e^{-} \times 2$   
 $Fe^{2+}(aq) + 2e^{-}$   $\longrightarrow Fe(s)$  ]×3

 $2Cr(s) + 3Fe^{2+}(aq) \longrightarrow 2Cr^{3+}(aq) + 3Fe(s), n = 6$ 

Here, n = 6,  $E_{cell}^{o} = 0.30 \text{ V}$ 

Substituting the values in the expression,  $\log K_c = \frac{n}{0.050} E_{cell}^0$ , we get

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

or

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

OI

$$K_c = 3.224 \times 10^{30}$$
  
$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

$$\Delta O = -hi$$

$$= -6 \times 96500 \times 0.30 = -173700 \text{ J mol}^{-1}$$

 $\Delta G^{\circ} = -173.7 \text{ kJ mol}^{-1}$ 

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

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

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

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

Molar Conductivity, 
$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

$$= \frac{0.01148 \,\mathrm{S \, cm^{-1}} \times 1000 \,\mathrm{cm^3 \, L^{-1}}}{0.05 \,\mathrm{mol \, L^{-1}}} = 229.6 \,\mathrm{S \, cm^2 \, mol^{-1}}$$

Q. 8. From the following molar conductivities at infinite dilution, calculate  $\Lambda_m^0$  for NH<sub>4</sub>OH.

 $\Lambda_m^0$  for Ba(OH)<sub>2</sub> = 457.6  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>

 $\Lambda_m^0$  for BaCl<sub>2</sub> = 240.6  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>

 $\Lambda_m^0$  for NH<sub>4</sub>Cl = 129.8  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>  $\Lambda_{m(NH,OH)}^{o} = \lambda_{NH}^{o} + \lambda_{OH}^{o}$ Ans.

$$\begin{array}{l} \Lambda_{m(\mathrm{NH_4OH})} - \Lambda_{\mathrm{NH_4^+}} - \Lambda_{\mathrm{OH}^-} \\ &= (\Lambda_{\mathrm{NH_4^+}}^{\circ} + \Lambda_{\mathrm{Cl}^-}^{\circ}) + \frac{1}{2} (\Lambda_{\mathrm{Ba}^2}^{\circ} + 2\Lambda_{\mathrm{OH}^-}^{\circ}) - \frac{1}{2} (\Lambda_{\mathrm{Ba}^2}^{\circ} + 2\Lambda_{\mathrm{Cl}^-}^{\circ}) \\ &= \Lambda_{m(\mathrm{NH_4Cl})}^{\circ} + \frac{1}{2} [\Lambda_{m(\mathrm{Ba}(\mathrm{OH})_2)}^{\circ}] - \frac{1}{2} [\Lambda_{m(\mathrm{BaCl}_2)}^{\circ}] \\ &= 129.8 + \frac{1}{2} \times 457.6 - \frac{1}{2} \times 240.6 \end{array}$$

$$= 238.3 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

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

[Given:  $\lambda^0(H^+) = 349.5 \text{ S cm}^2 \text{ mol}^{-1}$  and  $\lambda^0(HCOO^-) = 50.5 \text{ S cm}^2 \text{ mol}^{-1}$ .] [CBSE Allahabad 2015]

Ans.

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

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

$$\Lambda_{m}^{o}(\text{HCOOH}) = \Lambda_{\text{HCOO}}^{o} + \Lambda_{\text{H}^{+}}^{o}$$

$$= 50.5 \text{ S cm}^{2} \text{ mol}^{-1} + 349.5 \text{ S cm}^{2} \text{ mol}^{-1} = 400 \text{ S cm}^{2} \text{ mol}^{-1}$$

or

Degree of dissociation, 
$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^o} = \frac{210 \text{ S cm}^2 \text{ mol}^{-1}}{400 \text{ S cm}^2 \text{ mol}^{-1}} = 0.525$$
  
or  $\alpha = 52.5\%$ 

- Q. 10. (i) A current of 1.50 A was passed through an electrolytic cell containing AgNO3 solution with inert electrodes. The weight of Ag deposited was 1.50 g. How long did the current flow?
  - (ii) Write the reactions taking place at the anode and cathode in the above cell. (iii) Give reactions taking place at the two electrodes if these are made up of Ag.

(i) Ag<sup>+</sup> +  $e^ \longrightarrow$  Ag Ans.

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

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

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

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

(ii) Inert electrodes

Anode: 
$$2H_2O(l) \longrightarrow O_2(g) + 4H^{\dagger}(aq) + 4e^{-}$$
  
Cathode:  $Ag^{\dagger}(aq) + e^{-} \longrightarrow Ag(s)$ 

(iii) Ag electrodes

Anode: 
$$Ag(s) \longrightarrow Ag^{+}(aq) + e^{-}$$
  
Cathode:  $Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$ 

Cathode:

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

Zn | Zn<sup>2+</sup> (0.001 M) || H<sup>+</sup> (0.01 M) | H<sub>2</sub>(g) (1 bar) | Pt(s)  
Given: 
$$E_{Z_0}^{\Theta} = -0.76 \text{ V}$$
,  $E_{H^+/H_0}^{\Theta} = 0.00 \text{ V}$ , [log 10 = 1]

$$Zn | Zn^{2+} (0.001 \text{ M}) | H^{+} (0.01 \text{ M}) | H_{2}(g) (1 \text{ bar}) | Pt(s)$$

 $Zn \longrightarrow Zn^{2+} + 2e^{-}$ At anode:

 $2H^+ + 2e^- \longrightarrow H_2$ At cathode:

The net cell reaction  $Zn + 2H^+ \longrightarrow Zn^{2+} + H_2$ 

Nernst equation for the given cell is

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

$$= (0.00 + 0.76) - \frac{0.0591}{2} \log \frac{.0010}{.01 \times .01}$$

$$= \frac{.76}{1} - \frac{.0591}{2} = \frac{1.52 - .059}{2} = \frac{1.461}{2} = 0.7305 \text{ V}$$

(i) The cell in which the following reaction occurs:  $2Fe^{3+}(aq) + 2I^{-}(aq) \longrightarrow 2Fe^{2+}(aq) + I_{2}(s)$ 

has 
$$E_{\rm cell}^{\rm o}=0.236~{
m V}$$
 at 298 K. Calculate the standard Gibbs energy of the cell reaction. (Given : 1 F = 96500 C mol^1)

(ii) How many electrons flow through a metallic wire if a current of 0.5A is passed for 2 hours? (Given: 1 F = 96500 C mol<sup>-1</sup>) [CBSE (AI) 2017]

Ans. Given reaction is !-2 fe 3+ (ag) + 22 - (ag) -> 2 fe 2+ (ag) + 22(s) oo n-factor, n=2 E" = 0.236 V (given) 46° = 9 We know, -(2) (96500) (0.236) = 45648 Jmol-AG0 = - 45,548 K3 mol-(b) Givent- Current, I = 0.5A & time, t = Thes Let 'n' electrons pass through it. he know. charge, Q = It = ne 'e' is charge on one electron (e=1.6×10-19c) 0.5 x 2 x 3600 = x x 1.6 x10-19 ". N = 0.5x2 x 3600 1.6 × 10 -19 2 = 2.25 × 10 22 electrons [Topper's Answer (AI) 2017].

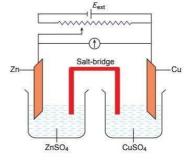
## **Long Answer Questions**

#### Each of the following questions are of 5 marks.

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

Ans. (i) Reaction continues to take place.

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



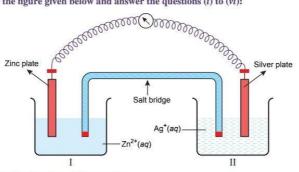
(ii) The reaction stops and no current flows.

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

(iii) Reaction takes place in opposite directions.

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

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



- (i) Write the direction of electron flow.
- (ii) Is silver plate the anode or cathode?
- (iii) What will happen if salt bridge is removed?
  - (iv) When will the cell stop functioning?
  - (v) How will concentration of Zn<sup>2+</sup> ions and Ag<sup>+</sup> ions be affected when the cell functions?
- (vi) How will the concentration of Zn<sup>2+</sup> ions and Ag<sup>+</sup> ions be affected after the cell becomes 'dead'? [NCERT Exemplar] [HOTS]
- Ans.
- (i) Electrons move from Zn to Ag.
- (ii) Ag is the cathode.
- (iii) Cell will stop functioning.
- (iv) When  $E_{\text{cell}} = 0$ .
- (v) Concentration of Zn<sup>2+</sup> ions will increase and concentration of Ag<sup>+</sup> ions will decrease.
- (vi) When  $E_{\text{cell}} = 0$ , equilibrium is reached and concentration of  $\text{Zn}^{2+}$  ions and  $\text{Ag}^{+}$  ions will not change.
- Q. 3. Calculate e.m.f and  $\Delta G$  for the following cell at 298 K:

$$Mg(s) | Mg^{2+} (0.01 M) | | Ag^{+} (0.0001 M) | Ag(s)$$

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

[CBSE Guwahati 2015]

Ans. At anode:

At cathode:

$$Mg \longrightarrow Mg^{2+} + 2e^{-}$$

$$[Ag^{+} + e^{-} \longrightarrow Ag] \times 2$$

$$Mg + 2Ag^{+} \longrightarrow Mg^{2+} + 2Ag; \quad n = 2$$

$$E_{\text{cell}}^{\text{o}} = E_{\text{cathode}}^{\text{o}} - E_{\text{anode}}^{\text{o}}$$
  
=  $E_{\text{Ag}^+/\text{Ag}}^{\text{o}} - E_{\text{Mg}^{2+}/\text{Mg}}^{\text{o}}$   
= 0.80 V - (-2.37 V) = 3.17 V

Substituting  $E_{\text{cell}}^0 = 3.17 \text{ V}$ , n = 2,  $[\text{Mg}^{2+}] = 1 \times 10^{-2} \text{ M}$ ,  $[\text{Ag}^{+}] = 1 \times 10^{-4} \text{ M}$  in Nernst equation for above cell reaction,

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

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

$$\begin{split} E_{\rm cell} &= 3.17 - 0.0295 \log \, 10^6 \\ E_{\rm cell} &= 3.17 - 0.177 \; \mathrm{V} \\ E_{\rm cell} &= 2.993 \; \mathrm{V} = \mathbf{2.993} \; \mathrm{V} \end{split}$$

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

$$\Delta G = -2 \times 96500 \text{ C mol}^{-1} \times 2.993 \text{ V}$$
  
 $\Delta G = -577649 \text{ J mol}^{-1} = -577.649 \text{ kJ mol}^{-1}$ 

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

Au(s) + Ca<sup>2+</sup>(1 M) 
$$\longrightarrow$$
 Au<sup>3+</sup>(1 M) + Ca(s)  
 $E_{\Lambda n^{3+}/\Lambda n}^{0}$  = + 1.50 V,  $E_{Ca^{2+}/Ca}^{0}$  = - 2.87 V

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

(ii) Tarnished silver contains Ag<sub>2</sub>S. Can this tarnish be removed by placing tarnished silver ware in an aluminium pan containing an inert electrolytic solution such as NaCl? The standard electrode potential for half reaction: [HOTS]

$$Ag_2S(s) + 2e^- \longrightarrow 2Ag(s) + S^{2-} \text{ is } -0.71V$$
  
 $A1^{3+} + 3e^- \longrightarrow 2A1(s) \text{ is } -1.66V$   
 $E^0_{\text{cell}} = E^0_{\text{Ca}^{2+}/\text{Ca}} - E^0_{\text{Au}^{3+}/\text{Au}}$   
 $= (-2.87 \text{ V}) - (1.50 \text{ V}) = -4.37 \text{ V}$   
 $\Delta_r G^0_{\text{cell}} = -nFE^0_{\text{cell}}$ 

Since  $\Delta_r G^0$  is positive, therefore, reaction is non-spontaneous.

Au<sup>3+</sup>/Au half cell will be an oxidising agent while Ca<sup>2+</sup>/Ca half cell will be a reducing agent.

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

(ii) E<sub>cell</sub> for reaction of tarnished silver ware with aluminium pan is

and for

(i)

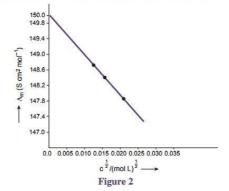
Ans.

Tarnished silver ware, therefore, can be cleaned by placing it in an aluminium pan as  $E^{o}_{cell}$  is positive.

Q. 5. (i) On the basis of  $E^0$  values identify which amongst the following is the strongest oxidising agent

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-$$
;  $E^0 = +1.36 \text{ V},$   
 $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ ;  $E^0 = +1.51 \text{ V}$   
 $Cr_2O_7^2 + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ ;  $E^0 = +1.33 \text{ V}$ 

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



- (a) Define molar conductivity.
- (b) Identify the nature of electrolyte on the basis of the above plot. Justify your answer.
- (c) Determine the value of  $\Lambda_m^0$  for the electrolyte.
- (d) Show how to calculate the value of A for the electrolyte using the above graph.

[CBSE Sample Paper 2021]

Ans. (i) MnO<sub>4</sub>

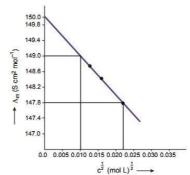
- (ii) (a) Molar conductivity of a solution at a given concentration is the conductance of the volume V of solution containing one mole of electrolyte kept between two electrodes with area of cross-section A and distance of unit length.
  - (b) The given plot shows that molar conductivity (\(\Lambda\_m\)) increases slowly with dilution so the electrolyte must be strong.

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

From the given plot we find that

$$\Lambda_m^0 = 150 \text{ S cm}^2 \text{ mol}^{-1}$$

(d)



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

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

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

$$2Al(s) + 3Ni^{2+}(0.1 M) \longrightarrow 2Al^{3+}(0.01 M) + 3Ni(s)$$

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

(ii) How does molar conductivity vary with increase in concentration for strong electrolyte and weak electrolyte? How can you obtain limiting molar conductivity (Λ<sup>0</sup><sub>m</sub>) for weak electrolyte? [CBSE 2019 (56/2/2)]

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

or

1

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

1/2

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

1

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

 $E_{\text{cell}} = 1.42 \text{ V}$ 

1/2

(ii)  $\Lambda_m$  decreases with increase in concentration for both strong and weak electrolyte  $\Lambda_m^o$  can be obtained for weak electrolyte by applying Kohlrausch law /  $\Lambda_m^o = v_+ \lambda_+^o + v_- \lambda_-^o$  1 + 1

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

Q. 7. At 291 K, the molar conductivities at infinite dilution of NH<sub>4</sub>Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 S cm<sup>2</sup> mol<sup>-1</sup> respectively. If the molar conductivity of a centinormal solution of NH<sub>4</sub>OH is 9.33 S cm<sup>2</sup> mol<sup>-1</sup>, what is the percentage dissociation of NH<sub>4</sub>OH at this dilution? Also calculate the dissociation constant of NH<sub>4</sub>OH.
[HOTS]

Ans. Here, we are given:

$$\Lambda_m^o$$
 for NH<sub>4</sub>Cl = 129.8 S cm<sup>2</sup> mol<sup>-1</sup>  
 $\Lambda_m^o$  for NaOH = 217.4 S cm<sup>2</sup> mol<sup>-1</sup>  
 $\Lambda_m^o$  for NaCl = 108.9 S cm<sup>2</sup> mol<sup>-1</sup>

By Kohlrausch's law,

$$\Lambda_{m}^{o} \text{ for NH}_{4}\text{OH} = \lambda_{\text{NH}_{4}^{s}}^{o} + \lambda_{\text{OH}^{-}}^{o}$$

$$= \Lambda_{m}^{o} (\text{NH}_{4}\text{CI}) + \Lambda_{m}^{o} (\text{NaOH}) - \Lambda_{m}^{o} (\text{NaCI})$$

$$= [129.8 + 217.4 - 108.9] \text{ S cm}^{2} \text{ mol}^{-1} = 238.3 \text{ S cm}^{2} \text{ mol}^{-1}$$

$$\Lambda_{m}^{c} = 9.33 \text{ S cm}^{2} \text{ mol}^{-1} (\text{Given})$$

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

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

Calculation of dissociation constant

$$\begin{array}{cccc} & \text{NH}_4\text{OH} & \Longrightarrow & \text{NH}_4^+ + \text{OH}^- \\ \text{Initial conc.} & c & 0 & 0 \\ \text{Equilibrium conc.} & c - c\alpha & c\alpha & c\alpha \end{array}$$

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

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

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

- Q. 8. (i) State Kohlrausch law of independent migration of ions. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch law.
  - (ii) Calculate  $\Lambda_m^0$  for acetic acid.

Given that 
$$\Lambda_m^0$$
 (HCl) = 426 S cm<sup>2</sup> mol<sup>-1</sup>,  $\Lambda_m^0$  (NaCl) = 126 S cm<sup>2</sup> mol<sup>-1</sup>  
 $\Lambda_m^0$  (CH<sub>3</sub>COONa) = 91 S cm<sup>2</sup> mol<sup>-1</sup>

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

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

(ii) 
$$\Lambda_{m}^{o}(CH_{3}COOH) = \Lambda_{CH_{3}COO^{-}}^{o} + \Lambda_{H^{+}}^{o}$$

$$= \Lambda_{CH_{3}COO^{-}}^{o} + \Lambda_{Na^{+}}^{o} + \Lambda_{Cl^{-}}^{o} + \Lambda_{Na^{+}}^{o} + \Lambda_{Cl^{-}}^{o} - (\Lambda_{Na^{+}}^{o} + \Lambda_{Cl^{-}}^{o})$$

$$= \Lambda_{m(CH_{3}COONa)}^{o} + \Lambda_{m(HCl)}^{o} - \Lambda_{m(NaCl)}^{o}$$

$$= (91 + 426 - 126) \text{ S cm}^{2} \text{ mol}^{-1} = 391 \text{ S cm}^{2} \text{ mol}^{-1}$$

- Q. 9. (i) What type of a battery is lead storage battery? Write the anode and cathode reactions and the overall cell reaction occurring in the operation of a lead storage battery.
  - (ii) Calculate the potential for half-cell containing  $0.10 \text{M K}_2\text{Cr}_2\text{O}_7(aq), 0.20 \text{ M Cr}^{3+}(aq) \text{ and } 1.0 \times 10^{-4} \text{ M H}^+(aq).$  The half cell reaction is

$$\text{Cr}_2\text{O}_7^{2-}(aq) + 14\text{H}^+(aq) + 6e^- \longrightarrow 2\text{Cr}^{3+}(aq) + 7\text{H}_2\text{O}(l)$$
  
and the standard electrode potential is given as  $E^0 = 1.33\text{V}$ . [CBSE (AI) 2011]

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

(ii) For half cell reaction

$$\operatorname{Cr}_2\operatorname{O}_7^{2-}(aq) + 14\operatorname{H}^+(aq) + 6e^- \longrightarrow 2\operatorname{Cr}^{3+}(aq) + 7\operatorname{H}_2\operatorname{O}(l)$$

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

Here, 
$$E^{\circ} = 1.33 \text{ V}$$
,  $n = 6$ ,  $[\text{Cr}_3^{3+}] = 0.2 \text{ M}$ ,  $[\text{Cr}_3\text{O}_7^{2-}] = 0.1 \text{ M}$ ,  $[\text{H}^{+}] = 1 \times 10^{-4} \text{ M}$ 

Substituting these values in the given expression, we get

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

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

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

$$= 1.33 \text{ V} - \frac{0.0591}{6} [2 \log 2 + 55 \log 10]$$

$$= 1.33 \text{ V} - \frac{0.0591}{6} [2 \times 0.3010 + 55]$$

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

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

- (a) Limiting molar conductivity (b) Fuel cell
- [CBSE (AI) 2014] (ii) Resistance of a conductivity cell filled with 0.1 mol L<sup>-1</sup> KCl solution is 100  $\Omega$ . If the resistance of
  - the same cell when filled with 0.02 mol L<sup>-1</sup> KCl solution is 520  $\Omega$ , 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  $1.29 \times 10^{-2} \,\Omega^{-1} \,\mathrm{cm}^{-1}$ .
- (i) (a) The limiting value of molar conductivity when concentration approaches to zero is called limiting Ans. molar conductivity.
  - (b) A fuel cell is a device which converts energy produced during the combustion of fuels like hydrogen, methane, methyl alcohol etc. directly into electrical energy. One such successful fuel cell is hydrogen-oxygen fuel cell.
  - (ii) For 0.1 mol L-1 KCl solution.

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

Cell constant = Conductivity × resistance  
= 
$$1.29 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1} \times 100 \Omega = 1.29 \text{ cm}^{-1}$$

For 0.02 mol L-1 solution.

Resistance =  $520 \Omega$ , Cell constant =  $1.29 \text{ cm}^{-1}$ 

Conductivity, 
$$\kappa = \frac{\text{Cell constant}}{\text{Resistance}}$$

$$= \frac{1.29 \text{ cm}^{-1}}{520 \Omega}$$

$$= 0.00248 \Omega^{-1} \text{ cm}^{-1}$$

Molar conductivity, 
$$\Lambda_m = \frac{\text{Conductivity } (\kappa) \times 1000 \text{ cm}^3 \text{ L}^{-1}}{\text{Molarity}}$$

$$= \frac{0.00248 \Omega^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.02 \text{ mol L}^{-1}}$$

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

(i) Conductivity of  $2 \times 10^{-3}$  M methanoic acid is  $8 \times 10^{-5}$  S cm<sup>-1</sup>. Calculate its molar conductivity Q. 11. and degree of dissociation if  $\wedge_m^0$  for methanoic acid is 404 S cm<sup>2</sup> mol<sup>-1</sup>. [CBSE 2023 (56/2/1)]

(ii) Calculate the  $\Delta rG^0$  and log  $K_c$  for the given reaction at 298 K:

$$Ni(s) + 2Ag^{+}(aq) = Ni^{2+}(aq) + 2Ag(s)$$

[Given:  $E_{\text{Ni}^{2+}/\text{Ni}}^0 = -0.25 \text{ V}, E_{\text{Ag}^+/\text{Ag}}^0 = +0.80 \text{ V}$ 1F = 96500 C mol-1.]

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

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

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

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

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

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

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

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

$$\log K_{c} = \frac{n}{0.059} \times E_{\text{cell}}^{\text{o}} = \frac{2}{0.059} \times 1.05 = 35.5932$$

$$\Delta_{r}G^{\text{o}} = -nFE_{\text{cell}}^{\text{o}} = -2 \times 96500 \times 1.05$$

$$\Delta_{r}G^{\text{o}} = -202650 \text{ J mol}^{-1} \text{ or } \Delta_{r}G^{\text{o}} = -202.65 \text{ KJ mol}^{-1}$$

(i) Calculate  $E_{\text{cell}}^{\text{o}}$  for the following reaction at 298 K: Q. 12.

$$2AI(s) + 3Cu^{2+}(0.01 M) \longrightarrow 2AI^{3+}(0.01 M) + 3Cu(s)$$

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

(ii) Using the  $E^0$  values of A and B, predict which is better for coating the surface of iron [  $E_{\text{Fe}^{2+}/\text{Fe}}^{\text{o}}$  = -0.44 V] to prevent corrosion and why?

[Given: 
$$E_{A^{2+}/A}^{0} = -2.37 \text{ V}, E_{B^{2+}/B}^{0} = -0.14 \text{ V}$$
] [CBSE Central 2016]

 $[Al(s) \longrightarrow Al^{3+}(aq) + 3e^{-}] \times 2$   $[Cu^{2+} + 2e^{-} \longrightarrow Cu] \times 3$ Ans. (i)

$$2Al + 3Cu^{2+} \longrightarrow 2Al^{3+} + 3Cu, n = 6$$

Here, n = 6,  $E_{\text{cell}} = 1.98 \text{ V}$ ,  $[\text{Al}^{3+}] = 1 \times 10^{-2} \text{ M}$ ,  $[\text{Cu}^{2+}] = 1 \times 10^{-2} \text{ M}$  $E_{\text{cell}} = E_{\text{cell}}^{0} - \frac{0.059}{n} \log \frac{[\text{Al}^{3+}]^2}{[\text{Co.}^{2+}]^3}$ 

ese values in the Nernst equation f
$$(10^{-2})^2$$

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

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

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

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

# **Questions for Practice**

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

1. A hypothetical electrochemical cell is shown below:

$$A \mid A^{+}(xM) \mid \mid B^{+}(yM) \mid B$$

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

- (a)  $A + B^+ \longrightarrow A^+ + B$
- (b) The cell reaction cannot be predicted.
- (c)  $A^+ + e^- \longrightarrow A$ ,  $B^+ + e^- \longrightarrow B$
- (d) A<sup>+</sup> + B  $\longrightarrow$  A + B<sup>+</sup>
- 2. When 0.1 mole of MnO $_4^{2-}$  is oxidised, the quantity of electricity required to completely oxidise MnO $_4^{2-}$  to MnO $_4^{-}$  is
  - (a) 96500 C

(b) 9650 C

(c) 96.50 C

- (d) 2 × 96500 C
- A voltaic cell is made by connecting two half cells represented by half equations below: [CBSE 2023 (56/5/2)]

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

$$Fe^{3+}(aq) + e^{-} \longrightarrow Fe^{2+}(aq) E^{0} = +0.77 V$$

Which statement is correct about this voltaic cell?

- (a)  $Fe^{2+}$  is oxidised and the voltage of the cell is -0.91 V.
- (b) Sn is oxidised and the voltage of the cell is 0.91 V.
- (c) Fe<sup>2+</sup> is oxidised and the voltage of the cell is 0.91 V.
- (d) Sn is oxidised and the voltage of the cell is 0.63 V.
- 4. In the electrolysis of aqueous sodium chloride solution, which of the following half cell reaction will occur at anode? [NCERT Exemplar]
  - (a)  $\text{Na}^+(aq) + e^- \longrightarrow \text{Na}(s);$   $E_{coll}^0 = -2.71 \text{ V}$
  - (b)  $2H_2O(1) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-; E_{cell}^o = 1.23 \text{ V}$
  - (c)  $H^{+}(aq) + e^{-} \longrightarrow \frac{1}{2}H_{2}(g);$   $E_{cell}^{o} = 0.00 \text{ V}$
  - (d)  $\operatorname{Cl}^-(aq) \longrightarrow \frac{1}{2} \operatorname{Cl}_2(g) + e^-;$
- $E_{\text{cell}}^{\text{o}} = 1.36 \text{ V}$
- 5. Which of the following cell was used in Apollo space programme?

[CBSE 2023 (56/5/2)]

(a) Mercury cell

(b) Daniel cell

(c) H2-O2 Fuel cell

(d) Dry cell

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

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

- 6. Assertion (A): Conductivity of an electrolyte decreases with decrease in concentration.
- Reason (R): Number of ions per unit volume increase on dilution. [CBSE 2023 (56/2/1)]
- 7. Assertion (A):  $\wedge_m$  for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.
- Reason (R): For weak electrolytes, degree of dissociation increases with dilution of solution. [CBSE 2023 (56/4/2)]
- Assertion (A): Rusting of iron is quicker in saline water than in ordinary water.
   Reason (R): Salt water helps in flow of current in the miniature cell developed on the iron surface.
- 9. Assertion (A): An electrochemical cell can be set up only if the redox reaction is spontaneous.

  Reason (R): A reaction is spontaneous if free energy change is negative.
- 10. Assertion (A): If  $\lambda_{Na^+}^{\circ}$  and  $\lambda_{Cl^-}^{\circ}$  are molar limiting conductivity of sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is
  - Reason (R): This is according to Kohlrausch law of independent migration of ions.

given by the equation:  $\lambda_{NaCl}^{o} = \lambda_{Na}^{o} + \lambda_{Cl}^{o}$ 

### Answer the following questions:

- In a plot of Λ<sub>m</sub> against the square root of concentration (C<sup>1/2</sup>) for strong and weak electrolyte, the value of limiting molar conductivity of a weak electrolyte cannot be obtained graphically.
   Suggest a way to obtain this value. Also state the related law, if any. [CBSE 2023 (56/4/2)]
- 12. (i) (a) What should be the signs (positive/negative) for  $E_{Cell}^{o}$  and  $\Delta G^{o}$  for a spontaneous redox reaction occurring under standard conditions?
  - (b) State Faraday's first law of electrolysis.
  - (ii) Calculate the emf of the following cell at 298 K:  $Fe(s) \mid Fe^{2+}(0.01M) \mid \mid H^{+}(1M) \mid H_{2}(g) \ (1 \ bar), Pt(s)$

Given:  $E_{Cell}^{o} = 0.44 \text{ V}.$ 

- 13. (i) For a weak electrolyte, molar conductance in dilute solution increases sharply as its concentration in solution is decreased. Give reason.
  - (ii) Write overall cell reaction for lead storage battery when the battery is being charged.
- 14. Two half-reactions of an electrochemical cell are given below:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l);$$
  $E^0 = +1.51 \text{ V}$   
 $Sn^{2+}(aq) \longrightarrow Sn^{4+}(aq) + 2e^-;$   $E^0 = +0.51 \text{ V}$ 

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

[CBSE 2019 (56/4/1)]

15. Calculate  $\Delta r G^{0}$  and  $\log K_{c}$  for the following reaction:

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

[Given:  $E_{\text{Cd}^{2+}/\text{Cd}}^{\text{o}} = -0.403 \text{ V}, \quad E_{\text{Zn}^{2+}/\text{Zn}}^{\text{o}} = -0.763 \text{ V}$ ]

- 16. Account for the following:
  - (i) Alkaline medium inhibits the rusting of iron.
    - (ii) Iron does not rust even if the zinc coating is broken in a galvanized iron pipe.

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

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

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

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

$$2Al(s) + 3Cd^{2+}(0.1M) \longrightarrow 3Cd(s) + 2Al^{3+}(0.01M)$$
 [CBSE Sample Paper 2022]

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

 $Zn \mid Zn^{2+} (0.001 \text{ M}) \mid \mid H^{+} (0.01 \text{ M}) \mid H_{2}(g) (1 \text{ bar}) \mid Pt(s)$ 

Given:  $E_{\mathrm{Zn^{2+}/Zn}}^{\Theta}$  =  $-0.76~\mathrm{V}$ ,  $E_{\mathrm{H^{+}/H_{2}}}^{\Theta}$  =  $0.00~\mathrm{V}$ , [log 10 = 1]

- 22. (i) The electrical resistance of a column of 0.02 M NaOH solution of diameter 1.40 cm and length 44 cm is 5.00 × 10<sup>3</sup> ohm. Calculate its resistivity, conductivity and molar conductivity.
  [CBSE (C) 2021(56/1/1)]
  - (ii) Depict the galvanic cell in which the reaction take place:

$$\operatorname{Ni}(s) + 2\operatorname{Ag}^+(aq) \longrightarrow \operatorname{Ni}^{2+}(aq) + 2\operatorname{Ag}(s)$$

Further show:

- (i) Which of the electrodes is positively charged?
- (ii) The carriers of the current in the outer circuit.
- 23. (i) State Faraday's first law of electrolysis. How much charge, in terms of Faraday, is required for the reduction of 1 mol Cu<sup>2+</sup> to Cu?
  - (ii) Calculate emf of the following cell at 298 K for

$$Mg(s) \mid Mg^{2+}(0.1 \text{ M}) \mid \mid Cu^{2+}(0.01 \text{ M}) \mid Cu(s)$$

$$[E_{\text{cell}}^0 = +2.71 \text{ V}, 1\text{F} = 96500 \text{ C mol}^{-1}, \log 10 = 1]$$

- 24. (i) The molar conductivities of NH<sub>4</sub><sup>+</sup> and Cl<sup>-</sup> ion are 73.8 S cm<sup>2</sup> mol<sup>-1</sup> and 76.2 S cm<sup>2</sup> mol<sup>-1</sup> respectively. The conductivity of 0.1 M NH<sub>4</sub>Cl is 1.29 × 10<sup>-2</sup> S cm<sup>-1</sup>. Calculate its molar conductivity and degree of dissociation.
  - (ii) Calculate the half-cell potential at 298 K for the reaction

$$Zn^{2^+} + 2e^- \longrightarrow Zn$$
  
if  $[Zn^{2^+}] = 0.1$  M and  $E_{7n^{2^+}/7n}^o = -0.76$  V

[CBSE 2023 (56/4/2)]

### **Answers**

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