ELECTROCHEMISTRY

1. **Specific conductivity** [κ] :- Conductivity is the reciprocal of specific resistance i.e.,

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

   Hence from R = $\rho \cdot \frac{\ell}{a} \cdot \frac{1}{C} = \frac{1}{\kappa} \cdot \frac{\ell}{a}$ or $\kappa = C \times \frac{\ell}{a}$

   Where $\frac{\ell}{a}$ = cell constant

   If ℓ = 1cm and a = 1 cm², κ = C, Hence conductivity is the conductance of 1 cm³ of the conductor. Units of κ = ohm⁻¹ cm⁻¹ or in SI units, these are $W^{-1}m^{-1}$ or Sm^{-1} (1 Scm⁻¹ = 100 Sm⁻¹)

2. **Relationship between Equivalent conductivity** $\left(\wedge_{eq} \right)$ **and Specific conductivity (K).**

   $$\wedge_{eq} = \kappa \times \frac{1000}{C_{eq}} = \kappa \times \frac{1000}{\text{Normality}}$$

   C_{eq} represents the concentration of the solution in gram equivalents per litre (i.e. normality of the solution).

3. **Units of equivalent conductivity =** ohm⁻¹ cm² eq⁻¹ or in SI units, these are S m² eq⁻¹ (1 S m² eq⁻¹ = 10⁴ S cm² eq⁻¹ or S cm² eq⁻¹ = 10⁻⁴ S m² eq⁻¹).

4. **Relationship between molar conductivity** $\left(\wedge_m \right)$ **and Specific conductivity (** κ **)**

   $$\wedge_m = \kappa \times V = \kappa \times \frac{1000}{C_m} = \kappa \times \frac{1000}{\text{Molarity}}$$

   Where V is volume of solution in cm³ containing one mole of the electrolyte and C_m is molar concentration (moles L⁻¹)

5. **Units of molar conductivity =** ohm⁻¹ cm² mol⁻¹ or in SI units, these are S m² mol⁻¹ (1 S m² mol⁻¹ = 10⁴ S cm² mol⁻¹ or 1 S cm² mol⁻¹ = 10⁻⁴ S m² mol⁻¹)

6. **Effect of dilution :** Conductance increases, specific conductivity decreases, equivalent and molar conductivity increase with dilution.

7. **Kohlrausch's law :** The law states that at infinite dilution where dissociation of all electrolytes is complete and all interionic effects disappear, each ion migrates independently of its co-ion and contributes to the total molar conductivities of an electrolyte a definate shape, which depends on its own nature and not at all on the ions with which it is associated.

   General formula : For molar conductance $\wedge_m^{\infty} = m\lambda_c^{\infty} + n\lambda_a^{\infty}$

   where m and n = moles of cation and anion λ_c^{∞} and λ_a^{∞} = ionic conductance at inifinite dilution for cation & anion

For equivalent conductance

$$\wedge_{eq}^{\infty} = \wedge_{eq}^{\infty}C + \wedge_{eq}^{\infty}A$$

Relation between in $\wedge_m$ and $\wedge_{eq}$
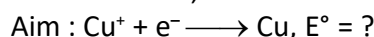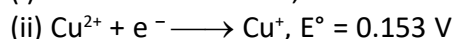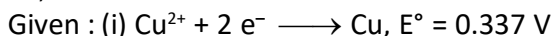
$$\wedge_{eq} = \frac{\wedge_m}{v.f.}$$
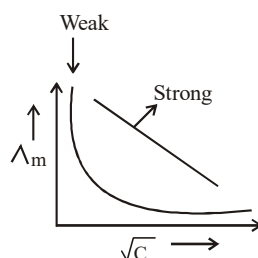
8. Absolute value of Electrode Potential cannot be Determined because oxidation or reduction half reaction cannot occur alone. Moreover, a reference electrode is required.

9. A negative value of standard reduction potential means that oxidation takes place on this electrode with reference to standard hydrogen electrode. The standard electrode potential of hydrogen electrode is taken as zero.

10. **(a)** Greater the reduction potential of a substance, stronger is the oxidizing agent.
   (b) A more reactive metal with greater oxidation potential (lower reduction potential) displaces the less reactive metal (higher reduction potential) from its aqueous solution.

11. An electrochemical cell or galvanic cell or voltaic cell is a device used to convert chemical energy produced in a redox reaction into electrical energy.
   LOAN → Left oxidation anode negative.

12. In galvanic cell, the electrode on which oxidation takes place is called anode or negative pole (because it is rich in electrons) and the electrode on which reduction takes place is called the cathode or **positive pole (being deficient in electrons)**

13. **Difference between Galvanic and Electrolytic cell** lies is the fact that the former is used convert chemical energy produced in the spontaneous redox reaction into electrical energy whereas in the latter, electrical energy is passed to bring about the redox reaction (electrolysis) which is otherwise non spontaneous.

14. In a salt brige the electrolytes commonly used are KCl or KNO_3 or NH_4NO_3. This is because their cations and anions move almost at the same speed and hence have almost the same transport number.

15. KCl / $NaCl/NH_4Cl$ etc. cannot be used in the salt bridge of a cell containing silver as one of the electrodes because they react to form a precipitate of $AgCl$.

16. $$E_{cell} = E^{\circ}_{O.P.(Anode)} - E^{\circ}_{O.P.(Cathode)}$$
   $$E_{cell} = E^{\circ}_{Red} (R.H.S. \text{ electrode}) - E^{\circ}_{Red} (L.H.S. \text{ electrode})$$
   $$E_{cell} = E^{\circ}_{R.P.(Cathode)} + E^{\circ}_{O.P.(Anode)}$$
   $$E_{cell} = E^{\circ}_{R.P.(Cathode)} - E^{\circ}_{R.P.(Anode)}$$

17. $E^{\circ}_{R.P.} = E^{\circ}_{O.P.}$ (For a same electrode)

18. In balancing of half cell reactions to get overall reaction, the equations may be multiplied by suitable integers but electrode potential are fixed quantities and are not multiplied with that integer.

19. For a given reaction to be spontaneous , E_{cell} must be positive.

20. When the cell reaction attains equilibrium , $E_{cell} = 0$.

ELECTROCHEMISTRY

21. The EMF of a cell (complete redox reaction) is found by adding the oxidation potential and reduction potential of the half-cell reaction. But the electrode potential of the half-cell form two other half-cells cannot be found by simply adding their electrode potentials.

For example, suppose we have to calculate standard electrode potential for Cu^+/Cu half-cell from known value for Cu^{2+}/Cu and Cu^{2+}/Cu^+ (which are 0.337 V and 0.153 V respectively) ie.,

Given : (i) $Cu^{2+} + 2e^- \longrightarrow Cu$, E° = 0.337 V

        (ii) $Cu^{2+} + e^- \longrightarrow Cu^+$, E° = 0.153 V

          Aim : $Cu^+ + e^- \longrightarrow Cu$, E° = ?

Substracting equation (ii) from equation (i). We have to calculate their free energy changes. Let the free energy changes of the above three reaction be $\Delta G°_1$, $\Delta G°_2$ and $\Delta G°_3$ respectively. Then $\Delta G°_3 = \Delta G°_1 - \Delta G°_2$

i.e., $-1 \times F \times E°_{Cu^+/Cu} = (-2 \times F \times 0.337) - (-1 \times F \times 0.153)$

$(\Delta G° = -nFE°)$

The gives $E°_{Cu^+/Cu}$ = 0.521V.

22. According to Faraday's first law of electrolysis, $\boxed{\dfrac{W}{E} = \dfrac{Q}{F}}$

Weight of substance liberated $\propto$ Quantity of electricity passed.

    $W \propto Q$ or $W = ZQ = Z \times i \times t$ (Z = electrochemical equivalent)

23. Z = Equivalent wt. of the substance / 96500 or $Z = \dfrac{E}{F}$

24. According to Faraday's second law of electrolysis for the same quantity of electricity passed through solutions of different electrolysis , (e.g, $CuSO_4$ and $AgNO_3$)

$$\frac{\text{Weight of Cu deposited}}{\text{Weight of Ag deposited}} = \frac{\text{Equivalent wt. of Cu}}{\text{Equivalent wt. of Ag}} \boxed{\frac{W_1}{E_1} = \frac{W_2}{E_2}}$$

25. In an aqueous solution of SO_4^{2-} and NO_3^-, at the anode these ions are not oxidised but H_2O is oxidized to give O_2 gas ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$).

26. For metals to be deposited on the cathode during electrolysis, the volage required is almost the same as the standard electrode potential. However for liberation of gases, some extra voltage is required than the theoretical value of the standard electrode potential. The extra voltage thus required is called over voltage or bubble voltage.

27. **Primary cell** are those which cannot be recharged i.e., dry cell and mercury cell.
Secondary cells are those which can be recharged i.e., lead storage battery and Ni – Cd cell.
Fuel cells are those in which energy produced from the combustion of fuels can be coverted into electrical energy e.g., H_2–O_2 fuel cell.

28. Main features of different cell.

	Name of the cell/Battery	Anode	Cathode	Electrolyte
(i)	Dry cell	Zinc	Graphite	MnO_2 + C black (touching cathode) $NH_4Cl + ZnCl_2$ (touching anode
(ii)	Mercury cell	Zn (Hg)	HgO and carbon	KOH and ZnO
(iii)	Lead storage battery	Lead	Lead dioxide	H_2SO_4(38% sol.)
(iv)	Ni-Cd cell	Cadmium	Nickel dioxide	KOH sol.
(v)	H_2–O_2 fuel cell	Porous carbon cont. catalysis H_2 passed	Porous carbon cont. catalysis O_2 passed	Conc. aq. KOH sol.

29. A dry cell does not have a long life because the acidic NH_4Cl corrodes the zinc container even when the cell is not in use.

30. Mercury cell gives a constant voltage (1.35 V) throughout its life and is used in hearing aids and watches.

31. **Reactions ocurring in lead storage battery** (a) Reactions occurring during discharge.
At anode : $Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$
At cathode : $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$
The complete reaction may be written as
$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$
As H_2SO_4 is consumed, the voltage of the battery drops.

32. In the Apollo moon flights, the source of electric energy and that of drinking water was the H_2— O_2 fuel cell.

33. Corrosion is the process of change of metal surface into salts like oxides, sulphides, carbonates etc. due to attack of atmospheric gases.

34. Rust is hydrate ferric oxide, $Fe_2O_3.xH_2O$

35. **Factors which enhance corrosion are**
(i) Presence of impurities in the metal (pure metals do not corrode).
(ii) Presence of moisture (e.g., in rainy season)
(iii) Presence of electrolytes (e.g., saline water)

36. Corrosion can be prevanted by the following methods.
(i) Barrier protection by oil/grease layer, paints or electroplating.
(ii) Sacrificial protection by coating the metal with more electropositive metal (e.g. Zn called galvanisation).
(iii) Electrical protection by connecting the iron pipe to a more electropositive metal with a wire. (Cathodic protection)

37. Corrrosion takes place faster in saline water than in pure water.

38. According to Nernst equation,
(i) For the reaction half reduction (electrode reaction)
$Mn^{n+} + ne^- \longrightarrow M$
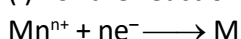
$$E_{R.P.} = E_{R.P.}^0 - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]} = E_{Red}^0 - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]} \text{ at 298 K}$$

(ii) For the cell reaction $a\,A + b\,B \rightleftharpoons x\,X + y\,Y$

$$E_{Cell} = E_{Cell}^0 - \frac{RT}{nF}\ln\frac{[X]^x[Y]^y}{[A]^a[B]^b} = E_{Cell}^0 - \frac{0.0591}{n}\log\frac{[X]^x[Y]^y}{[A]^a[B]^b} \text{ at 298 K}$$

For a pure solid, pure liquid at 1 atm. put molar conc. 1.
e.g. for $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$.

$$E_{Cell} = E_{Cell}^0 - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} = E_{Cell}^0 - \frac{0.0591}{n}\log\frac{[Product]}{[Reactant]}$$

39. $$E_{cell}^{\circ} = \frac{RT}{nF}\ln K = \frac{2.303}{nF}\log K = \frac{0.0591}{n}\log K \text{ at 298 K}$$

(K = Equilibrium constant of the cell reaction).

40. Thermodynamic efficiency of a fuel cell $(\eta) = \dfrac{\Delta G}{\Delta H} = \dfrac{-nFE}{\Delta H}$

41. Calculation of ΔG and ΔS for cell reactions.
(i) $\Delta G = - n\,FE_{cell}$

(ii) $\Delta S = nF\left(\dfrac{\partial E}{\partial T}\right)_P$
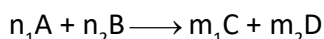
where $\left(\dfrac{\partial E}{\partial T}\right)_P$ = temperature coefficient of e.m.f = $\dfrac{E_2 - E_1}{T_2 - T_1}$ at constant pressure

(iii) $\Delta G = \Delta H - T\Delta S$.

CHEMICAL KINETICS

1. Rate of Reaction :

$n_1A + n_2B \longrightarrow m_1C + m_2D$

$$ROR = \frac{1}{n_1} \cdot \frac{-d[A]}{dt} = \frac{1}{n_2} \cdot \frac{-d[B]}{dt} = \frac{1}{m_1} \cdot \frac{+d[C]}{dt} = \frac{1}{m_2} \cdot \frac{+d[D]}{dt}$$

Rate of disappearance of A = $-\dfrac{d[A]}{dt}$

Rate of disappearance of B = $-\dfrac{d[B]}{dt}$

Rate of appearance of C = $\dfrac{d[C]}{dt}$

Rate of appearance of D = $\dfrac{d[D]}{dt}$

Order of Reaction :

Order of reaction (R) is defined as "the total number of reacting molecules whose concentration determines the rate of reaction or the total number of reacting molecules whose concentration changes during the chemical change. In general order of a reaction is defined as, "the sum of the powers to which the concentration terms of reactant must be raised in order to determine the reaction rate."

For a reaction, $mA + nD \longrightarrow C$
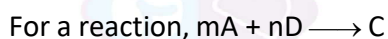
Rate equation is $\dfrac{dx}{dt} = k[A]^x[D]^y$

Order of reaction with respect to A = x
Order of reaction with respect to B = y
Total order of reaction = x + y
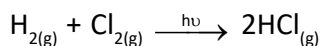Here k is a rate constant and value depend on
(1) Temperature
(2) Catalyst
(3) Nature of reactant

CHEMICAL KINETICS

Zero Order Reaction

Eg. decomposition of gases on metal surface
Eg. Photochemical reaction

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{h\upsilon} 2HCl_{(g)}$$

Integrated rate equation

$$[A]_t = [A]_0 - kt \qquad ......(1)$$
$$x = kt \qquad ......(2)$$

Half life $\quad t_{1/2} = \dfrac{[A]_o}{2k} \implies t_{100\%} = \dfrac{a}{k} \implies t_{100\%} = 2 \times t_{1/2}$

Rate equation : $\dfrac{-d[A]}{dt} = k[A]^0$

First order Reaction

Eg. All radio active disintegration

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$
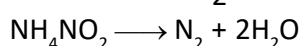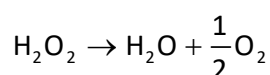
Hydrolysis of ester in acidic medium

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$
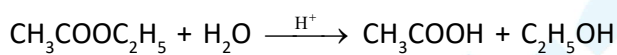
Inversion of cane sugar in acidic medium

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
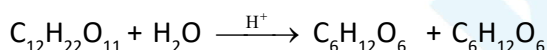
Rate equation : $\dfrac{-d[A]}{dt} = k[A]^1$

First Order Rate Expression :

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Half - life $(t_{1/2}) = \dfrac{0.693}{k}$

$t_{75\%} = 2 \times t_{1/2}$, $t_{87.5\%} = 3 \times t_{1/2}$, $t_{93.75\%} = 4 \times t_{1/2}$, $t_{100\%} = \infty$

Integrated rate equation for n^{th} order reaction :

$$kt = \frac{1}{(n-1)}\left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right]$$

$$t_{1/2} = \frac{1}{(n-1)}\left[\frac{2^{n-1}-1}{a^{n-1}}\right] \times k \implies t_{1/2} \propto \frac{1}{a^{n-1}}$$

$$\boxed{\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}}$$

half life method to determine order of reaction.

CHEMICAL KINETICS

Activation Energy :

- Only those collisions, in which the colliding molecules possess certain minimum energy called threshold energy result in a chemical reaction.
- The excess energy that is supplied to the reactant molecules in order to raise them to the level of threshold energy is called activation energy.
- Arrhenius gave a relationship between the temp. and rate constant of a reaction called Arrhenius equation

$$K = Ae^{-\frac{E_a}{RT}}$$

Where, k_1 = rate constant at temp. T_1

k_2 = rate constant at temp. T_2

- Temperature coefficient $\mu = \dfrac{k_{T+10}}{k_T}$

    range of $\mu = 2 \leq \mu \leq 3$

    $\mu^{\Delta T/10} = \dfrac{k_2}{k_1} = \dfrac{r_2}{r_1}$ at any two different temperatures.

    Factors which affecting activation energy
    (1) Catalyst
    (2) Nature of reactant

1. Factors affecting rate of reaction

(i) Nature of reactant.
(a) Physical state (b) Physical Nature (c) Chemical nature
(ii) Concentration of reactant
(iii) Pressure
(iv) Temperature
(v) Catalyst
(vi) Exposure to radiation

2. Collision theory - Arrhenius

Two conditions must be satisfied at a line for effective collision.
(i) Reacting molecules must posses a minimum amount of energy. which is equal to threshold energy.
(ii)Proper orientation of collision.

- Threshold energy = Potential energy of reactant + activation energy.

$$\Delta H = H_P - H_R = (E_a)_f - (E_a)_b$$