

Chapter 22: Introduction to Electroanalytical Chemistry

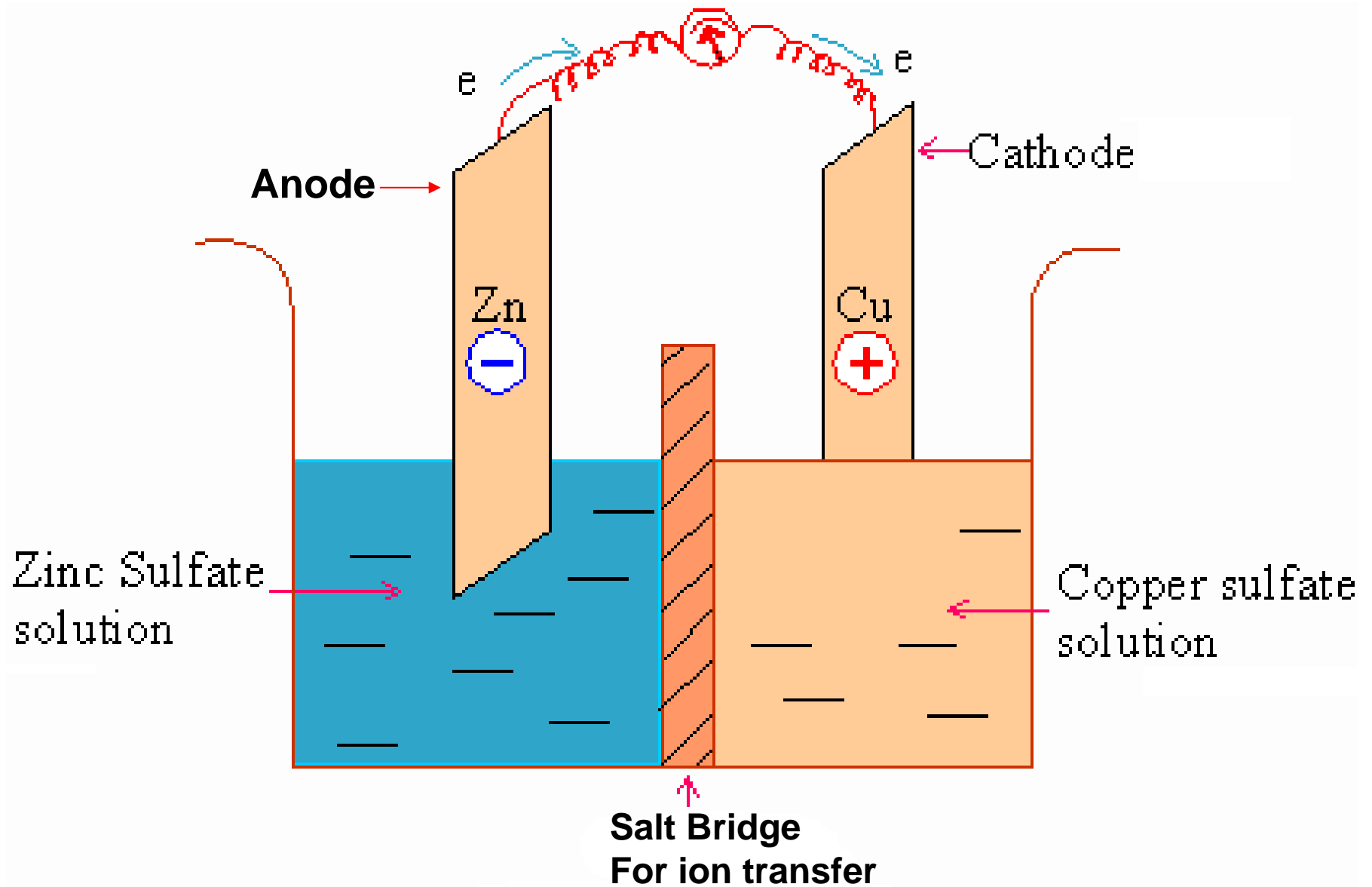
Two general categories:

- 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



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

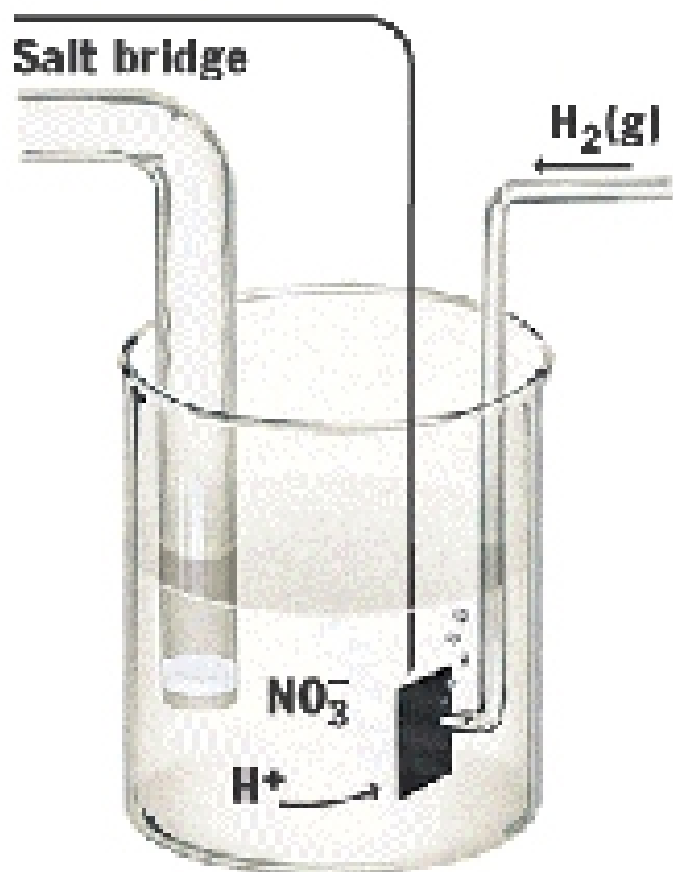
Nernst Equation

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

Where

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

Normal Hydrogen Electrode (NHE)



- Hydrogen gas is bubbled over an inert platinum electrode

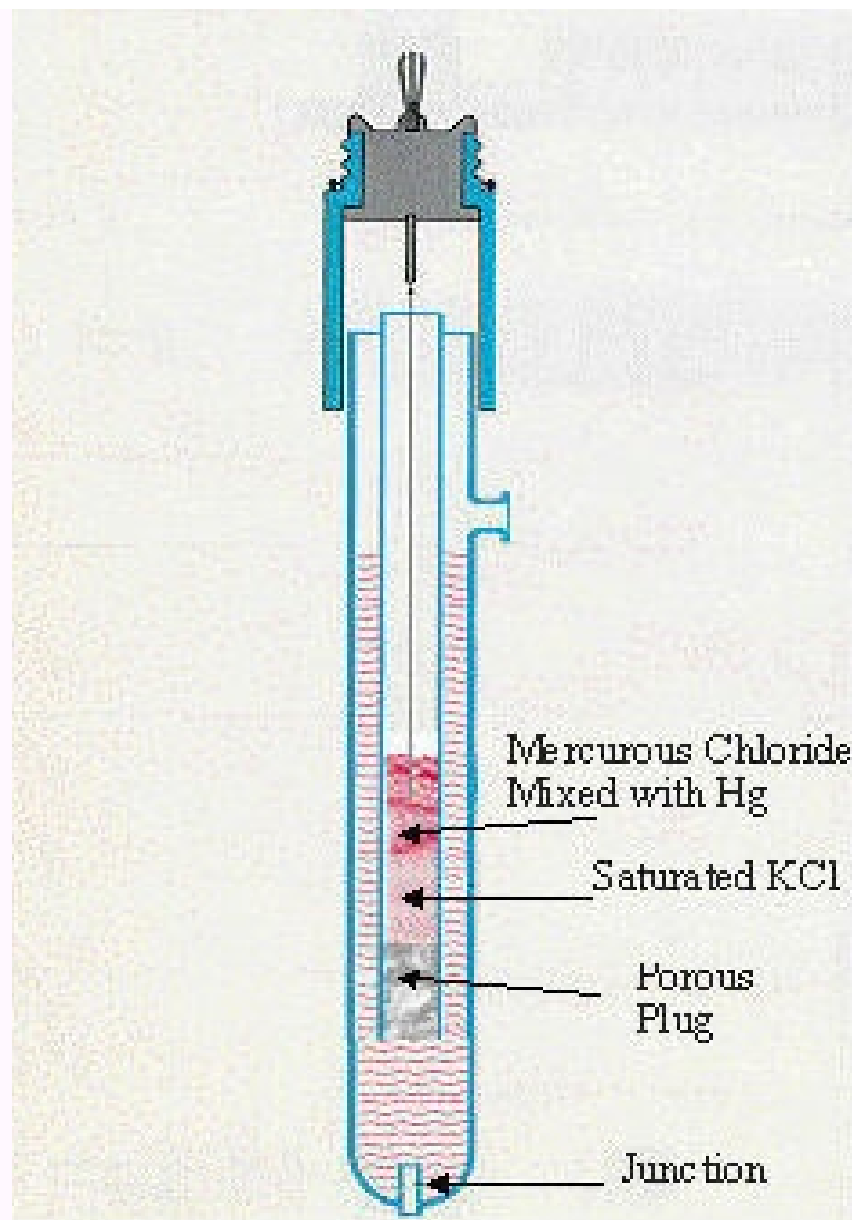
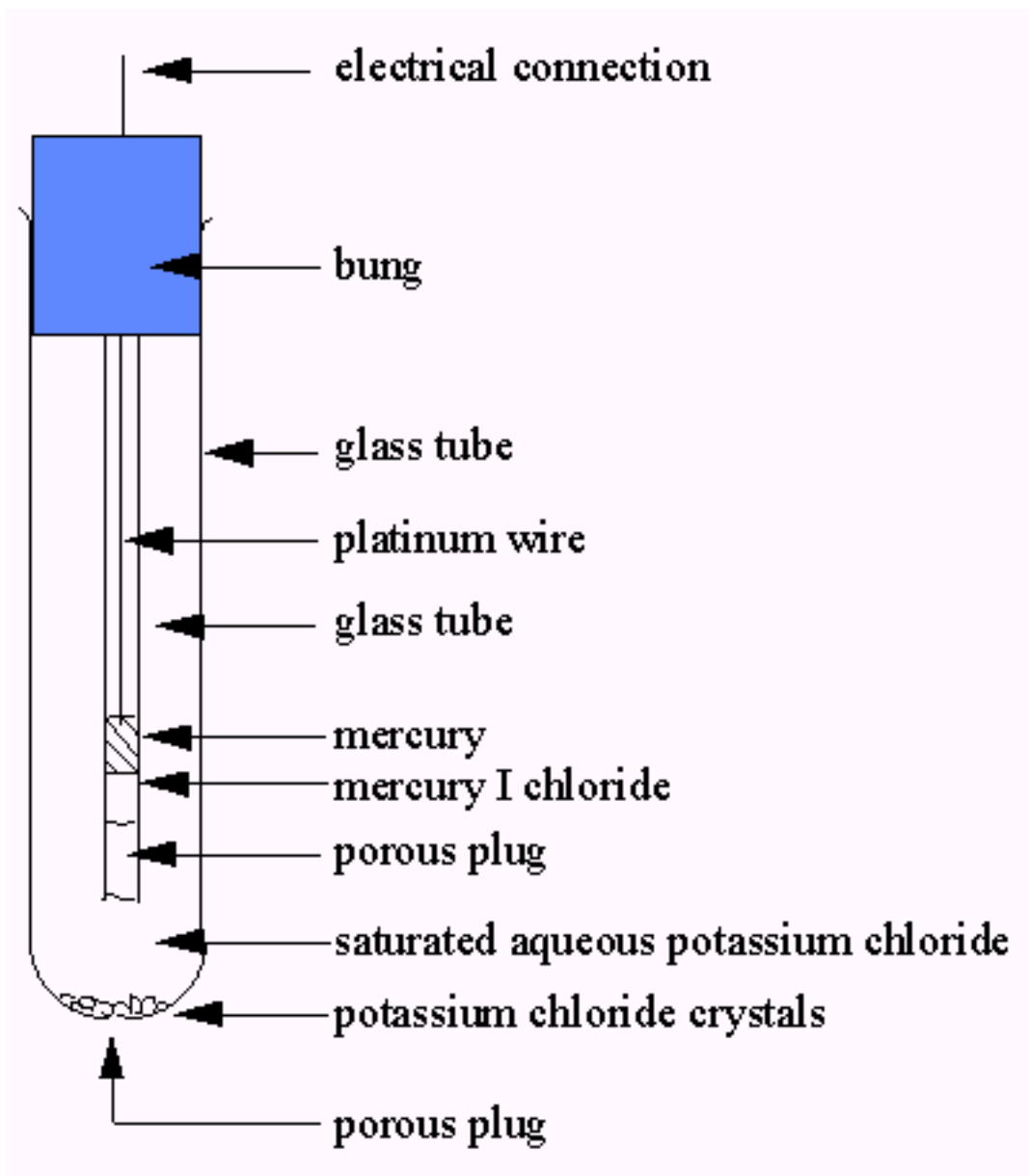
$$E^\circ = 0.000 \text{ v}$$



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
- $\text{Hg}_2\text{Cl}_2 + 2 e^- \leftrightarrow 2 \text{Hg} + 2\text{Cl}^- \quad E^\circ = 0.242 \text{ v}$

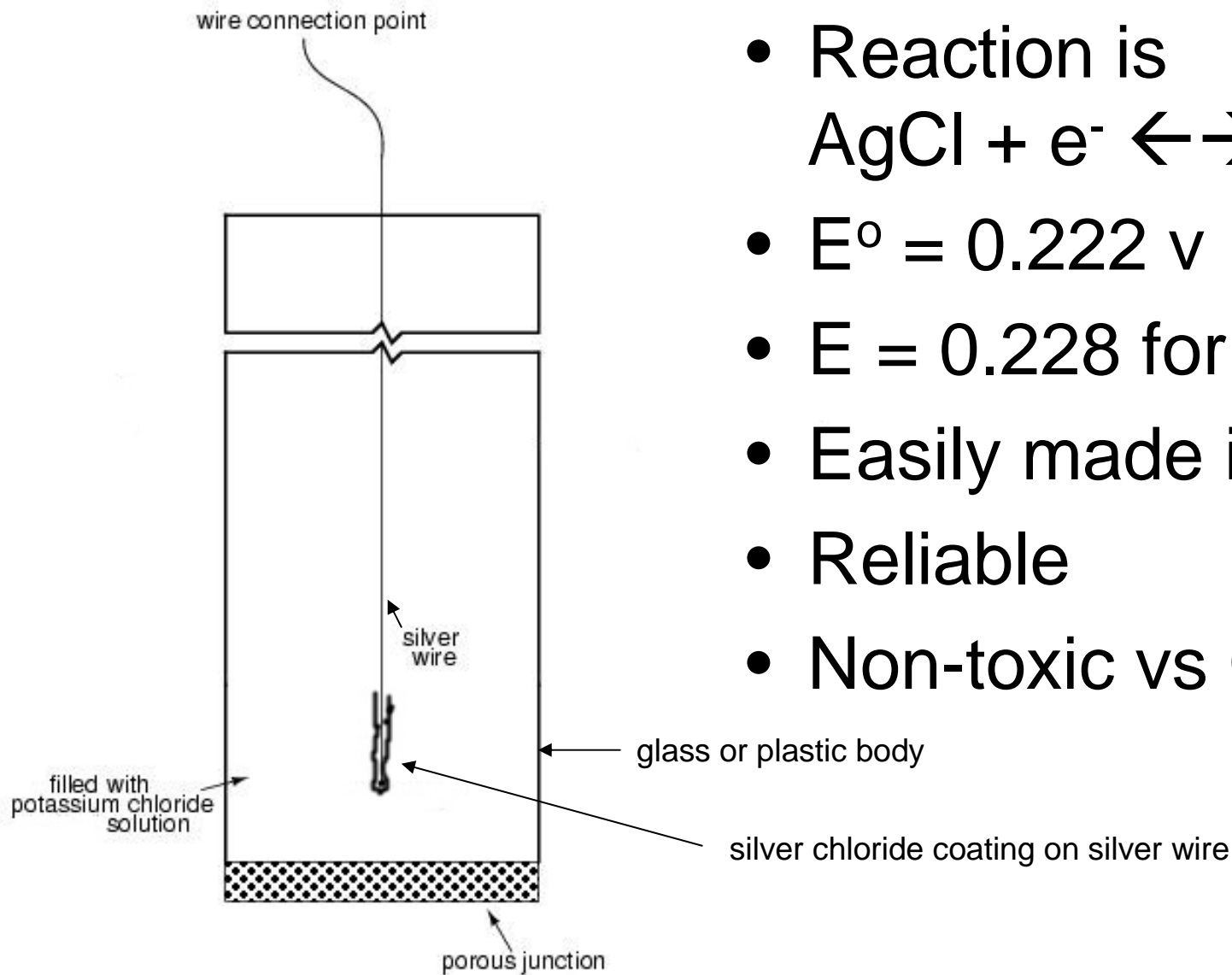
Calomel Reference Electrode



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



- Reaction is $\text{AgCl} + e^- \leftrightarrow \text{Ag} + \text{Cl}^-$
- $E^\circ = 0.222 \text{ v}$
- $E = 0.228$ for 1 M KCl
- Easily made in the lab
- Reliable
- Non-toxic vs Calomel

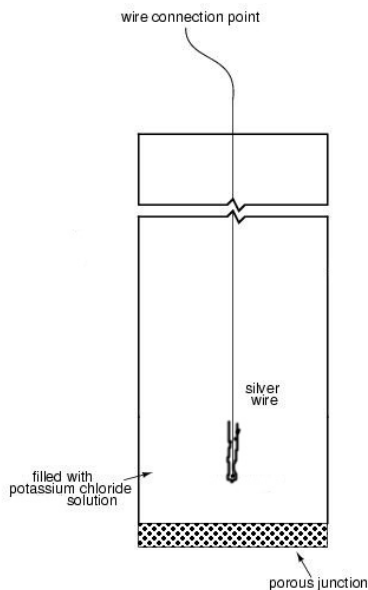
Silver/Silver Chloride Reference



silver chloride
coating on wire

silver wire

potassium
chloride
solution



Nernst Equation

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

Reference Electrode Summary

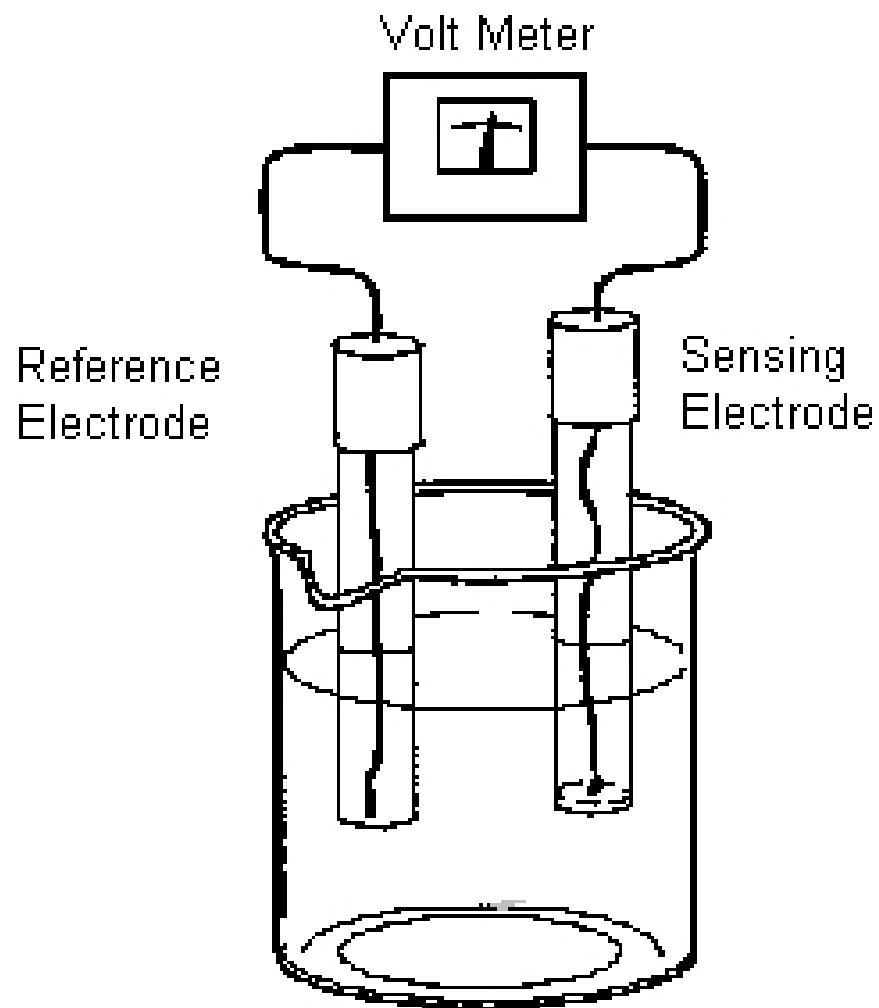
- Normal Hydrogen Electrode (NHE)
- $2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2 \quad E^\circ = 0.000 \text{ v}$

- Saturated Calomel Electrode (SCE)
- $\text{Hg}_2\text{Cl}_2 + 2 \text{e}^- \leftrightarrow 2 \text{Hg} + 2\text{Cl}^- \quad E^\circ = 0.268 \text{ v}$

- Silver/Silver Chloride Electrode (AgCl)
- $\text{AgCl} + \text{e}^- \leftrightarrow \text{Ag} + \text{Cl}^- \quad E^\circ = 0.222 \text{ v}$

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



Nernst Equation

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

At 25 °C this becomes

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

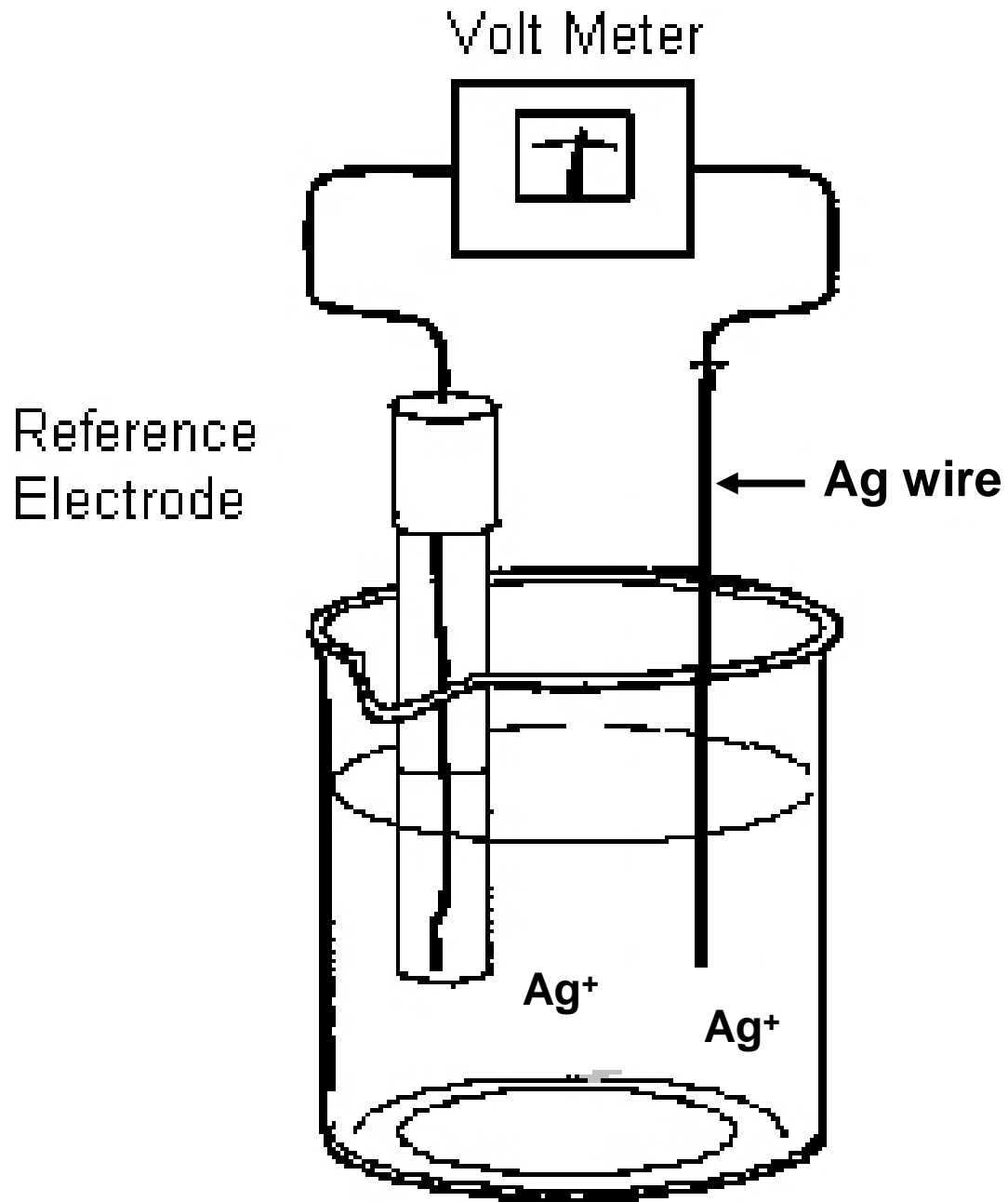
For the Silver/Silver ion system



this becomes

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

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



**Silver metallic
Electrode to
Measure
Ag⁺ ions**



Indicator Electrodes

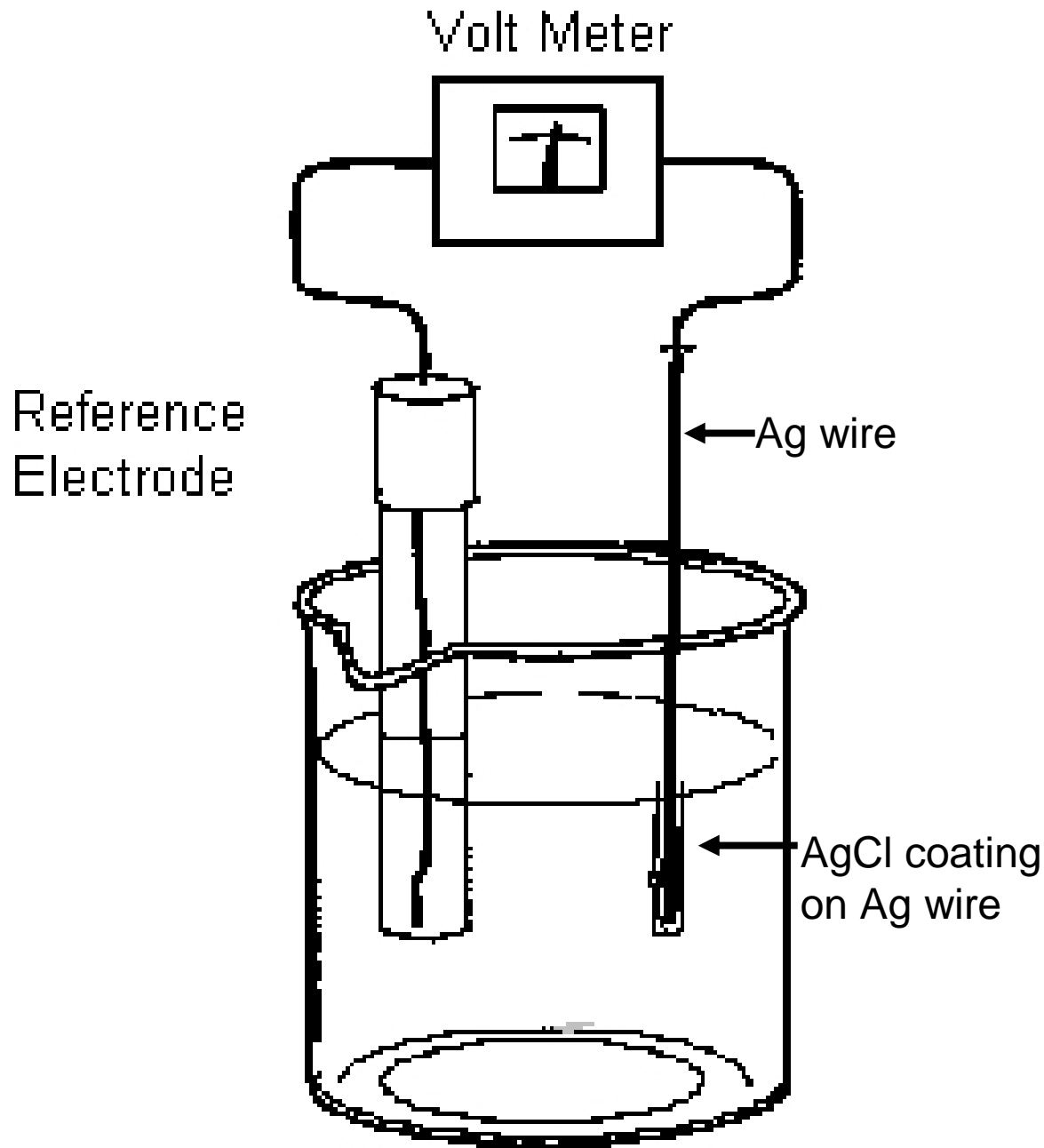
– Metallic Indicator Electrodes

2) Active metal in contact with slightly soluble precipitate involving the metal cation
–responds to anion concentration

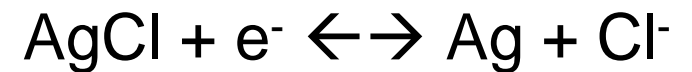
This is an **Electrode of the Second Kind**

e.g., Silver/Silver Chloride Electrode (AgCl)

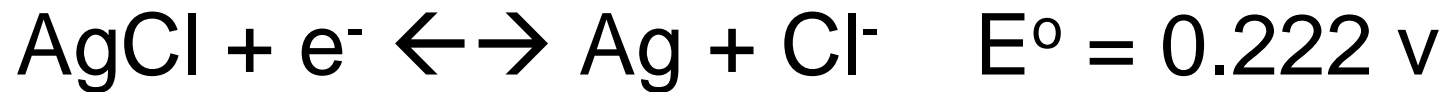




**Silver/Silver
Chloride
Electrode
to measure
Cl⁻ ions**



For the Silver/Silver Chloride system



The Nernst equation becomes

$$E = 0.222 - \frac{0.0591}{1} \log \frac{[\text{Cl}^-]}{1}$$

Electrode potential is **directly** proportional to the concentration of the chloride ions for This Electrode of the Second Kind

Indicator Electrodes

– Metallic Indicator Electrodes

3) Inert Electrodes e.g., Pt or Au (noble metal)

Don't participate in the reaction, but serve only as a source or sink for electrons.

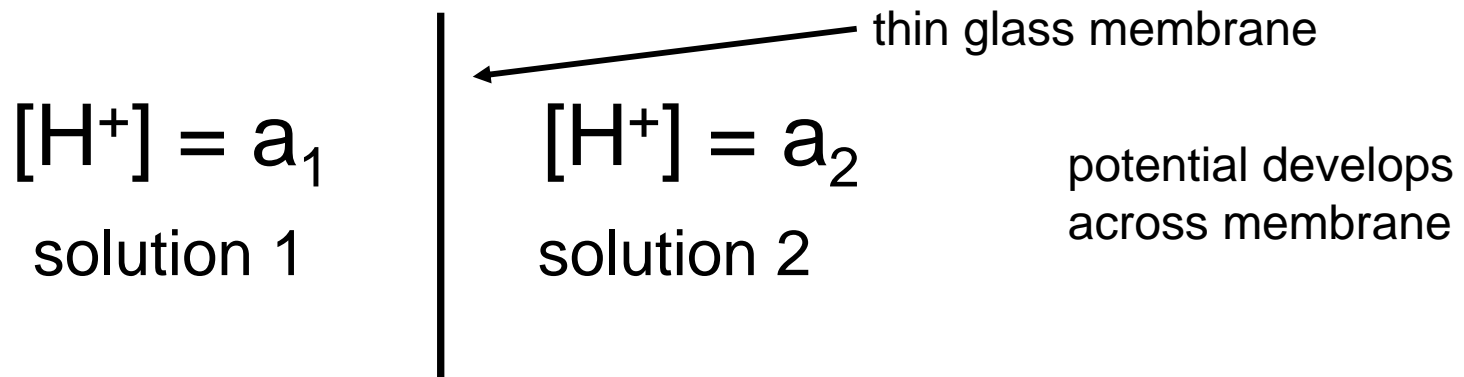
Respond to the ratio of [Ox] to [Red] when both oxidized and reduced species are soluble e.g., could be used to follow a redox titration like Fe^{2+} with MnO_4^-

Summary of Metallic Electrodes

- Important historically for development of potentiometric sensors
- Not very practical in modern electrochem because of poor detection limits
- Inert electrodes are used in redox titrations
- Better systems now available for Cl^- , etc.
- Electrode of the Third Kind can be made that senses an ion that reacts with Cl^- and changes the activity of Cl^- detected

Membrane Electrodes

- Several types – Glass membrane electrode
 - Solid State “ “
 - Liquid Junction “ “
 - Permeable “ “
- Most important is glass electrode for pH



Glass Membrane Electrode for pH

$$E = K + 0.0591 \log \frac{a_1}{a_2}$$

where K is constant at fixed temp

In Glass Electrode, a_2 is fixed at 0.1 M HCl

$$E = K' + 0.0591 \log a_1$$

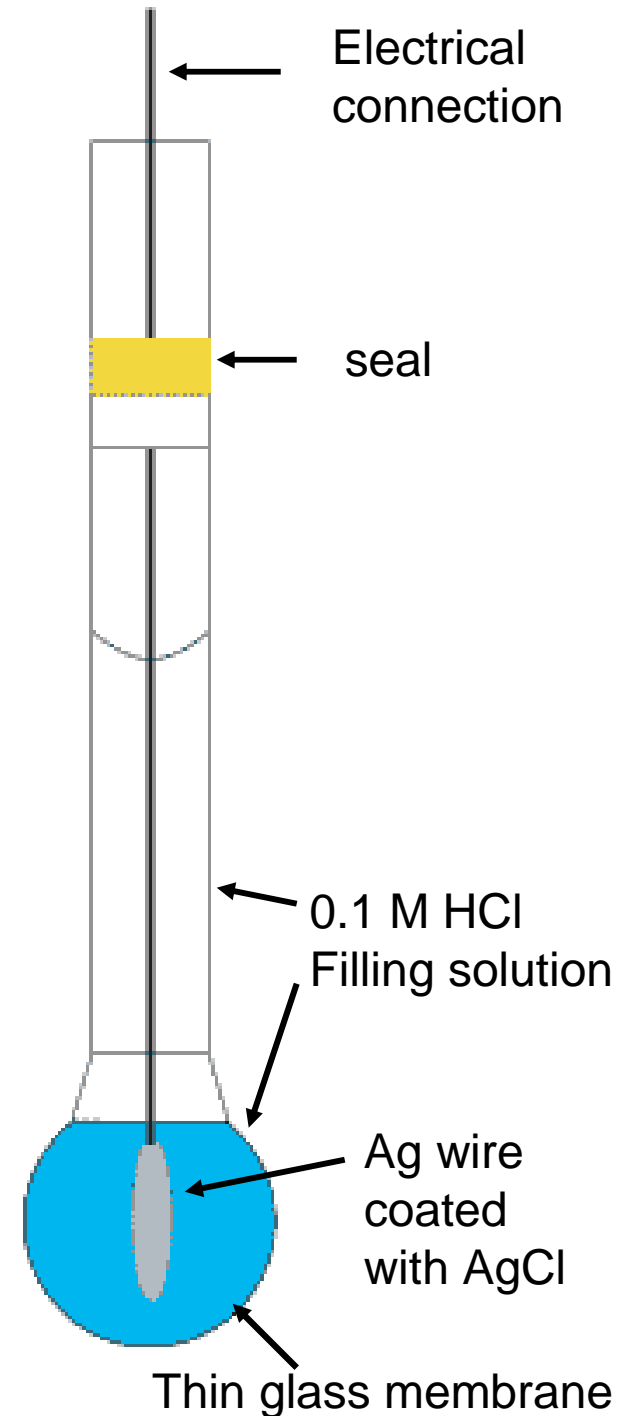
K' new constant that includes a_2

$$E = K' - 0.0591 \text{ pH}$$

since $\text{pH} = -\log a_{\text{H}^+}$

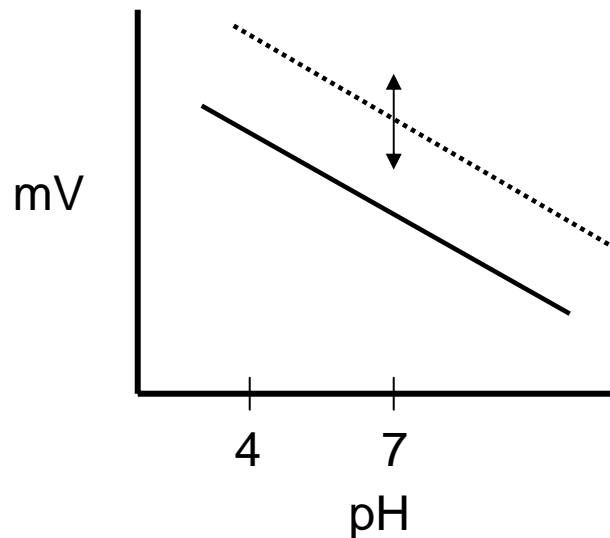
Glass pH Electrode

- $E = K' - 0.0591 \text{ pH}$
- Combine with reference electrode and meter
- Half cell voltage proportional to pH
- Nernstian slope
- Intercept is K' , no E°
- Calibrate with buffers



Proper pH Calibration

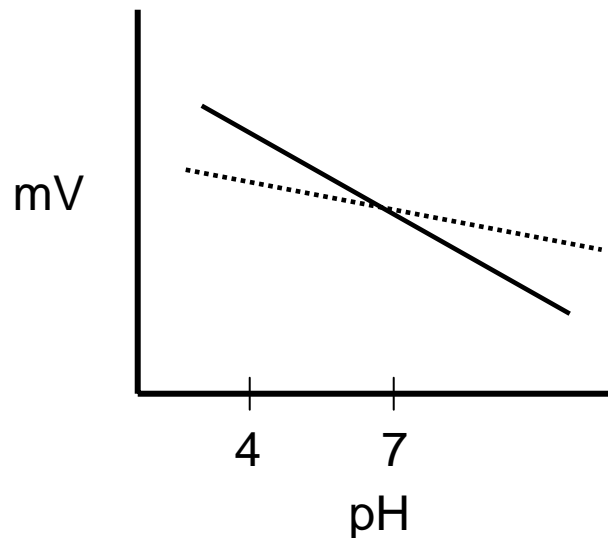
- $E = K' - 0.0591 \text{ pH}$
- Meter measures E vs pH – must calibrate both slope & intercept on meter with buffers
- Meter has two controls – calibrate & slope
- 1st use $\text{pH } 7.00$ buffer to adjust calibrate knob



Calibrate knob raises and lowers the line without changing slope

Proper pH Calibration (cont.)

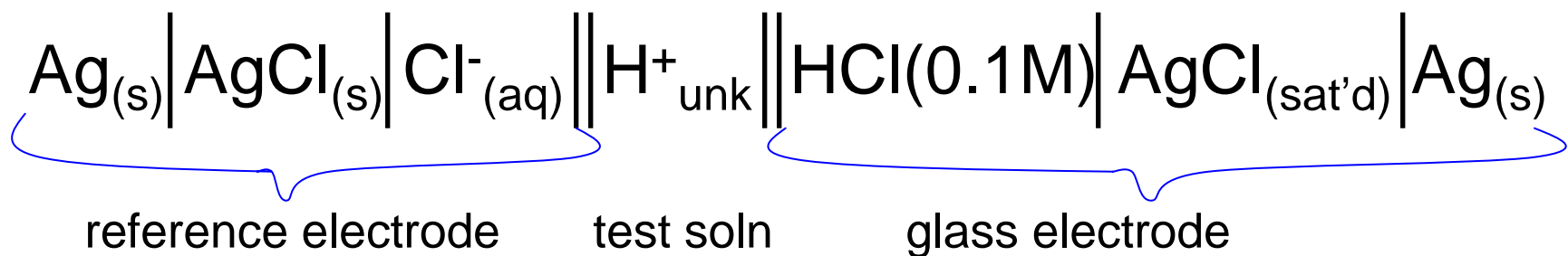
- 2nd step is to use any other pH buffer
- Adjust slope/temp control to correct pH value
- This will pivot the calibration line around the isopotential which is set to 7.00 in all meters



Slope/temp control pivots line around isopotential without changing it

- Slope comes from RT/nF in Nernst Equation
- Slope is temperature sensitive
- Other factors influence slope including
 - Impurities in glass membrane
 - Overall quality of electrode construction
- Many electrodes exhibit “full Nernstian response” while others may give only 90%

Cell for pH measurement (shorthand notation)



Errors in pH Measurement 1

- pH measurements are only as good as the buffers used to calibrate
 - Accuracy good to ± 0.01 units
 - Precision may be good to ± 0.001 units
- Junction potential dependent on ionic strength of solution – E_j may be a significant error if test solution has different ionic strength than buffers

Errors in pH Measurement 2

- Asymmetry potential is another non-ideal potential that arises possibly from strain in the glass. When both internal & external H^+ solutions are the same, potential should be 0 but it's not

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} + E_j + E_a$$