UNIT – 3

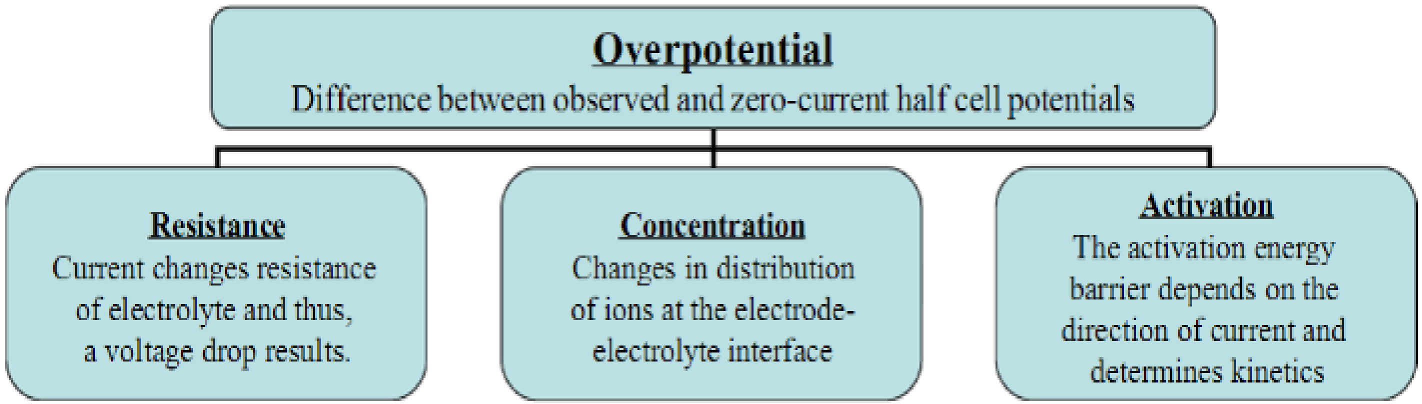
BIOPOTENTIAL ELECTRODES

& CONFIGURATION

Polarization effects of electrode

Polarization

- **with current** flowing the half-cell voltage changes this voltage change is called **overpotential** or **polarization.**



$$V_p = V_r + V_c + V_a$$

- V_a: activation, depends on direction of reaction
- V_c: concentration (change in double layer)
- V_r: ohmic (voltage drop)

Note: Polarization and impedance of the electrode are two of the most important electrode properties to consider.

- **Perfectly Polarizable Electrodes**

The current across the interface is a displacement current and the electrode behaves like a capacitor. No electrodes' ions transfer. Instead, the ions and electrons (of the solution) at the surface of the metal become polarized. The charges orient at the interface to create an electric double layer; the metal then acts like a capacitor.

Example : Silver/silver chloride (Ag/AgCl) electrode, Platinum (Pt) electrode, metal electrodes.[5]

- **Perfectly Non-Polarizable Electrode**

Current passes freely across the electrode-electrolyte interface, requiring no energy to make the transition. No overpotentials. Non-polarizable electrodes are reversible (ions in the solution are charged and discharged).

Example: Silver/silver chloride (Ag/AgCl) electrode. Mercury/mercurous chloride (Hg/Hg_2Cl_2) (Calomel).

Nernst equation

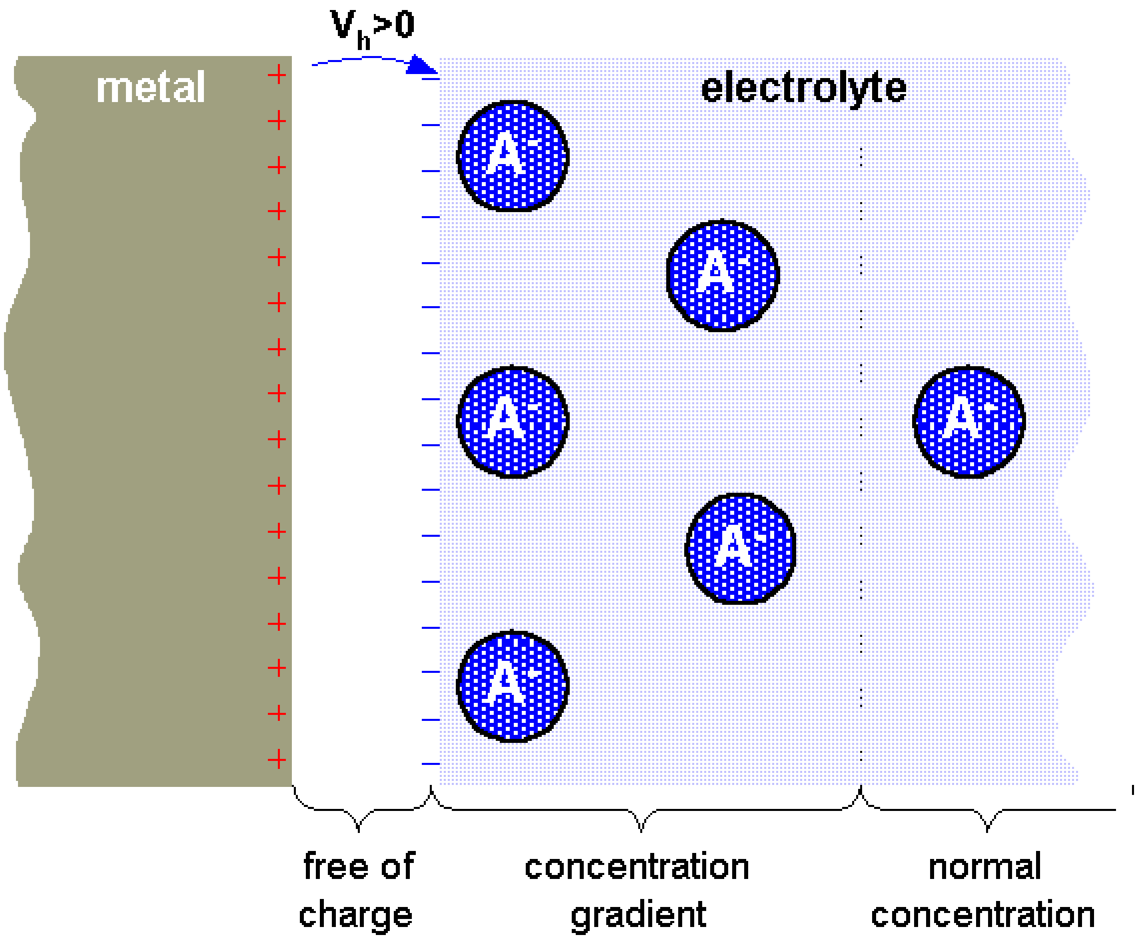
For arbitrary concentration and temperature

$E = RT/(zF) \cdot \ln(c/K)$

E – electrode potential
R = 8.314 J /(mol*K) – molar gas constant
T – absolute temperature
z – valence
F = 96485 C/mol – Faraday’s constant
c – concentration of metal ion in solution
K – “metal solution pressure”,
or tendency to dissolve

electrode double layer

No current



current influence

- **with current** flowing
  the half-cell voltage changes
- this voltage change is called
  overpotential or **polarization:**
- $V_p = V_r + V_c + V_a$

  - V_a: activation, depends on direction of reaction
  - V_c: concentration (change in double layer)
  - V_r: ohmic (voltage drop)

polarizable electrode

- “perfectly” polarizable electrode:
  - only **displacement** current, electrode behave like a **capacitor**
- example: noble metals like platinum Pt

nonpolarizable electrode

- “perfectly” nonpolarizable electrode:
  - current passes freely across interface,
  - no **overpotential**
- examples:
  - silver/silver chloride (Ag/AgCl),
  - mercury/mercurous chloride (Hg/Hg_2Cl_2) (calomel)