

ELECTROCHEMISTRY

SOLVED SUBJECTIVE EXERCISE

Very Short Answer Type Questions (1 mark)

1. Why is it necessary to use a salt bridge in a Galvanic cell ?

Ans. To complete the inner circuit and to maintain electrical neutrality of the electrolytic solutions of the half-cells.

2. Find the charge in coulombs on 1 g-ion of N^{3-} .

Ans. Charge on one ion of $N^{3-} = 3 \times 1.6 \times 10^{-19}$ coulombs

One g-ion = 6.02×10^{23} ions

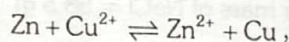
\therefore Charge on 1 g-ion of $N^{3-} = 3 \times 1.6 \times 10^{-19} \times 6.02 \times 10^{23} = 2.89 \times 10^5$ coulombs

3. On electrolysis of an aqueous solution of NaCl, why H_2 and not Na is liberated at the cathode ?

Ans. This is because H^+ ions produced from ionization of water have lower discharge potential than Na^+ ions produced from ionization of NaCl or reduction potential of water is greater than that of sodium ions.

4. Equilibrium constant is related to E_{cell}^0 but not to E_{cell} . Explain why ?

Ans. When equilibrium is reached in the cell reaction, E_{cell} becomes equal to zero. However, E_{cell}^0 is a constant quantity. Hence, applying Nernst equation to the cell reaction, e.g., to the reaction:



$$E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]} = E_{cell}^0 - \frac{RT}{nF} \ln K_c. \text{ At equilibrium } E_{cell} = 0. \text{ Hence, } E_{cell}^0 = \frac{RT}{nF} \ln K_c.$$

5. On the basis of standard electrode potential values stated for acid solution, predict whether Ti^{4+} species may be used to oxidize Fe^{II} to Fe^{III}

Reaction	E/V
$Ti^{4+} + e^- \rightarrow Ti^{3+}$: + 0.01
$Fe^{3+} + e^- \rightarrow Fe^{2+}$: - 0.77

Ans. We want to check the spontaneity of the reaction : $Ti^{4+} + Fe^{2+} \rightarrow Ti^{3+} + Fe^{3+}$

E.M.F. of this reaction = + 0.01 + (-0.77) = -0.76 V

As EMF is -ve, the reaction is non-spontaneous, i.e., Ti^{4+} cannot be used to oxidize Fe^{II} to Fe^{III} .

6. Why fluorine cannot be obtained by electrolysis of aqueous HF solution, though it is a good conductor of electricity?

Ans. H_2O has higher oxidation potential than F^- ions. Hence, in aqueous solution, as compared to F^- ions, H_2O is more easily oxidized to give O_2 gas. Therefore, F_2 cannot be obtained by electrolysis of aqueous HF solution.

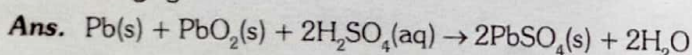
7. Why a mercury cell gives a constant voltage throughout its life ?

Ans. This is because the electrolyte KOH is not consumed in the reaction.

8. Which type of cells are rechargeable ?

Ans. Those cells are rechargeable in which the products formed during discharge are deposited on the electrodes and these can be decomposed to give the original substances when electrical energy is supplied.

9. Write down the overall cell reaction for lead storage battery. (a) When the battery is in use (b) When the battery is on charging.



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

Ans. Zinc container corrodes in presence of NH_4Cl (acidic salt). Thus, dry cell becomes dead after a long time even if it has not been used.

11. Rusting of iron is quicker in saline water than in ordinary water. Why is it so?

Ans. Electrolytes present in saline water help in transport of electrons between cathodic and anodic sites developed on the surface of iron.

Short Answer Type Questions (2 mark)

12. A zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential ($E_{Zn^{2+}/Zn}^0 = -0.76V$)

Ans. The electrode reaction written as reduction reaction is : $Zn^{2+} + 2e^- \rightarrow Zn(n = 2)$

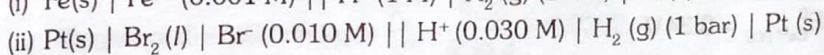
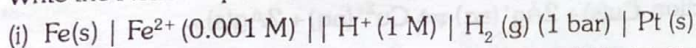
Applying Nernst equation, we get $E_{Zn^{2+}/Zn} = E_{Zn^{2+}/Zn}^0 - \frac{0.0591}{2} \log \frac{1}{[Zn^{2+}]}$

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

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

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

13. Write the Nernst equation and the e.m.f. of the following cells at 298 K:



Given $E_{Fe^{2+}/Fe}^0 = -0.44V$, $E_{Br_2/Br^-}^0 = +1.08V$.

Ans. (i) Cell reaction : $Fe + 2H^+ \rightarrow Fe^{2+} + H_2(n = 2)$

Nernst equation : $E_{cell} = E_{cell}^0 - \frac{0.0591}{2} \log \frac{[Fe^{2+}]}{[H^+]^2}$

$$\therefore E_{cell} = 0 - (-0.44) - \frac{0.0591}{2} \log \frac{10^{-3}}{(1)^2} = 0.44 - \frac{0.0591}{2} \times (-3) = 0.44 + 0.0887 = \mathbf{0.523 V}$$

(ii) Cell reaction : $2Br^- + 2H^+ \rightarrow Br_2 + H_2$ (**Note carefully**)

Nernst equation : $E_{cell} = E_{cell}^0 - \frac{0.0591}{2} \log \frac{1}{[Br^-]^2 [H^+]^2}$

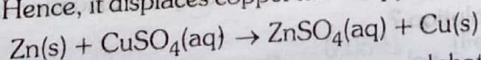
$$\therefore E_{cell} = (0 - 1.08) - \frac{0.0591}{2} \log \frac{1}{(0.01)^2 (0.03)^2}$$

$$= -1.08 - \frac{0.0591}{2} \log(1.111 \times 10^7) = -1.08 - \frac{0.0591}{2} (7.0457) = -1.08 - 0.208 = \mathbf{-1.288 V}$$

Thus, oxidation will occur at the hydrogen electrode and reduction on the Br_2 electrode. $E_{cell} = -1.288 V$

14. Can you store copper sulphate solution in a zinc pot ?

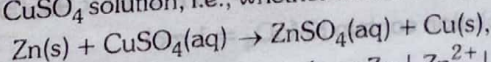
Ans. Zinc is more reactive than copper. Hence, it displaces copper from copper sulphate solution as follows :



Thus, zinc reacts with $CuSO_4$ solution. Hence, we cannot store copper sulphate solution in a zinc pot.

Alternatively, $E_{Zn^{2+}/Zn}^0 = -0.76V$, $E_{Cu^{2+}/Cu}^0 = 0.34V$

To check whether zinc reacts with $CuSO_4$ solution, i.e., whether the following reaction takes place or not

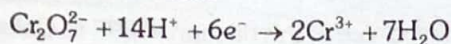


find the EMF of this cell reaction. The cell may be represented as : $Zn | Zn^{2+} || Cu^{2+} | Cu$

$$E_{cell}^0 = E_{Cu^{2+}/Cu}^0 - E_{Zn^{2+}/Zn}^0 = 0.34V - (-0.76V) = 1.10V$$

As E_{cell}^0 is positive, the reaction takes place and we cannot store.

15. Consider the reaction:



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

Ans. From the given reaction, 1 mol of $\text{Cr}_2\text{O}_7^{2-}$ ions require $6F = 6 \times 96500 \text{ C} = 579000 \text{ C}$ of electricity for reduction to Cr^{3+} .

16. Iodine (I_2) and bromine (Br_2) are added to a solution containing iodide (I^-) and bromide (Br^-) ions. What reaction would occur if the concentration of each species is 1 M? The electrode potentials for the reactions are : $E_{\text{I}_2/\text{I}^-}^0 = 0.54\text{V}$, $E_{\text{Br}_2/\text{Br}^-}^0 = 1.08\text{V}$

Ans. The reaction can be either $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$ or $\text{I}_2 + 2\text{Br}^- \rightarrow 2\text{I}^- + \text{Br}_2$

For 1st reaction, E.M.F. = $E_{\text{Br}_2/\text{Br}^-}^0 - E_{\text{I}_2/\text{I}^-}^0 = 1.08 - 0.54 = 0.54\text{V}$

For 2nd reaction, E.M.F. = $E_{\text{I}_2/\text{I}^-}^0 - E_{\text{Br}_2/\text{Br}^-}^0 = 0.54 - 1.08 = -0.54\text{V}$

As E.M.F. is positive for the 1st reaction, hence the cell reaction is $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$.

17. Calculate the equilibrium constant for the reaction $\text{Cu(s)} + 2\text{Ag}^+(\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2\text{Ag(s)}$,

Given that $E_{\text{Ag}^+/\text{Ag}}^0 = 0.80\text{V}$ and $E_{\text{Cu}^{2+}/\text{Cu}}^0 = 0.34\text{V}$

Ans. The cell may be represented as : $\text{Cu} | \text{Cu}^{2+}(\text{aq}) || \text{Ag}^+(\text{aq}) | \text{Ag}$

$$E_{\text{cell}}^0 = E_{\text{RHS}}^0 - E_{\text{LHS}}^0 = 0.80\text{V} - (0.34\text{V}) = 0.46\text{V}$$

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

For the given reaction, $n = 2$, $E_{\text{cell}}^0 = 0.46 \text{ V}$

$$\therefore 0.46 = \frac{0.0591}{n} \log K_c \text{ or } \log K_c = \frac{0.46 \times 2}{0.0591} = 15.5668$$

$$\therefore K_c = \text{antilog } 15.5668 = 3.6 \times 10^{15}$$

18. In each of the following pairs, which will allow greater conduction of electricity and why ?

- (a) Silver wire at 20°C, Same silver wire at 50°C
- (b) NaCl solution at 20°C, Same NaCl solution at 50°C
- (c) NH_4OH solution at 20°C, Same NH_4OH solution at 50°C
- (d) 0.1 M acetic acid solution, 1 M acetic acid solution.

Ans. (a) Silver wire at 20°C because with increase in temperature, metallic conduction decreases due to vibration of kernels.
 (b) NaCl solution at 50°C because in case of a strong electrolyte with increase in temperature, the ionic mobilities increase.
 (c) NH_4OH at 50°C because in case of a weak electrolyte, dissociation increases with increase in temperature.
 (d) 0.1 M acetic acid because with dilution, dissociation/ionization increases.

19. How many coulombs of electricity are required for (i) Complete oxidation of 90g of H_2O ? (ii) Complete reduction of 100 mL of 0.1 M KMnO_4 solution ?

Ans. (i) $90 \text{ g of } \text{H}_2\text{O} = \frac{90}{18} \text{ moles} = 5 \text{ moles}$

As explained in example 2 above, 1 mole of H_2O requires electricity = 2 F

$$\therefore 5 \text{ moles of } \text{H}_2\text{O} \text{ will require electricity} = 5 \times 2 \text{ F} = 10 \text{ F} = 10 \times 96500 = 965000 \text{ C}$$

(ii) 1000 mL of 1 M KMnO_4 solution contain $\text{KMnO}_4 = 1 \text{ mol}$

$$\therefore 100 \text{ mL of } 0.1 \text{ M } \text{KMnO}_4 \text{ solution contain } \text{KMnO}_4 = \frac{1}{1000} \times 100 \times 0.1 \text{ mol} = 0.01 \text{ mol}$$

As explained in example 1 above, 1 mole of KMnO_4 requires electricity = 5 F

$$\therefore 0.01 \text{ mol of } \text{KMnO}_4 \text{ will require electricity} = 0.01 \times 5 \text{ F} = 0.05 \text{ F} = 0.05 \times 96500 \text{ C} = 4825 \text{ C}$$

20. Define molar conductivity of an electrolyte solution. What is the effect of temperature on molar conductivity?

Ans. Conductance of an electrolyte solution containing 1 mol of electrolyte is called molar conductance.

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

It increases with temperature.

Short Answer Type Questions (3 mark)

21. At 291 K, the molar conductivities at infinite dilution of NH_4Cl , NaOH and NaCl are 129.8, 217.4 and 108.9 S cm^2 respectively. If the molar conductivity of a centinormal solution of NH_4OH is 9.33 S cm^2 , what is the percentage dissociation of NH_4OH at this dilution? Also calculate the dissociation constant of NH_4OH .

Ans. Here, we are given: Λ° for $\text{NH}_4\text{Cl} = 129.8 \text{ S cm}^2$, Λ° for $\text{NaOH} = 217.4 \text{ S cm}^2$, Λ° for $\text{NaCl} = 108.9 \text{ S cm}^2$

By Kohlrausch's law, Λ° for $\text{NH}_4\text{OH} = \lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{OH}^-}^\circ = \Lambda^\circ(\text{NH}_4\text{Cl}) + \Lambda^\circ(\text{NaOH}) - \Lambda^\circ(\text{NaCl})$

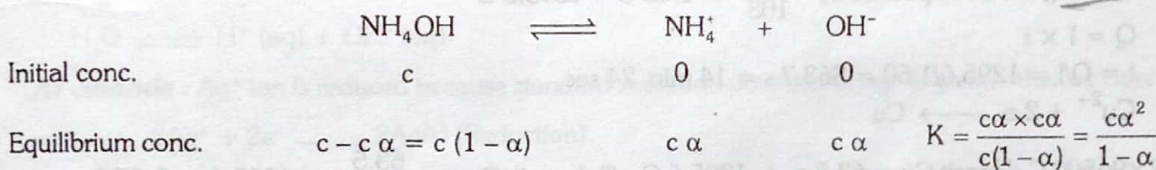
$$= 129.8 + 217.4 - 108.9 = 238.3 \text{ S cm}^2$$

$$\Lambda_c = 9.33 \text{ S cm}^2 \text{ (Given)}$$

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

or percentage dissociation = $0.0392 \times 100 = 3.92\%$

Calculation of dissociation constant



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

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

22. A galvanic cell is constructed with Ag/Ag^+ as one electrode and $\text{Fe}^{2+}/\text{Fe}^{3+}$ as the second electrode. Calculate the concentration of Ag^+ ions at which the E.M.F. of the cell will be zero at equimolar concentrations of Fe^{2+} and Fe^{3+} ions. Given $E_{\text{Ag}^+/\text{Ag}}^\circ = 0.80\text{V}$, $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = 0.77\text{V}$.

Ans. Given electrode potential values show that EMF of the cell will be positive only if reduction occurs at silver electrode.

Therefore, the cell reaction will be: $\text{Fe}^{2+} + \text{Ag}^+ \rightarrow \text{Fe}^{3+} + \text{Ag}$

Hence, the cell may be represented as: $\text{Fe}^{2+} | \text{Fe}^{3+} || \text{Ag}^+ | \text{Ag}$

$$\therefore E_{\text{cell}}^\circ = E_{\text{Ag}^+/\text{Ag}}^\circ - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = 0.80 - 0.77 = 0.03\text{V}$$

Applying Nernst equation to the above reaction, $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}][\text{Ag}]}{[\text{Fe}^{2+}][\text{Ag}^]}$

But $[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$ (Given) and $[\text{Ag}] = 1$.

$$\therefore E_{\text{cell}} = E_{\text{cell}}^\circ - 0.0591 \log \frac{1}{[\text{Ag}^]}$$

$$\therefore 0 = 0.03 + 0.0591 \log [\text{Ag}^]$$

$$\text{or } \log [\text{Ag}^] = -\frac{0.03}{0.0591} = -0.5076 = 1.4924 \text{ or } [\text{Ag}^] = \text{Antilog } 1.4924 = 3.1 \times 10^{-1} = 0.31 \text{ M}$$

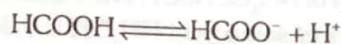
23. The molar conductivity of 0.025 mol L⁻¹ methanoic acid is 46.1 S cm² mol⁻¹. Calculate its degree of dissociation and dissociation constant.

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

Ans. $\Lambda_m^\circ(\text{HCOOH}) = \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{HCOO}^-) = 349.6 + 54.6 \text{ S cm}^2 \text{ mol}^{-1} = 404.2 \text{ S cm}^2 \text{ mol}^{-1}$

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

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



Initial conc.

$c \text{ mol L}^{-1}$

Conc. at eqm.

$c(1 - \alpha)$

$$\therefore K_a = \frac{c\alpha \cdot c\alpha}{c(1 - \alpha)} = \frac{c\alpha^2}{1 - \alpha} = \frac{0.025 \times (0.114)^2}{1 - 0.114} = \mathbf{3.67 \times 10^{-4}}$$

24. Three electrolytic cells A, B and C containing electrolytes ZnSO₄, AgNO₃ and CuSO₄ respectively were connected in series. A steady current of 1.50 ampere was passed through them until 1.45 g of Ag were deposited at the cathode of cell B. How long did the current flow? What mass of copper and zinc were deposited?

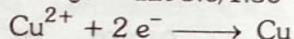
(At. wts. of Cu = 63.5, Zn = 65.3, Ag = 108)

Ans. $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$, i.e., 108 g of Ag are deposited by 1 F = 96500 C

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

$$Q = I \times t$$

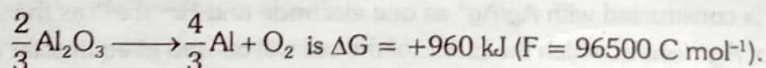
$$\text{or } t = Q/I = 1295.6/1.50 = 863.7 \text{ s} = 14 \text{ min, } 24 \text{ sec.}$$



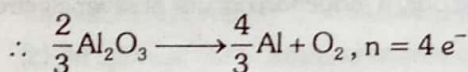
$$\text{i.e., } 2 \times 96500 \text{ C deposit Cu} = 63.5 \text{ g} \therefore 1295.6 \text{ C will deposit Cu} = \frac{63.5}{2 \times 96500} \times 1295.6 = \mathbf{0.426 \text{ g}}$$

$$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn} \therefore \text{Zn deposited} = \frac{65.3}{2 \times 96500} \times 1295.6 = \mathbf{0.438 \text{ g.}}$$

25. Estimate the minimum potential difference needed to reduce Al₂O₃ at 500°C. The free energy change for the decomposition reaction



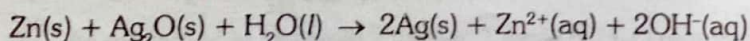
Ans. $\text{Al}_2\text{O}_3(2 \text{ Al}^{3+} + 3 \text{ O}^{2-}) \longrightarrow 2 \text{ Al} + \frac{3}{2} \text{ O}_2, n = 6 e^-$



Substituting $\Delta G = +960 \text{ kJ} = +960,000 \text{ J}$ and $n = 4$ in the equation, $\Delta G = -nFE$, we get $960,000 = -4 \times 96500 \times E$ or $E = -2.487 \text{ V}$

\therefore Minimum potential difference needed to reduce Al₂O₃ is **2.487 V**.

26. Calculate the equilibrium constant for the reaction.



when $E_{\text{cell}}^\circ = 1.11 \text{ volt}$ at 298 K

Ans. We know, $k_c = \text{Antilog} \left(\frac{nE^\circ}{0.0591} \right)$

$$= \text{Antilog} \left(\frac{2 \times 1.11}{0.0591} \right) = \mathbf{3.65 \times 10^{37}}$$

29. 1.0 N solution of a salt surrounding two platinum electrodes 2.1 cm apart and 4.2 sq cm in area was found to offer a resistance of 50 ohm. Calculate the equivalent conductivity of the solution.

Ans. Given, $l = 2.1$ cm, $a = 4.2$ sq cm, $R = 50$ ohm

$$\text{Specific conductance, } k = \frac{l}{a} \cdot \frac{1}{R}$$

$$\text{or } k = \frac{2.1}{4.2} \times \frac{1}{50} = 0.01 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$$

$$\text{Equivalent conductivity} = k \times V$$

$V =$ the volume containing 1 g equivalent = 1000 mL

So, Equivalent conductivity = 0.01×1000

$$= \mathbf{10 \text{ ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}}$$

30. The measured resistance of a conductivity cell containing 7.5×10^{-3} M solution of KCl at 25°C was 1005 ohm. Calculate :

(i) Specific conductance;

(ii) Molar conductance of the solution. [Cell constant = 1.25 cm^{-1}]

Ans. We know,

$$\text{(i) Specific conductance, } k = \frac{1}{R} \times \text{cell constant}$$

$$= \frac{1}{1005} \times 1.25$$

$$= 1.243 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$$

(ii) Molar conductance \wedge_m of solution may be calculated as,

$$\wedge_m = k \times \frac{1000}{M}$$

$$= 1.243 \times 10^{-3} \times \frac{1000}{7.5 \times 10^{-3}}$$

$$= \mathbf{165.73 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}}$$

EXERCISE-1

PREVIOUS YEARS BOARD PROBLEMS

CBSE 2016

- (a) Calculate $E_{\text{cell}}^{\circ} = 0.261\text{V}$ for the following reaction at 298 K:
 $2\text{Cr}(s) + 3\text{Fe}^{2+}(0.01\text{M}) \rightarrow 2\text{Cr}^{3+}(0.01\text{M}) + 3\text{Fe}(s)$
 Given : $E_{\text{cell}}^{\circ} = 0.261\text{V}$

(b) Using the E° values of A and B, predict which one is better for coating the surface of iron [$E^{\circ}(\text{Fe}^{2+}/\text{Fe}) = -0.44\text{V}$] to prevent corrosion and why?
 Given : $E^{\circ}(\text{A}^{2+}/\text{A}) = -2.37\text{V}$; $E^{\circ}(\text{B}^{2+}/\text{B}) = -0.14\text{V}$
- (a) The conductivity of 0.001 mol L^{-1} solution of CH_3COOH is $3.905 \times 10^{-5}\text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociations (α).
 Given $\lambda^{\circ}(\text{H}^{+}) = 349.6\text{ S cm}^2\text{ mol}^{-1}$ and $\lambda^{\circ}(\text{CH}_3\text{COO}^{-}) = 40.9\text{ S cm}^2\text{ mol}^{-1}$.

(b) Define electrochemical cell. What happens if external potential applied becomes greater than E_{cell}° of electrochemical cell?

CBSE 2015

- Calculate the time to deposit 1.5 g of silver at cathode when a current of 1.5 A was passed through the solution of AgNO_3 . (Molar mass of Ag = 108 g mol^{-1} , $1\text{ F} = 96500\text{ C mol}^{-1}$)
- Calculate E_{cell}° and $\Delta_r G^{\circ}$ for the following reaction at 25°C :
 $\text{A}^{2+} + \text{B}^{+} \rightarrow \text{A}^{3+} + \text{B}$
 Given : $K_c = 10^{10}$, $1\text{ F} = 96500\text{ C mol}^{-1}$

CBSE 2014

- (a) Calculate $\Delta_r G^{\circ}$ for the reaction
 $\text{Mg}(s) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu}(s)$
 Given: $E_{\text{cell}}^{\circ} = +2.71\text{V}$, $1\text{ F} = 96500\text{ C mol}^{-1}$

(b) Name the type of cell which was used in Apollo space program for providing electrical power.
- Define the following terms :
 (a) Molar conductivity (\wedge_m)
 (b) Secondary batteries

CBSE 2013

- The standard electrode potential (E°) for Daniel cell is $+1.1\text{ V}$. Calculate the ΔG° for the reaction
 $\text{Zn}(s) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(s)$ ($1\text{ F} = 96500\text{ C mol}^{-1}$) [$\Delta G^{\circ} = 212300\text{ J mol}^{-1}$]
- Calculate the emf of the following cell at 25°C
 $\text{Ag}(s) | \text{Ag}^{+}(10^{-3}\text{M}) || \text{Cu}^{2+}(10^{-1}\text{M}) | \text{Cu}(s)$
 Given, $E_{\text{cell}}^{\circ} = +0.46\text{V}$ and $\log 10^n = n$. [0.3125 V]

CBSE 2012

1. A voltaic cell is set up at 25° C with the following half cells.
 Al | Al³⁺ (0.001 M) and Ni | Ni²⁺ (0.50 M)
 Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.
 $E_{\text{Ni}^{2+}/\text{Ni}}^0 = -0.25\text{V}$ and $E_{\text{Al}^{3+}/\text{Al}}^0 = -1.66\text{V}$ ($\log 8 \times 10^{-6} = -5.0969$)
2. The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm² mol⁻¹. Calculate the conductivity of this solution.
[0.208 S cm⁻¹]
3. The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm is 5.55 × 10³ Ω. Calculate its resistivity, conductivity and molar conductivity.
[ρ = 7.135 W cm, k = 1.148 × 10² S cm⁻¹, Λ_m = 229.5 S cm² mol⁻¹]

CBSE 2011

1. Calculate the potential for half cell containing 0.10 MK₂Cr₂O₇(aq), 0.20 MCr³⁺(aq) and 1.0 × 10⁻⁴ MH⁺(aq). The half cell reaction is Cr₂O₇²⁻(aq) + 14H⁺(aq) + 6e⁻ → 2Cr³⁺(aq) + 7H₂O(l) and the standard electrode potential is given as E⁰ = 1.33 V
[0.7823 V]
2. Calculate the equilibrium constant, K for the reaction at 298 K, Zn(s) + Cu²⁺(aq) ⇌ Zn²⁺(aq) + Cu(s);
 ΔG⁰ = -212.300 kJ mol⁻¹ [Given, E_{Zn²⁺/Zn}⁰ = -0.76V, E_{Cu²⁺/Cu}⁰ = +0.34V]
[1.6 × 10³⁷]
3. What type of a battery is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery when current is drawn from it.
4. How many moles of mercury will be produced by electrolysis of 1.0 M Hg(NO₃)₂ solution with a current of 2.00 A for three hours? [Hg(NO₃)₂ = 200.6 g mol⁻¹]
[0.112 mol]
5. In the electrolysis of aqueous sodium bromide, there are two possible anodic reactions.
 2H₂O(l) → O₂(g) + 4H⁺(aq) + 4e⁻, E⁰ = 1.23V ; 2Br⁻(aq) → Br₂(g) + 2e⁻, E⁰ = 1.08V
 Which reaction occurs at anode and why?
6. Give an example of a fuel cell and write the cathode and anode reactions for it.
7. Write the overall reaction that occurs during use (discharging) of nickel-cadmium cell. Is it a primary or a secondary cell? Mention its one merit over the lead storage cell.
8. An aqueous solution of copper sulphate, CuSO₄ was electrolysed between platinum electrodes using a current of 0.1287 ampere for 50 minutes. [Given atomic mass of Cu = 63.5 g mol⁻¹]
 (i) Write the cathodic reaction.
 (ii) Calculate (a) Electric charge massed during electrolysis. (b) Mass of copper deposited at the cathode.
 [Given, If = 96500 C mol⁻¹]
[(a) 386.1C (b) 0.127 g]

CBSE 2010

- Given that the standard electrode potentials (E°) of metals are
 $K^+ / K = -2.93 \text{ V}$, $Ag^+ / Ag = 0.80 \text{ V}$, $Cu^{2+} / Cu = 0.34 \text{ V}$, $Mg^{2+} / Mg = -2.37 \text{ V}$,
 $Cr^{3+} / Cr = -0.74 \text{ V}$, $Fe^{2+} / Fe = -0.44 \text{ V}$,
 Arrange these metals in an increasing order of their reducing power.
- What is meant by limiting molar conductivity?
- State and explain Kohlrausch's law of independent migration of ion. Write an expression for the molar conductivity of acetic acid at infinite dilution according to Kohlrausch law.
- State and explain Kohlrausch's law of independent migration of ions. How can the degree of dissociation of acetic acid be calculated from its molar conductance data?
- What is a nickel-cadmium cell? State its one merit and one demerit over lead storage cell. Write the overall reaction that occurs during discharging of this cell.

CBSE 2009

- Two half reactions of an electrochemical cell are given below
 $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$; $E^\circ = +1.51 \text{ V}$
 $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$; $E^\circ = +0.15 \text{ V}$
 Construct the redox equation from the standard potential of the cell and predict if the reaction is reactant favoured or product favoured.
- A copper-silver cell is set up. The copper ion concentration is 0.10 M. The concentration of silver ion is not known. The cell potential when measured was 0.422 V. Determine the concentration of silver ions in the cell.
 [Given, $E^\circ_{Ag^+/Ag} = +0.80 \text{ V}$, $E^\circ_{Cu^{2+}/Cu} = +0.34 \text{ V}$] **[[Ag⁺] = 7.17 × 10⁻² M]**
- Calculate the cell emf and $\Delta_r G^\circ$ for the cell reaction at 25°C.
 $Zn(s) | Zn^{2+} (0.1 \text{ M}) || Cd^{2+} (0.01 \text{ M}) | Cd (s)$
 [Given, $E^\circ_{Zn^{2+}/Zn} = -0.763 \text{ V}$, $E^\circ_{Cd^{2+}/Cd} = -0.403 \text{ V}$, $1 \text{ F} = 96500 \text{ C mol}^{-1}$, $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$]
- Calculate the standard electrode potential of Ni²⁺ | Ni electrode if emf of the cell,
 $Ni(s) | Ni^{2+} (0.01 \text{ M}) || Cu^{2+} (0.1 \text{ M}) | Cu(s)$ is 0.059 V. (Given, $E^\circ_{Cu^{2+}/Cu} = +0.34 \text{ V}$) **[0.31 V]**
- (a) What type of 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.
 (b) Calculate the potential for half-cell containing 0.10 M $K_2Cr_2O_7(aq)$, 0.20 M $Cr^{3+}(aq)$ and $1.0 \times 10^{-4} \text{ M H}^+(aq)$
 The half-cell reaction is $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ and the standard electrode potential is given as $E^\circ = 1.33 \text{ V}$. **[0.7824 V]**

EXERCISE-1

SOLUTIONS OF PREVIOUS YEARS BOARD PROBLEMS

ELECTROCHEMISTRY

CBSE 2016

Sol.1 (a) $E_{\text{cell}} = E_{\text{cell}}^{\ominus} - \frac{0.059}{n} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3}$

$$0.261 \text{ V} = E_{\text{cell}}^{\ominus} - \frac{0.059}{6} \log \frac{[0.01]^2}{[0.01]^3}$$

$$0.261 \text{ V} = E_{\text{cell}}^{\ominus} - \frac{0.059}{6} \log 100$$

$$E_{\text{cell}}^{\ominus} = 0.261 + 0.0197$$

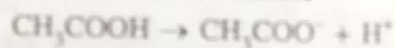
$$= 0.2807 \text{ V}$$

(b) A because low value of SRP

Sol.2 (a) $\Lambda_m^{\ominus} = \kappa \times 1000 / C$

$$= 3.905 \times 10^{-5} \times 1000 / 0.001$$

$$= 39.05 \text{ S cm}^2 / \text{mole}$$



$$\Lambda^{\ominus} \text{CH}_3\text{COOH} = \lambda^{\ominus} \text{CH}_3\text{COO}^- + \lambda^{\oplus} \text{H}^+$$

$$= 40.9 + 349.6$$

$$\Lambda^{\ominus} \text{CH}_3\text{COOH} = 390.5 \text{ S cm}^2 / \text{mol}$$

$$\alpha = \frac{\Lambda_m^{\ominus}}{\Lambda^{\ominus}}$$

$$= 39.05 / 390.5$$

$$= 0.1$$

(b) An electrochemical cell is a device in which chemical energy of the redox reaction is converted into electrical energy. While electrolytic cell do the reverse.

→ e^- flow from Cu to Zn and current flows from Zn to Cu.

CBSE 2015

Sol.1 Wt. of Ag = 1.5g Current = $i = 1.5 \text{ amp}$

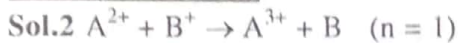
Molecular mass = 108 g/mol $F = 96500 \text{ C/mol}$

$n =$ number of electron transferred

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

$$\therefore t = \frac{W \times n \times F}{M \times I} = \frac{1.5 \times 1 \times 96500}{108 \times 1.5}$$

$$= 893.51 \text{ s or } 14.89 \text{ min}$$



$K_c = 10^{10}$ $F = 96500 \text{ C/mol}$ $T = 25^\circ\text{C} = 298\text{K}$

$\Delta G^\circ = ?$ $E^\circ = ?$ $R = 8.314 \text{ J/K/mol}$

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

$\Delta G^\circ = -2.303 \times 8.314 \text{ J/K/mol} \times 298\text{K} \times \log 10^{10}$

$\therefore \Delta G^\circ = -57058.4 \text{ J/mol}$ or -57.0584 kJ/mol

$\Delta G^\circ = -57058.4 \text{ J/mol} = -nFE^\circ = -1 \times 96500 \times E^\circ$

$\therefore E^\circ = \frac{-57058.4}{-96500} = 0.591\text{V}$

$\therefore \Delta G^\circ = -nFE^\circ$
 $E^\circ_{\text{cell}} = \frac{\Delta G^\circ}{-nF}$

CBSE 2014

Sol.1 (a) $\Delta G^\circ = -nFE^\circ$

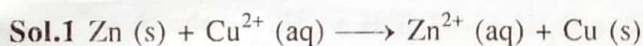
$= -2 \times 96500 \times (2.71) = -523030 \text{ J}$

(b) Fuel cell

Sol.2 (i) Molar conductivity, \wedge_m , is defined by k/c where c is the concentration. Conductivity decreases but molar conductivity increases with decrease in concentration. It increases slowly with decrease in concentration for strong electrolytes while the increase is very steep for weak electrolytes in very dilute solutions.

(ii) A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. A good secondary cell can undergo a large number of discharging and charging cycles.

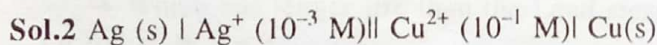
CBSE 2013



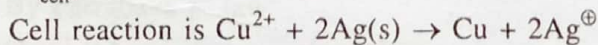
$E^\circ = 1.1\text{V}$

$\Delta G^\circ = -nFE^\circ$

$= -2 \times 96500 \times (1.1) = -212300 \text{ J}$



$E^\circ_{\text{cell}} = +0.46 \text{ V}$



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

$E_{\text{cell}} = 0.46 - \frac{0.059}{2} \log 10^{-5}$

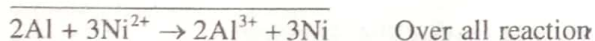
$= 0.46 + .147 = .6075 \text{ V}$

CBSE 2012

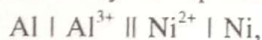
Sol.1 Given :

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

Half cell equations are



The cell may be represented as



$$E^\circ_{\text{cell}} = E^\circ_{\text{right}} - E^\circ_{\text{left}}$$

$$= (-0.25) - (-1.66)$$

$$= -0.25 + 1.66 \Rightarrow E^\circ_{\text{cell}} = 1.41 \text{ V.}$$

Sol.2 $\lambda_m = \frac{K \times 1000}{C}$

$$K = \frac{138.9 \times 1.5}{1000} = 0.20835 \text{ Scm}^{-1}$$

Sol.3 $R = \rho \frac{\ell}{A}$ or $\rho = \frac{RA}{\ell} = \frac{5.55 \times 10^3 \Omega \times 0.785 \text{ cm}^2}{50 \text{ cm}} = 87.135 \Omega \text{ cm}$

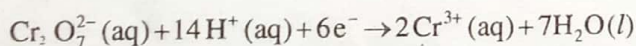
$$\text{Conductivity} = K = \frac{1}{\rho} = \left(\frac{1}{87.135} \right) \text{ Scm}^{-1} = 0.01148 \text{ Scm}^{-1}$$

$$\text{Molar conductivity } \lambda_m = \frac{K \times 1000}{C}$$

$$= \frac{0.01148 \text{ Scm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.05 \text{ mol L}^{-1}} = 229.6 \text{ Scm}^2 \text{ mol}^{-1}$$

CBSE 2011

Sol.1 The cell reaction for the cell:



$$E = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Cr}^{3+}(\text{aq})]^2}{[\text{H}^+(\text{aq})]^{14} [\text{Cr}_2\text{O}_7^{2-}]}$$

$$E_{\text{cell}} = 1.33 - \frac{0.059}{6} \log \frac{(0.2)^2}{(1.0 \times 10^{-4})^{14} (0.1)}$$

$$E_{\text{cell}} = 1.33 - 0.556 = 0.774$$

Sol.2 $\Delta G^\circ = -2.303 RT \log K_c$

$$+212.300 = +2.303 \times 8.314 \times 298 \log K_c$$

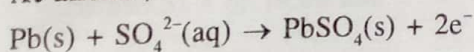
$$\log K_c = \frac{212.300}{5705.84} = 0.037$$

$$K_c = \text{Anti log } 0.037, K_c = 1.6 \times 10^{37}$$

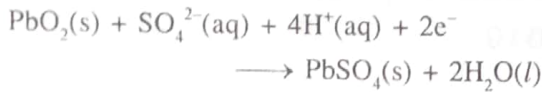
Sol.3 The lead storage battery is the most important secondary cell.

The cell reactions when the battery is in use are given below.

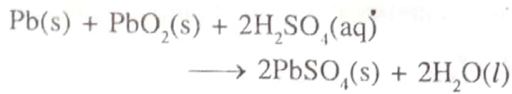
At anode ;



At cathode :



the overall cell reaction is



Sol.4 Time = 3 hours

$$= 3 \times 60 \times 60 = 10800 \text{ Sec.}$$

$$\text{Current} = 2\text{A}$$

$$\text{Charge} = \text{Current} \times \text{time}$$

$$= 2 \times 10800 = 21600 \text{ C}$$

According to the questions

deposited mass of mercury

$$W = ZIt = \frac{E}{96487} \times I \times t \quad \because I \times t = 21600 \text{ C}$$

$$W = \frac{200.6}{2 \times 96487} \times 21600 = 22.45 \text{ g}$$

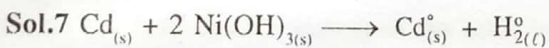
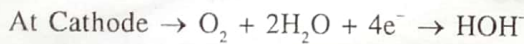
$$\text{Number of mole of Hg} = \frac{22.45}{200}$$

$$\text{Number of moles of mercury} = 0.11 \text{ mole}$$

Log n

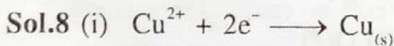
Sol.5 Br⁻/Br At anode due to low SRP value.

Sol.6 H₂O₂ Fuel Cell



→ It is a secondary cell

→ Which has longer life than the Lead storage cell but more expensive to manufacture.



By Faradays Ist law

$$\begin{aligned} \text{(ii) } Q &= I \times t \\ &= 0.1287 \times 3000 \\ &= 386.1 \text{ C} \end{aligned} \quad \begin{cases} t = 50 \text{ min} \\ s = 50 \times 60 \text{ sec.} \\ = 3000 \text{ sec.} \end{cases}$$

$$\text{(b) } m = z \times i \times t$$

$$m = \frac{\text{Eq. wt}}{96500} \times i \times t$$

$$m = \frac{63.5}{2 \times 96500} \times 386.1$$

$$m = 0.127 \text{ g}$$

CBSE 2010

Sol.1 $\text{Ag} < \text{Cu} < \text{Fe} < \text{Cr} < \text{Mg} < \text{K}$

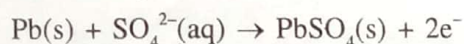
Sol.2 Limiting molar conductivity: The molar conductivity of a solution at infinite dilution is called limiting molar conductivity and is represented by the symbol \wedge_m° .

Sol.3 The law states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contribution of its anion and cation.

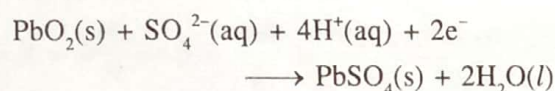
Sol.4 The lead storage battery is the most important secondary cell.

The cell reactions when the battery is in use are given below.

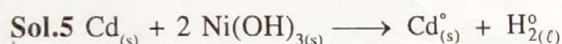
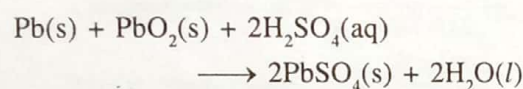
At anode ;



At cathode :



the overall cell reaction is

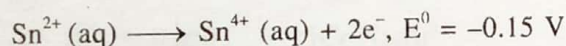


→ It is a secondary cell

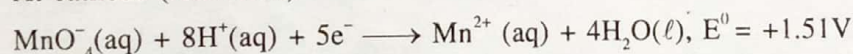
→ Which has longer life than the Lead storage cell but more expensive to manufacture.

CBSE 2009

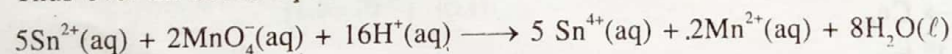
Sol.1 At anode (oxidation)



At cathode (reduction)



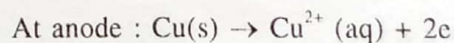
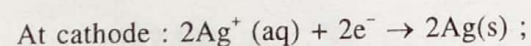
Thus over all redox equation is



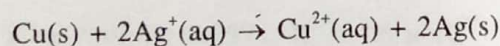
$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = 1.51 - 0.15 = 1.36 \text{ V}$$

Hence the reaction favours formation of product.

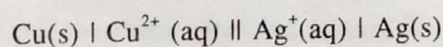
Sol.2 Half cell reactions :



The cell reaction is



The cell can be represented as



$$\begin{aligned} \therefore E_{\text{cell}}^0 &= E_{\text{cathode}}^0 - E_{\text{anode}}^0 \\ &= 0.80 - 0.34 = 0.46 \text{ V} \end{aligned}$$

