# Advanced Analytical Chemistry 84.514

Dr. David Ryan

Olney 318A

978-934-3698

http://faculty.uml.edu/David_Ryan

# 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

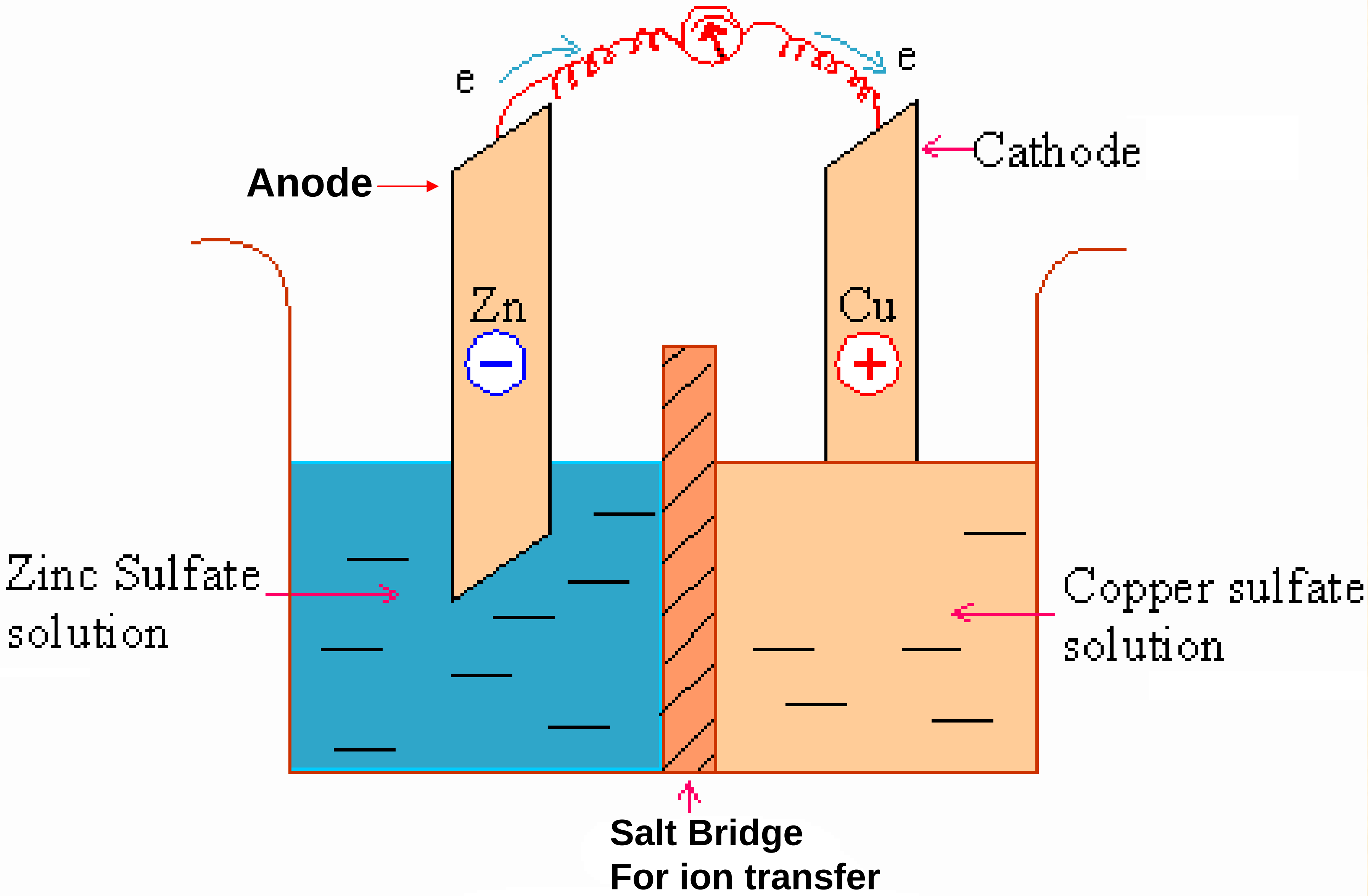
- Determine concentrations by measuring the potential (i.e., voltage) of an electrochemical cell (galvanic cell)

- Two electrodes are required

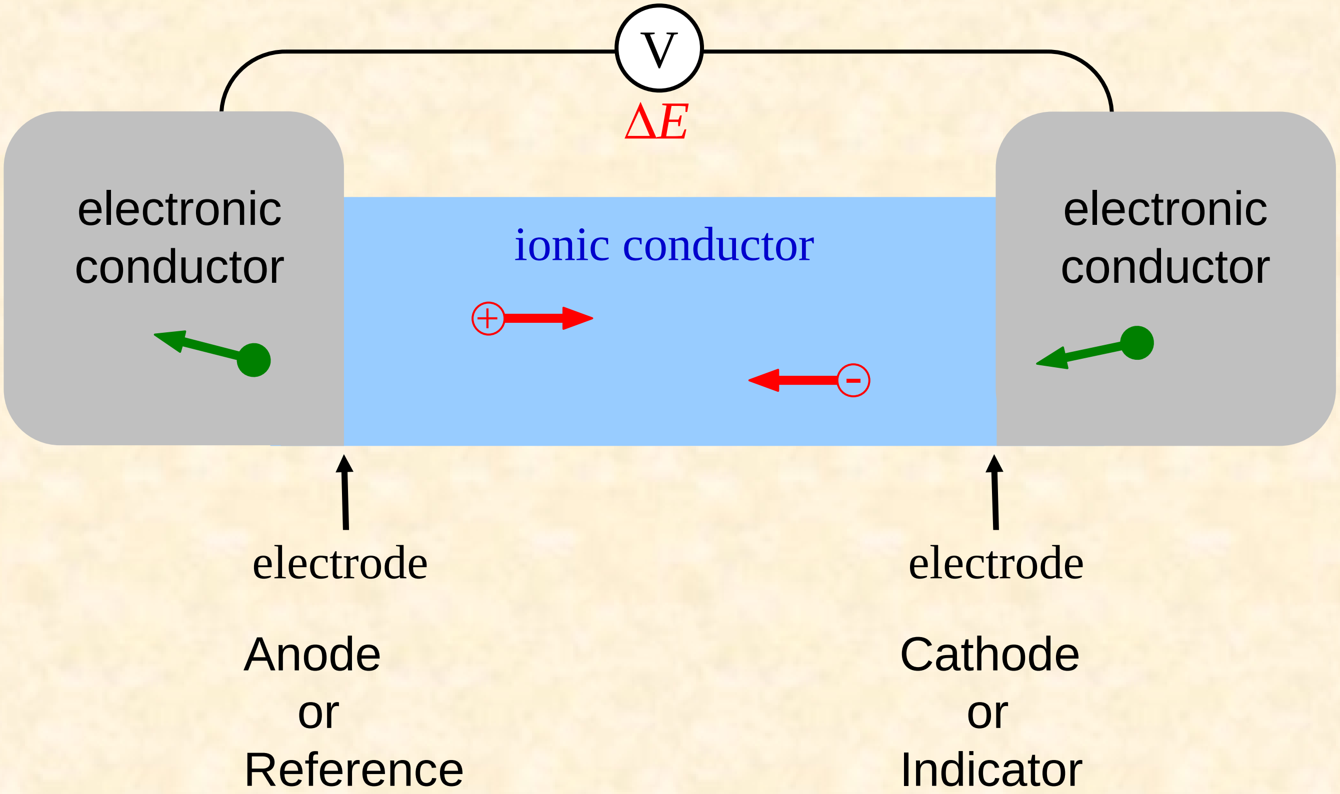
  1) Indicator Electrode – potential responds to activity of species of interest

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

# Electrochemical Cell



# 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)

# 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

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

# Nernst Equation

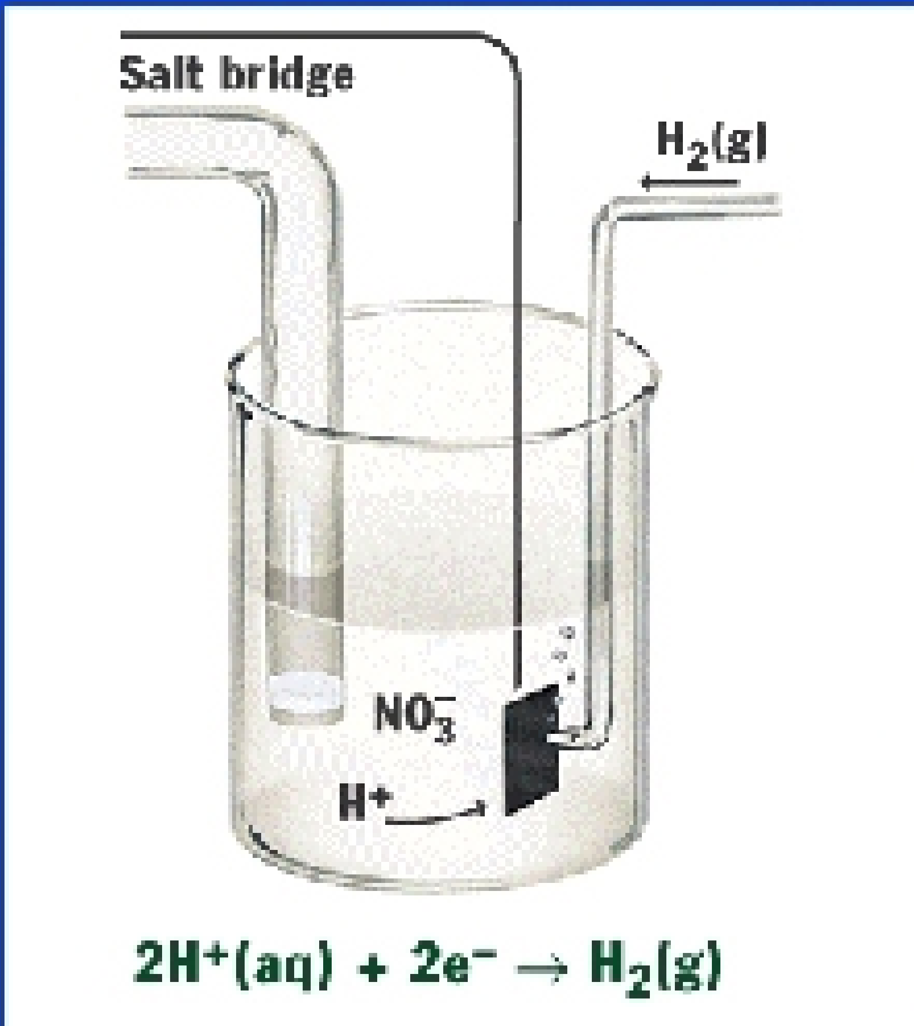
$$E = E^o - \frac{RT}{nF} \ln \frac{[Red]}{[Ox]}$$

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

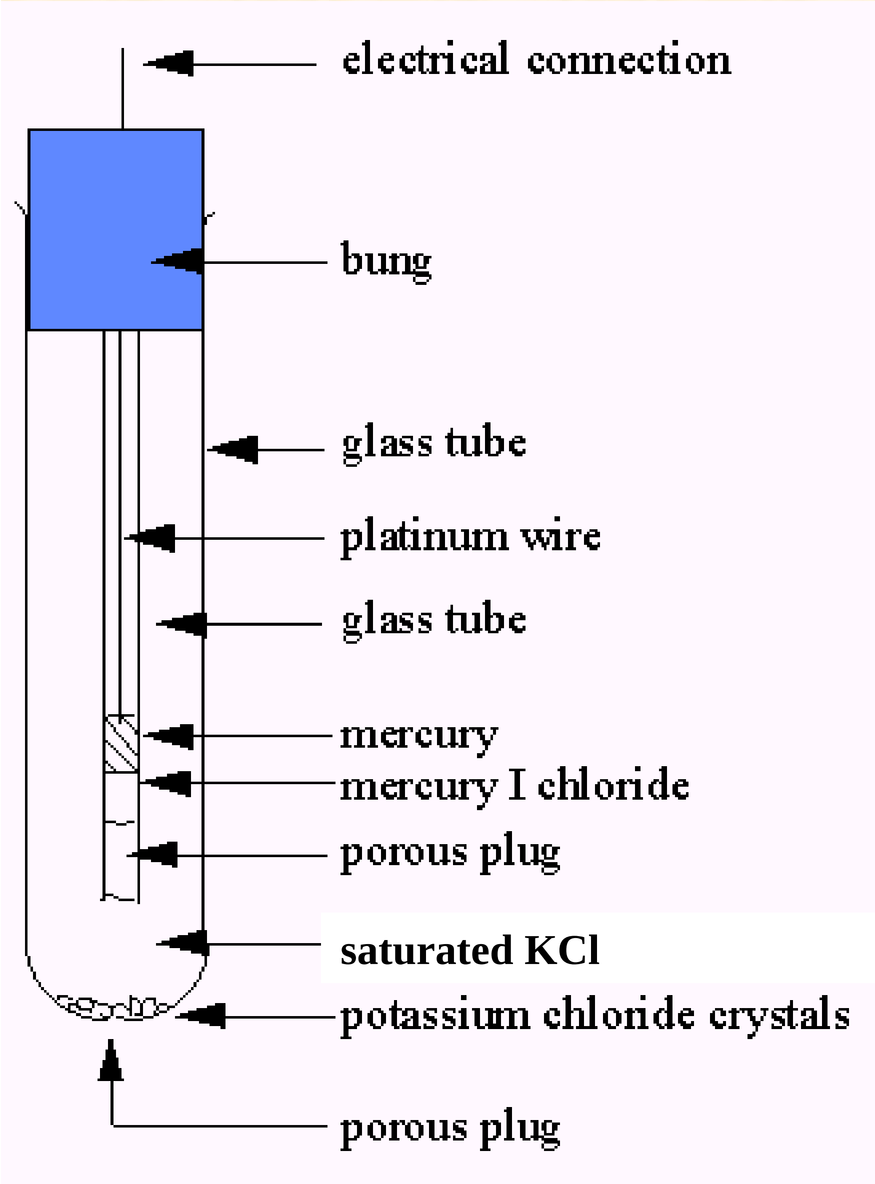


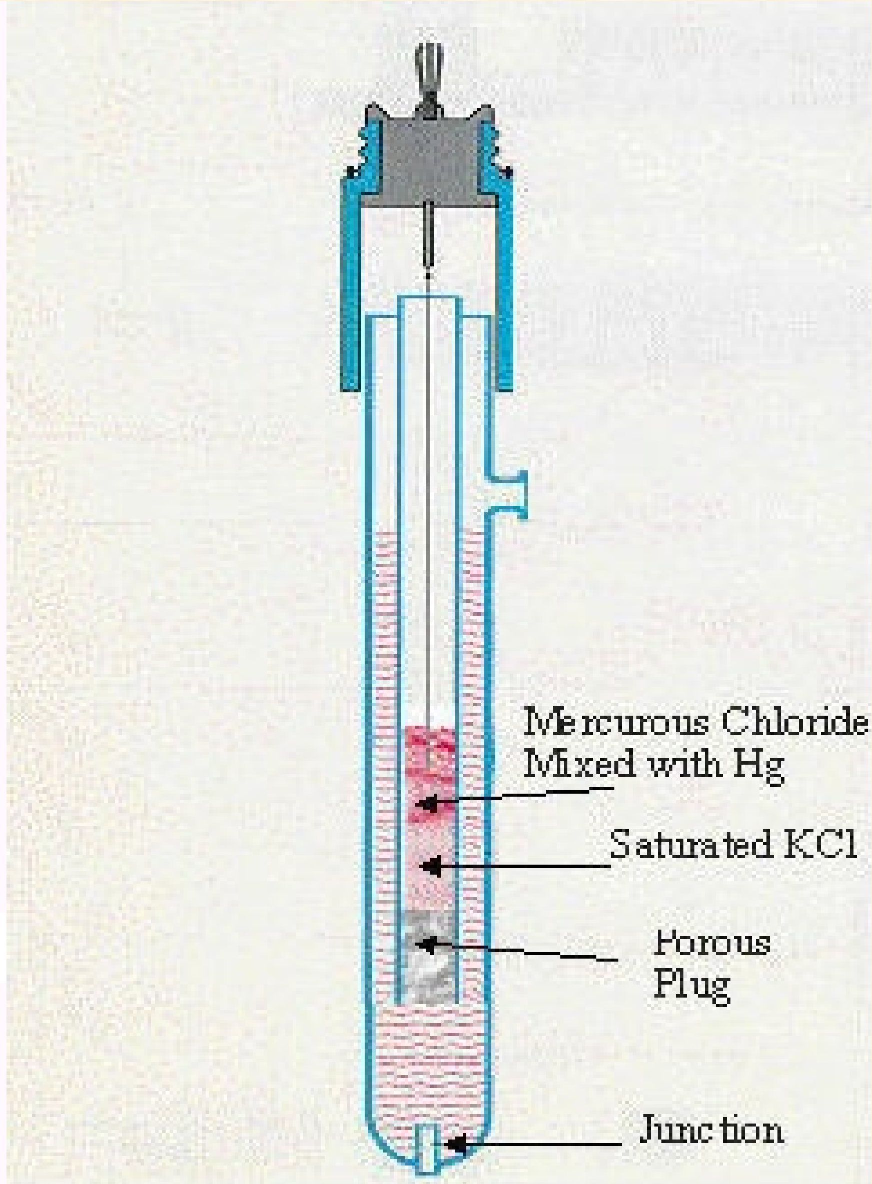

- Hydrogen gas is bubbled over an inert platinum electrode

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

# Calomel Reference Electrode

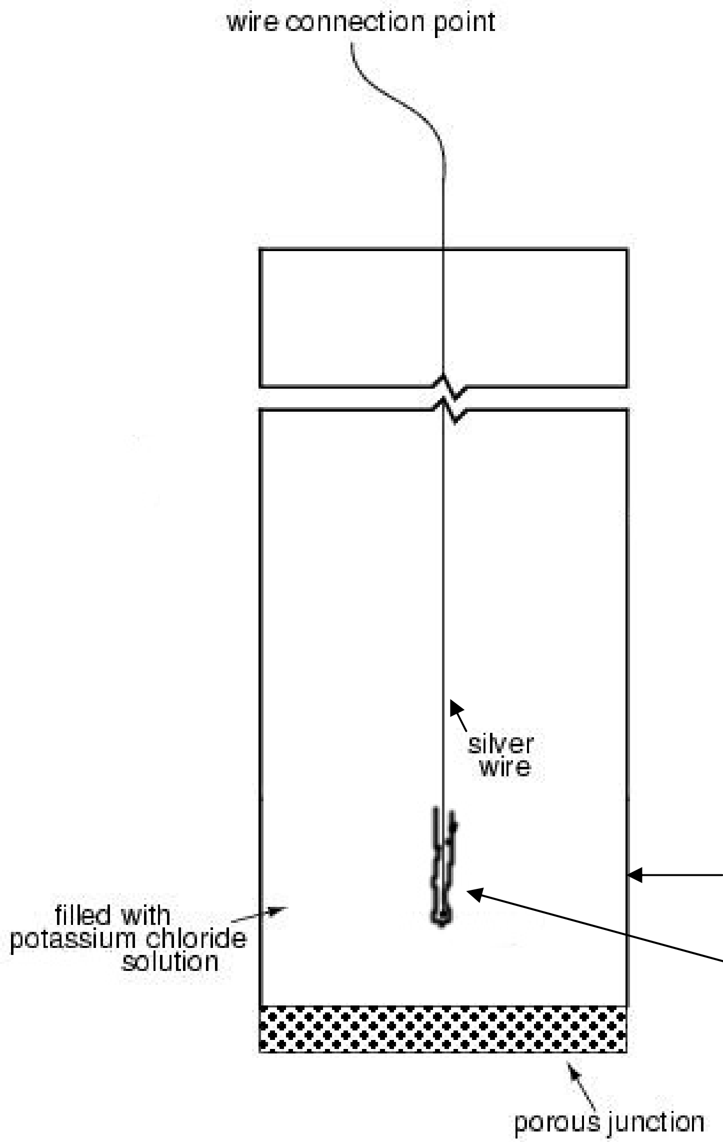


# Calomel Reference Electrode

- 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 + $e^-$ ←→ Ag + $Cl^-$
- $E^o$ = 0.222 v
- E = 0.228 for 1 M KCl
- Easily made in the lab
- Reliable
- Non-toxic vs Calomel

glass or plastic body

silver chloride coating on silver wire

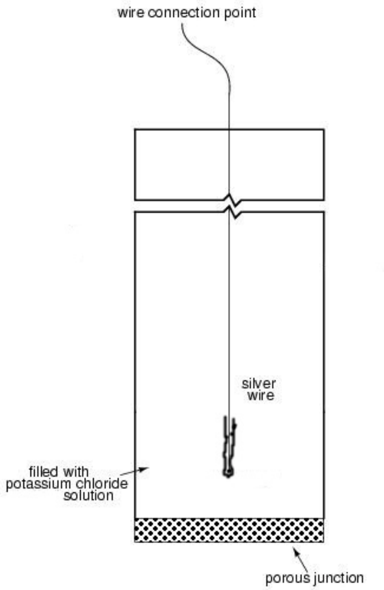
# Silver/Silver Chloride Reference Electrode

$$AgCl + e^- \leftarrow\rightarrow Ag + Cl^-$$

silver chloride coating on wire

silver wire

potassium chloride solution




Nernst Equation

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

# Reference Electrodes

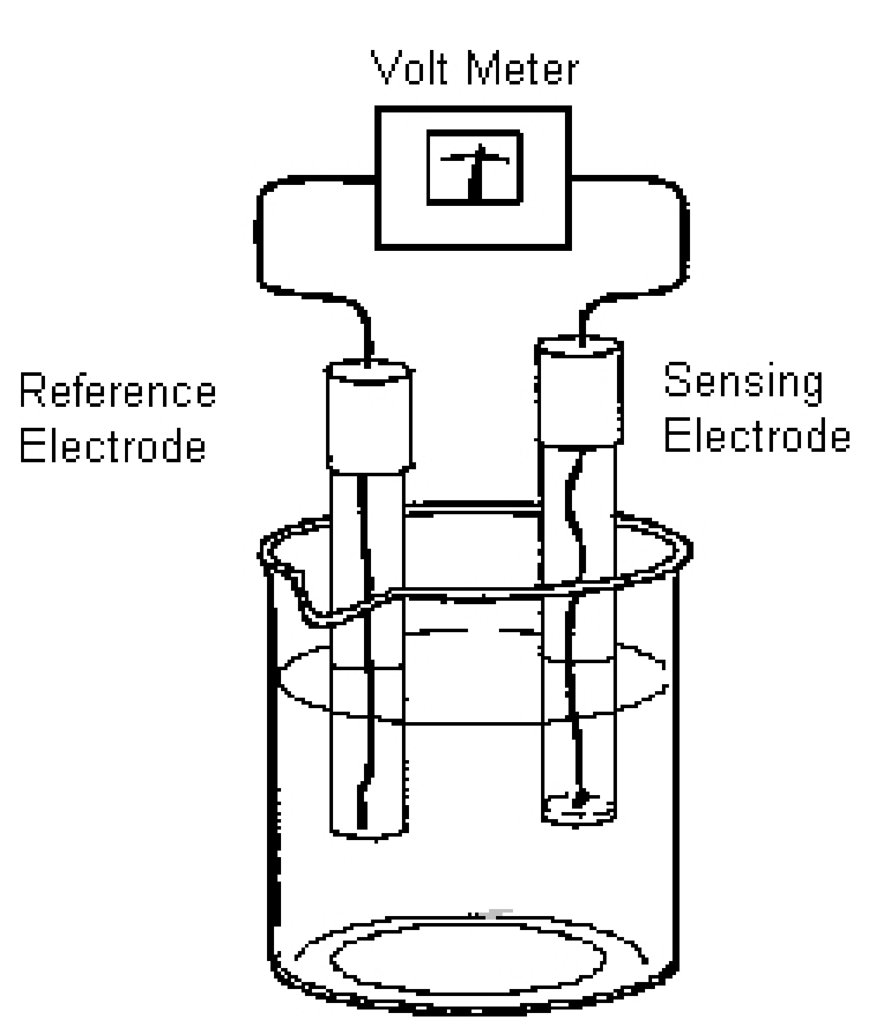
- Normal Hydrogen Electrode (NHE)
- $2H^+ + 2e^- \leftarrow\rightarrow H_2$  $E^o = 0.000$ v

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

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

$Ag^+ + e^- \leftrightarrow Ag \qquad E^o = 0.799$ 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