2. ELECTRO CHEMISTRY

STUDY NOTES

2. 0 **Electrochemistry** deals with the relation between **electrical energy** & **chemical change**. In Electrochemistry, we use

i) Chemical reactions for the production of electrical energy (electrochemical- cells).

ii) Electrical energy from the dissociation of chemical compounds (electrolysis).

iii) Electrical energy in the study and preparation of chemical substances which are ecofriendly.

2.1 **Electro chemical cells :**An electrochemical cell consists of two metallic electrodes dipping in electrolytic solution(s). They are two types (i) Galvanic cell (ii) Electrolytic cell

2.2.1 **Galvanic cell:** In a Galvanic cell, **chemical energy is converted into electrical energy**. When plates of two dissimilar metals are placed in a conducting liquid ,such as an aqueous solution of a salt or an acid, the resulting system becomes a source of electricity; and is called as Galvanic cell or Voltaic cell . **Ex: Daniel cell**

2.2.2 **Electrolytic cell:** In an Electrolytic cell, electrical energy is converted into chemical energy. **Ex:** Rechargeable batteries, Electroplating, Electrolysis of water.

2.2.3 **SHE :** A Standard Hydrogen Electrode is the universal reference electrode used to measure the potential of other electrodes. It consists of a platinum electrode coated with platinum black immersed in a 1M HCl solution, with 1 atm hydrogen gas bubbled over it.

2.3. **Nernst Equation:** This equation gives the relationship between the electrode potential and concentration of the electrolyte (C) in a half cell.

Nernst Equation: $E = E^0 + \frac{RT}{nF} ln[M^{n+}]$

2.3.1 **Equilibrium Constant (K_c):** The equilibrium (K_c)is a numerical value that describes the ratio of product concentration to reactant concentration in a chemical reaction at equilibrium.

For the reaction, aA +bB = cC + dD

the equilibrium constant (K_c)= $\frac{[C]^c[D]^d}{[A]^a[B]^b}$, [ ] indicate molar conductivity.

Larger K values (>>>1) favour products and smaller K values (<<<1) favour reactants.

Equilibrium constant from Nernst equation : $E^o_{cell} = \frac{2.303RT}{nF} \log K_c$

2.3.2 Gibbs Energy (ΔG): In galvanic cells, the Gibbs energy of redox reaction is converted into electrical work which is used in electrical gadgets like fans, heaters, geysers.

It is the maximum electrical work a system can perform at constant temperature, defined by $\Delta G = -nFE_{cell}$

ΔG determines the spontaneity of a redox reaction

If $\Delta G < 0$, the reaction is spontaneous. **Ex:** Galvanic cell

If $\Delta G > 0$, the reaction is non- spontaneous. **Ex:** Electrolytic cell

Gibbs energy is used to find

(i) voltage of a cell $E_{cell} = \dfrac{-\Delta G}{nF}$ (ii) equilibrium constant $\Delta G^o = -2.303RT \log K_c$

(iii) the maximum work done by a battery. (iv) maximum efficiency of batteries

2.4. Conductance of Electrolytic Solutions:

It is the conductance of electricity by ions present in the solution.

It depends on nature of the solvent and its viscosity, concentration of the electrolyte, temperature.

Conductivity $k = \dfrac{\text{cell constant}}{R}$, R is the resistance of the solution.

2.4.1 Molar Conductivity: It is the conductance of the solution containing one gram-mole of the electrolyte when the electrodes are unit distance apart

Molar conductivity $\Lambda_m = \dfrac{k \times 1000}{M}$, where k is conductivity, 'M' is molarity.

2.4.2 Limiting molar conductivity (Λ_m^0) is the molar conductivity at infinite dilution.

It is defined as the molar conductivity of any electrolyte when the concentration of electrolyte approaches zero (i.e., at infinite dilution)

2.4.3 Kohlrausch's law: The limiting molar conductivity of an electrolyte is equal to the sum of the limiting molar conductivities of cation (λ_+^0) and anion (λ_-^0) of the electrolyte at infinite dilution.

Formula: $\lambda_{m+}^0 = \lambda_+^0 + \lambda_-^0$

For NaCl , $\Lambda_{(NaCl)}^o = \lambda_{Na^+}^0 + \lambda_{Cl^-}^0$

2.5 Electrolytic Cells and Electrolysis:

- An electrolytic cell is defined as an electro chemical device that converts electrical energy into chemical energy.
- **Electrolysis:** It is the decomposition of a chemical compound in the molten state or in its solution state into its constituent elements under the influence of an applied EMF.

2.5.1 Faradays laws of Electrolysis:

Faraday's first law: "The mass (W) of the substance deposited or liberated at the electrode is directly proportional to the quantity of electric charge (Q) passing through the electrolyte". Thus, $W \propto Q$

Faraday's second law : "When same quantity of electric charge is passed through different electrolytes, connected in series the amount of different substances deposited at the electrodes is directly proportional to their equivalent masses". Mathematically, $\frac{m_1}{m_2} = \frac{E_1}{E_2}$

2.5.2 Products of Electrolysis:

Electrolysis of aq.NaCl solution. **Cathode:** H_2 gas **Anode:** Cl_2 gas

Electrolysis of H_2SO_4 solution. **Cathode:** H_2 gas **Anode:** O_2 gas

2.6 Batteries : Battery is basically a galvanic cell where the chemical energy in the redox reaction is converted into electrical energy.

They are two types i.e., primary and secondary batteries.

2.6.1 Primary Batteries (Non rechargeable) Ex: Dry cell, mercury button cell

2.6.2 Secondary Batteries (Rechargeable) Ex: Lead storage battery, Nickel Cadmium cells

2.7. Fuel Cells: A fuel cell is a device that converts combustion energy of fuel (Hydrogen, methane, methanol) directly into electrical energy.

2.8. Corrosion: Corrosion of metals is an electrochemical phenomenon.

FORMULA BOX

1. Deposited mass $m = \frac{E \times C \times t}{96500}$, $e = \frac{E}{96500}$; $m = \frac{Z \times i \times t}{96500}$ (or) $m = \frac{At.wt \times i \times t}{n \times 96500}$, n= valency

2. $\frac{m_1}{E_1} = \frac{m_2}{E_2} = \frac{m_3}{E_3}$ **3.Kohlrausch's law Formula:** $\Lambda^0_{m+} = \Lambda^0_+ + \Lambda^0_-$

4. **EMF = $E_{RHS} - E_{LHS}$:** Gibbs energy change $\Delta G = \Delta G^0 + RT\,ln K_{eq}$.

$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln K_{eq}$ $E = E^0 - \frac{2.303\,RT}{nF} \log \frac{[Products]}{[Reactants]}$

5.1. Nernst equation : $E = E^0 + \frac{0.059}{n} \log C$, [cation], for metal electrode.

6.2. Nernst equation : $E = E^0 - \frac{0.059}{n} \log C$, [anion], for non-metal electrode.