Short Notes for CUET UG Chemistry

Unit II: Electrochemistry

1. Electrochemical Cells & Galvanic Cells

An **electrochemical cell** is a device capable of either converting chemical energy into electrical energy or vice versa.

Galvanic (Voltaic) Cells

These cells convert the chemical energy of a spontaneous redox reaction into electrical energy.

- **Anode:** The electrode where **oxidation** occurs. It has a negative potential.
- **Cathode:** The electrode where **reduction** occurs. It has a positive potential.
- **Salt Bridge:** A U-tube containing an inert electrolyte (like KCl or NH_4NO_3) in agar-agar. It completes the electrical circuit and maintains electrical neutrality in the two half-cells.

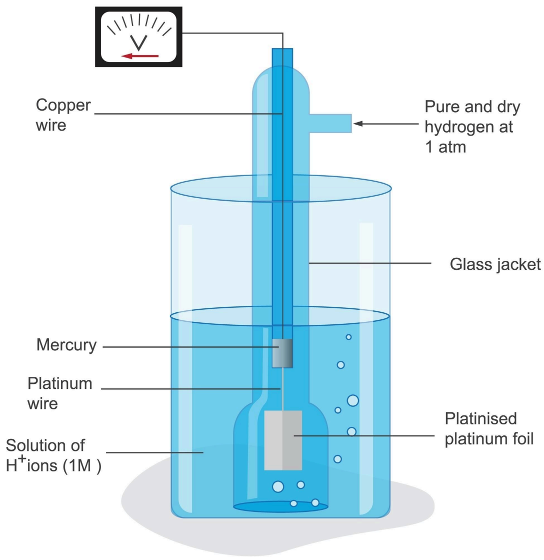
Example: Daniell Cell

- Zinc acts as the anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
- Copper acts as the cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
- Overall reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

2. Standard Electrode Potential and EMF

- **Electrode Potential (E):** The potential difference established between the metal electrode and its ions in the solution.
- **Standard Electrode Potential ($E^\ominus$):** The potential measured when the concentration of all species involved in a half-cell is unity at 298 K.
- **Standard Hydrogen Electrode (SHE):** Used as a reference electrode. Its standard reduction potential is arbitrarily taken as **0.00 V** at all temperatures.

Standard Hydrogen Electrode



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Electromotive Force (EMF) of a Cell

The potential difference between the two electrodes of a galvanic cell when no current is drawn through the circuit:

$$E^\ominus_{cell} = E^\ominus_{cathode} - E^\ominus_{anode}$$

(Note: Always use standard reduction potentials for this calculation).

3. Nernst Equation and Its Applications

The Nernst equation relates the electrode potential to the concentration of the electrolytic solution. For a general reduction reaction $M^{n+} + ne^- \rightarrow M$:

$$E = E^\ominus - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

For a general cell reaction: $aA + bB \rightarrow cC + dD$

At 298 K, substituting the values of R, T, and F (Faraday constant = 96487 C mol^{-1}), the equation simplifies to:

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0591}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Where n is the number of electrons transferred in the cell reaction.

Applications of the Nernst Equation

A. Calculation of Equilibrium Constant (K_c):

At equilibrium, the cell is completely discharged, and $E_{cell} = 0$.

$$E^{\ominus}_{cell} = \frac{0.0591}{n} \log K_c$$

B. Electrochemical Cell & Gibbs Energy ($\Delta_r G$):

The reversible work done by a galvanic cell is equal to the decrease in its Gibbs energy.

$$\Delta_r G = -nFE_{cell}$$

For standard state conditions:

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

(Note: For a spontaneous reaction, E_{cell} must be positive so that $\Delta_r G$ is negative).

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4. Conductance of Electrolytic Solutions

- **Resistance (R):** Opposition to the flow of current.
- **Specific Conductivity (κ):** The conductance of 1 cm³ of a solution. It is the reciprocal of resistivity (ρ).
  $$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A}$$
  Where l/A is the **Cell Constant** (G^*).
- **Molar Conductivity (Λ_m):** The conducting power of all the ions produced by dissolving one mole of an electrolyte in solution.
  $$\Lambda_m = \frac{\kappa \times 1000}{M}$$

(Where κ is in S cm⁻¹ and M is molarity. Units of Λ_m are S cm² mol⁻¹).

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5. Variation of Conductivity and Kohlrausch Law

- **Conductivity (κ)** always *decreases* with a decrease in concentration (dilution) because the number of ions per unit volume decreases.
- **Molar Conductivity (Λ_m)** always *increases* with a decrease in concentration. For strong electrolytes, this is due to a decrease in interionic attractions. For weak electrolytes, it is due to an increase in the degree of dissociation.

Kohlrausch Law of Independent Migration of Ions

It states that limiting molar conductivity ($\Lambda^{\ominus}_m$) of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

$$\Lambda^{\ominus}_m = \nu_+ \lambda^{\ominus}_+ + \nu_- \lambda^{\ominus}_-$$

Where ν_+ and ν_- are the number of cations and anions, and $\lambda_+^\ominus$ and $\lambda_-^\ominus$ are their limiting molar conductivities.

Applications:

1. Calculating $\Lambda_m^\ominus$ for weak electrolytes.
2. Calculating the degree of dissociation (α) for weak electrolytes:
   $$\alpha = \frac{\Lambda_m}{\Lambda_m^\ominus}$$
3. Calculating the dissociation constant (K_a):
   $$K_a = \frac{c\alpha^2}{1-\alpha}$$

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6. Electrolytic Cells & Electrolysis

Electrolytic cells use electrical energy to drive non-spontaneous chemical reactions.

Faraday's Laws of Electrolysis

- **First Law:** The mass of a substance deposited or liberated at any electrode is directly proportional to the quantity of electricity (Q) passed through the electrolyte.
  $m = ZIt$
  (Where Z is electrochemical equivalent, I is current in Amperes, and t is time in seconds).
- **Second Law:** When the same quantity of electricity is passed through different electrolytes connected in series, the masses of the substances produced are proportional to their equivalent weights.

Products of Electrolysis

The product depends on the nature of the material being electrolyzed and the electrodes used. Generally, the cation with the higher standard reduction potential is reduced at the cathode, and the anion with the lower standard reduction potential is oxidized at the anode (Preferential Discharge Theory).

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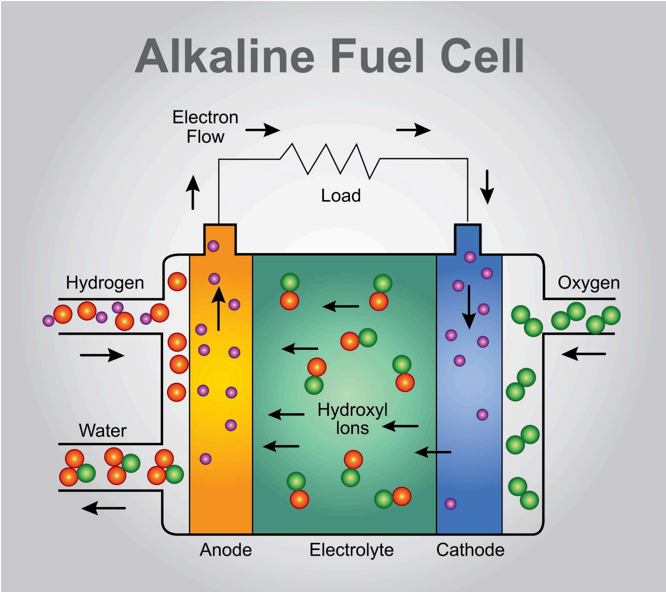
7. Batteries and Fuel Cells

A battery is essentially a series of galvanic cells.

- **Primary Batteries:** The cell reaction occurs only once and becomes dead after use (e.g., Dry cell/Leclanche cell, Mercury cell).
- **Secondary Batteries:** Can be recharged by passing current through them in the opposite direction (e.g., Lead storage battery, Nickel-Cadmium cell).
- **Fuel Cells:** Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane, or methanol directly into electrical energy. They are highly efficient and pollution-free.



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8. Corrosion

Corrosion is an electrochemical process where a metal is oxidized by its environment (e.g., rusting of iron).

- **Anode (Oxidation):** $2Fe(s) \rightarrow 2Fe^{2+} + 4e^-$
- **Cathode (Reduction):** $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
- **Prevention Methods:** Barrier protection (painting, oiling), galvanization (coating with zinc), and cathodic protection.
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