BRUSH UP YOUR CONCEPTS

Class XII

This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.in. The queries will be entertained by the author.*

ELECTROCHEMISTRY

In continuation to the last article :

- **Conductance (*G*) :** The ease with which current flows through an electrolyte is called conductance. Its unit is ohm^{-1} (Ω^{-1}) or mho or Siemens(S).

  $$G = \frac{1}{\text{resistance } (R) \text{ due to solvent}}$$

  Remember : Mobility of ions increases with dilution which outweighs the increase in resistance and hence conductance increases with increase in dilution.

- **Conductivity or Specific Conductance (κ) :** It is inverse of specific resistance and is directly proportional to the number of ions in unit volume. Hence, decrease with increase in dilution is observed.

  $$R \text{ (resistance)} \propto \frac{l \text{ (distance between electrodes)}}{a \text{ (area of cross section of two parallel plates of electrodes)}}$$

  $$R = \rho\left(\frac{l}{a}\right) \quad \Rightarrow \quad \frac{1}{\rho} = \frac{1}{R}\left(\frac{l}{a}\right) \quad \text{or} \quad \kappa = G\,G^*$$

  $G^*\left(=\frac{l}{a}\right)$ is cell constant of conductivity cell.

  Unit of κ is Siemens cm^{-1} or Siemens m^{-1}.
  Conductivity = conductance $\times$ cell constant
  Conductivity of a solution of a given concentration is equal to conductance when it is kept between two electrodes of unit area separated by unit length (cm or m in both the cases).

- **Molar Conductivity or Molar Conductance (Λ_m) :** It is the conductance of all the ions produced by 1 mole of electrolyte present in V cm^3 (*i.e.*, mL) solution.

  $\Lambda_m = \kappa V$ [κ is in S cm^{-1}]

  If C moles are present in 1000 cm^3, $V = \frac{1000}{C}$

  $$\Lambda_m = \frac{\kappa \times 1000}{C} \text{ S cm}^2\text{mol}^{-1}$$

  If κ is in S m^{-1}, and C moles are present in 1 L, *i.e.*, 10^{-3} m^3,

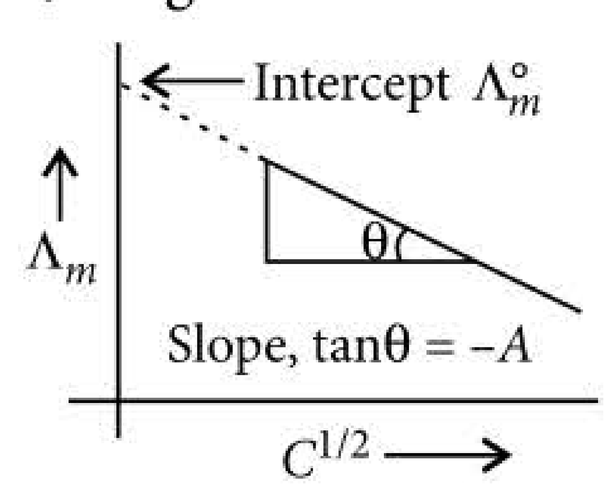
  $$V = \frac{10^{-3}}{C} \text{ m}^3$$

  $$\Lambda_m = \kappa \times \frac{1}{1000\,C} \text{ S m}^2 \text{ mol}^{-1}$$

  It increases with dilution because of higher mobility of ions.

- **Debye-Huckel-Onsager Equation :**
  For strong electrolytes, Λ_m increases by small value, on dilution because of high degree of ionisation.
  $\Lambda_m = \Lambda^\circ_m - A\, C^{1/2}$
  Λ°_m is limiting molar conductivity at infinite dilution.

  Λ_m when plotted against $\sqrt{C}$, we get

  $-A$ is slope which depends upon the nature of solute and temperature. All 1 – 1 electrolytes NaCl, KBr, etc, have same value of A. $CaCl_2$, $BaBr_2$, etc. 2 – 1 electrolytes have the same value of A but different from 1 – 1 electrolytes, etc.

- **Kohlrausch's Work :**
  He found that difference of Λ°_m of electrolytes KX and NaX for any X is nearly constant.
  $\Lambda^\circ_m(\text{KCl}) - \Lambda^\circ_m(\text{NaCl}) = \Lambda^\circ_m(\text{KBr}) - \Lambda^\circ_m(\text{NaBr})$
  $= \Lambda^\circ_m(\text{KI}) - \Lambda^\circ_m(\text{NaI}) \approx 23.4 \text{ S cm}^2 \text{ mol}^{-1}$

*By **R.C. Grover**, having 45+ years of experience in teaching chemistry.

Similarly,
$\Lambda^\circ_m(NaBr) - \Lambda^\circ_m(NaCl) = \Lambda^\circ_m(KBr) - \Lambda^\circ_m(KCl)$
≈ 1.8 S cm^2 mol^{-1}

He enunciated Kohlrausch Law of Independent Migration of Ions : Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of anions and cations of the electrolyte.

$\Lambda^\circ_m(X_aY_b) = a\lambda^\circ_X + b\lambda^\circ_Y$
or $\Lambda^\circ_m = \upsilon_+ \lambda^\circ_+ + \upsilon_- \lambda^\circ_-$

Approximate degree of dissociation $= \dfrac{\Lambda_m}{\Lambda^\circ_m}$

Acid dissociation constant K_a or base dissociation constant K_b

$$= \frac{C\alpha^2}{1-\alpha} = \frac{C\left(\dfrac{\Lambda_m}{\Lambda^\circ_m}\right)^2}{1-\dfrac{\Lambda_m}{\Lambda^\circ_m}} = \frac{C\Lambda_m^2}{\Lambda^\circ_m(\Lambda^\circ_m - \Lambda_m)}$$

- **Equivalent Conductivity or Equivalent Conductance (Λ_{eq}) :**
It is the conductivity of all the ions produced by one gram-equivalent of an electrolyte in given solution.
$\Lambda_{eq} = \kappa V$
For normality N, $\Lambda_{eq} = \kappa \times \dfrac{1000}{N}$ ohm^{-1} cm^2 eq^{-1}
It should be noted that $M\Lambda_m = N\Lambda_{eq}$
(a) $\Lambda^\circ_{m[Al_2(SO_4)_3]} = 2\lambda^\circ_{Al^{3+}} + 3\lambda^\circ_{SO_4^{2-}}$
$\Lambda^\circ_{eq[Al_2(SO_4)_3]} = \dfrac{1}{3}\lambda^\circ_{Al^{3+}} + \dfrac{1}{2}\lambda^\circ_{SO_4^{2-}}$
Here, $\lambda^\circ_{Al^{3+}}$ and $\lambda^\circ_{SO_4^{2-}}$ are molar conductances at infinite dilution.
(b) $\Lambda^\circ_{eq[Al_2(SO_4)_3]} = \lambda^\circ_{Al^{3+}} + \lambda^\circ_{SO_4^{2-}}$
Here, $\lambda^\circ_{Al^{3+}}$ and $\lambda^\circ_{SO_4^{2-}}$ are equivalent conductances at infinite dilution.

- **Corrosion :** It is layer by layer destructive oxidation of metals under environmental conditions. Corrosion of iron is called rusting. Chemically rust is hydrated ferric oxide, $Fe_2O_3.xH_2O$.
Rusting is a redox reaction having EMF = 1.67 V
Anode (under water drop that forms H_2CO_3 on dissolving CO_2 from atmosphere) :
$2Fe_{(s)} \rightarrow 2Fe^{2+} + 4e^-$; $E^\circ_{Fe^{2+}/Fe} = -0.44$ V
Cathode (on periferi of the water drop) :
$O_{2(g)} + 4H^+ + 4e^-; \rightarrow 2H_2O$; $E^\circ_{H^+/O_2/H_2O} = 1.23$ V
Net reaction : $2Fe + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O$; $E^\circ_{cell} = 1.67$ V
$2Fe^{2+} + (2+x)\,H_2O + \dfrac{1}{2}O_2 \rightarrow 4H^+ + Fe_2O_3.xH_2O$

- **Rusting can be prevented by**
(a) Coating iron objects by oil, grease, paint.
(b) Coating iron objects by more active metals (Zn-galvanisation). It is sacrificial protection where the coated metal like Zn gets oxidised and Fe is saved.
(c) Sometimes a less reactive metal which forms protective oxide layer can also be used for coating, *e.g.*, Cr.
(d) Iron pipes placed in marsh or water are connected to Mg, Zn, Al, etc, through wires which lose electrons easily and protect iron objects. It is called electrical protection.

- **Primary cells or Batteries :** These are not rechargeable, once consumed, are thrown.
(a) Dry (Leclanche) cell : Cathode is graphite rod surrounded by $MnO_2 + C + NH_4Cl$ powder placed in Zn container as anode. A paste of $ZnCl_2$ and NH_4Cl is used as packing between the two electrodes.
Anode reaction : $Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$; $E^\circ = -0.76$ V
Cathode reaction : $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$; $E^\circ = 0.74$ V
Net potential (E°_{cell}) = 1.5 V
Zn^{2+} forms complex $[Zn(NH_3)_4]^{2+}$.
(b) Mercury cell : It is commonly called as button cell and is used in hearing aids, watches, calculators, etc. Anode is Zn – Hg amalgam, cathode is paste of HgO and carbon and paste of KOH and ZnO as electrolyte.
Anode reaction : $Zn_{(s)}(Hg) + 2OH^- \rightarrow ZnO_{(s)} + H_2O_{(l)} + 2e^-$
Cathode reaction : $HgO_{(s)} + H_2O_{(l)} + 2e^- \rightarrow Hg_{(l)} + 2OH^-$
Net reaction : $Zn_{(s)}(Hg) + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$; $E^\circ_{cell} = 1.36$ V
Since, no ions are involved in the net reaction. The potential of the cell does not fall during its life.

- **Secondary cells or Batteries :** These batteries or cells can be recharged by passing current in the reverse direction. The most common is lead storage battery used in invertors and automobiles.
Lead-storage battery : Anode has compressed spongy lead plates, cathode has lead plates packed

with PbO_2, electrolyte is 3.7 M (approximately 38% by mass) H_2SO_4 of specific gravity 1.215.

Cell needs recharging when specific gravity falls to about 1.15.

Maximum voltage per cell is 2.15 V which should not fall below 1.7 V, otherwise lead plates will break.

Cell representation :

$Pb_{(s)}, PbSO_{4(s)} | H_2SO_{4(aq)} | PbO_{2(s)}, Pb_{(s)}$

During discharging :

Anode reaction : $Pb_{(s)} + SO^{2-}_{4(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

Cathode reaction : $PbO_{2(s)} + 4H^+_{(aq)} + SO^{2-}_{4(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O$

Net reaction : $Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O$

During recharging, these reactions get reversed.

- **H_2 — O_2 Fuel Cell (Bacon Cell) :**

This cell has the highest efficiency of about 70% among all known systems of the world.

Anode contains finely divided Pt or Pd while cathode has Ag_2O with Pt or Pd packed in compressed carbon. Electrolyte is NaOH.

Anode reaction : $H_{2(g)} + 2OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + 2e^-$

Cathode reaction : $H_2O_{(l)} + \frac{1}{2}O_{2(g)} + 2e^- \rightarrow 2OH^-_{(aq)}$

Net reaction : $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}; E° = 1.2$ V

MULTIPLE CHOICE QUESTIONS

1. Which of the following has the highest efficiency among all the known systems so far?
(a) Human being
(b) Steam plant generating electricity
(c) Hydrogen – oxygen fuel cell
(d) Lead accumulator

2. In the $H_2 - O_2$ fuel cell the anode reaction is
(a) $Zn \rightarrow Zn^{2+} + 2e^-$
(b) $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
(c) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
(d) $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$

3. If a fuel cell, $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ has $\Delta G° = -240$ kJ, the $E°_{cell}$ is
(a) 1 V (b) 1.24 V
(c) 2.15 V (d) 1.36 V

4. Which of the following is not correct for lead accumulator?
(a) Electrolyte is 3.7 M H_2SO_4.
(b) EMF per cell is 2.15 V.
(c) Anode is Pb plate packed with PbO_2.
(d) Cell needs recharging when specific gravity of H_2SO_4 falls to 1.15.

5. Which of the following is the correct cathode reaction in dry cell?
(a) $HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$
(b) $H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2OH^-$
(c) $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
(d) $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

6. What is rust chemically?
(a) $Fe(OH)_3$ (b) $Fe_2O_3 \cdot xH_2O$
(c) $Fe_3O_4 \cdot xH_2O$ (d) $FeO \cdot xH_2O$

7. Galvanisation is basically a method of preventing rusting under sacrificial protection. The metal coated on iron objects is
(a) Cr (b) Sn (c) Mg (d) Zn

8. Rusting of iron is basically a redox reaction. The EMF of the cell formed is
(a) 1.67 V (b) 1.24 V
(c) 2.15 V (d) 1.36 V

9. The net reaction of rusting, combination of cathode reaction and anode reaction is
$2Fe + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O; E° = 1.67$ V
Which of the following is oxidised in this reaction?
(a) Fe (b) O_2 (c) H^+ (d) Fe^{2+}

10. In dry (Leclanche) cell graphite rod at cathode is surrounded by
(a) $ZnCl_2 + NH_4Cl$ (b) $ZnCl_2 + NH_4Cl + C$
(c) $MnO_2 + NH_4Cl$ (d) $MnO_2 + NH_4Cl + C$

11. Which of the following cell is commonly used in wrist watches?
(a) Dry cell (b) Bacon cell
(c) Ni-Cd cell (d) Hg-cell

12. Which of the following is correct when lead storage battery is discharged (working)?
(a) $PbSO_4$ is formed at anode and PbO_2 at cathode.
(b) $PbSO_4$ is formed at cathode and PbO_2 at anode.
(c) $PbSO_4$ is formed at cathode and anode both.
(d) PbO_2 is formed at cathode and anode both.

13. The values of $\overset{\circ}{\Lambda}_{CH_3COONa}$ and $\overset{\circ}{\Lambda}_{HCl}$ are 91 S cm^2 mol^{-1} and 426.2 S cm^2 mol^{-1} respectively. Which of the following will you need for calculating the value of $\overset{\circ}{\Lambda}_{CH_3COOH}$?