Chapter 3
Electrochemistry

---

1 Marks Questions

1. Can you store AgCl solution in Zinc pot?

Ans. No. We can't store AgCl solution in Zinc pot because standard electrode potential of Zinc is less than silver.

2. Define the term – standard electrode potential?

Ans. When the concentration of all the species involved in a half-cell is unity, then the electrode potential is called standard electrode potential.

3. What is electromotive force of a cell?

Ans. Electromotive force of a cell is also called the cell potential. It is the difference between the electrode potentials of the cathode and anode.

$$E_{cell} = E_{cathode} - E_{anode}$$

4. Can an electrochemical cell act as electrolytic cell? How?

Ans. Yes, An electrochemical cell can be converted into electrolytic cell by applying an external opposite potential greater than its own electrical potential.

5. Single electrode potential cannot be determined. Why?

Ans. A single half cell does not exist independently as reduction and oxidation occur simultaneously therefore single electrode potential cannot be measured.

6. What is SHE? What is its electrode potential?

Ans. SHE stands for standard Hydrogen electrode. By convention, its electrode potential is taken as 0 (zero).

7. What does the positive value of standard electrode potential indicate?

Ans. The positive value of standard electrode potential indicates that the element gets reduced more easily than H^+ ions and its reduced form is more stable than Hydrogen gas.

8. What is an electrochemical series? How does it predict the feasibility of a certain redox reaction?

Ans. The arrangement of metals and ions in increasing order of their electrode potential values is known as electrochemical series.

The reduction half reaction for which the reduction potential is lower than the other will act as anode and one with greater value will act as cathode. Reverse reaction will not occur.

9. Give some uses of electrochemical cells?

Ans. Electrochemical cells are used for determining the

a) pH of solutions

b) solubility product and equilibrium constant

c) in potentiometric titrations

10. A cell is represented by notation – $Cu(s) / cu^{2+}(aq) // Ag^+(aq) / Ag(s)$

Calculate e.m.f of the cell if $E^0 Cu^{2+} / Cu = +0.34V$ **and** $E^0 Ag^+ / Ag = 0.08V$ **?**

Ans. $E^0_{cell} = E^0_{cathode} - E^0_{Anode}$

$= E^0_{Ag+/Ag} - E^0_{Cu^{2+}/Cu}$

=0.80V – (+0.34V)

=+0.46V

11. What would happen if Nickel spatula is used to stir a solution of $CuSO_4$ **?**

$E^0 Cu^{2+} / Cu = 0.34\ V$, $E^0_{Ni}\ 2^+ / Ni = -0.25V$ **?**

Ans. From the reduction potential values, it is indicated that Nickel (more negative value) is more reactive than copper and will, then displace copper from $CuSO_4$

$$Ni(s)+Cu^{2+}(aq)\rightarrow \grave{a}Ni^{2}+(aq)+Cu(s).$$

12. State the factors that affect the value of electrode potential?

Ans. Factors affecting electrode potential values are –

a) Concentration of electrolyte

b) Temperature.

13. Write Nernst equation for a Daniel cell?

Ans. Daniel cell:

$$Zn(s)/Zn^{2}+(aq)//Cu^{2}+(aq)/Cu(s)$$

Nernst equation – at 298 K

$$E_{cell}=\left(E^{0}{}_{Cu^{2}+/Cu}-E^{0}{}_{Zn^{2}+/Zn}\right)-\frac{0.059}{2}\log\frac{[Zn^{2+}]}{[cu^{2+}]}$$

14. Define the term specific resistance and give its SI unit

Ans. The specific resistance of a substance is its resistance when it is one meter long and its area of cross Section is one m^2. Its SI unit is Ωm (ohm meter)

15. Give the unit of conductance?

Ans. The SI unit of conductance is Siemens, denoted by the symbol, S & is equal to Ω^{-1}.

16. What do you understand by the term- conductivity?

Ans. Conductivity of a material in Sm^{-1} is its conductance when it is 1m long and its area of cross - section is $1m^{2}$. It is represented by κ.

17. What do you understand by strong and weak electrolytes?

Ans. An electrolyte that ionises completely in solution is a strong electrolyte eg. NaCl, $CaCl_2$ etc and an electrolyte that ionizes partially in solution is weak electrolyte eg CH_3COOH, NH_4OH etc .

18. State kohlrausch's Law?

Ans. Kohlrausch Law of independent migration of ion states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

19. What is meant by Faraday's constant?

Ans. Faraday's constant is the quantity of electricity carried by one mole of electrons.

1 F = 96500 C/mol

20. How many faradays are needed to reduce 3g mole of Cu^{2+} to Cu metal?

Ans. $Cu^{2+} + 2e^- \rightarrow Cu$

Two faradays are needed to reduce 1g mole Cu^{2+} $\therefore$ 6 Faradays will be needed to reduce 3g mole of Cu^{2+} .

21. Give the reaction taking place in lead storage battery when it is on charging?

Ans. When the lead storage battery is on charging –

$$2\ PbSO_4(s) + 2H_2O(e) \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$$

22. A Leclanche cell is also called dry cell. Why?

Ans. Leclanche cell consists of zinc anode (container) and carbon cathode. The electrolyte is a moist paste of MnO_2, $ZnCl_2$, NH_4Cl and carbon black. Because there is no free liquid in the cell, it is called dry cell.

23. Why is the voltage of a mercury cell constant during its working?

Ans. As all the products and reactants are either in solid or liquid state, their concentration does not change with the use of the cell.

24. What are fuel cells?

Ans. A fuel cell is a galvanic cell for converting the energy of a fuel directly into electrical energy without use of a heat engine.

25. What do you understand by corrosion?

Ans. Corrosion is an electrochemical phenomenon in which metal gets decomposed in the presence of air and water and forms compounds like oxides, sulphates, carbonates, sulphides etc.

26. Name two metals that can be used for cathodic protection of iron?

Ans. Names of the metals are – Zinc and Magnesium.

27. 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. The following is the order in which the given metals displace each other from the solution of their salts. Mg, Al, Zn, Fe, Cu

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

Ans. Methane and methanol can be used as fuels in fuel cells.

29. Suggest a list of metals that are extracted electrolytically.

Ans. Metals that are on the top of the reactivity series such as sodium, potassium, calcium, lithium, magnesium, aluminium are extracted electrolytically.

2 Marks Questions

1. How is standard electrode potential of a cell related to :-

1) Equilibrium constant?

2) Gibbs free energy change.

Ans. (i) Standard electrode potential and equilibrium constant

$$E^0_{cell} = \frac{2.303RT}{nF}\log k_c$$

Where E^0_{cell} = standard electrode potential of cell

R = Gas constant

T = temperature in Kelvin

n = no. of electrons.

F = Faraday’s constant and

Kc = Equilibrium constant

(ii) Standard electrode potential and Gibbs free energy change-

$$\Delta G^0 = -n\,F\,E^0 cell$$

Where ΔG^0 = Change in Gibbs’ free energy

n = No. of electrons

F = Faraday’s Constant

E^0_{cell} = Standard electrode Potential of cell.

2. What is the half cell potential for Fe^{3+}/Fe electrode in which $\left[Fe^{3+}\right] = 0.1\,m$.

$$E^0 Fe^{3+}/Fe = +0.771V$$

Ans. $Fe^{3+} + 3e^- \rightarrow Fe$

According to Nernst Equation –

$$E_{Fe^{3+}/Fe} = E^{0}_{Fe^{3+}/Fe} - \frac{0.059}{n} \log \frac{1}{[Fe^{3+}]}$$

$= 0.771\ V - \frac{0.059}{3} \log \frac{1}{0.1}$

$= 0.771\ V - 0.0197\ V$

$= +0.7513V$

3. Calculate pH of following half cell. Pt , H_2 / H_2SO_4, if its electrode potential is 0.03V.

Ans. $P^{H} = -Log\left[H^{+}\right]$

The cell reaction is –

$$H^{+} + e \longrightarrow H_2(g)$$

According to Nearest Equation

$$E = E^{0} - \frac{0.059}{n} \log \frac{1}{[H^{+}]}$$

$0.03V = 0 + \frac{0.059}{1} \left(-\log \frac{1}{[H^{+}]} \right)$

$= 0 + 0.059_{P}{}^{H}$

$PH = \frac{0.03V}{0.059} = 5.07\ V$

4. What are the factors on which conductivity of an electrolyte depend?

Ans. The conductivity of an electrolyte depends upon

i) The nature of electrolyte

ii) Size of the ions produced

iii) Nature of solvent and its viscosity.

iv) Concentration of electrolyte.

v) Temperature

5. How is molar conductance related to conductivity of an electrolyte ?

Ans. Molar conductance, Ωm is related to conductively by the relation.

$$\Omega m = \frac{k}{c}$$

Where κ = conductivity in s/m.

C = concentration in mol / m^3

6. Write an expression relating cell constant and conductivity?

Ans. Cell constant and conductivity are related by the expression-

$\kappa = \frac{G}{R}$ where G = Cell constant

κ = conductivity

R = Resistance.

7. The conductivity of an aqueous solution of NaCl in a cell is $92\Omega^{-1}\ cm^{-1}$ the resistance offered by this cell is 247.8Ω. Calculate the cell constant?

Ans. Specific conductivity = $\frac{\text{cell constant}}{\text{Resistance}}$

Or cell constant = $conductivity \times Resistance$

= 92 $\Omega^{-1}\ \text{cm}^{-1} \times 247.8\ \Omega$

= 22797.6 Ω^{-1}

8. The molar conductivity of 0.1M CH_3COOH solution is $4.6\ cm^2\ mol^{-1}$. What is the conductivity and resistivity of the solution?

Ans. $\lambda m = \frac{\kappa}{C} \times 1000\ \text{S cm}^2\ \text{mol}_{-1}$

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

κ = $\frac{\lambda m \times M}{1000}$

= $\frac{4.6\ S\ cm^2 / mol \times 0.1\text{m}}{100}$

= 0.00046 s/cm

Resistivity = $\frac{1}{\kappa}$

= $\frac{1}{0.00046\ \text{S cm}^{-1}} = 2174\ \Omega\ \text{cm}$.

9. The conductivity of metals decreases while that of electrolytes increases with increases in temperature. Why?

Ans. With increase in temperature, the K.E. of metal cation increases and obstructs the free flow of electrons decreasing the conducts of metal while in case of electrolytes, increased temperature increases the mobility of ions this increases the conductance of ions.

10. The measured resistance of a cell containing $7.5 \times 10^{-3} M$ solution of KCl at $25^0 C$ was 1005 Ω calculate

(a) Specific conductance and

(b) Molar conductance of the solution. Cell Constant = $1.25\ cm^{-1}$

Ans. $k = 1.2\ 2/3 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}$

$\lambda m = 165.7\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$.

11. How is Limiting molar conductivity related to

i) degree of ionization and

ii) dissociation constant

Ans. Relation between limiting molar conductance and degree of dissociation –

$\alpha = \dfrac{\Omega m}{\Omega^{\circ} m}$ where α = degree of dissociation

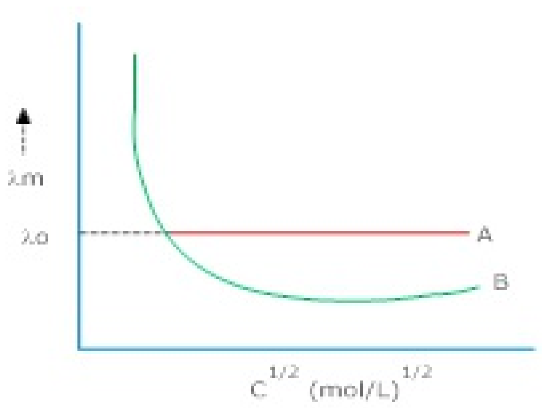
$\lambda m =$ molar conductance molar

λm^0 Limiting molar conductance

Relation between dissociation constant and limiting molar conductance –

$Ka = \dfrac{C\ \lambda \text{m}^2}{\lambda m^0\ (\lambda \text{m}^0 - \lambda \text{m})}$ where c = concentration

12. In fig. (1), identify the nature of electrolyte A& B. In which case it is not possible to obtain value of limiting molar conductance?



Ans. A = strong Electrolyte

B = weak Electrolyte

In case of B , it is not possible to get an exact value of limiting molar conductance.

13. At 298 K , the molar conductivities at infinite dilution of NH_4Cl , NaOH and NaCl are 129.8 , 217.4 and $108.9\ s\ cm^2\ mol^{-1}$ respectively .It molar conductivity of 0.01M NH_4OH solution is $9.33\ s\ cm^2\ mol^{-1}$,calculate the degree of dissociation of NH_4OH at this dilution?

Ans. $\lambda_m^0\ (NH_4OH) = \lambda_m^\circ\ (Na_4Cl) + \lambda_m^\circ\ (NaOH) - \lambda_m^\circ\ (NaCl)$

= 129.8 +217.4 – 108.9 $= 237.35\ cm^2 / mol$

Degree of dissociation, $\alpha = \dfrac{\lambda m}{\lambda m^0} = \dfrac{9.33\ 5\ cm^2 / mol}{237.3\ 5\ cm^2 / mol}$

= 0.039 or 3.9 %.

14. State Faraday's Laws of electrolysis?

Ans. Faraday's Laws of electrolysis

<u>First Law:</u> The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.

<u>Second Law:</u> The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution is proportional to their chemical equivalent weights.

15. How many g of chlorine can be produced by the electrolysis of molten NaCl with a current of 1 amp. for 15 min?

Ans. Q = It $=1\times15\times60=900C$

The reaction is $2Cl^- Cl_2+2e^-$

2mol 1mol 2mol

$\therefore$ 2F . produces 1 mol of Cl_2

1mol of $Cl_2 =$ $71g$

$\therefore$ $2\times$ 96500 C produces 71g of Cl_2

900 C will produce $\frac{71}{2}\times\frac{900}{96500}$ g $=$ $0.331\,g\ of\ Cl_2$.

16. How many electrons flow when a current of 5 amps is passed through a solution for 193 sec. Given f = 96500 C. $N_A=6.002\times10^{23}mol^{-1}$?

Ans. Q = It $=5\times193=965\ C$

96500C = 1 mol of electrons $= 6.022\times10^{23}\,mol^{-1}$

965 C = $6.022\times10^{23}\times\frac{965}{96500}$

$= 6.022\times10^{21}$ electrons.

17. There are two possible reactions for cathode in the electrolysis of aqueous $ZnCl_2$:

$Zn^{2+}(aq)+\rightarrow 2e^- Zn(s)$ **E = -0.76v,** $2H_2O(l)+2e^-\rightarrow H_2(g)+2OH^-(aq)$ **E = - 0.83v**

Which one will take place ?

Ans. Zn^{2+} has higher reduction potential (-0.76v) Than H_2O $(-\ 0.83v)$ and therefore Zn^{2+} is reduced to Zn preferentially at cathode.

18. Silver is deposited on a metallic vessel by passing a current of 0.2 amps. for 3 hrs. Calculate the weight of silver deposited. (At mass of silver = 108 amu, F = 96500 C?

Ans. 2.417 g of silver.

19. What do you mean by primary and secondary battery?

Ans. In the primary batteries, the reaction occurs only once and after the use over a period of time battery becomes dead and cannot be reused again. A secondary battery , after used, can be recharged by passing current through it in the opposite direction so that it can be used again.

20. Name the cell used for low current devices like hearing aids, watches etc. Also give the half cell reactions for such a cell?

Ans. This cell is mercury cell – Half cell reactions are Anode
$Zn(Hg)+2OH^- \rightarrow ZnO+H_2O+2e^-$ and those
$HgO+H_2O+2e^- \rightarrow Hg(e)+2OH^-$

21. Rusting of iron is quicker in saline water than in ordinary water. Explain?

Ans. Saline water consists of greater no. of ions than normal water which increases the electrochemical reaction. This increases rate of corrosion.

22. Enlist the factors affecting corrosion?

Ans. Factors affecting corrosion are -

1) Water and air

2) Presence of electrolytes in water.

3) Presence of gases like CO_2, SO_2.

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

Ans. Given,

$K = 0.0248\ \mathrm{S\ cm^{-1}}$

c = 0.20 M

Therefore, Molar conductivity, $\Lambda_m = \dfrac{K \times 1000}{c}$

$$= \frac{0.0248 \times 1000}{0.2}$$

$$= 124\ \mathrm{Scm^2mol^{-1}}$$

24. The resistance of a conductivity cell containing 0.001M KCl solution at 298 K is 1500Ω. What is the cell constant if conductivity of 0.001M KCl solution at 298 K is $0.146 \times 10^{-3}\ \mathrm{Scm^{-1}}$.

Ans. Given,

Conductivity, $K = 0.146 \times 10^{-3}\ \mathrm{S\ cm^{-1}}$

Resistance, R = 1500Ω

Therefore, Cell constant = $K \times R$

= $0.146 \times 10^{-3} \times 1500$

= $0.219\ \mathrm{cm^{-1}}$

25. In the button cells widely used in watches and other devices the following reaction takes place: $Zn(s) + Ag_2O(s) + H_2O(l) \rightarrow Zn^{2+}(aq) + 2Ag(s) + 2OH^-(aq)$ Determine $\Delta_r G^\ominus$ and $E^\ominus$ for the reaction.

Ans.

$$\begin{array}{l}
Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^- \ ; \ E^\ominus = 0.76\mathrm{V} \\
Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \longrightarrow 2Ag_{(s)} + 2OH^-_{(aq)} \ ; \ E^\ominus = 0.344\ \mathrm{V} \\
\hline
Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)} + 2OH^-_{(aq)} ; \ E^\ominus = 1.104\ \mathrm{V}
\end{array}$$

Therefore, $E^{\ominus}$ = 1.104 V

We know that,

$$\Delta_r G^{\ominus} = -nFE^{\ominus}$$

= $-2 \times 96487 \times 1.04$

= –213043.296 J

= –213.04 kJ

26. Given the standard electrode potentials,

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

$Hg^{2+} / Hg = 0.79V$

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

Arrange these metals in their increasing order of reducing power.

Ans. The lower the reduction potential, the higher is the reducing power. The given standard electrode potentials increase in the order of $K^+ / K < Mg^{2+} / Mg < Cr^{3+} / Cr < Hg^{2+} / Hg < Ag^+ / Ag$.

Hence, the reducing power of the given metals increases in the following order:

Ag < Hg < Cr < Mg < K

27. What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$? Consider the reaction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 8H_2O$

Ans. The given reaction is as follows: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Therefore, to reduce 1 mole of $Cr_2O_7^{2-}$, the required quantity of electricity will be:

=6 F = $6 \times 96487\ C$

= 578922 C

28. Why does the conductivity of a solution decrease with dilution?

Ans. The conductivity of a solution is the conductance of ions present in a unit volume of the solution. The number of ions (responsible for carrying current) decreases when the solution is diluted. As a result, the conductivity of a solution decreases with dilution.

29. Suggest a way to determine the Λ_m^0 value of water.

Ans. Applying Kohlrausch's law of independent migration of ions, the Λ_m^0 value of water can be determined as follows:

$$\Lambda^0_{m(H_2O)} = \lambda^0_{H^+} + \lambda^0_{OH^-}$$

$$= \left(\lambda^0_{H^+} + \lambda^0_{Cl^-}\right) + \left(\lambda^0_{Na^+} + \lambda^0_{OH^-}\right) - \left(\lambda^0_{Na^+} + \lambda^0_{Cl^-}\right)$$

$$= \Lambda^0_{m(HCl)} + \Lambda^0_{m(NaOH)} - \Lambda^0_{m(NaCl)}$$

Hence, by knowing the Λ_m^0 values of HCl, NaOH, and NaCl, the Λ_m^0 value of water can be determined.

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

Ans. Zinc is more reactive than copper. Therefore, zinc can displace copper from its salt solution. If copper sulphate solution is stored in a zinc pot, then zinc will displace copper from the copper sulphate solution.

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

Hence, copper sulphate solution cannot be stored in a zinc pot.

31. Consult the table of standard electrode potentials and suggest three substances that can oxidise ferrous ions under suitable conditions.

Ans. Substances that are stronger oxidising agents than ferrous ions can oxidise ferrous ions.

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-1};\ E^{\circ} = -0.77V$$

This implies that the substances having higher reduction potentials than +0.77 V can oxidise ferrous ions to ferric ions. Three substances that can do so are F_2, Cl_{12}, and O_2.

3 Marks Questions

1.What is the cell potential for the cell at 25^0C $Cr/Cr^{3+}10.1\ m]//Fe^{2+}(0.01m)/Fe$

$E^0_{cr+/cr} = -0.74V$; $E^0Fe^{2+}/Fe = -0.44V$ ·

Ans. The cell reaction is

$2Cr + 3Fe^{2+}\ 6e^{-} \rightarrow 2Cr^{3+} + 3Fe$

Nernst Equation –

$$E_{cell} = \left(E^0{}_{Fe}{}^{2}+/_{Fe} - E^0{}_{cr}{}^{3+}/_{cr}\right) - \frac{0.059}{6}\log\frac{\left[Cr^{3+}\right]^2}{\left[Fe^{2+}\right]^3}$$

=(-0.44v – (-0.74v) - $\frac{0.059}{6}\log\frac{(0.10)^2}{(0.01)^3}$

= $0.3V - \frac{0.059}{6}\log 10^4$

= 0.3V – 0.0394V

= +0.2606 V

2.Calculate ΔG^0 **for the reaction at** 25^0C

$Zn(s)1Zn^2+[0.0004m]11cd^2+(0.2m)1cd(s)$ $E^0{}_{Zn}{}^{2+}/_{Zn} = -0.763V$,

$E^0{}_{cd}{}^{2+}/cd = -0.403v$, $F = 96500\ CMol^{-1}$, **R = 8.314 J/K.**

Ans. The half cell reactions are

Anode: $Zn(s) \rightarrow Zn^2 + (aq) + 2e^-$

Cathode: $Cd^2 + (aq) + 2e^- \rightarrow Cd(s)$

Nernst Equation

$$E_{cell} = \left(E^0{}_{Cathode} - E^0{}_{anode}\right) - \frac{0.059}{n}\log\frac{\left[Zn^{2+}\right]}{\left[Cd^{2+}\right]}$$

= (- 0.403 – (-0.763) - $\frac{0.059}{2}\log\frac{0.0004}{0.2}$

= 0.36V - 0.0798V = 0.4398V

$$\Delta G^0 = -n\,F\,E^0{}_{cell}$$

$$= \frac{-2mol \times 96500\ C}{mol \times 0.4398V}$$

= -8488 J mol^{-1}

3.Calculate Equilibrium constant K for the reaction at $298K\ Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}/aq) + Cu\ E^0{}_{Zn}{}^{2+}1Zn = -0.076v; E^0Cu^2 + /Cu$ = **+0.34v.**

Ans.From the reaction, n =2

$$E^0{}_{cell} = E^0cu^2 + /cu - E^0Zn^2 + /Zn$$

= + 0.34v - (-0.76v) = 1.10V

$$E^0{}_{cell} = \frac{2.303RT}{nF}\log k_c$$

At 298k , $E^0{}_{cell} \times \frac{n}{0.059}\log k_c$

Log k_c = $E^0{}_{cell} \times \frac{n}{0.059}$

$$= 1.10 \times \frac{2}{0.059} = 37.29$$

$$K_c = Antilog\ 37.29$$

$$= 1.95 \times 10^{37}$$

4. For what concentration of $Ag+(aq)$ **will the emf of the given cell be zero at** 25^0C

if the concentration of $CU^{2+}(aq)$ **is 0.1 M ?**

$Cu(s)/Cu^{2+}(0.1M)//Ag^+(aq)/Ag(s)\ E^0Ag^+/Ag=+0.80V;$
$E^0{}_{Cu}{}^{2+/Cu}=0.34\ V$

Ans. $\left[Ag^+\right]=5.3\times10^{-9}M$

5.Calculate the standard free energy change for the cell- reaction.

$Fe^{2+}(aq)+Ag^+(s)\dot{a}\rightarrow Fe^3+(aq)+Ag(s)$ **How is it related to the equilibrium constant of the reaction?** $E^0{}_{Fe}{}^{3+}/Fe^{2+}=+0.77V$ **,** $E^0{}_{Ag}{}^{+1/Ag}=+0.08V\ F$
$=96500\ C/mol.$

Ans. $E^0{}_{cell}=\ 0.03V$

$\Delta G^0=-2895J$

6.How much charge is required for the following reductions:

(i) 1 mol of Al^{3+} **to Al.**

(ii) 1 mol of Cu^{2+} **to Cu.**

(iii) 1 mol of MnO_4^- **to** Mn^{2+} **.**

Ans.(i) $Al^{3+}+3e^-\rightarrow Al$

Therefore, Required charge = 3 F

$=3\times96487\ C$

= 289461 C

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

Therefore, Required charge = 2 F

$= 2 \times 96487\ C$

= 192974 C

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

i.e., $Mn^{7+} + 5e^- \rightarrow Mn^{2+}$

Therefore, Required charge = 5 F

$= 5 \times 96487\ C$

= 482435 C

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

(i) 20.0 g of Ca from molten $CaCl_2$.

(ii) 40.0 g of Al from molten Al_2O_3.

Ans.(i) According to the question,

$$Ca^{2+} + 2e^{-1} \rightarrow \underset{40g}{Ca}$$

Electricity required to produce 40 g of calcium = 2 F

Therefore, electricity required to produce 20 g of calcium = $\frac{2 \times 20}{40} F$

= 1 F

(ii) According to the question,

$$Al^{3+} + 3e^{-1} \rightarrow \underset{27g}{Al}$$

Electricity required to produce 27 g of Al = 3 F

Therefore, electricity required to produce 40 g of Al = $\frac{3 \times 40}{27} F$

= 4.44 F

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

(i) 1 mol of H_2O to O_2.

(ii) 1 mol of FeO to Fe_2O_3.

Ans.(i) According to the question,

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

Now, we can write:

$$O^{2} \rightarrow \frac{1}{2}O_2 + 2e^{-}$$

Electricity required for the oxidation of 1 mol of H_2O to O_2 = 2 F

= 2×96487 C

= 192974 C

(ii) According to the question,

$$Fe^{2+} \rightarrow Fe^{3+} + e^{-1}$$

Electricity required for the oxidation of 1 mol of FeO to Fe_2O_3 = 1 F

= 96487 C

9. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode?

Ans. Given,

Current = 5A

Time = 20×60 = 1200 s

Therefore, $\text{Charge} = \text{current} \times \text{time}$

$= 5 \times 1200$

= 6000 C

According to the reation,

$$Ni^{2+}_{(aq)} + 2e^- \rightarrow \underset{58.7g}{Ni_{(s)}}$$

Nickel deposited by $2 \times 96487\ C$ = 58.71 g

Therefore, nickel deposited by 6000 C $= \frac{58.71 \times 6000}{2 \times 96487} g$

= 1.825 g

Hence, 1.825 g of nickel will be deposited at the cathode.

10. Depict the galvanic cell in which the reaction 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 galvanic cell in which the given reaction takes place is depicted as:

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

(i) Zn electrode (anode) is negatively charged.

(ii) Ions are carriers of current in the cell and in the external circuit, current will flow from silver to zinc.

(iii) The reaction taking place at the anode is given by,

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

The reaction taking place at the cathode is given by,

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

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

Ans.A lead storage battery consists of a lead anode, a grid of lead packed with lead oxide (PbO_2) as the cathode, and a 38% solution of sulphuric acid (H_2SO_4) as an electrolyte.

When the battery is in use, the following cell reactions take place:

At anode: $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

At cathode: $PbSO_{4(s)} + SO_4^{2-}{}_{(aq)} + 4H^-{}_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

The overall cell reaction is given by,

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

When a battery is charged, the reverse of all these reactions takes place.

Hence, on charging, $PbSO_{4(s)}$ present at the anode and cathode is converted into $Pb_{(s)}$ and $PbO_{2(s)}$ respectively.

12. If a current of 0.5 ampere flows through a metallic wire for 2 hours, then how many electrons would flow through the wire?

Ans. $I = 0.5$ A

t = 2 hours = $2 \times 60 \times 60 \text{ s} = 7200 \text{ s}$

Thus, $Q = It$

= $0.5 \text{ A} \times 7200 \text{ s}$ = 3600 C

We know that $96487 \text{ C} = 6.023 \times 10^{23}$ number of electrons.

Then, $3600 \text{ C} = \dfrac{6.023 \times 10^{23} \times 3600}{96487}$ number of electrons

$= 2.25 \times 10^{22}$ number of electrons

Hence, 2.25×10^{22} number of electrons will flow through the wire.

13. Calculate the potential of hydrogen electrode in contact with a solution whose pH is 10.

Ans. For hydrogen electrode, $H^+ + e^- \rightarrow \frac{1}{2}H_2$, it is given that pH = 10

Therefore, $[H^+]$ = 10 - 10M

Now, using Nernst equation:

$$H_{\left(H^+/\frac{1}{2}H^2\right)} = E^{\circ}_{\left(H^+/\frac{1}{2}H^2\right)} - \frac{RT}{nF} \mathrm{In} \frac{1}{[H^+]}$$

$$= E^{\circ}_{\left(H^+/\frac{1}{2}H^2\right)} - \frac{0.0591}{1} \log \frac{1}{[H^+]}$$

$$0 - \frac{0.0591}{1} \log \frac{1}{[10^{-10}]}$$

= - 0.0591 log 10^{10} = - 0.591 V

14. Calculate the emf of the cell in which the following reaction takes place:

$$Ni_{(s)} + 2Ag^{+}(0.002M) \rightarrow Ni^{2+}(0.160M) + 2Ag_{(s)}$$

Given that $E^{\ominus}_{(cell)} = 1.05V$

Ans. Applying Nernst equation we have:

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{0.0591}{n} \log \frac{[Ni^{2+}]}{[Ag^{2}]^{+}}$$

$$= 1.05 - \frac{0.0591}{2} \log \frac{(0.160)}{(0.002)^{2}}$$

$$= 1.05 - 0.02955 \log \frac{0.16}{0.000004}$$

= 1.05 - 0.02955 log 4 × 104

= 1.05 - 0.02955 (log 10000 + log 4)

= 1.05 - 0.02955 (4 + 0.6021)

= 0.914 V

15. The cell in which the following reactions occurs:

$2Fe^{3+}_{(aq)} + 2I^{-}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}$ **has** $E^{\ominus}_{cell}$ **= 0.236 V at 298 K. Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.**

Ans. Here, *n* = 2, $E^{\ominus}_{cell} = 0.236V$ T = 298 K

We know that:

$$\Delta_r G^{\ominus} = nFE^{\ominus}_{cell}$$

= - 2 × 96487 × 0.236

= - 45541.864 J mol - 1

= - 45.54 kJ mol - 1

Again, $\Delta_r G^\ominus = -2.303RT\log Kc$

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

$$= -\frac{-45.54\times 10^3}{2.303\times 8.314\times 298}$$

= 7.981

∴*K*c= Antilog (7.981) = 9.57 × 107

16. How would you determine the standard electrode potential of the systemMg2+| Mg?

Ans. The standard electrode potential of Mg^{2+} | Mg can be measured with respect to the standard hydrogen electrode, represented by Pt(*s*), $H_{2(g)}$ (1 atm) | H^+(*aq*) (1M).

A cell, consisting of Mg | $MgSO_4$(*aq* 1 M) as the anode and the standard hydrogen electrode as the cathode, is set up.

$$Mg\,|\,Mg^{2+}(aq, 1M)\,||\,H^+(aq, 1M)\,|\,H_2(g, 1bar), Pt_{(s)}$$

Then, the emf of the cell is measured and this measured emf is the standard electrode potential of the magnesium electrode.

$$E^\ominus = E^\ominus_R - E^\ominus_L$$

Here, $E^\ominus_R$ for the standard hydrogen electrode is zero.

Therefore, $E^\ominus = 0 - E^\ominus_L$

$= -E^\ominus_L$

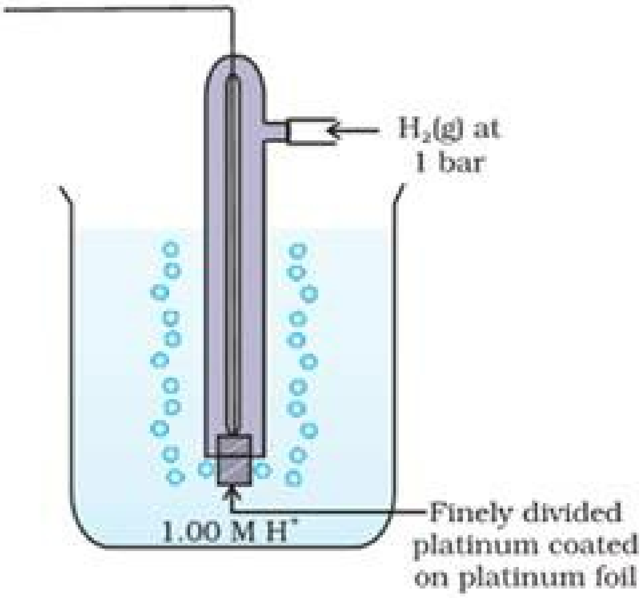
5 Marks Questions

1. Explain construction and working of standard Hydrogen electrode?

Ans. Construction :

SHE consists of a platinum electrode coated with platinum black. The electrode is dipped in an acidic solution and pure Hydrogen gas is bubbled through it. The concentration of both the reduced and oxidized. Forms of Hydrogen is maintained at unity i.e) pressure of H_2 gas is 1 bar and concentration of Hydrogen ions in the solution is 1 molar.

Working – The reaction taking place in SHE is $H^+(aq)+e^- \rightarrow \grave{a} H_2(g)$ At 298 K , the emf of the cell constructed by taking SHE as anode and other half cell as cathode, gives the reduction potential of the other half cell where as for a cell constructed by taking SHE as anode gives the oxidation potential of other half cell as conventionally the electrode potential of SHE is zero.



2. The molar conductivity of 0.025 mol L-1 methanoic acid is 46.1 S $cm^2\ mol^{-1}$.

Calculate its degree of dissociation and dissociation constant. Given $\lambda^\circ H^+$ = 349.6 S $cm^2\ mol^{-1}$ and $\lambda^\circ(HCOO-) = 54.6 S\ cm^2\ mol$

Ans. *C* = 0.025 $mol\ L^{-1}$

$$\Lambda_m = 46.1\, \text{S cm}^2\, \text{mol}^{-1}$$

$$\lambda^\circ(H^+) = 349.6\, \text{S cm}^2\, \text{mol}^{-1}$$

$$\lambda^\circ(HCOO^-) = 54.6\, \text{S cm}^2\, \text{mol}^{-1}$$

$$\Lambda_m^\circ(HCOOH) = \lambda^\circ(H^+) + \lambda^\circ(HCOO^-)$$

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

Now, degree of dissociation:

$$\alpha = \frac{\Lambda_m(HCOOH)}{\Lambda_m^0(HCOOH)}$$

$$= \frac{46.1}{404.2}$$

= 0.114 (approximately)

Thus, dissociation constant:

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

$$= \frac{(0.025\, \text{mol L}^{-1})(0.114)^2}{(1-0.114)}$$

$$= 3.67 \times 10^{-4}\, \text{mol L}^{-1}$$

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

Ans. In the process of corrosion, due to the presence of air and moisture, oxidation takes place at a particular spot of an object made of iron. That spot behaves as the anode. The reaction at the anode is given by, $Fe_{(s)} \rightarrow Fe^{2+}{}_{(aq)} + 2e^-$

Electrons released at the anodic spot move through the metallic object and go to another spot of the object.

There, in the presence of H^+ ions, the electrons reduce oxygen. This spot behaves as the cathode. These H+ ions come either from H_2CO_3, which are formed due to the dissolution of carbon dioxide from air into water or from the dissolution of other acidic oxides from the atmosphere in water.

The reaction corresponding at the cathode is given by, $O_{2(g)} + 4H^+{}_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$

The overall reaction is: $2Fe_{(s)} + O_{2(g)} + 4H^+{}_{(aq)} \rightarrow 2Fe^{2+}{}_{(aq)} + 2H_2O_{(l)}$

Also, ferrous ions are further oxidized by atmospheric oxygen to ferric ions. These ferric ions combine with moisture, present in the surroundings, to form hydrated ferric oxide $(Fe_2O_3 . xH_2O)$ i.e., rust.

Hence, the rusting of iron is envisaged as the setting up of an electrochemical cell.

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

(i) $2Cr_{(s)} + 3Cd^{2+}{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 3Cd$ **(ii)** $Fe^{2+}{}_{(aq)} + Ag^+{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + Ag_{(s)}$

Calculate the $\Delta_r G^\ominus$ **, and equilibrium constant of the reactions**

Ans. (i) $E^\ominus_{Cr^{3+}/Cr} = 0.74V$

$E^\ominus_{Cd^{2+}/Cd} = 0.40V$

The galvanic cell of the given reaction is depicted as: $Cr_{(s)} | Cr^{3+}{}_{(aq)} || Cd^{2+}{}_{(aq)} | Cd_{(s)}$

Now, the standard cell potential is $E^\ominus_{cell} = E^\ominus_R - E^\ominus_L$

= 0.40 – (–0.74)

= +0.34 V

$$\Delta_r G^\ominus = -nFE^\ominus_{cell}$$

In the given equation,

n = 6

F = 96487 C mol - 1

$E^\ominus_{cell}$ = +0.34 V

Then, $\Delta_r G^\ominus = -\ 6 \times 96487\ \text{C mol}^{-1} \times 0.34\ \text{V}$

= –196833.48 CV mol^{-1}

= –196833.48 J mol^{-1}

= –196.83 kJ v

Again, $\Delta_r G^\ominus = -RT\ \text{In}\ K$

$$\Delta_r G^\ominus = -2.303\,RT\ \text{In}\ K$$

$$\log K = -\frac{\Delta_r G}{2.303\,RT}$$

$$= \frac{196.83 \times 10^3}{2.303 \times 8.314 \times 298}$$

= 34.496

Therefore, K = antilog (34.496)

$= 3.13 \times 1034$

(ii) $E^\ominus{}_{Fe^{3+}/Fe^{2+}} = 0.77\,V$

$E^{\ominus}_{Ag^+/Ag} = 0.80\,V$

The galvanic cell of the given reaction is depicted as: $Fe^{2+}_{(aq)} \,|\, Fe^{3+}_{(aq)} \,||\, Ag^{+}_{(aq)} \,|\, Ag_{(s)}$

Now, the standard cell potential is $E^{\ominus}_{cell} = E^{\ominus}_{R} - E^{\ominus}_{L}$

= 0.80 – 0.77

= 0.03 V

Here, *n* = 1.

Then, $\Delta_r G^{\ominus} = -nFE^{\ominus}_{cell}$

= $-1 \times 96487\ C\ mol^{-1} \times 0.03\ V$

= –2894.61 J mol^{-1}

= –2.89 kJ mol^{-1}

Again, $\Delta_r G^{\ominus} = 2.303\,RT\ In\,K$

$$\log K = -\frac{\Delta_r G}{2.303\,RT}$$

$$= \frac{-2894.61}{2.303 \times 8.314 \times 298}$$

= 0.5073

Therefore, K = antilog (0.5073)

= 3.2 (approximately)

5. Write the Nernst equation and emf of the following cells at 298 K:

(i) $Mg_{(s)} \,|\, Mg^{2+} + (0.001M) \,||\, Cu^{2+}(0.0001M)$

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

(iii) $\mathrm{Sn_{(s)}\,|\,Sn^{2+}(0.050\,M)\,||\,H^{+}(0.020\,M)\,|\,H^{2}{}_{(g)}\,(1\,bar)\,|\,Pt_{(s)}}$

(iv) $\mathrm{Pt_{(s)}\,|\,Br^{2}(l)\,|\,Br^{-}(0.010\,M)\,||\,H^{+}(0.030M)\,|\,H^{2}{}_{(g)}\,(1\,bar)\,|\,Pt_{(s)}}$

Ans. (i) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{\left[Mg^{2+}\right]}{\left[Cu^{2+}\right]}$$

$$= \{0.34-(-236)\} - \frac{0.0591}{2}\log\frac{.001}{.0001}$$

$$= 2.7 - \frac{0.0591}{2}\log 10$$

= 2.7 – 0.02955

= 2.67 V (approximately)

(ii) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{\left[Fe^{2+}\right]}{\left[H^{+}\right]^{2}}$$

$$= \{0-(-0.44)\} - \frac{0.0591}{2}\log\frac{0.001}{1^{2}}$$

= 0.44–0.02955(–3)

= 0.52865 V

= 0.53 V (approximately)

(iii) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{\left[Sn^{2+}\right]}{\left[H^{+}\right]^{2}}$$

$$= \{0-(-0.14)\} - \frac{0.0591}{2}\log\frac{0.050}{(0.020)^2}$$

$= 0.14 - 0.0295 \times \log 125$

= 0.14–0.062

= 0.078 V

= 0.08 V (approximately)

(iv) For the given reaction, the Nernst equation can be given as:

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n}\log\frac{1}{[Br^-]^2[H^+]^2}$$

$$= (0-1.09) - \frac{0.0591}{2}\log\frac{1}{(0.010)^2(0.030)^2}$$

$$= -1.09 - 0.02955 \times \log\frac{1}{0.00000009}$$

$$= -1.09 - 0.02955 \times \log\frac{1}{9 \times 10^{-8}}$$

$$= -1.09 - 0.02955 \times \log(1.11 \times 10^7)$$

= –1.09–0.02955(0.0453+7)

= –1.09–0.208

= –1.298 V

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

Ans. Conductivity of a solution is defined as the conductance of a solution of 1 cm in length and area of cross-section 1 sq. cm. The inverse of resistivity is called conductivity or specific conductance. It is represented by the symbol *K*. If ρ is resistivity, then we can write: $K = \frac{1}{\rho}$

The conductivity of a solution at any given concentration is the conductance (*G*) of one unit volume of solution kept between two platinum electrodes with the unit area of cross-section and at a distance of unit length.

i.e., $G = K\frac{a}{1} = k.1 = k$

(Since a = 1, l = 1)

Conductivity always decreases with a 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 with a decrease in concentration.

Molar conductivity:

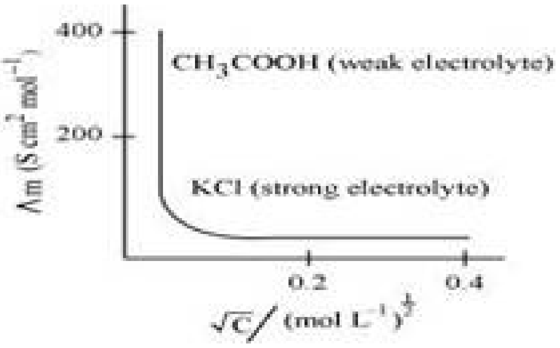
Molar conductivity of a solution at a given concentration is the conductance of volume V of a solution containing 1 mole of the electrolyte kept between two electrodes with the area of cross-section *A* and distance of unit length. $A_m = K\frac{A}{1}$

Now, l = 1 and A = V (volume containing 1 mole of the electrolyte).

Therefore, $A_m = \kappa V$

Molar conductivity increases with a decrease in concentration. This is because the total volume V of the solution containing one mole of the electrolyte increases on dilution.

The variation of A_m with $\sqrt{c}$ for strong and weak electrolytes is shown in the following plot:



7. 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 $10^2 \times \kappa / \mathrm{Sm}^{-1} 1.23711.85\ 23.15\ 55.53\ 106.74$

Calculate A_m **for all concentrations and draw a plot between** A_m **and** $c\frac{1}{2}$**. Find the value of** A_m^0**.**

Ans. Given, $K = 1.237 \times 10^{-2}\ \mathrm{Sm}^{-1}, c = 0.001\mathrm{M}$

Then, $K = 1.237 \times 10^{-4}\ \mathrm{S\ cm}^{-1},\ c\frac{1}{2} = 0.0316\ \mathrm{M}^{1/2}$

Therefore, $A_m = \frac{K}{c}$

$$= \frac{1.237 \times 10^{-4}\ \mathrm{S cm}^{-1}}{0.001 \mathrm{mol\,L}^{-1}} \times \frac{1000\ \mathrm{cm}^3}{\mathrm{L}}$$

$= 123.7\ \mathrm{S cm}^2\mathrm{mol}^{-1}$

Given,

$K = 11.85 \times 10^{-2}\ \mathrm{S\ m}^{-1},\ c = 0.010\mathrm{M}$

Then, $K = 11.85 \times 10^{-4}\mathrm{S\ cm}^{-1},\ c½ = 0.1\ \mathrm{M}^{1/2}$

Therefore, $A_m = \frac{K}{c}$

$$= \frac{11.85 \times 10^{-4}\ \mathrm{S cm}^{-1}}{0.010 \mathrm{mol\,L}^{-1}} \times \frac{1000\ \mathrm{cm}^3}{\mathrm{L}}$$

$= 118.5\ \mathrm{S\ cm}^2\mathrm{mol}^{-1}$

Given,

$K = 23.15\times10^{-2}\ \text{S m}^{-1}, c = 0.020\ \text{M}$

Then, $K = 23.15\times10^{-4}\ \text{S cm}^{-1},\ c^{1/2} = \ 0.1414\ \text{M}^{1/2}$

Therefore, $A_m\ = \dfrac{K}{c}$

$$= \frac{23.15\times10^{-4}\,\text{S cm}^{-1}}{0.020\,\text{mol L}^{-1}}\times\frac{1000\,\text{cm}^3}{\text{L}}$$

$= 115.8\ \text{S cm}^2\text{mol}^{-1}$

Given,

$K = 55.53\times10^{-2}\ \text{S m}^{-1},\ c = 0.050\ \text{M}$

Then, $K = 55.53\times10^{-4}\ \text{S cm}^{-1},\ c^{1/2} = 0.2236\ \text{M}^{1/2}$

Therefore, $K = \dfrac{K}{c}$

$$= \frac{55.53\times10^{-4}\,\text{S cm}^{-1}}{0.050\,\text{mol L}^{-1}}\times\frac{1000\,\text{cm}^3}{\text{L}}$$

$=\ 111.11\ \text{S cm}^2\text{mol}^{-1}$

Given,

$K = 106.74\times10^{-2}\ \text{S m}^{-1},\ c = 0.100\ \text{M}$

Then, $K = 106.74\times10^{-4}\ \text{S cm}^{-1},\ c^{1/2} = 0.3162\ \text{M}^{1/2}$

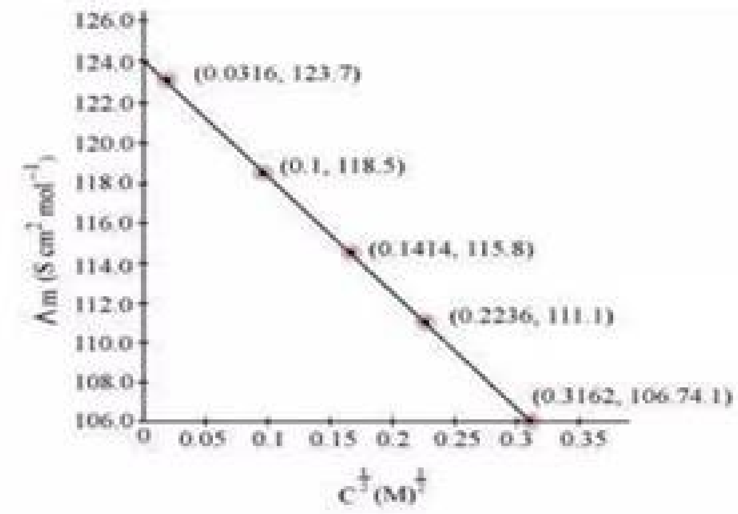
Therefore, $A_m\ = \dfrac{K}{c}$

$$= \frac{106.74\times10^{-4}\,\text{S cm}^{-1}}{0.100\,\text{mol}^{-1}}\times\frac{1000\,\text{cm}^3}{\text{L}}$$

$= 106.74 \text{ S cm}^2\text{mol}^{-1}$

Now, we have the following data:

$\frac{C^{\frac{1}{2}}}{M^{\frac{1}{2}}}$	0.0316	0.1	0.1414	0.2236	0.3162
$\Lambda_m (\text{S cm}^2 \text{ mol}^{-1})$	123.7	118.5	115.8	111.1	106.74



Since the line interrupts Λ_m at $124.0 \text{ S cm}^2 \text{ mol}^{-1}$, $\Lambda_m^0 = 124.0 \text{ S cm}^2\text{mol}^{-1}$

8. Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and if Λ_m^0 for acetic acid is $390.5 \text{cm}^2 \text{ mol}^{-1}$, what is its dissociation constant?

Ans. Given, $K = 7.896 \times 10^{-5} \text{ S m}^{-1}$

$c = 0.00241 \text{ mol L}^{-1}$

Then, molar conductivity, $\Lambda_m = \frac{K}{c}$

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

$= 32.76 \text{ S cm}^2\text{mol}^{-1}$

Again, $\Lambda_m^0 = 390.5 \text{ S cm}^2\text{mol}^{-1}$

Now, $\alpha = \dfrac{\Lambda_m}{\Lambda_m^0} = \dfrac{32.76 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}}$

= 0.084

Therefore, Dissociation constant, $K_a = \dfrac{c\alpha^2}{(1-\alpha)}$

$$= \frac{(0.00241 \text{mol L}^{-1})(0.084)^2}{(1-0.084)}$$

$$= 1.86 \times 10^{-5} \text{ mol L}^{-1}$$

9. Three electrolytic cells A,B,C containing solutions of $ZnSO_4$, $AgNO_3$ and $CuSO_4$ respectively are 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. According to the reaction:

$$Ag^+_{(aq)} + e^- \rightarrow \underset{108g}{Ag_{(s)}}$$

i.e., 108 g of Ag is deposited by 96487 C.

Therefore, 1.45 g of Ag is deposited by = $\dfrac{96487 \times 1.45}{108} C$

= 1295.43 C

Given,

Current = 1.5 A

Therefore, Time $= \dfrac{1295.43}{1.5} s$

= 863.6 s

= 864 s

= 14.40 min

Again,

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow \underset{63.5g}{Cu_{(s)}}$$

i.e., 2×96487 C of charge deposit = 63.5 g of Cu

Therefore, 1295.43 C of charge will deposit = $\frac{63.5 \times 1295.43}{2 \times 96487}$ g

= 0.426 g of Cu

$$Zn^{2+}_{(aq)} + 2e^- \rightarrow \underset{65.4g}{Zn_{(s)}}$$

i.e., 2×96487 C of charge deposit = 65.4 g of Zn

Therefore, 1295.43 C of charge will deposit = $\frac{65.4 \times 1295.43}{2 \times 96487}$ g

= 0.439 g of Zn

10. Using the standard electrode potentials given in Table 3.1, predict if the reaction between the following is feasible:

(i) $Fe^{3+}(aq)$ **and** $I^-(aq)$

(ii) $Ag^+(aq)$ **and Cu(s)**

(iii) $Fe^{3+}(aq)$ **and** $Br^-(aq)$

(iv) Ag(s) and $Fe^{3+}(aq)$

(v) $Br^2(aq)$ **and** $Fe^{2+}(aq)$.

Ans.

$$\begin{array}{llr}
\text{(i)} & \left.\mathrm{Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}}\right] \times 2; & E^\circ = +0.77\ \mathrm{V} \\
& \mathrm{2I^-_{(aq)} \longrightarrow I_{2(s)} + 2e^-}; & E^\circ = -0.54\ \mathrm{V} \\
\hline
& \mathrm{2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}}\ ; & E^\circ = +0.23\ \mathrm{V}
\end{array}$$

Since E° for the overall reaction is positive, the reaction between $\mathrm{Fe^{3+}(aq)}$ and $\mathrm{I^-(aq)}$ is feasible.

$$\begin{array}{llr}
\text{(ii)} & \left.\mathrm{Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}}\right] \times 2\ ; & E^\circ = +0.80\ \mathrm{V} \\
& \mathrm{Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-}\ ; & E^\circ = -0.34\ \mathrm{V} \\
\hline
& \mathrm{2Ag^+_{(aq)} + Cu_{(s)} \longrightarrow 2Ag_{(s)} + Cu^{2+}_{(aq)}}\ ; & E^\circ = +0.46\ \mathrm{V}
\end{array}$$

Since E° for the overall reaction is positive, the reaction between $\mathrm{Ag^+(aq)}$ and Cu(*s*) is feasible.

$$\begin{array}{llr}
\text{(iii)} & \left.\mathrm{Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}}\right] \times 2\ ; & E^\circ = +0.77\ \mathrm{V} \\
& \mathrm{2Br^-_{(aq)} \longrightarrow Br_{2(l)} + 2e^-}\ ; & E^\circ = -1.09\ \mathrm{V} \\
\hline
& \mathrm{2Fe^{3+}_{(aq)} + 2Br^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)}}\ \text{and}\ \mathrm{Br_{2(l)}}\ ; & E^\circ = -0.32\ \mathrm{V}
\end{array}$$

Since E° for the overall reaction is negative, the reaction between $\mathrm{Fe^{3+}(aq)}$ and $\mathrm{Br^-(aq)}$ is not feasible.

$$\begin{array}{llr}
\text{(iv)} & \mathrm{Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e^-}\ ; & E^\circ = -0.80\ \mathrm{V} \\
& \mathrm{Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}}\ ; & E^\circ = +0.77\ \mathrm{V} \\
\hline
& \mathrm{Ag_{(s)} + Fe^{3+}_{(aq)} \longrightarrow Ag^+_{(aq)} + Fe^{2+}_{(aq)}}\ ; & E^\circ = -0.03\ \mathrm{V}
\end{array}$$

Since E° E for the overall reaction is negative, the reaction between Ag(*s*) and $\mathrm{Fe^{3+}(aq)}$ is not feasible.

$$\begin{array}{llll}
\text{(iv)} & Br_{2(aq)} + 2e^- \longrightarrow 2Br^-_{(aq)} & & ; \; E^\circ = +1.09\text{ V} \\
 & Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^- \left.\right] \times 2 & & ; \; E^\circ = -0.77\text{ V} \\
\hline
 & Br_{2(aq)} + 2Fe^{2+}_{(aq)} \longrightarrow 2Br^-_{(aq)} + 2Fe^{3+}_{(aq)} & & ; \; E^\circ = +0.32\text{ V}
\end{array}$$

Since E° for the overall reaction is positive, the reaction between $Br^2(aq)$ and $Fe^{2+}(aq)s$ is feasible.

11. Predict the products of electrolysis in each of the following:

(i) An aqueous solution of $AgNO_3$ with silver electrodes.

(ii) An aqueous solution of $AgNO_3$ with platinum electrodes.

(iii) A dilute solution of H_2SO_4 with platinum electrodes.

(iv) An aqueous solution of $CuCl_2$ with platinum electrodes.

Ans. (i) At cathode:

The following reduction reactions compete to take place at the cathode.

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

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

The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

At anode:

The Ag anode is attacked by NO_3^- ions. Therefore, the silver electrode at the anode dissolves in the solution to form Ag^+.

(ii) At cathode:

The following reduction reactions compete to take place at the cathode.

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

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

The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of silver will take place at the cathode.

At anode:

Since Pt electrodes are inert, the anode is not attacked by NO_3^- ions. Therefore, OH^- or NO_3^- ions can be oxidized at the anode. But OH^- ions having a lower discharge potential and get preference and decompose to liberate O_2.

$$OH^{-} \rightarrow OH^{+}e^{-}$$

$$4OH^{-} \rightarrow 2H_2O + O_2$$

(iii) At the cathode, the following reduction reaction occurs to produce H_2 gas.

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

At the anode, the following processes are possible.

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-}; E^{\circ} = +1.23V \text{ ....(1)}$$

$$2SO_4^{2-}{}_{(aq)} \rightarrow S_2O_6^{2-}{}_{(aq)} + 2e^{-}; \; E^{\circ} = +1.96V \text{ ....(2)}$$

For dilute sulphuric acid, reaction (i) is preferred to produce O_2 gas. But for concentrated sulphuric acid, reaction (ii) occurs.

(iv) At cathode:

The following reduction reactions compete to take place at the cathode.

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

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

The reaction with a higher value of E° takes place at the cathode. Therefore, deposition of copper will take place at the cathode.

Atanode:
The following oxidation reactions are possible at the anode.

$Cl^{-}_{(aq)} \rightarrow \frac{1}{2}Cl_{2(g)} + e^{-1};E^{\circ} = 1.36V$

$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-};\ E^{\circ} = +1.23V$

At the anode, the reaction with a lower value of E° is preferred. But due to the over-potential of oxygen, Cl^{-} gets oxidized at the anode to produce Cl_2 gas.