Chapter 22: Introduction to Electroanalytical Chemistry

Two general categories:

1) Potentiometric Systems – measure voltage (i.e., potential) of a galvanic cell (produces electricity spontaneously)
2) Voltammetric Systems – control potential & usually measure current in an electrolytic cell (consumes power to cause an electrochemical reaction to occur)

Potentiometry

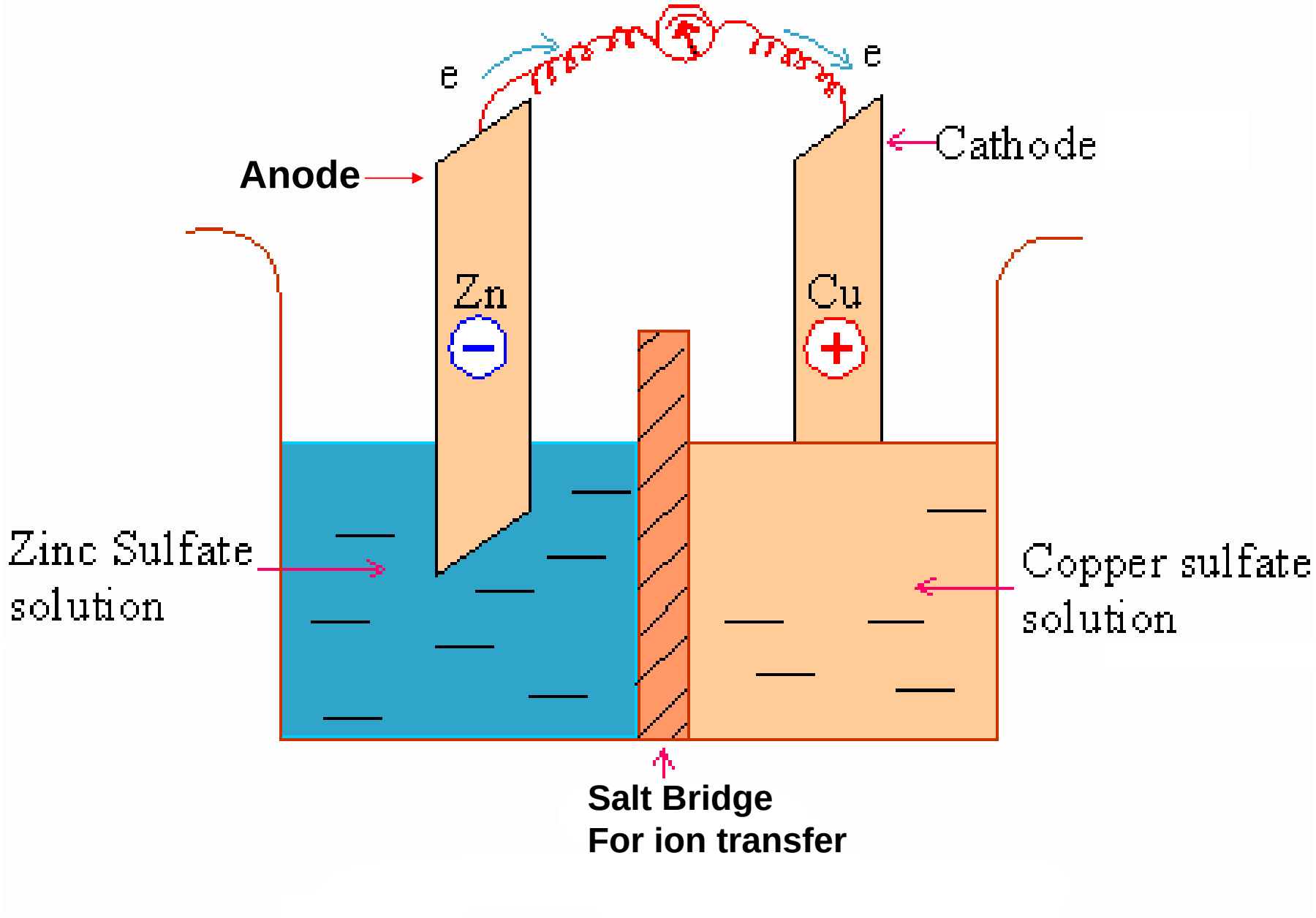
- Determine concentrations by measuring the potential (i.e., voltage) of an electrochemical cell (galvanic cell)

- Two electrodes are required

    1) Indicator Electrode – potential responds to activity of species of interest

    2) Reference Electrode – chosen so that its potential is independent of solution composition.

Representation of Electrochemical Cell



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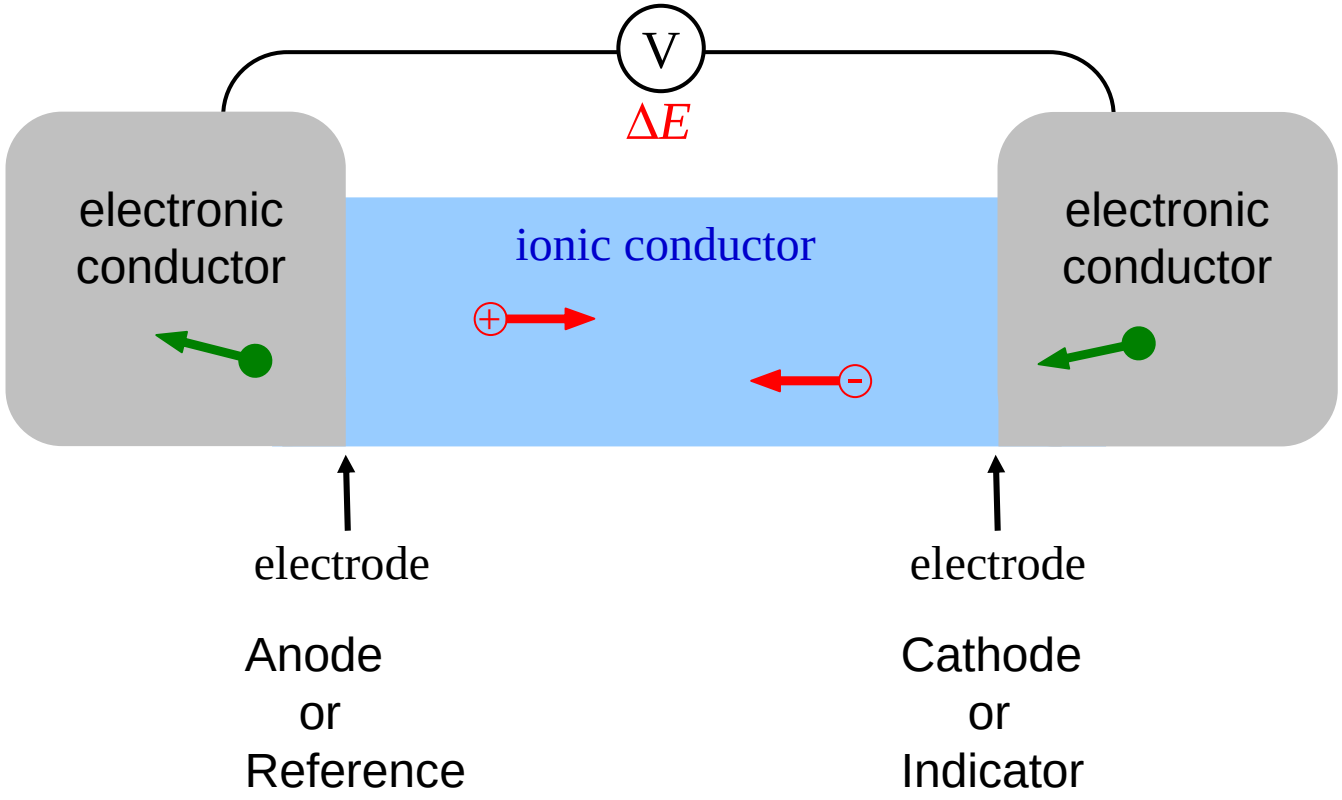


Ⓥ - Represents device to measure potential (voltage) without drawing significant current i.e potentiometer or electrometer (high input impedance ≥ 100 MΩ (mega ohms)

$$E_{cell} = E_{ind} - E_{ref} \ (+ E_J)$$

E_J = junction potential, a non-ideal potential which develops across the interface between two dissimilar solutions

$$E_{cell} = E_{ind} - E_{ref} \ (+ E_J)$$

Nernst Equation

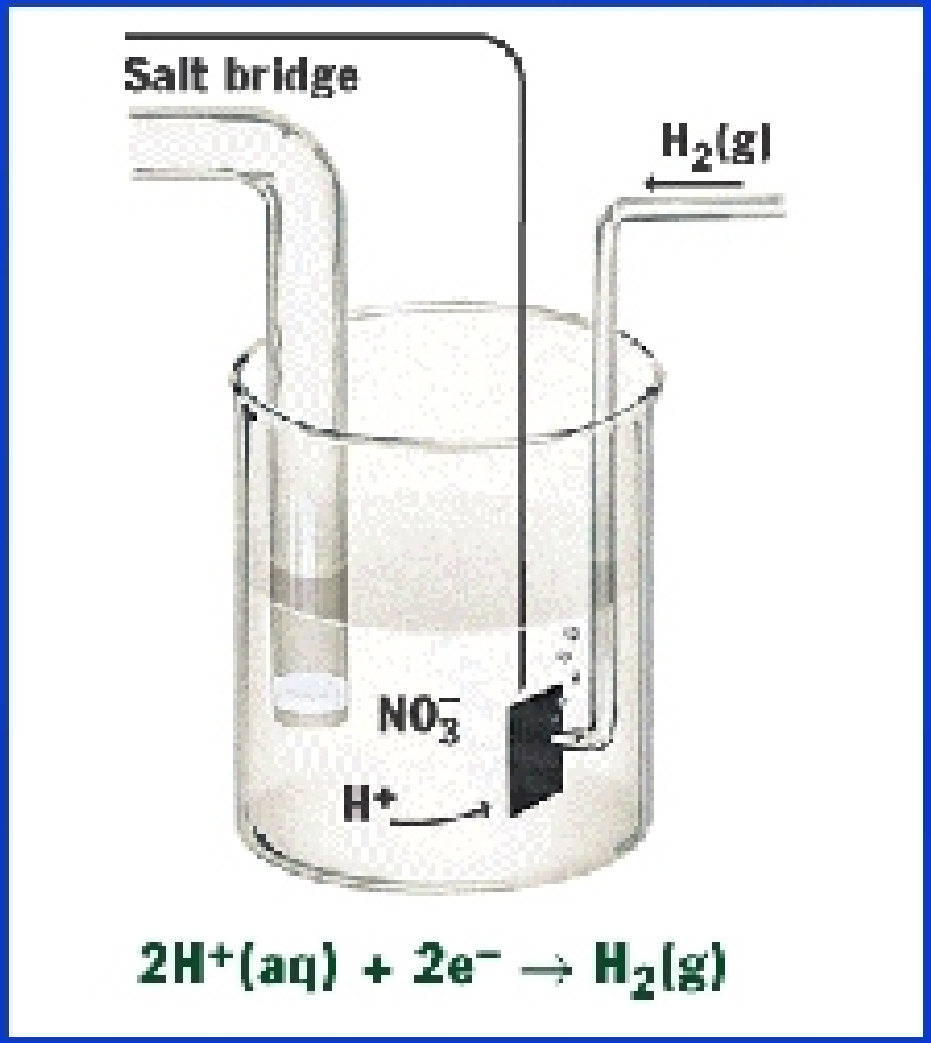
$$E = E^o - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]}$$

Where R = gas constant
T = absolute temperature
n = number of electrons in reaction
F = Faraday's constant
E = potential
E^o = standard potential
[Red] = molar concentration of reduced form of species
[Ox] = molar concentration of oxidized form of species

Reference Electrodes

- The Normal Hydrogen Electrode (NHE) is important historically and could serve as a reference electrode today, however, it is impractical, requiring a source of H_2 gas at constant pressure, and is highly flammable.

The Hydrogen Electrode

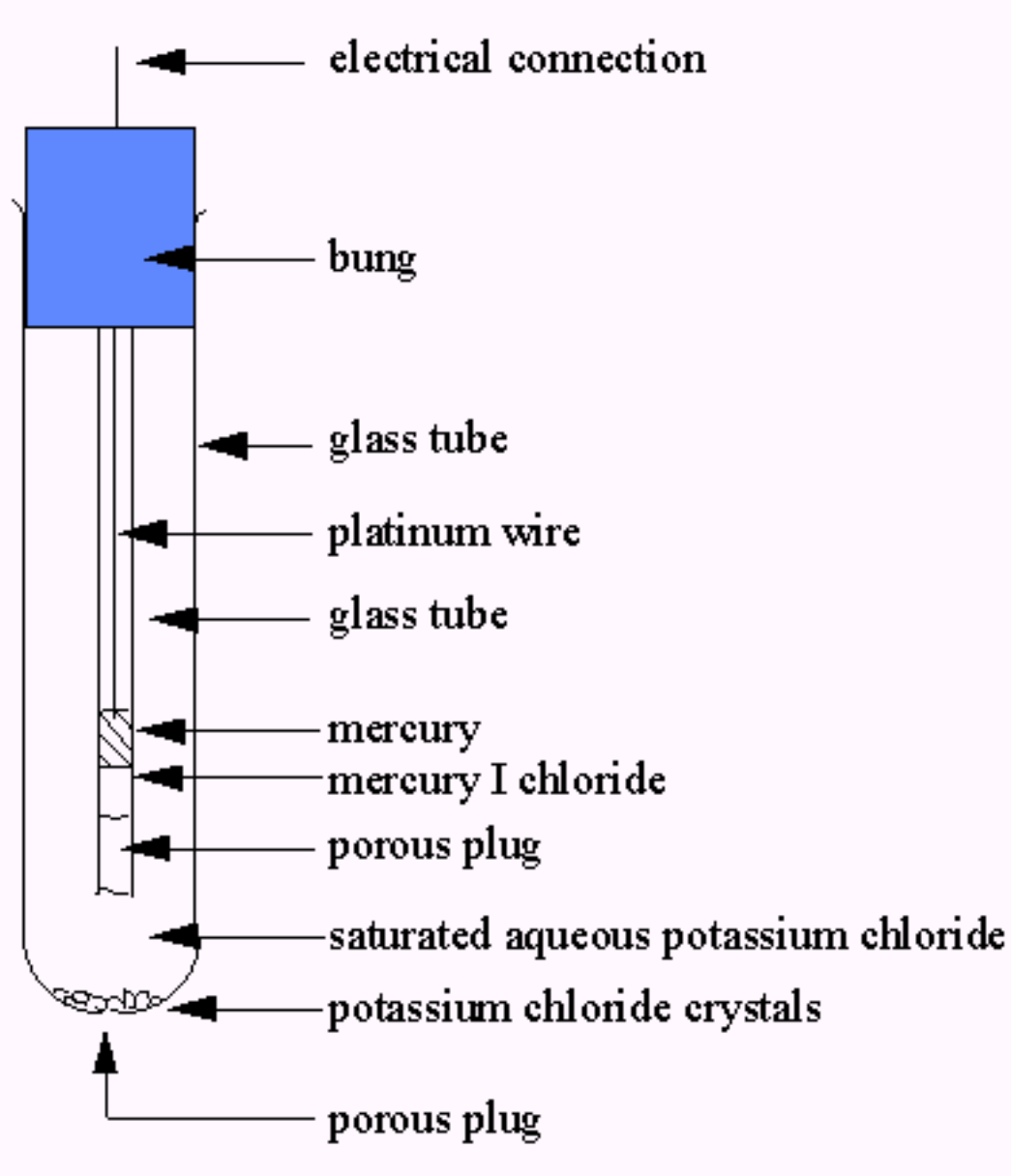


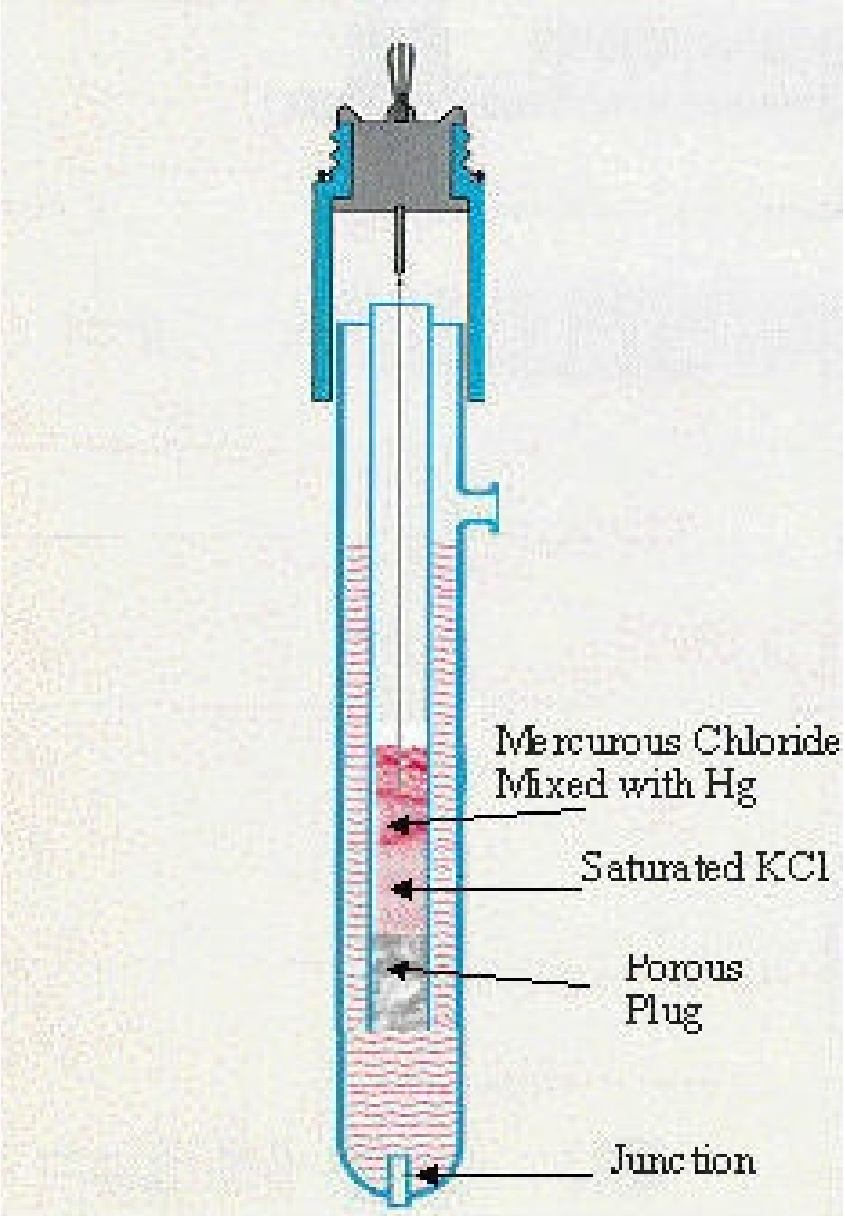
- Hydrogen gas is bubbled over an inert platinum electrode

Reference Electrodes

- The Calomel Electrode or Saturated Calomel Electrode (SCE) is the next most important reference electrode historically and was used almost exclusively for many decades as the reference electrode of choice
- Calomel is the insoluble compound Hg_2Cl_2
- The electrode half reaction is
- $Hg_2Cl_2 + 2\ e^- \leftrightarrow 2\ Hg + 2Cl^-$ $E^o = 0.242$ v

Calomel Reference Electrode





Calomel Reference Electrode

- Can use 1 M or 0.1 M KCl rather than a saturated solution
- E for reference changes slightly with any change in concentration from the Nernst Eq
- Temperature coefficient of reference electrode is less with 1 M or 0.1 M than for SCE
- SCE often gets clogged if solution dries out