Chapter 3

Electrochemistry

Solutions (Set-1)

Very Short Answer Type Questions :

1. Express mathematically the relation among resistance, specific conductivity and cell constant.

Sol. $K = \frac{1}{R} \times \frac{l}{a}$

Where K = specific conductivity, R = Resistance, (l/a) = cell constant

2. What is the effect of dilution on (i) conductivity and (ii) molar conductivity?

Sol. Conductivity of an electrolyte decreases with dilution whereas molar conductivity increases.

3. Why does molar conductivity of strong electrolytes increase marginally with dilution even though they are completely ionised?

Sol. Molar conductivity of strong electrolytes is less in the high concentration region as the mobility of ions is slow due to inter ionic attractions. As the concentration decreases, the conductance marginally increases as the mobility of ions increases due to weaker inter ionic attractions.

4. What happens to the reduction potential of $Pt \mid H_2$ (P atm) $\mid H^+$ (1 M) at 298 K when P increases from 1 atm to 10 atm?

Sol. $E_{H^+/H_2} = -\frac{0.059}{2}\log\frac{(p_{H_2})}{[H^+]^2}$.

As p_{H_2} increases from 1 atm to 10 atm keeping $[H^+]$ = 1 M at 25°C, the reduction potential of hydrogen electrode decreases from 0 to –0.0295 V.

5. What is the effect of increase in concentration of Zn^{2+} ions on the electrode potential of zinc electrode $(E_{Zn^{2+}/Zn})$?

Sol. $E_{Zn^{2+}/Zn} = E^o_{Zn^{2+}/Zn} - \frac{RT}{2F}\ln\frac{1}{[Zn^{2+}]}$.

As the concentration of Zn^{2+} ions increases the reduction potential of Zn/Zn^{2+} half cell increases.

6. Predict whether F_2 and Na will react with each other or not? Also give suitable explanation.

Given $E^o_{F_2/F^-} = 2.87$ V; $E^o_{Na^+/Na} = -2.71$ V.

Sol. $2Na + F_2 \longrightarrow 2NaF$

$$E^o_{cell} = E^o_{F_2/F^-} - E^o_{Na^+/Na} = 2.87 - (-2.71) = 5.58\ V$$

Since, E^o_{cell} is positive, sodium will react with fluorine.

7. How do we measure the conductance of an electrolytic conductor?

Sol. The conductance of an electrolytic conductor is measured by immersing the conductivity cell into the electrolyte and connecting it to one of the arms of Wheatstone bridge.

8. Write electrode reactions taking place in Ni – Cd cell. Is it primary or secondary cell?

Sol. Anode : $Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^-$

Cathode : $NiO_2 + 2H_2O + 2e^- \longrightarrow Ni(OH)_2 + 2OH^-$

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

It is a secondary cell.

9. How does standard reduction potential of Ag | AgX | X^- vary with the solubility product of AgX at 25°C?

Sol.

$$AgX \rightleftharpoons Ag^+ + X^- \quad \Delta G^o_1 = -RT\ln K_{sp}$$

$$Ag^+ + e \longrightarrow Ag \quad \Delta G^o_2 = -FE^o_{Ag^+/Ag}$$

$$AgX + e \longrightarrow Ag + X^- \quad \Delta G^o_3 = -FE^o_{Ag^+/Ag} - RT\ln K_{sp}$$

$$\therefore \quad -FE^o_{X^-|AgX|Ag} = -FE^o_{Ag^+|Ag} - RT\ln K_{sp}$$

$$E^o_{X^-|AgX|Ag} = E^o_{Ag^+|Ag} + \frac{RT}{F}\ln K_{sp}$$

As K_{sp} increases, the standard reduction potential of Ag|AgX|X^- half cell increases.

10. What are the products obtained at cathode and anode during electrolysis of an aqueous solution $CdCl_2$ using mercury cathode and platinum anode?

Sol. $CdCl_2 \longrightarrow Cd^{2+} + 2Cl^-$

$$H_2O \rightleftharpoons H^+ + OH^-$$

Cathode : $Cd^{2+} + 2e \longrightarrow Cd$; $\quad Cd + Hg \longrightarrow$ Amalgam

Anode : $2Cl^- \longrightarrow Cl_2 + 2e$

Short Answer Type Questions :

11. Define specific conductivity of a solution. The specific conductivity of 0.15 M. NaOH solution is 0.48 S cm^{-1}. Calculate its equivalent conductance.

Sol. Specific conductivity of a solution is the conductance of 1 cubic centimeter of the solution. If 'K' is the specific conductivity, 'C' the conductance, 'l' the distance between electrodes and 'a' is the area of cross-section of the electrodes then $K = C \times \frac{l}{a}\ S\ cm^{-1}$.

Equivalent conductance (Λ_{eq}) of an electrolyte is given by

$$\Lambda_{eq} = \frac{K \times 1000}{\text{Normality}} = \frac{0.48 \times 1000}{0.15} = 3.2 \times 10^3\ S\ cm^2\ eq^{-1}$$

12. Calculate pH of electrolyte in the half cell Pt | H_2 (1 atm) | H^+, if its reduction potential at 25°C is –0.30 V.

Sol. Pt | H_2 (1 atm) | H^+

$$E_{H^+/H_2} = -\frac{0.059}{2}\log\frac{p_{H_2}}{[H^+]^2}$$

$-0.30 = -0.059\ (pH)$

$\Rightarrow$ pH = 5.08

13. The standard emf of the following cell reaction is 0.89 V

$3Sn^{4+} + 2Cr \longrightarrow 3Sn^{2+} + 2Cr^{3+}$

Calculate standard free energy change for the reaction.

Sol. $3Sn^{4+} + 2Cr \longrightarrow 3Sn^{2+} + 2Cr^{3+}$ $\quad E^\circ_{cell} = 0.89$ V

$\Delta G^\circ = -nFE^\circ_{cell} = -6 \times 96500 \times 0.89 = 515.31$ kJ

14. Explain Kohlrausch's law of independent migration of ions. Mention one application of Kohlrausch's law.

Sol. Kohlrausch's law states that at infinite dilution when dissociation is complete molar conductivity of an electrolyte is equal to sum of contributions due to cation as well as anion. For example, molar conductivity of Na_2SO_4 at infinite dilution is given by

$$\Lambda_m^\infty(Na_2SO_4) = 2\lambda_m^\infty(Na^+) + \lambda_m^\infty(SO_4^{2-})$$

It helps to calculate Λ_m^∞ of weak electrolytes. Example

$$\Lambda_m^\infty(CH_3COOH) = \lambda_m^\infty(H^+) + \lambda_m^\infty(CH_3COO^-)$$

$$\Lambda_m^\infty(NaCl) = \lambda_m^\infty(Na^+) + \lambda_m^\infty(Cl^-)$$

$$\Lambda_m^\infty(HCl) = \lambda_m^\infty(H^+) + \lambda_{Cl}^\infty(Cl^-)$$

$$\Lambda_m^\infty(CH_3COONa) = \lambda_m^\infty(Na^+) + \lambda_m^\infty(CH_3COO^-)$$

$$\therefore \quad \Lambda_m^\infty(CH_3COOH) = \Lambda_m^\infty(CH_3COONa) + \Lambda_m^\infty(HCl) - \Lambda_m^\infty(NaCl)$$

15. Consider the given E° values in volts for 1 M solution

$Fe^{2+} | Fe = -0.4$ V; $Fe^{3+} | Fe^{2+} = +0.80$ V

$Mn^{2+} | Mn = -1.2$ V; $Mn^{3+} | Mn^{2+} = +1.5$ V

Comment on the relative stabilities of +2 and +3 oxidation states of iron and manganese.

Sol. Since $E^\circ_{Mn^{3+}/Mn^{2+}} > E^\circ_{Fe^{3+}/Fe^{2+}}$ and $E^\circ_{Mn^{2+}/Mn} < E^\circ_{Fe^{2+}/Fe}$, Fe^{3+} is more stable than Fe^{2+} whereas Mn^{2+} is more stable than Mn^{3+}. This is supported by their electronic configuration also. Both Fe^{3+} and Mn^{2+} have stable configuration *i.e.*, $3d^5$.

16. The same quantity of electrical charge deposited 0.583 g of Ag when passed through $AgNO_3$ and $AuCl_3$ solutions. Calculate the weight of gold deposited. [Atomic mass : Ag = 108, Au = 197]

Sol. Equivalents of gold = Equivalents of silver [$\because$ Q is same]

$$\frac{W_{Au}}{(197/3)} = \frac{0.583}{108}$$

$\Rightarrow$ $W_{Au} = 0.354$ g

17. Calculate the volume of Cl_2 at STP produced during electrolysis of $MgCl_2$ which produces 5.4 g Mg (Atomic mass of Mg = 24).

Sol. Equivalents of Cl_2 = Equivalents of Mg $= \frac{5.4}{12}$

Volume of one equivalent of Cl_2 at STP = 11.2 litre

$\therefore$ Volume of Cl_2 at STP $= \frac{5.4 \times 11.2}{12} = 5.04$ litre

18. In a fuel cell H_2 and O_2 react to produce electricity. In the process H_2 gas is oxidised at anode and O_2 gas is reduced at cathode. If 67.2 litre of H_2 at STP reacts in 20 min, what is the average current produced?

Sol. In a fuel cell

$$\text{Anode : } [H_2 + 2OH^- \longrightarrow 2H_2O + 2e] \times 2$$
$$\text{Cathode : } \underline{O_2 + 2H_2O + 4e \longrightarrow 4OH^-}$$
$$2H_2 + O_2 \longrightarrow 2H_2O$$

Volume of 1 equivalent of H_2 at STP = 11.2 litre

$\therefore$ Number of equivalents of $H_2 = \frac{67.2}{11.2} = 6$

$\therefore$ Charge (Q) = 6 F = 6 × 96500 C

$$\text{Current (amp)} = \frac{\text{Charge (C)}}{\text{Time (s)}} = \frac{6 \times 96500}{20 \times 60} = 482.5 \text{ A}$$

19. E_{cell} of Pt | H_2 (1 atm) | H^+ (pH = 6) | | H^+ (pH = x) | H_2 (1 atm) | Pt at 25°C is 0.118 V. What is the value of x?

Sol. Pt | H_2 (1 atm) | H^+ (pH = 6) | | H^+ (pH = x) | H_2 (1 atm) | Pt

$$\text{Anode : } \frac{1}{2}H_2 \longrightarrow H^+ + e$$
$$\text{Cathode : } \underline{H^+ + e \longrightarrow \frac{1}{2}H_2}$$
$$(H^+)_{cathode} \longrightarrow (H^+)_{anode}$$

$$E_{cell} = -0.059 \log \frac{[H^+]_{anode}}{[H^+]_{cathode}}$$

$0.118 = 0.059\ [(pH)_{anode} - (pH)_{cathode}]$

$(pH)_{cathode} = 4$

20. The E° of a cell in which the following reaction occurs is 0.59 V at 25°C

$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

What is equilibrium constant (K_C) of the given reaction?

Sol. $E^o_{cell} = 0.59$ V at 25°C

$$E^o_{cell} = \frac{RT}{nF} \ln K = \frac{0.059}{n} \log K \text{ at } 25°C$$

$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Here, n = 5

$$\therefore \quad 0.59 = \frac{0.059}{5}\log K$$

$$\Rightarrow \quad K = 10^{50}$$

21. How much copper is deposited on the cathode of an electrolytic cell if a current of 5 ampere is passed through a solutions of $CuSO_4$ for 45 minutes? [Atomic mass of Cu = 63.5]

Sol. i = 5 amp, t = 45 × 60 s

$$Q = it = 5 \times 45 \times 60 \text{ C} = 13500 \text{ C} = \frac{13500}{96500}\text{ F}$$

Mass of copper deposited = Q(F) × Eq. wt. of Cu

$$= \frac{135}{965} \times \frac{63.5}{2} = 4.44 \text{ g}$$

22. How many grams of Ag could be plated on a shield by electrolysis of a solution containing Ag^+ ions for a period of 4 hours at a current strength of 8.5 ampere?

Sol. i = 8.5 A, t = 4 × 3600 s

$$Q = it = 8.5 \times 4 \times 3600 \text{ C} = 122400 \text{ C} = \frac{1224}{965}\text{ F}$$

$$\text{Mass of silver deposited} = \frac{1224}{965} \times 108 = 137 \text{ g}$$

23. What is corrosion? Describe the role of zinc in cathodic protection of iron. Can we use tin in place of zinc for this purpose? Give reasons.

Sol. Corrosion is a process in which metals are oxidised on exposure to moist air. The rusting of iron, tarnishing of silver, development of green layer on the surface of copper are examples of corrosion. Metal looses electrons to other electronegative elements like oxygen or sulphur to form metal oxide or sulphide on its surface. Corrosion is essentially an electrochemical phenomenon. For example, corrosion of iron is the electrochemical oxidation of iron to Fe^{2+} and reduction of O_2 in presence of H^+ formed due to dissolution of CO_2 and other acidic oxides present in air into water

Anode :	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e$	$(E^o_{Fe^{2+}/Fe} = -0.44 \text{ V})$
Cathode :	$O_2(g) + 4H^+(aq) + 4e \longrightarrow 2H_2O(l)$	$(E^o_{H^+/O_2/H_2O} = 1.23 \text{ V})$
	$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2H_2O(l)$	$(E^o_{cell} = 1.67 \text{ V})$

The Fe^{2+} ions are oxidised by atmospheric oxygen to form hydrated ferric oxide which is called rust

$$2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) + 4H^+(aq)$$

Corrosion of iron can be prevented by covering its surface by Zn which itself undergoes oxidation in preference to Fe and thus saves the iron. Tin can also be used in place of Zn.

24. Zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 90% ionised at this concentration at 25°C. Calculate the electrode potential.

Given $E^o_{Zn^{2+}/Zn} = -0.76$ V

Sol. $Zn \mid ZnSO_4$ (0.1 M) at 25°C

$$\underset{\text{Conc. } 0.1(1-0.9)\text{ M}}{ZnSO_4} \rightleftharpoons \underset{0.09\text{ M}}{Zn^{2+}} + \underset{0.09\text{ M}}{SO_4^{2-}}$$

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

$$E_{Zn^{2+}/Zn} = E^o_{Zn^{2+}/Zn} - \frac{0.059}{2}\log\frac{1}{[Zn^{2+}]}$$

$$= -0.76 - \frac{0.059}{2}\log\frac{1}{0.09}$$

$$= -0.79 \text{ V}$$

25. Calculate the emf of the following cell at 25°C

$Fe \mid Fe^{2+}$ (0.1 M) $\mid\mid Ag^+$ (0.1 M) $\mid Ag$

Given : $E^o_{Fe^{2+}/Fe} = -0.44$ V and $E^o_{Ag^+/Ag} = 0.80$ V

Sol. $Fe \mid Fe^{2+}$ (0.1 M) $\mid\mid Ag^+$ (0.1 M) $\mid Ag$ at 25°C

$E^o_{Fe^{2+}/Fe} = -0.44$ V and $E^o_{Ag^+/Ag} = 0.80$ V

Anode : $Fe \longrightarrow Fe^{2+} + 2e$

Cathode : $2Ag^+ + 2e \longrightarrow 2Ag$

$$Fe + 2Ag^+ \longrightarrow Fe^{2+} + 2Ag$$

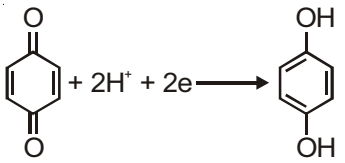
$$E_{cell} = E^o_{cell} - \frac{0.059}{2}\log\frac{[Fe^{2+}]}{[Ag^+]^2}$$

$$= [0.80 - (-0.44)] - \frac{0.059}{2}\log\frac{0.1}{(0.1)^2}$$

$$= 1.2105 \text{ V}$$

26. Calculate the quantity of charge in coulombs required to reduce 16.2 g of p-benzoquinone if current efficiency is 75%.

Sol.



Moles of p-benzoquinone $= \frac{16.2}{108} = 0.15$

Charge (Q) = 0.15 × 2 = 0.30 F

$$\text{Current efficiency} = \frac{Q_{theoretical}}{Q_{experimental}} \times 100$$

$$Q_{experimental} = \frac{0.30 \times 100}{75} = 0.40 \text{ F} = 38600 \text{ C}$$

Long Answer Type Questions :

27. 0.05 N solution of a weak acid has a conductivity 4.65×10^{-4} S cm^{-1}. The degree of dissociation of acid at this dilution is 0.055. Calculate the equivalent conductivity of weak acid at infinite dilution.

Sol. Degree of dissociation, $\alpha = 0.055$

Conductivity, $K = 4.65 \times 10^{-4}$ S cm^{-1}

$$\Lambda_{eq} = \frac{K \times 1000}{\text{Normality}} = \frac{4.65 \times 10^{-4} \times 1000}{0.05} = 9.3 \text{ S cm}^2 \text{ eq}^{-1}$$

$$\alpha = \frac{\Lambda^c_{eq}}{\Lambda^o_{eq}}; \ \Lambda^o_{eq} = \frac{9.3}{0.055} = 169.09 \text{ S cm}^2 \text{ eq}^{-1}$$

28. The equivalent conductivity of 0.15 N $CaCl_2$ solution is 89.6 S cm^2 eq^{-1} at 298 K. A conductivity cell with a cell constant 0.28 cm^{-1} is filled with 0.16 N $CaCl_2$ solution. How much current flows when the potential difference between the electrodes is 5 V?

Sol. Equivalent conductivity $= \frac{\text{Conductivity} \times 1000}{\text{Normality}}$

or Conductivity $= \frac{89.6 \times 0.15}{1000} = 13.44 \times 10^{-3}$ S cm^{-1}

Conductivity = Conductance × Cell constant

or Conductance $= \frac{13.44 \times 10^{-3}}{0.28} = 0.048$ S

Resistance $= \frac{1}{0.048}$ ohm

Current $= \frac{\text{Potential difference}}{\text{Resistance}} = 5 \times 0.048 = 0.24$ amp

29. At 25°C the molar conductivities of H^+ and CH_3COO^- ions at infinite dilution are 345 and 40 S cm^2 mol^{-1} respectively. The conductivity of 0.003 N solution of acetic acid is 1.62×10^{-4} S cm^{-1} at the same temperature. What is the degree of dissociation of acetic acid?

Sol. $\Lambda^o_m(CH_3COOH) = \lambda^o_m(H^+) + \lambda^o_m(CH_3COO^-) = 345 + 40 = 385$ S cm^2 mol^{-1}

$$\Lambda^c_m = \frac{K \times 1000}{\text{Molarity}} = \frac{1.62 \times 10^{-4} \times 1000}{0.003} = 54 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda^c_m}{\Lambda^o_m} = \frac{54}{385} = 0.14 \text{ or } 14\%$$

30. A cell consists of two hydrogen electrodes dipped into the same 0.1 M HCl. One electrode is supplied with pure H_2 at 1 atm pressure, the other with a mixture of H_2 and Ar also at 1 atm pressure. What is the mole fraction of H_2 in this mixture when emf of the cell is 10 mV at 298 K?

Sol. Pt | H_2 (1 atm) | HCl (0.1 M) | H_2 (P atm) | Pt $\quad E_{cell} = 10$ mV at 298 K

Anode : $H_2 \longrightarrow 2H^+ + 2e$

Cathode : $2H^+ + 2e \longrightarrow H_2$

$(H_2)_{anode} \longrightarrow (H_2)_{cathode}$

$$E_{cell} = -\frac{0.059}{2}\log\frac{(p_{H_2})_{cathode}}{(p_{H_2})_{anode}}$$

$$10^{-2} = -\frac{0.059}{2}\log\frac{P}{1}$$

$\Rightarrow$ P = 0.458 atm

In cathode half cell H_2 and Ar are present at 1 atm pressure

$$\therefore \quad \text{Mole fraction of } H_2 = \frac{\text{Partial pressure of } H_2}{\text{Total pressure}} = 0.458$$

31. If K_w of water at 25°C is 10^{-14}, calculate the standard reduction potential of the following reaction at 25°C

$2H_2O + 2e \longrightarrow H_2 + 2OH^-$

Given $H^+ + e^- \longrightarrow \frac{1}{2}H_2 \qquad E^o = 0V$

Sol.

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \Delta G_1^\circ = -RT \ln K_w$$

$$H^+ + e \longrightarrow \frac{1}{2}H_2 \qquad \Delta G_2^\circ = 0$$

$$H_2O + e \longrightarrow \frac{1}{2}H_2 + OH^- \qquad \Delta G_3^\circ = -RT \ln K_w$$

$$2H_2O + 2e \longrightarrow H_2 + 2OH^- \qquad \Delta G^\circ = -2RT \ln K_w$$

$-2FE^\circ = -2RT \ln K_w$

$$E = \frac{RT}{F}\ln K_w = 0.059 \log 10^{-14} = -0.826 \text{ V}$$

32. Find the solubility product of a saturated solution of silver chromate in water at 298 K if emf of the cell Ag | Ag_2CrO_4 (saturated solution) | | Ag^+ (0.1 M) | Ag is 0.164 V at 298 K.

Sol. Ag | Ag_2CrO_4 (satd. sol.) | | Ag^+ (0.1 M) | Ag $\qquad E_{cell} = 0.164$ V at 298 K

If x mol L^{-1} is the solubility of Ag_2CrO_4

Ag | Ag^+ (2x M) | | Ag^+ (0.1 M) | Ag

$$E_{cell}^\circ = -0.059 \log\frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}}$$

$$0.164 = -0.059 \log\frac{2x}{0.1}$$

$\Rightarrow$ $x = 8.3 \times 10^{-5}$ M

$$Ag_2CrO_4(s) \rightleftharpoons \underset{2x}{2Ag^+(aq)} + \underset{x}{CrO_4^{2-}}$$

$K_{sp} = (2x)^2 x = 4x^3 = 4(8.3 \times 10^{-5})^3 = 2.29 \times 10^{-12}$

33. An electrode is prepared by dipping a silver strip into a solution saturated with AgSCN and containing 0.1 M SCN^-. The emf of the voltaic cell constructed by connecting this as the cathode to the standard hydrogen half-cell as the anode is 0.45 V at 25°C. What is K_{sp} of AgSCN? [Given $E^o_{Ag^+/Ag} = 0.80$ V]

Sol. $Pt \mid H_2\ (1\ atm) \mid H^+\ (1\ M) \mid\mid SCN^-\ (0.1\ M) \mid AgSCN \mid Ag$ $\quad E_{cell} = 0.45\ V$ at 25°C

$$E_{cell} = E_{SCN^- \mid AgSCN \mid Ag} - 0$$

$$\therefore \quad E_{SCN^- \mid AgSCN \mid Ag} = 0.45$$

$$E_{SCN^- \mid AgSCN \mid Ag} = E^o_{SCN^- \mid AgSCN \mid Ag} - 0.059 \log \frac{1}{[SCN^-]}$$

$$E^o_{SCN^- \mid AgSCN \mid Ag} = 0.45 + 0.059 \log 0.1 = 0.391\ V$$

$$E^o_{SCN^- \mid AgSCN \mid Ag} = E^o_{Ag^+/Ag} + \frac{RT}{F} \ln K_{sp}$$

$0.391 = 0.80 + 0.059 \log K_{sp}$

$\therefore \quad K_{sp} = 1.17 \times 10^{-7}$

34. An excess of liquid mercury was added to 10^{-3} M acidified solution of Fe^{3+} ions. It was found that only 5% Fe^{3+} ions remained as Fe^{3+} ions at equilibrium at 25°C. Calculate $E^o_{Hg/Hg_2^{2+}}$ at 25°C for

$$2Hg + 2Fe^{3+} \longrightarrow Hg_2^{2+} + 2Fe^{2+} \quad (E^o_{Fe^{2+}/Fe^{3+}} = -0.7)$$

Sol.

$2Hg$ +	$2Fe^{3+}$	$\longrightarrow$	Hg_2^{2+} +	$2Fe^{2+}$
	$10^{-3}(1-0.95)$		$\frac{0.95\times10^{-3}}{2}$	0.95×10^{-3}

$$K_C = \frac{[Hg_2^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2} = \frac{(0.95\times10^{-3})^3}{2\times(0.05\times10^{-3})^2} = 0.171$$

$$E^o_{cell} = \frac{RT}{nF} \ln K_C$$

$$E^o_{Fe^{3+}/Fe^{2+}} - E^o_{Hg_2^{2+}/Hg} = \frac{0.059}{2} \log 0.171$$

$$E_{Hg^{2+}/Hg} = 0.77 - (-0.0226) = 0.793\ V$$

$$\therefore \quad E_{Hg/Hg_2^{2+}} = -0.793$$

35. A solution containing 4.5 mM of $Cr_2O_7^{2-}$ and 15 mM of Cr^{3+} shows a pH of 2.0. Calculate the potential of half cell reaction. The standard potential of the reaction $Cr_2O_7^{2-} \longrightarrow Cr^{3+}$ is 1.33 V.

Sol. $Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O \quad E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33\ V$

$[Cr_2O_7^{2-}] = 4.5 \times 10^{-3}$ M; $[Cr^{3+}] = 15 \times 10^{-3}$ M; $[H^+] = 10^{-2}$ M

$$E_{Cr_2O_7^{2-}/Cr^{3+}} = E^o_{Cr_2O_7^{2-}/Cr^{3+}} - \frac{0.059}{6} \log \frac{[Cr^{3+}]^2}{(Cr_2O_7)[H^+]^{14}}$$

$$= 1.33 - \frac{0.059}{6} \log \frac{(15\times10^{-3})^2}{(4.5\times10^{-3})(10^{-2})^{14}}$$

$$= 1.07\ V$$

36. During the discharge of a lead storage battery, the density of H_2SO_4 falls from 1.294 g/cc to 1.139 g/cc. H_2SO_4 of density 1.294 g/cc is 39% by weight and that of density 1.139 g/cc is 20% by weight. The battery holds 3.5 litre of acid. Calculate the number of ampere-hours for which the battery must have been used.

Sol. In a lead storage battery, the following reaction takes place

$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$

Total charge drawn from the battery = Moles of H_2SO_4 consumed

Initial moles of $H_2SO_4 = \dfrac{3500 \times 1.294 \times 39}{98 \times 100} = 18.023$

Final moles of $H_2SO_4 = \dfrac{3500 \times 1.139 \times 20}{98 \times 100} = 8.136$

Moles of H_2SO_4 consumed = 18.023 – 8.136 = 9.887

Charge drawn = 9.887 F = 9.887 × 96500 C

1 amp. – hour = 3600 C

$\therefore$ Number of amp. hour $= \dfrac{9.887 \times 96500}{3600} = 265.03$

37. A lead storage cell is discharged which causes H_2SO_4 electrolyte to change from a concentration of 34.6% by weight (density 1.261 g/cc at 25°C) to one of 27% by weight. The original volume of electrolyte is 1 litre. Calculate the total charge used at the anode.

Sol. $Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$

Charge drawn from the cell = Moles of H_2SO_4 consumed

= Moles of H_2O formed

Initial mass of $H_2SO_4 = \dfrac{1000 \times 1.261 \times 34.6}{100} = 436.3$ g

Percentage of H_2SO_4 in the final solution = 27%

Let xF charge is drawn from the cell

Final mass of H_2SO_4 = (436.3 – 98x) g

Final mass of solution = 1261 – 98x + 18x

= (1261 – 80x) g

$\therefore \quad \dfrac{436.3 - 98x}{1261 - 80x} = \dfrac{27}{100}$

$\Rightarrow$ x = 1.255 F

38. An acidic solution of Cu^{2+} salt containing 0.4 g of Cu^{2+} is electrolysed untill all the copper is deposited. The electrolysis is continued for 7 more minutes with the volume of solution kept at 100 ml and the current at 1.2 amp. Calculate volume of gases evolved at NTP during the entire electrolysis. (Atomic mass of Cu = 63.5)

Sol. Let the Cu^{2+} salt the $CuSO_4$ and the acidic medium be dil H_2SO_4. In the first part of electrolysis when copper is deposited at the cathode

Cathode : $Cu^{2+} + 2e \longrightarrow Cu$

Anode : $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

Equivalents of O_2 = Equivalents of Cu $= \frac{0.4 \times 2}{63.5}$

Volume of O_2 at NTP $= \frac{0.8 \times 5600}{63.5} = 70.55$ ml

In the second part of electrolysis

Cathode : $2H^+ + 2e \longrightarrow H_2$

Anode : $4OH^- \longrightarrow 2H_2O + O_2 + 4e$

$Q = \frac{1.2 \times 7 \times 60}{96500} = 5.2 \times 10^{-3}$ F

Equivalents of H_2 = Equivalents of $O_2 = 5.2 \times 10^{-3}$

Volume of H_2 at NTP = $5.2 \times 10^{-3} \times 11200 = 58.24$ ml

Volume of O_2 at NTP = $5.2 \times 10^{-3} \times 5600 = 29.12$ ml

Total volume of O_2 at NTP = 70.55 × 29.12 = 99.67 ml

39. A current of 15 amp per hour is employed to Ni plate in a $NiSO_4$ solution. Both Ni and H_2 are formed at the cathode and volume of hydrogen produced is 2.5 litre at STP.

(i) How many gm of Ni is plated on the metal sheet per hour?

(ii) What is the thickness of coating if the cathode consists of 4 × 4 cm square metal sheet which is coated on both faces. The density of Ni is 8.9 g/cc and atomic mass of Ni = 58.7?

Sol. $Q = \frac{15 \times 3600}{96500}$ F $= 0.56$ F

Equivalents of Ni + Equivalents of $H_2 = 0.56$

Equivalents of $H_2 = \frac{2.5}{11.2} = 0.2232$

$\therefore$ Equivalents of Ni = 0.56 – 0.2232 = 0.3368

Mass of Ni deposited per hour $= 0.3368 \times \frac{58.7}{2} = 9.88$ g

Volume of Ni deposited per hour $= \frac{9.88}{8.9}$ cc

Thickness of coating $= \frac{9.88}{8.9 \times 2 \times 16} = 0.035$ cm

40. The $E^o_{Cu^{2+}/Cu}$ and $E^o_{Ag^+/Ag}$ are 0.337 V and 0.799 V respectively. Construct a galvanic cell using these electrodes so that E^o_{cell} is +ve. For what silver ion concentration will the emf of the cell at 25°C be zero if $[Cu^{2+}] = 0.01$ M?

Sol. $Cu \mid Cu^{2+}$ (1 M) $\mid\mid Ag^+$ (1 M) $\mid Ag$

$E^o_{cell} = E^o_{Ag^+/Ag} - E^o_{Cu^{2+}/Cu} = 0.799 - 0.337 = 0.462$ V

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{2} \log \frac{[Cu^{2+}]}{[Ag^{+}]^2}$$

If $[Cu^{2+}] = 0.01$ M and $E_{cell} = 0$

$$E^{o}_{cell} = \frac{0.059}{2} \log \frac{0.01}{[Ag^{+}]^2}$$

$$\frac{0.462 \times 2}{0.059} = \log \frac{0.01}{[Ag^{+}]^2}$$

$\Rightarrow$ $[Ag^{+}] = 1.477 \times 10^{-9}$ M

❑ ❑ ❑

Chapter 3

Electrochemistry

Solutions (Set-2)

[Conductance]

1. The correct order of equivalent conductance at infinite dilution of LiCl, NaCl, KCl is

(1) KCl > NaCl > LiCl (2) LiCl > NaCl > KCl (3) LiCl > KCl > NaCl (4) LiCl $\simeq$ NaCl < KCl

Sol. Answer (1)

The ions formed are Li^+, Na^+ and K^+, the hydration is maximum in case of Li^+ because of which its mobility is least and has least conductance.

Hence, the following order.

KCl > NaCl > LiCl

2. The specific conductance of a saturated solution of AgCl is $K\Omega^{-1}$ cm^{-1}. The limiting ionic conductances of Ag^+ and Cl^- are x and y, respectively. The solubility product of AgCl is

(1) $\frac{1000\,K}{x+y}$ (2) $\left(\frac{1000\,K}{x+y}\right)^2$ (3) $\frac{1000\times143.5\times K}{x+y}$ (4) $\left(\frac{10^3\times143.5\times K}{x+y}\right)^2$

Sol. Answer (2)

$AgCl \rightleftharpoons Ag^+ + Cl^-$

Specific conductance = $K\Omega^{-1}cm^{-1}$

$$\Lambda = \frac{K\times1000}{C}$$

$$\Lambda_{AgCl} = \lambda^o_{Ag^+} + \lambda^o_{Cl^+} = (x + y)$$

$$\therefore\ (x + y) = \frac{K\times1000}{C}$$

$$\therefore\ C = \frac{1000K}{(x+y)}$$

$$\therefore\ \text{Solubility product} = C^2 = \left[\frac{1000K}{(x+y)}\right]^2$$

3. The equivalent conductances of CH_3COONa, HCl and NaCl at infinite dilution are 91, 426 and 126 S cm^2 eq^{-1} respectively at 25°C. The equivalent conductance of 1 M CH_3COOH solution is 19.55 S cm^2 eq^{-1}. The pH of solution is

(1) 5.3 (2) 4.3 (3) 2.3 (4) 1.3

Sol. Answer (4)

$\Lambda^{\infty}_{CH_3COONa} = \lambda^{o}_{CH_3COO^-} + \lambda^{o}_{Na^+}$

$\Lambda^{o}_{HCl} = \lambda^{o}_{H^+} + \lambda^{o}_{Cl^-}$

$\Lambda^{\infty}_{NaCl} = \lambda^{\infty}_{Na^+} + \lambda^{o}_{Cl^-}$

$\Lambda^{\infty}_{CH_3COOH} = \Lambda^{\infty}_{CH_3COONa} + \Lambda^{\infty}_{HCl^-} - \Lambda^{\infty}_{NaCl}$

$\Rightarrow$ 91 + 426 + (–126) = 391 = $\Lambda^{\infty}_{CH_3COOH}$

$\Lambda_C = 19.55$

$\alpha = \frac{\Lambda_C}{\Lambda^{\infty}} = \frac{19.55}{391} = 0.05$

$[H^+] = \alpha C = 1 \times 0.05$ M

$pH = -\log [H^+] = -\log (5 \times 10^{-2})$

$\Rightarrow$ 2–log 5 = 2 – 0.7 =1.3

4. The limiting equivalent conductance of NaCl, KCl and KBr are 126.5, 150.0 and 152.0 S cm^2 eq^{-1} respectively. The limiting equivalent ionic conductance of Br^- is 76 S cm^2 eq^{-1}. The limiting equivalent ionic conductance of Na^+ is

(1) 25.5 (2) 52.5 (3) 75.5 (4) 57.5

Sol. Answer (2)

$\Lambda^{\infty}_{NaCl} = \lambda^{o}_{Na^+} + \lambda^{o}_{Cl^-} = 126.5$ ...(i)

$\Lambda^{\infty}_{KCl} = \lambda^{o}_{K^+} + \lambda^{o}_{Cl^-} = 150$ ...(ii)

$\Lambda^{\infty}_{KBr} = \lambda^{o}_{K^+} + \lambda^{o}_{Br^-} = 152$ ...(iii)

Adding (i) & (iii) subtract (ii)

$\lambda^{o}_{Na^+} + \lambda^{o}_{Cl^-} + \lambda^{o}_{K^+} + \lambda^{o}_{Br^-} - \lambda^{o}_{K^+} - \lambda^{o}_{Cl^-} = \lambda^{o}_{Na^+} + \lambda^{o}_{Br^-}$

$= (126.5 + 152 - 150) = (76) + \lambda^{o}_{Na^+}$

$\lambda^{o}_{Na^+} = 52.5$

$\therefore$ Equivalent ionic conductance for Na^+ is 52.5.

5. The molar conductances at infinite dilution of $BaCl_2$, NaCl and NaOH are respectively 280×10^{-4}, 126.5×10^{-4}, 248×10^{-4} S m^2 mol^{-1}. The molar conductance at infinite dilution for $Ba(OH)_2$ is

(1) 523×10^{-4} S m^2 mol^{-1} (2) 52.3×10^{-4} S m^2 mol^{-1}

(3) 5.23×10^{-4} S m^2 mol^{-1} (4) 65×10^{-4} S m^2 mol^{-1}

Sol. Answer (1)

$\mu^{\infty}_{BaCl_2} = \mu^{\infty}_{Ba^{2+}} + 2\mu^{\infty}_{Cl^-}$ ...(i)

$\mu^{\infty}_{NaCl} = \mu^{\infty}_{Na^+} + \mu^{\infty}_{Cl^-}$ ...(ii)

$\mu^{\infty}_{NaOH} = \mu^{\infty}_{Na^+} + \mu^{\infty}_{HO^-}$ ...(iii)

for $Ba(OH)_2$

(i) + 2(iii) –2(ii)

$\Rightarrow \mu_{(Ba(OH)_2)} = (280 \times 10^{-4}) + 2(248 \times 10^{-4}) - 2(126.5 \times 10^{-4})$

$= 523 \times 10^{-4}\ Sm^2\ mol^{-1}$.

6. At 25°C, the equivalent conductances at infinite dilution of HCl, CH_3COONa and NaCl are 426.1, 91.0 and 126.45 $cm^2\ \Omega^{-1}eq^{-1}$ respectively. Λ_∞ for CH_3COOH (in $cm^2\ \Omega^{-1}eq^{-1}$) is

(1) 391.6 (2) 390.6 (3) 380.6 (4) 309.6

Sol. Answer (2)

According to given condition:

$\Lambda^{\infty}_{HCl} = \lambda^{o}_{H^+} + \lambda^{o}_{Cl^-}$ ...(i)

$\Lambda^{\infty}_{CH_3COONa} = \Lambda^{\infty}_{CH_3COO^-}\ \lambda^{o}_{Na^+}$ ...(ii)

$\Lambda^{\infty}_{NaCl} = \lambda^{o}_{Na^+} + \lambda^{o}_{Cl^-}$ ...(iii)

Doing the operation

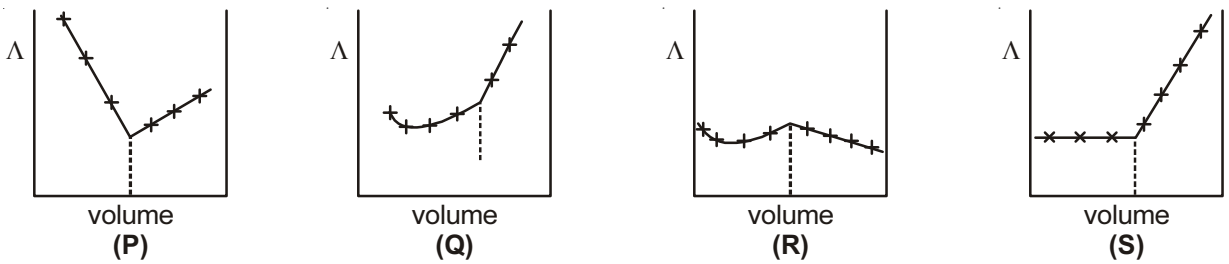
Equation (i) + (ii) – (iii)

$\Lambda^{\infty}_{HCl} + \Lambda^{\infty}_{CH_3COONa} - \Lambda^{\infty}_{NaCl} = \lambda^{o}_{CH_3COO^-} + \lambda^{o}_{H^+}$

$\Rightarrow (426.1 + 91.0 - 126.45) = \Lambda^{\infty}_{CH_3COOH}$

$\therefore \Lambda^{\infty}_{CH_3COOH} = 390.6\ cm^2\ \Omega^{-1}/eq$

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

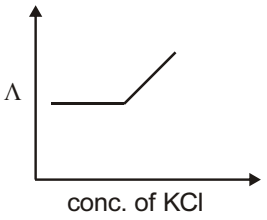


(1) (P) (2) (Q) (3) (R) (4) (S)

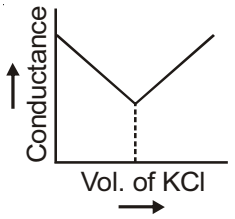
Sol. Answer (4)

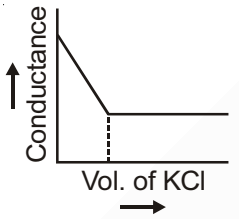
Ag^+ and K^+ have nearly same ionic mobility.

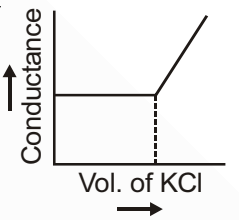
$AgNO_3 + KCl \longrightarrow AgCl(s) + KNO_3$

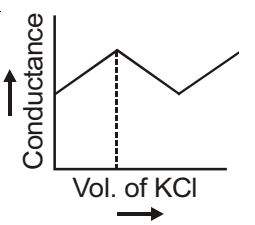


8. Which of following type of plot would you expect from the titration of $AgNO_3$ against KCl solution?

(1) 

(2) 

(3) 

(4) 

Sol. Answer (3)

Fact.

[Electrolysis]

9. During electrolysis of aqueous solution of a salt under inert electrodes, pH in the space near one of the electrode is increased. Which of the following salt solution was electrolysed?

(1) KCl (2) $CuCl_2$ (3) $Cu(NO_3)_2$ (4) $CuSO_4$

Sol. Answer (1)

In KCl solution the reaction at the electrodes are

$2H^+ + 2e^- \rightarrow H_2$

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

$\therefore$ $[H^+]$ decreases in the solution because of which $[\bar{O}H]$ increases hence increasing the pH.

10. On passing 3 faradays of electricity through three electrolytic cells connected in series containing Ag^+, Ca^{+2} and Al^{+3} ion respectively, the molar ratio in which three metal ions are liberated at the electrode is

(1) 1 : 2 : 3 (2) 3 : 2 : 1 (3) 6 : 3 : 2 (4) 3 : 4 : 2

Sol. Answer (3)

i × t is same for all the electrolytic solutions

$$\left(\frac{W}{M}\right)_{Ag} = \frac{it}{nF} = \frac{it}{F} \quad (Ag^+ + e^- \rightarrow Ag)$$

$$\left(\frac{W}{M}\right)_{Ca} = \frac{it}{2F} \quad (Ca^{2+} + 2e^- \rightarrow Ca)$$

and $$\left(\frac{W}{M}\right)_{Al} = \frac{it}{3F} \quad (Al^{3+} + 3e \rightarrow Al)$$

$\therefore$ Molar ratio is $1 : \frac{1}{2} : \frac{1}{3}$ or 6 : 3 : 2

11. A current of 2.0 A when passed for 5 hrs through a molten salt, deposits 22.2 g of metal (of atomic weight 177). The oxidation state of metal in metal salt is

(1) +1 (2) +2 (3) +3 (4) +4

Sol. Answer (3)

i = 2A, t = 5 hrs = 5 × 60 × 60 s

w_M = 22.2 g; A = 177

Applying the equation

$$w = \frac{Eit}{F} \Rightarrow w = \frac{Ait}{nF}$$

$$\therefore \quad n = \frac{A \times i \times t}{wF} = \frac{177 \times 2 \times 5 \times 60 \times 60}{22.2 \times 96500} = 2.97$$

$\therefore$ n = 3

$M^{3+} + 3e^- \rightarrow M$

$\therefore$ Oxidation state is +3.

12. In the electrolysis of aqueous solution of NaOH, 2.8 litre of oxygen at NTP was liberated at the anode. How much hydrogen was liberated at cathode?

(1) 5.6 litre (2) 56 ml (3) 560 ml (4) 0.056 litre

Sol. Answer (1)

NaOH is electrolysed.

$NaOH \rightarrow Na^+ + HO^-$

$H_2O \rightarrow H^+ + HO^-$

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

At anode: $4HO^- \rightarrow 2H_2O + O_2 + 4e^-$

$$\left(\frac{w}{M}\right)_{H_2} = \frac{it}{2F}; \left(\frac{w}{M}\right)_{O_2} = \frac{it}{4F}$$

$$\therefore \quad n_{H_2} : n_{O_2} = \frac{it}{2F} : \frac{it}{4F} \Rightarrow 2 : 1 \quad \therefore \text{ Volume ratio } V_{H_2} : V_{O_2} = 2 : 1$$

$$\frac{V_{H_2}}{2.8} = \frac{2}{1} \qquad \therefore \quad V_{H_2} = 2.8 \times 2 = 5.6 \text{ L}$$

13. Passage of one ampere current through 0.1 M $Ni(NO_3)_2$ solution using Ni electrodes bring in the concentration of solution to _____ in 60 seconds.

(1) 0.1 M (2) 0.05 M (3) 0.2 M (4) 0.025 M

Sol. Answer (1)

The reaction taking place at the electrodes are

Anode : $Ni \rightarrow Ni^{2+} + 2e$

Cathode : $Ni^{2+} + 2e^- \rightarrow Ni$

Hence $[Ni^{2+}]$ does not change.

$\therefore$ Concentration of Ni^{2+} is 0.1M.

14. When electricity is passed through a solution of $AlCl_3$ 13.5 g of Al is deposited. The number of faradays must be

(1) 1.0 (2) 1.5 (3) 0.5 (4) 2

Sol. Answer (2)

The reaction at cathode is

$Al^{3+} + 3e^- \rightarrow Al$ (n = 3)

Applying the equation

$$w = \frac{Eit}{F} \Rightarrow \frac{w}{E} \times F$$

$$\therefore \quad i \times t = \frac{13.5}{\left(\frac{27}{3}\right)} \times F = \frac{13.5}{9} F = 1.5 F$$

15. 0.5 faraday of electricity was passed to deposit all the copper present in 500 ml of $CuSO_4$ solution. What was the molarity of this solution?

(1) 1 M (2) 0.5 M (3) 0.25 M (4) 2.5 M

Sol. Answer (2)

$i \times t = 0.5$ F

Applying the equation

$$w = \frac{E \times it}{F} \Rightarrow \left(\frac{w}{M}\right) = \frac{it}{2F} = \frac{0.5F}{2F} = 0.25 \text{ moles}$$

V × molarity = No. of moles

$$\Rightarrow \quad 500 \times x \times 10^{-3} = 0.25$$

$$\therefore \quad x = \frac{0.25 \times 10^3}{500} = 0.5$$

Molarity = 0.5 M

16. 25 g of a metal is deposited on cathode during the electrolysis of metal nitrate solution by a current of 5 A passing for 4 hours. If atomic weight of the metal is 100. The valency of metal in metal nitrate is

(1) 1 (2) 2 (3) 3 (4) 4

Sol. Answer (3)

$w_M = 25$ g, i = 5 A, t = 5 hrs = 4 × 60 × 60 second

A = 100 (metal nitrate was electrolysed)

Applying the equation,

$$w = \frac{E \times it}{F}$$

$$\Rightarrow \quad 25 = \frac{100}{n} \times \frac{5 \times 4 \times 60 \times 60}{96500}$$

$$\therefore \quad n = \frac{100 \times 5 \times 4 \times 60 \times 60}{(96500 \times 25)} = 3$$

Hence, valency = 3

17. A well stirred (1 L) solution of 0.1 M $CuSO_4$ is electrolysed at 25°C using copper electrodes with a current of 25 mA for 6 hours. If current efficiency is 50%. At the end of the duration what would be the concentration of copper ions in the solution?

(1) 0.0856 M (2) 0.092 M (3) 0.0986 M (4) 0.1 M

Sol. Answer (3)

18. 50 ml of a buffer of 1 M NH_3 and 1 M NH_4^+ are placed in two volatic cells separately. A current of 3.0 amp is passed through both cells for 10 min. If electrolysis of water takes place as

$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$ (R.H.S.)

$2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$ (L.H.S.)

then pH of the

(1) L.H.S. will increase (2) R.H.S. will increase

(3) R.H.S. will decrease (4) Both side will increase

Sol. Answer (2)

Because of the reactions of electrolysis, $[H^+]$ concentration will decrease as a result of which pH will increase.

19. 1 M aqueous solution of NaCl undergo electrolysis if 50 mA current is passed for 12 hours. Assume current efficiency is 25%. The total volume of gas produced at standard state is

(1) 137 ml (2) 68.5 ml (3) 125.44 ml (4) 62.72 ml

Sol. Answer (3)

NaCl aq. solution undergoes electrolysis

$NaCl \rightarrow Na^+ + Cl^-$

$H_2O \rightarrow H^+ + HO^-$

Reactions :

At cathode : $2H^+ + 2e \rightarrow H_2(g)$

At anode : $2Cl^- \rightarrow Cl_2 + 2e$

$$\left(\frac{w}{M}\right)_T = \frac{it}{2F} + \frac{it}{2F} = \frac{it}{F}$$

$$\Rightarrow \quad 50\times10^{-3}\,\frac{25}{100}\times\frac{12\times60\times60}{96500} = n_T$$

$\Rightarrow \quad n_T = 0.005595$

$\therefore \quad V = 0.005595 \times 22400$

$\therefore \quad \approx 125.44$ ml.

20. Vanadium electrode is oxidised electrically. If the mass of electrode decreases by 100 mg during the passage of 570 coulomb, the oxidation state of vanadium in the product is (At. wt. of V = 51)

(1) 6 (2) 5 (3) 4 (4) 3

Sol. Answer (4)

$i \times t = 570$ C

$w = 100\ mg = 100 \times 10^{-3}\ g$

$$w = \frac{E \times it}{F}$$

$$\Rightarrow \frac{100 \times 10^{-3}}{51} = \frac{570}{96500 \times n}$$

$$\therefore\ n = \frac{570 \times 51}{100 \times 10^{-3} \times 96500} = 3$$

21. Which is correct increasing order of deposition?

(1) $Na^+ < Mg^{+2} < Zn^{+2} < Ag^+$ (2) $Ag^+ < Zn^{+2} < Mg^{+2} < Na^+$

(3) $Mg^{+2} < Na^+ < Zn^{+2} < Ag^+$ (4) $Mg^{+2} < Zn^{+2} < Na^+ < Ag^+$

Sol. Answer (1)

Increasing order of deposition is related to the order of reduction and oxidation potential (in accordance with preferential discharge theory)

$\therefore\ Na^+ < Mg^{2+} < Zn^{2+} < Ag^+$

22. Which is the correct order of deposition of anion?

(1) $SO_4^{-2} > OH^- > Cl^- > Br^- > I^-$ (2) $SO_4^{-2} < OH^- < Cl^- < Br^- < I^-$

(3) $SO_4^{-2} > Cl^- > Br^- > I^- > OH^-$ (4) $Br^- > Cl^- > I^- > SO_4^{-2} > OH^-$

Sol. Answer (2)

It is in the order of discharge potential.

$\therefore$ In anion order of deposition is

$SO_4^{2-} < HO^- < Cl^- < Br^- < I^-$

23. Rate of corrosion is maximum when

(1) An electrolyte is present in water (2) Metal has low S.R.P.

(3) Metal has high standard oxidation potential (4) All of these

Sol. Answer (4)

When metal has high standard oxidation potential, it has more tendency to undergo oxidation. In presence of electrolyte, rate of Corrosion is maximum.

24. Which of the following cannot be extracted by electrolysis from aqueous solution of their salts?

(1) Zn (2) Ag (3) Cu (4) Pt

Sol. Answer (1)

As $E^{\circ}_{Zn^{2+}/Zn}$ is less than $E^{\circ}_{H^+/H_2}$

25. Zn amalgam is prepared by electrolysis of aqueous $ZnCl_2$ using 9 gram Hg cathode. How much current is to be passed through $ZnCl_2$ solution for 1000 seconds to prepare a Zn amalgam with 20% by weight? (Atomic mass, Zn = 65.4 g)

(1) 5.6 A (2) 7.2 A (3) 8.85 A (4) 11.2 A

Sol. Answer (3)

Let, x gram of Zn deposited on 9 gram of Hg. % of Zn in amalgam $= \frac{x}{9+x} \times 100 = 25$

$\Rightarrow$ x = 3 gram

Equivalent of Zn $= \frac{3 \times 2}{65.4}$

Current $= \frac{6}{65.4} \times \frac{96500}{1000} = 8.85$ A

[E.M.F. (E° and K_{eq})]

26. By how much will the potential of half cell Cu^{+2}/Cu change, if the solution is diluted to 100 times at 298 K?

(1) Increases by 59 mV (2) Decreases by 59 mV

(3) Increases by 29.5 mV (4) Decreases by 29.5 mV

Sol. Answer (2)

For $Cu^{2+} + 2e^- \rightarrow Cu(s)$

$$E_{Cu^{2+}/Cu} = E^\circ - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$$

When Cu^{2+} solution is diluted to 100 times $[Cu^{2+}]$ decreases to 1/100

$$E'_{Cu^{2+}/Cu} = E^\circ - \frac{0.0591}{2} \log \frac{100}{[Cu^{2+}]}$$

$$E' = E^\circ - \frac{0.0591}{2} [[\log 100 - \log [Cu^{2+}]]$$

$$\therefore \quad E' = E^\circ - \frac{0.0591}{2} \times 2 - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$$

$$\therefore \quad E' = E^\circ - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]} - 0.0591$$

$\therefore$ E′ = E – 0.0591, Hence, Potential decreases by 59 mV.

27. The E°_{cell} of the reaction

$MnO_4^- + Fe^{+2} + H^+ \rightarrow Mn^{+2} + Fe^{+3} + H_2O$ is 0.59 V at 25°C. The equilibrium constant for the reaction is

(1) 50 (2) 10 (3) 10^{50} (4) 10^5

Sol. Answer (3)

E^o_{cell} = 0.59 V

$MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$

$$E = E^o_{cell} - \frac{0.0591}{5} \log Q_c$$

At equilibrium, $E = 0$; $Q_c = K_c$

$\therefore \quad E^o_{cell} = \frac{0.0591}{5} \log K_c$

$\therefore \quad \frac{5 \times 0.59}{0.59} = \log K_c$

$50 = \log K_c$

$\therefore \quad K_c = 10^{50}$.

28. Some Indian scientists tried to use a metal x for electroplating iron pillar in Mehrauli but they ended up with E_{cell} of the reaction to be negative. They concluded that

(1) Reaction is spontaneous (2) Reaction is non-spontaneous

(3) Reaction is reversible (4) Reaction is non-reversible

Sol. Answer (2)

For electroplating Iron a metal 'x' is used.

E_{cell} is negative, it means that no reaction takes place and the reaction is non-spontaneous.

29. The equilibrium constant for the reaction $Sr(s) + Mg^{+2}(aq) \rightleftharpoons Sr^{+2}(aq) + Mg(s)$ is 2.69×10^{12} at 25°C. The E° for a cell made up of Sr/Sr^{+2} and Mg^{+2}/Mg half cells is

(1) 0.3667 V (2) 0.7346 V (3) 0.1836 V (4) 3.667 V

Sol. Answer (1)

The reaction is

$Sr(s) + Mg^{2+}(aq) \rightarrow Mg(s) + Sr^{2+}(aq)$

$K_c = 2.69 \times 10^{12}$

At equilibrium, $E = 0$; $Q = K_c$

$\Rightarrow \quad 0 = E^o - \frac{0.0591}{2} \log K_c$

$\Rightarrow \quad E^o = \frac{0.0591}{2} \log K_c = \frac{0.0591}{2} \log (2.69 \times 10^{12}) = 0.3667 \text{ V}$

30. In which of the following pair, first specie is a better oxidising agent than second specie under standard conditions?

(1) Br_2 & Au^{3+} (2) H_2 & Ag^+

(3) Cr^{3+} & Cd^{2+} (4) O_2 in acidic medium & O_2 in basic medium

Sol. Answer (4)

31. M^+ is not stable and undergoes disproportionation to form M and M^{2+}. Calculate E° for M^+ disproportionation

$E^\circ_{M^{2+}/M} = +0.153 \text{ V}, \; E^\circ_{M^+/M} = 0.53 \text{ V}$

(1) +0.683 V (2) –0.367 V (3) 0.754 V (4) +0.3415 V

Sol. Answer (3)

Given

$E^o_{Cu^{2+}/Cu} = +0.153 \text{ V}$ and $E^o_{Cu^+/Cu} = 0.53 \text{ V}$

The reaction

$2Cu^{+} \rightarrow Cu + Cu^{2+}$

$\therefore \quad E^{o}_{Cell} = E^{o}_{Cu^{+}/Cu^{2+}} + E^{o}_{Cu^{+}/Cu}$

we required $E^{o}_{Cu^{+}/Cu^{2+}}$

$Cu^{2+} + 2e \rightarrow Cu; \ 0.153$

$Cu \rightarrow Cu^{+} + e^{-}; \ -0.53$

$\Rightarrow \quad Cu^{2+} + e^{-} \rightarrow Cu^{+}$

$\Rightarrow \quad -1 \times F \times E^{o} = [-2 \times F \times (0.153)] + [F \times 0.53]$

$\Rightarrow \quad -FE^{o} = -2F\ (0.153) + 0.53\ F$

$\therefore \quad E^{o} = -0.53 + (2 \times 0.153)$

$\therefore \quad E^{o}_{Cu^{2+}/Cu^{+}} = -0.224$

or $E^{o}_{Cu^{+}/Cu^{2+}} = 0.224$

$\therefore \quad E^{o} = 0.224 + 0.53 = 0.754\ V$

32. $E^{\circ}_{(Na^{+}/Na)} = -2.71\,V, \quad E^{\circ}_{(Mg^{+2}/Mg)} = -2.37\ V$

$E^{\circ}_{(Fe^{+2}/Fe)} = -0.44\ V, \ E^{\circ}_{(Cr^{+3}/Cr)} = -0.41\,V$

Based on this data, which is the poorest reducing agent?

(1) Na^{+} (2) Mg^{+2} (3) Fe^{+2} (4) Cr^{+3}

Sol. Answer (4)

Cr^{3+} is the poorest reducing agent because of least value of oxidation potential.

33. The standard reduction potential of Cu^{+2}/Cu and Cu^{+2}/Cu^{+} are 0.337 V and 0.153 V respectively. The standard reduction potential of Cu^{+}/Cu half cell is

(1) 0.521 V (2) 0.490 V (3) 0.321 V (4) 0.290 V

Sol. Answer (1)

Given (i) ... $Cu^{2+} + 2e^{-} \rightarrow Cu(s); \ E^{o}_{1} = 0.337\ V$

(ii)... $Cu^{2+} + e^{-} \rightarrow Cu^{+} \ E^{o}_{2} = 0.153\ V$

Reversing equation (ii); we get

$Cu^{+} \rightarrow Cu^{2+} + e^{-}$ ...(iii)

Adding equation (i) and (iii)

We get, $Cu^{+} + e^{-} \rightarrow Cu$

$$\Delta G^{o} = \Delta G^{o}_{1} + \Delta G^{o}_{2} = (-1 \times F \times E^{o}) = \left(-2 \times F \times E^{o}_{1}\right) + \left(-1 \times F \times E^{o}_{2}\right)$$

$\therefore \quad -FE^{o} = [-2 \times F \times (0.337)] + [-F \times -0.153]$

$-FE^{o} = -2 \times 0.337 \times F + (0.153)\ F$

$\Rightarrow \quad E^{o} = (2 \times 0.337) - (0.153) = 0.521\ V$

34. What is ΔG° for the following reaction?

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

$E^\circ_{Cu^{+2}/Cu} = 0.34\ V, \quad E^\circ_{Ag^+/Ag} = 0.8\ V$

(1) –44.5 kJ (2) 44.5 kJ (3) –89 kJ (4) 89 kJ

Sol. Answer (4)

The reaction given is

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

$E^\circ_{Cell} = E^\circ_{Ag/Ag^+} + E^\circ_{Cu^{2+}/Cu}$

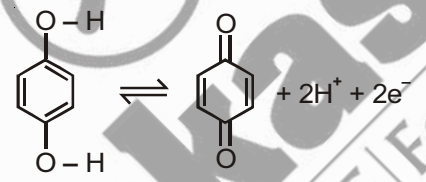
$\therefore \quad E^\circ_{Cell} = (-0.8) + (0.34) = -0.46$

$\Delta G^\circ = -nF \times E^\circ = -2 \times F \times (-0.46)$

$= -2 \times -0.46 \times 96500 = 88780\ J$

or $\Delta G^\circ = +89\ kJ.$

35. For the reduction half reaction $E^\circ_{Quinhydrone} = 1.30\ V$



At pH = 3 at 298 K, electrode reduction potential is (Consider quinone and hydroquinone have identical concentration)

(1) 1.48 V (2) 1.42 V (3) 1.36 V (4) 1.3 V

Sol. Answer (1)

For the reaction, on applying Nernst equation

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

$$E_{cell} = 1.30 - \frac{0.0591}{2} \log (10^{-3})^2$$

$$= -\frac{0.0591}{2} \times (-6) \log 10 + 1.30 = 0.0591 \times 3 + 1.30 = 1.477 \approx 1.48$$

36. Emf of the cell

$Zn \mid Zn^{+2}(aq) \parallel Cu^{+2}(aq) \mid Cu$ is independent of

(1) Quantity of Cu^{+2} and Zn^{+2} in solution (2) Concentration of Cu^{+2}

(3) Concentration of Zn^{+2} (4) Temperature

Sol. Answer (1)

For the given cell

$$E = E^{o} - \frac{0.0591}{2} \log \frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

When Zn^{2+} & Cu^{2+} quantity is changed the emf does not change because EMF depends upon concentration and not the quantity.

37. Which metal oxide is thermally unstable?

(1) Al_2O_3 (2) Na_2O (3) BaO (4) Ag_2O

Sol. Answer (4)

Ag_2O decomposes as

$$Ag_2O \xrightarrow{\Delta} 2Ag + \frac{1}{2} O_2.$$

[Miscellaneous]

38. 135 g of water is electrolysed during an experiment. If the efficiency of current is 75% then select the correct statement.

(1) 168 L of $O_2(g)$ will be evolved at anode at STP

(2) 84 L of $H_2(g)$ will be evolved at cathode at STP

(3) 15 F electricity will be consumed

(4) 20 F electricity will be consumed

Sol. Answer (4)

$$H_2O \xrightarrow{\text{electrolysis}} H_2(g) + \frac{1}{2}O_2(g)$$

Moles of $H_2O = \frac{135}{18} = 7.5$

$\therefore$ Electricity consumed $= 7.5 \times 2 \times \frac{4}{3} F$

$= 20$ F

39. Limiting value of equivalent conductance of $BaSO_4$, $BaCl_2$ and H_2SO_4 are X, Y and Z respectively. Equivalent conductance of HCl at infinite dilution is

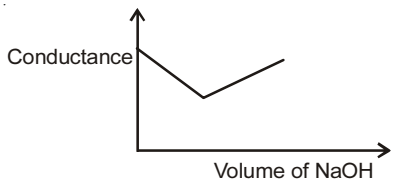
(1) Y + Z – X (2) $\frac{1}{2}(X + Y - Z)$ (3) $\frac{1}{2}(Z + X - Y)$ (4) $\frac{1}{2}(Y + Z - X)$

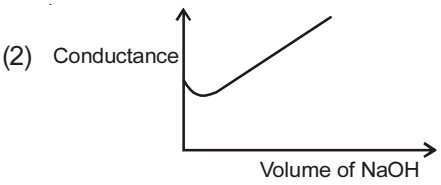
Sol. Answer (4)

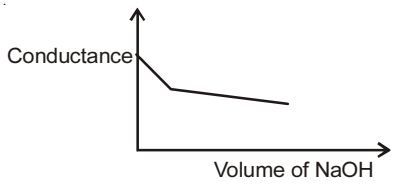
Equivalent conductance of HCl at infinite dilution

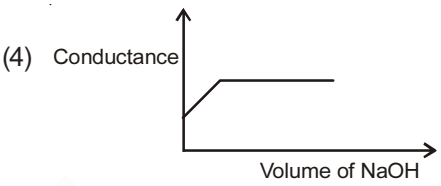
$$= \left[\left(\lambda^{\circ}_{eq}\right)_{BaCl_2} + \left(\lambda^{\circ}_{eq}\right)_{H_2SO_4} - \left(\lambda^{\circ}_{eq}\right)_{BaSO_4}\right]$$

40. If weak monobasic acid is titrated with NaOH, which of the following is correct graph ?

(1) 

(2) 

(3) 

(4) 

Sol. Answer (2)

Option (2) graph represent the correct variation of conductance with volume of NaOH

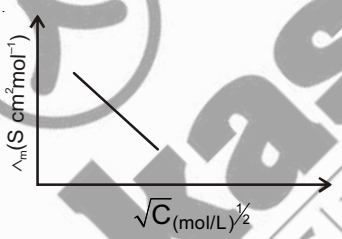
41. The product of electrolysis of aqueous Na_2SO_4 with inert electrodes are

(1) Na and H_2 (2) H_2 and O_2 (3) Na and O_2 (4) H_2 and SO_2

Sol. Answer (2)

H_2 at cathode and O_2 at anode.

42. For an electrolyte, consider the below graph



For which of the following electrolyte above graph is not possible?

(1) NaCl (2) KCl (3) CsCl (4) CH_3COOH

Sol. Answer (4)

Given graph is possible for strong electrolytes

43. pH of 0.1 M CH_3COOH solution is 3 at 25 °C. If limiting molar conductivity of CH_3COO^- and H^+ are 40 and 350 S cm^{2}mol^{-1}. The molar conductance(in Scm^{2}mol^{-1}) at 25 °C for 0.1 M CH_3COOH is

(1) 3.9 (2) 39 (3) 92 (4) 340

Sol. Answer (1)

pH of 0.1 M CH_3COOH solution = 3

$[H^+] = c\,\alpha = 10^{-3}$

$$\alpha = \frac{10^{-3}}{10^{-1}} = 10^{-2}$$

$$\alpha = \frac{\lambda_m}{\lambda_m^\circ} \Rightarrow \frac{1}{100} = \frac{\lambda_m}{390}$$

$\lambda_m = 3.9$ S cm^2 mol^{-1}

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