Advanced Analytical Chemistry CHEM.5140

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Electroanalytical Methods

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

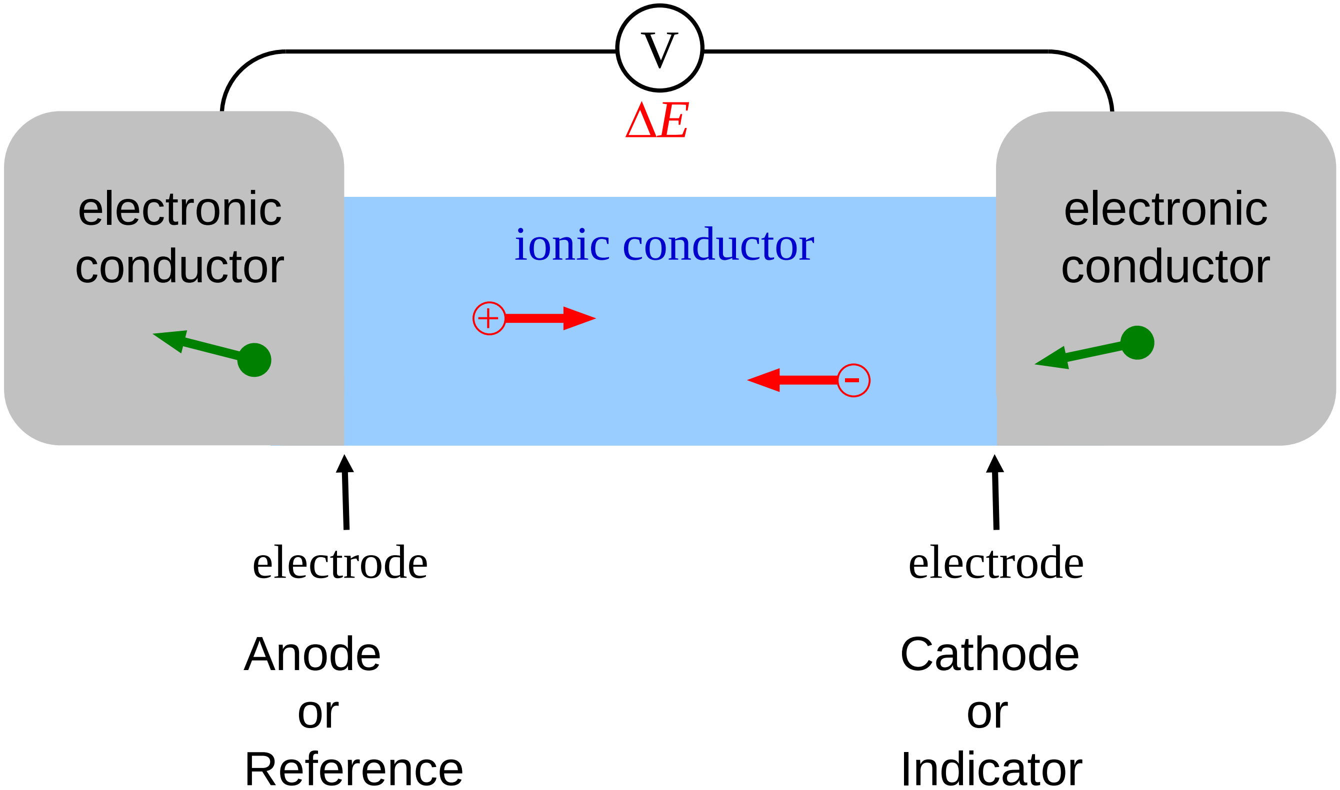
- Determine concentrations by measuring the potential (i.e., voltage) of an electrochemical cell (galvanic cell)

- Two electrodes are required (2 half cells)

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

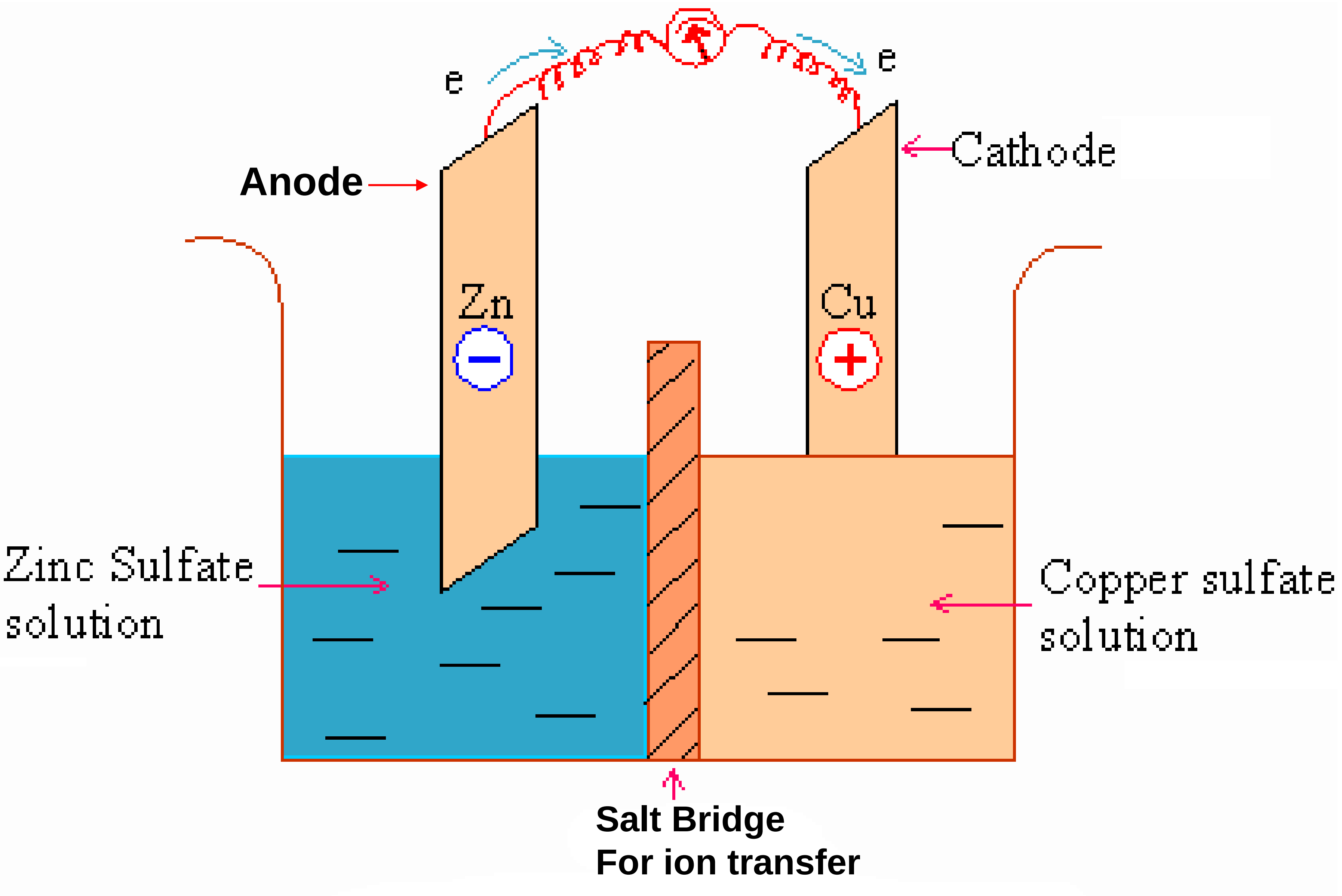
  2) Reference Electrode – chosen so that its potential is independent of solution composition.

Electrochemical Cell



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

Electrochemical Cell



Cell Potential (Voltage)

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

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

Half reactions written as reductions

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

Nernst Equation

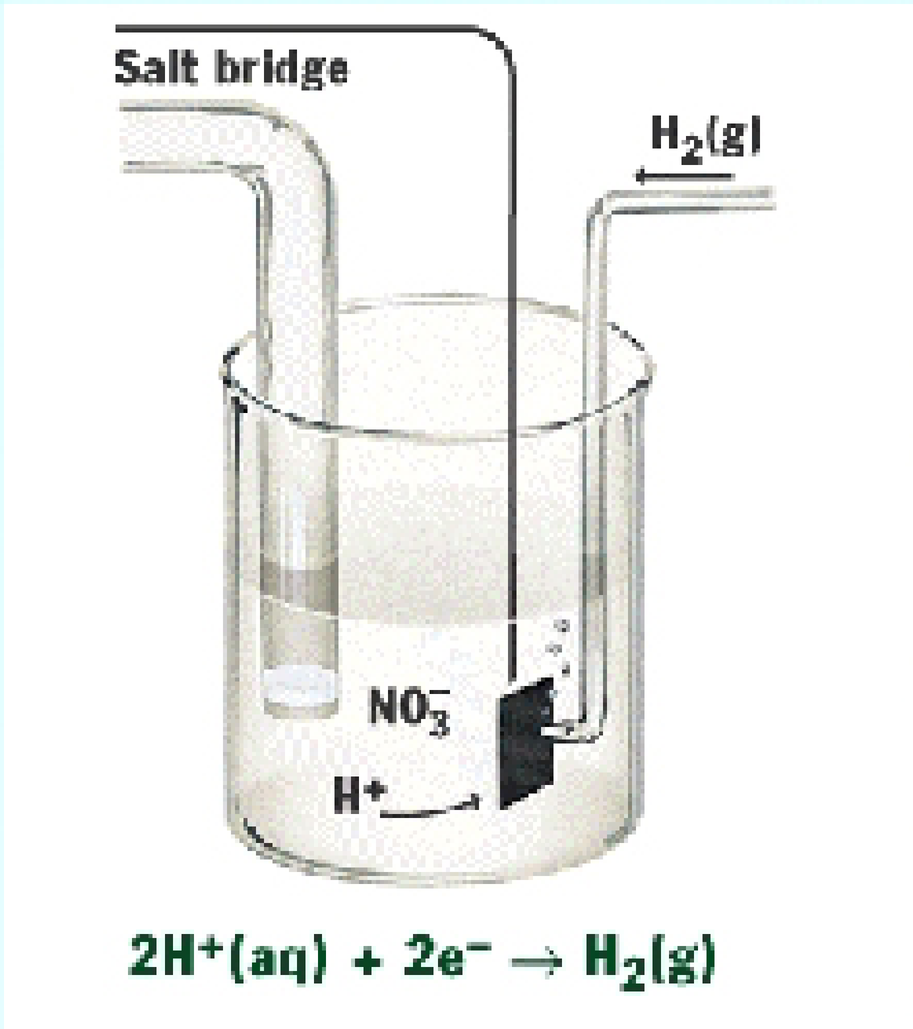
$$E = E^o - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]}$$

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

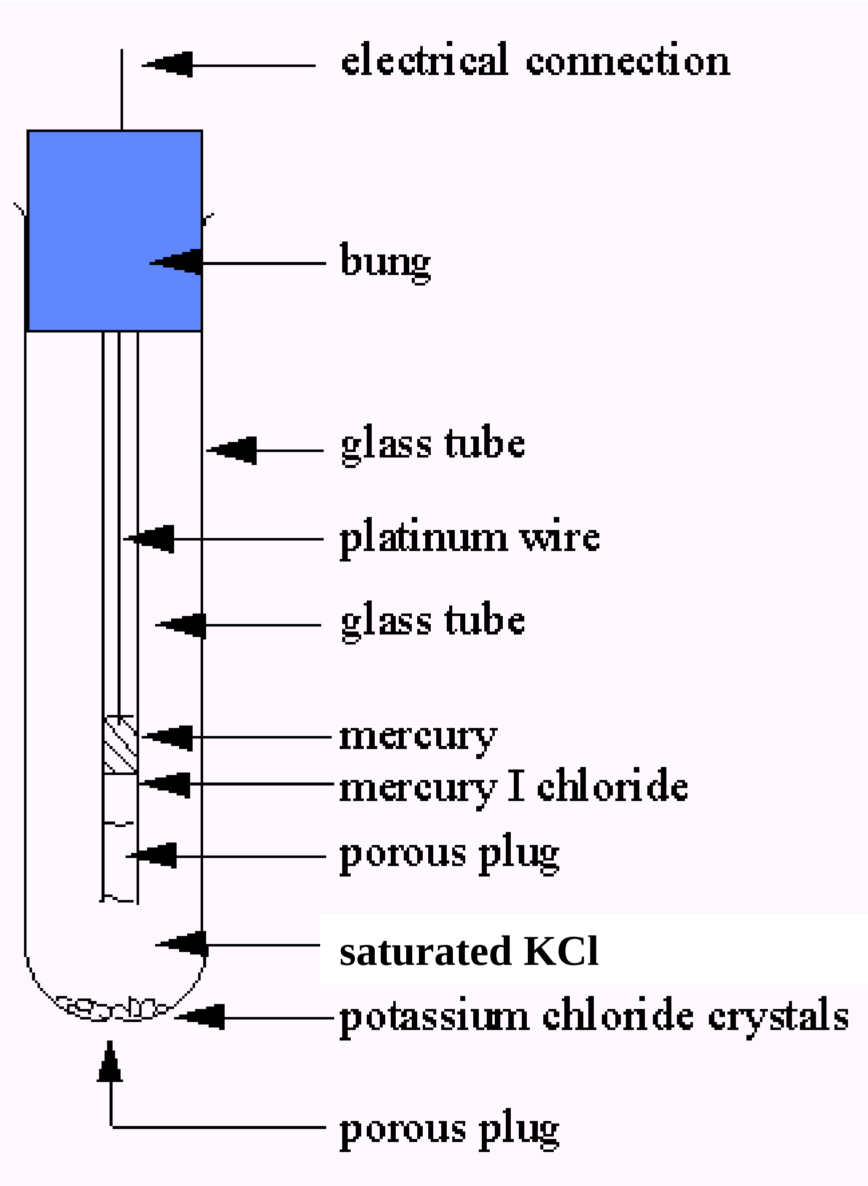


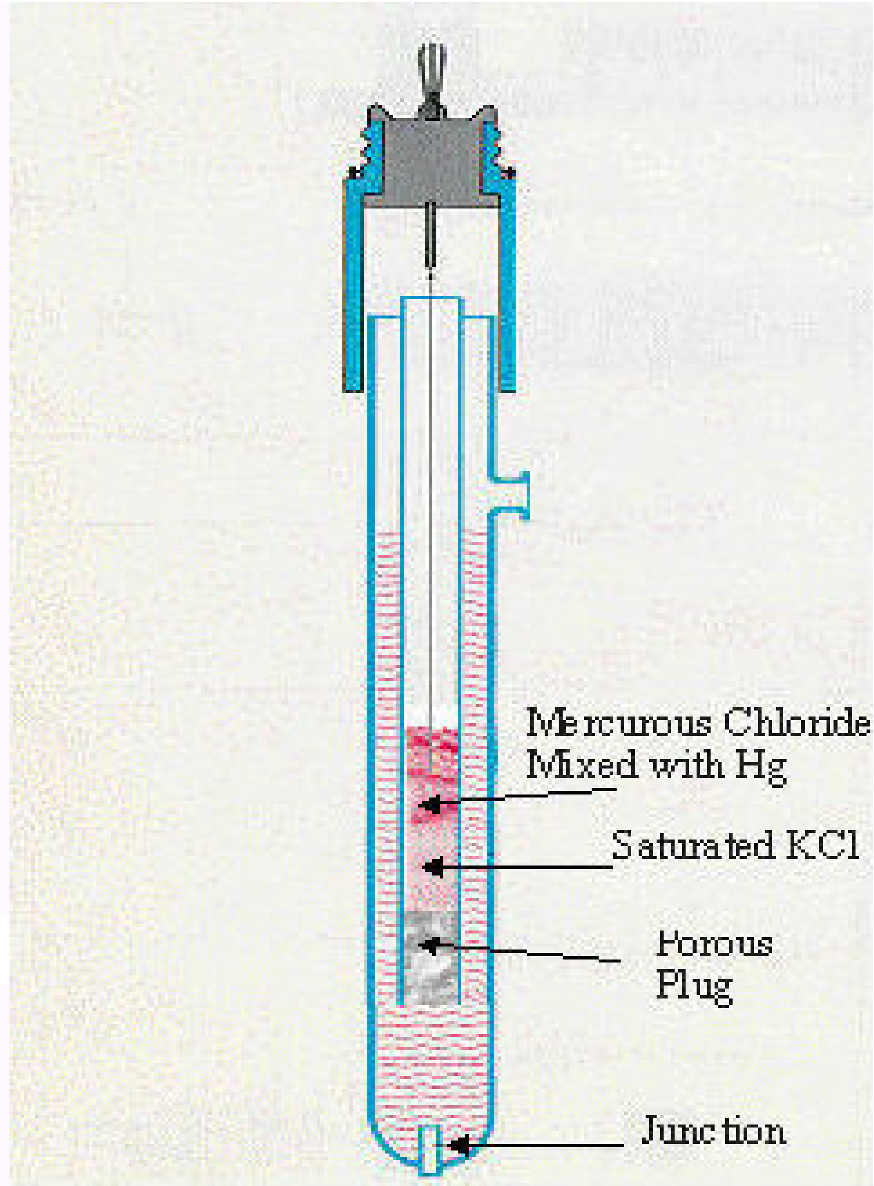
- Hydrogen gas is bubbled over an inert platinum electrode

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
- $Hg_2Cl_2 + 2\ e^- \leftrightarrow 2\ Hg + 2Cl^-\quad E^o = 0.242\ v$

Calomel Reference Electrode

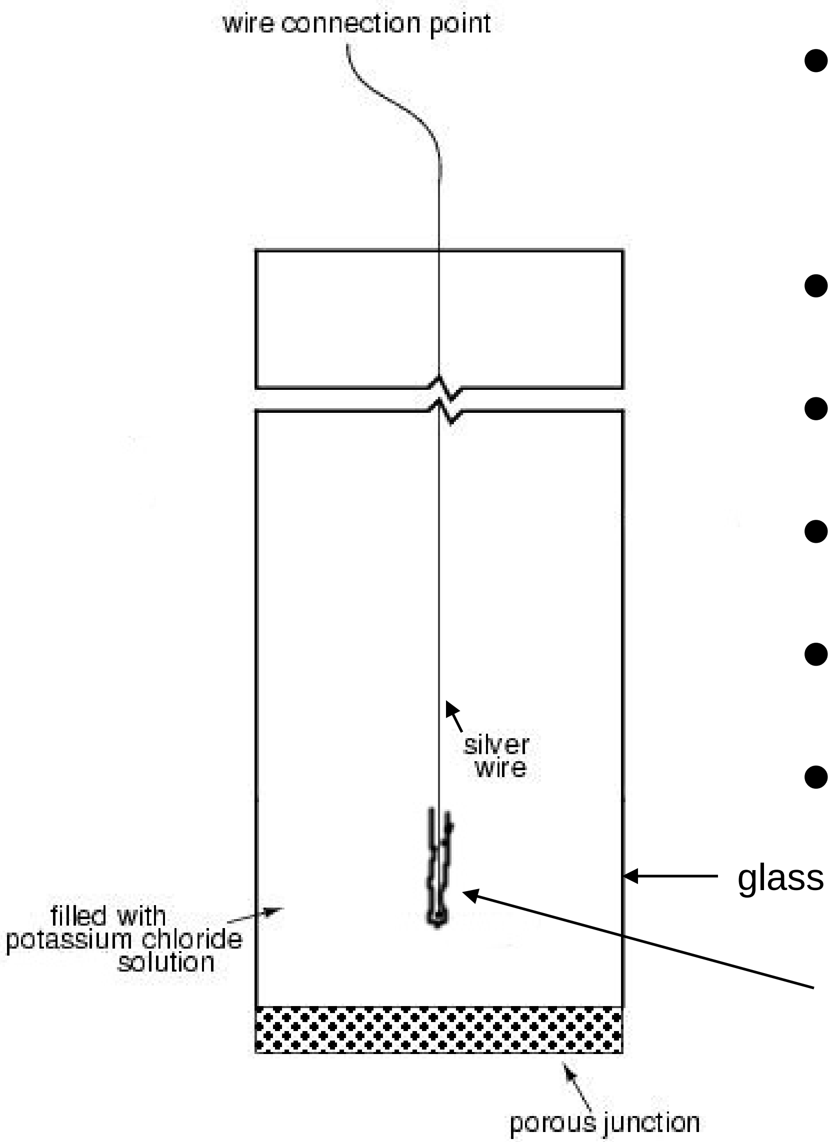




Calomel Reference Electrode

- 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

Silver/Silver Chloride Reference Electrode



- Reaction is
  $AgCl + e^- \leftarrow\rightarrow Ag + Cl^-$
- $E^o = 0.222$ v
- E = 0.228 for 1 M KCl
- Easily made in the lab
- Reliable
- Non-toxic vs Calomel

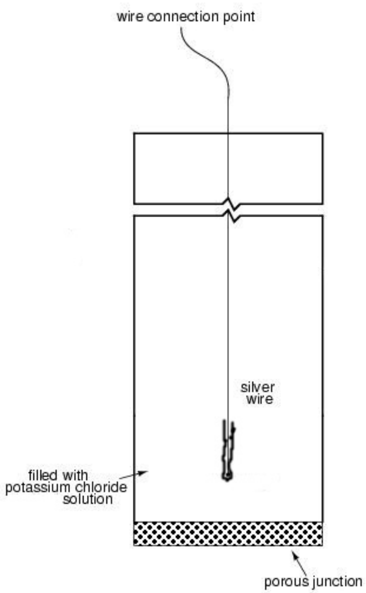
Silver/Silver Chloride Reference Electrode

$$AgCl + e^- \leftrightarrow Ag + Cl^-$$

silver chloride coating on wire

silver wire

potassium chloride solution



Nernst Equation

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

Reference Electrodes

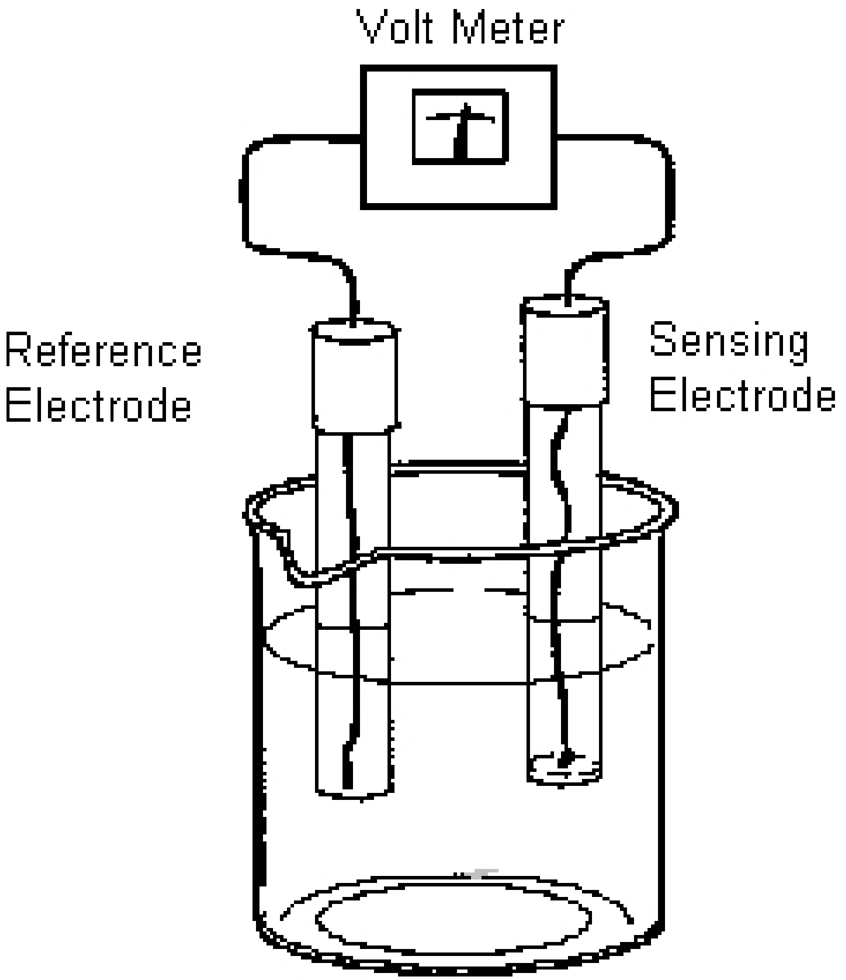
- Normal Hydrogen Electrode (NHE)
- $2H^+ + 2e^- \leftrightarrow H_2$ $E^o = 0.000$ v

- Saturated Calomel Electrode (SCE)
- $Hg_2Cl_2 + 2\ e^- \leftrightarrow 2\ Hg + 2Cl^-$ $E^o = 0.268$ v

- Silver/Silver Chloride Electrode (AgCl)
- $AgCl + e^- \leftrightarrow Ag + Cl^-$ $E^o = 0.222$ v

Indicator Electrodes

- potential "indicates" activity of species
- terms Working Electrode or Sensing Electrode are sometimes used
- Coupled to reference and meter as usual



Indicator Electrodes

Electrode of the First Kind

– Metallic Indicator Electrodes

1) Active metals (e.g., Ag, Cu, Hg, Pb, Cd) can serve as indicators for their own ions

$$Ag^{+} + e^{-} \leftrightarrow Ag \qquad E^{o} = 0.799 \text{ v}$$

Nernst Equation

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

At 25 ^{o}C this becomes

$$E = E^{o} - \frac{0.0591}{n} \log \frac{[Red]}{[Ox]}$$

For the Silver/Silver ion system

$$Ag^+ + e^- \leftrightarrow Ag \qquad E^o = 0.799 \text{ v}$$

this becomes

$$E = 0.799 - \frac{0.0591}{1} \log \frac{1}{[Ag^+]}$$

Electrode potential is inversely proportional to the concentration of the silver ions, even for a simple electrode made only of Ag metal