SYNOPSIS :

- **Electrochemistry:** The study of production of electricity from energy released during spontaneous chemical reactions.

- **Use of Electrochemistry:** To use electrical energy to bring about non-spontaneous chemical transformations.

- **Daniell cell** converts the chemical energy liberated during the redox reaction. This is a cell in which the following redox reaction occurs: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

- **A galvanic cell** is an electrochemical cell that converts the chemical energy of a spontaneous redox reaction into electrical energy. In this device the **Gibbs energy** of the spontaneous redox reaction is converted into **electrical work**.

- **Half-cells or Redox couples:** The reduction half reaction occurs on the copper electrode while the oxidation half reaction occurs on the zinc electrode.

- **Electrode potential:** A potential difference develops between the electrode and the electrolyte. In a galvanic cell, the half-cell in which oxidation takes place is called **anode** and it has a negative potential with respect to the solution.

- The potential difference between the two electrodes of a galvanic cell is called the **cell potential** and is measured in **volts**.

- The **cell potential** is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the **cell electromotive force (emf)** of the cell when no current is drawn through the cell.

- **The pressure of hydrogen gas** is one bar and the concentration of hydrogen ion in the solution is one molar.

- The positive value of the **standard electrode potential** in the first case indicates that Cu^{2+} ions get reduced more easily than H^{+} ions.

- **Inert electrodes:** Metals like platinum or gold are used as Inert electrodes. They do not participate in the reaction but provide their surface for oxidation or reduction reactions and for the conduction of electrons.

- **E(cell)** is an intensive parameter. It depends on the concentration of both Cu^{2+} and Zn^{2+} ions. It increases with increase in the concentration of Cu^{2+} ions and decreases in the concentration of Zn^{2+} ions.

- **Electrical work done in one second = electrical potential multiplied by total charge passed.**

- **$\Delta_r G$** is an extensive hermodynamic property and the value depends on n.

- **The electrical resistance** is represented by the symbol **'R'** and it is measured in ohm **(Ω).**

- The **electrical resistance** of any object is directly proportional to its **length**, **l**, and **inversely proportional** to its area of cross section, A.

$$R \propto \frac{l}{A} \text{ or } R = \rho \frac{l}{A}$$

- The **constant of proportionality**, ρ (Greek, rho), is called **resistivity**. The inverse of resistance, R, is called **conductance.**

$$G = \frac{1}{R} = \frac{A}{\rho l} = \frac{A}{l}$$

- The **SI unit of conductance** is siemens, represented by the symbol **'S'** and is equal to **ohm−1** (mho) or Ω−1.

- The inverse of resistivity, called **conductivity** (specific conductance) is represented by the symbol, **κ** (Greek, kappa).

- **Materials:** They are classified into **conductors**, **insulators** and **semiconductors** depending on the magnitude of their conductivity.

- Conductivity between conductors and insulators are called **semiconductors** and are important electronic materials.

- Superconductors have zero resistivity or infinite conductivity.

- **The electronic conductance depends on:**
  - The nature and structure of the metal
  - The number of valence electrons per atom
  - Temperature (it decreases with increase of temperature).

- The conductance of electricity by ions present in the solutions is called **electrolytic** or **ionic conductance**.

- **The conductivity of electrolytic (ionic) solutions depends on:**
  - The nature of the electrolyte added
  - Size of the ions produced and their solvation
  - The nature of the solvent and its viscosity
  - Concentration of the electrolyte
  - Temperature (it increases with the increase of temperature).

- **Conductivity Cell:** It consists of two platinum electrodes coated with platinum black.

- The quantity l/A is called **cell constant** denoted by the symbol, **G***. It depends on the distance between the electrodes and their area of cross-section and has the dimension of length–1 and can be calculated if we know l and A.

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

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- **Faraday's Laws of Electrolysis:**
  - **First Law:** '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 (solution or melt)'.
  - **Second Law:** 'The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation)'.

- **Products of electrolysis** depend on the nature of material being electrolysed and the type of electrodes being used.

- **Any battery** or **cell** that we use as a source of **electrical energy** is basically a galvanic cell where the chemical energy of the redox reaction is converted into electrical energy.

- **Dry cell (Leclanche cell):** The cell consists of a zinc container that also acts as anode and the cathode is a carbon (graphite) rod surrounded by powdered manganese dioxide and carbon. It is used commonly in transistors and clocks.

- **Mercury cell:** Consists of zinc – mercury amalgam as anode and a paste of HgO and carbon as the cathode. It is suitable for low current devices like hearing aids, watches, etc.

- A **secondary cell** after use can be recharged by passing current through it in the opposite direction, so that it can be used again.

- **Galvanic cells:** Designed to convert the energy of combustion of fuels like hydrogen, methane, methanol, etc. directly into electrical energy are called **fuel cells**.

- **Oxidation of Metals:** By loss of electrons to oxygen and formation of oxides. Corrosion of iron (rusting) occurs in presence of water and air.

- **Methods of preventing corrosion:**
  - To prevent the surface of the metallic object to come in contact with atmosphere, done by covering the surface with paint or by some chemicals (e.g. bisphenol).
  - To cover the surface by other metals (Sn, Zn, etc.) that are inert or react to save the object.
  - An electrochemical method is to provide a sacrificial electrode of another metal (like Mg, Zn, etc.) which corrodes itself but saves the object.