84.514 Advanced Analytical Chemistry

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.

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

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

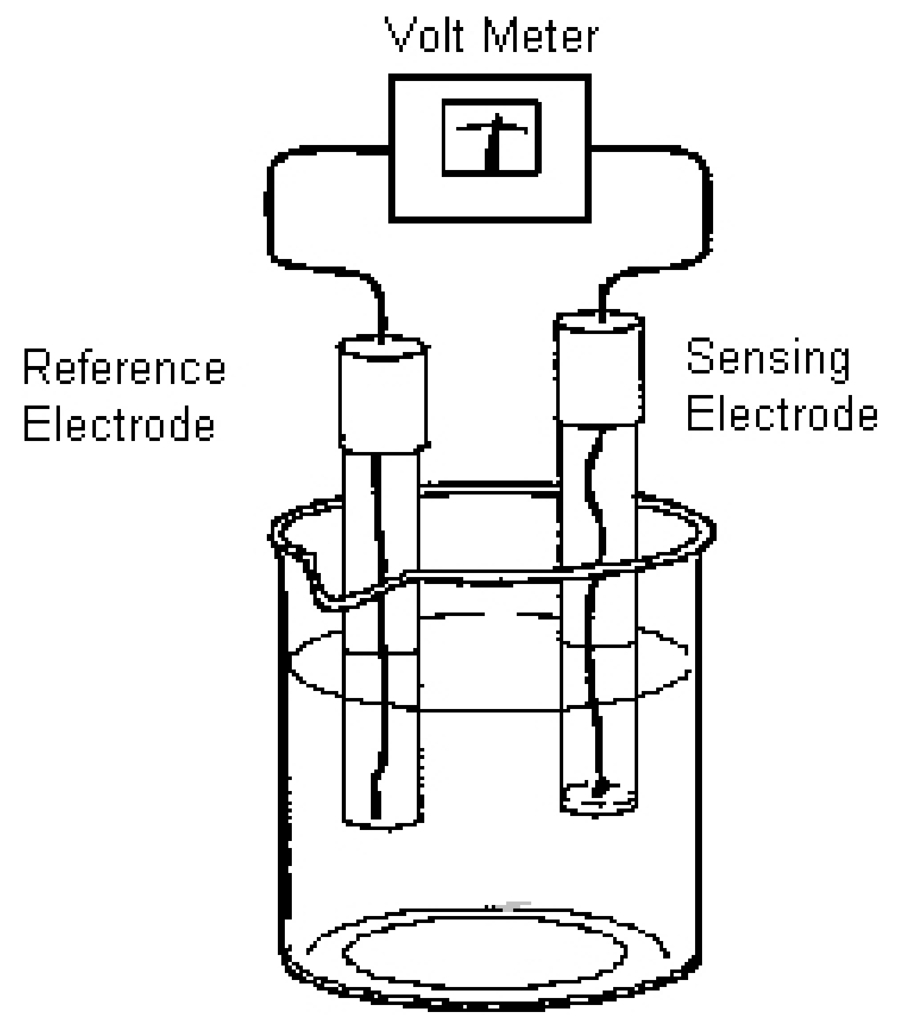
- Normal Hydrogen Electrode (NHE)
- $2H^+ + 2e^- \leftrightarrow H_2$ $E^o = 0.000$ v

- 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

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

Nernst Equation

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

At 25 °C this becomes

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

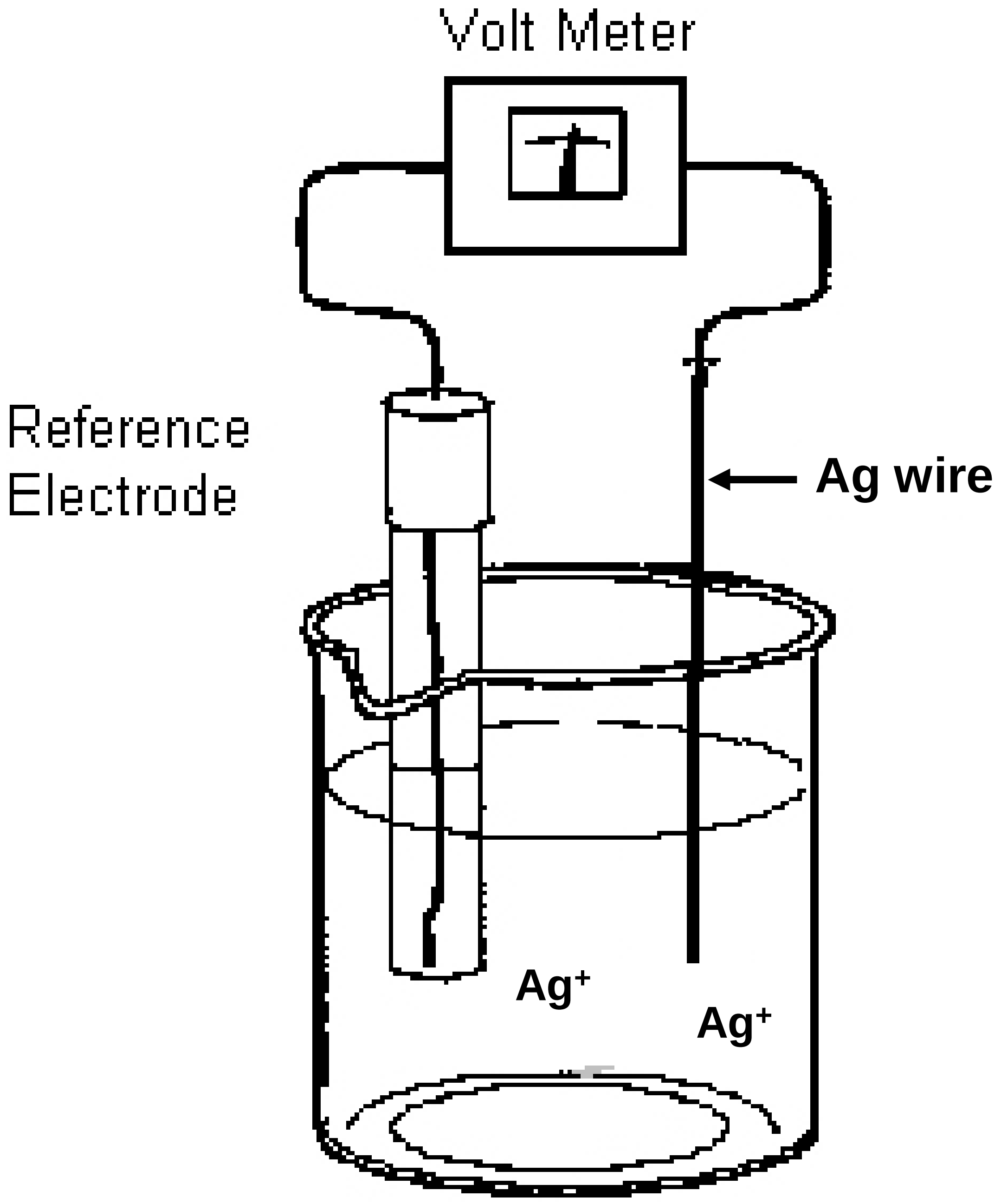
For the Silver/Silver ion system

$Ag^+ + e^- \leftarrow\rightarrow Ag$ $E^o = 0.799$ v

this becomes

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

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



Silver metallic Electrode to Measure Ag^+ ions

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

Indicator Electrodes

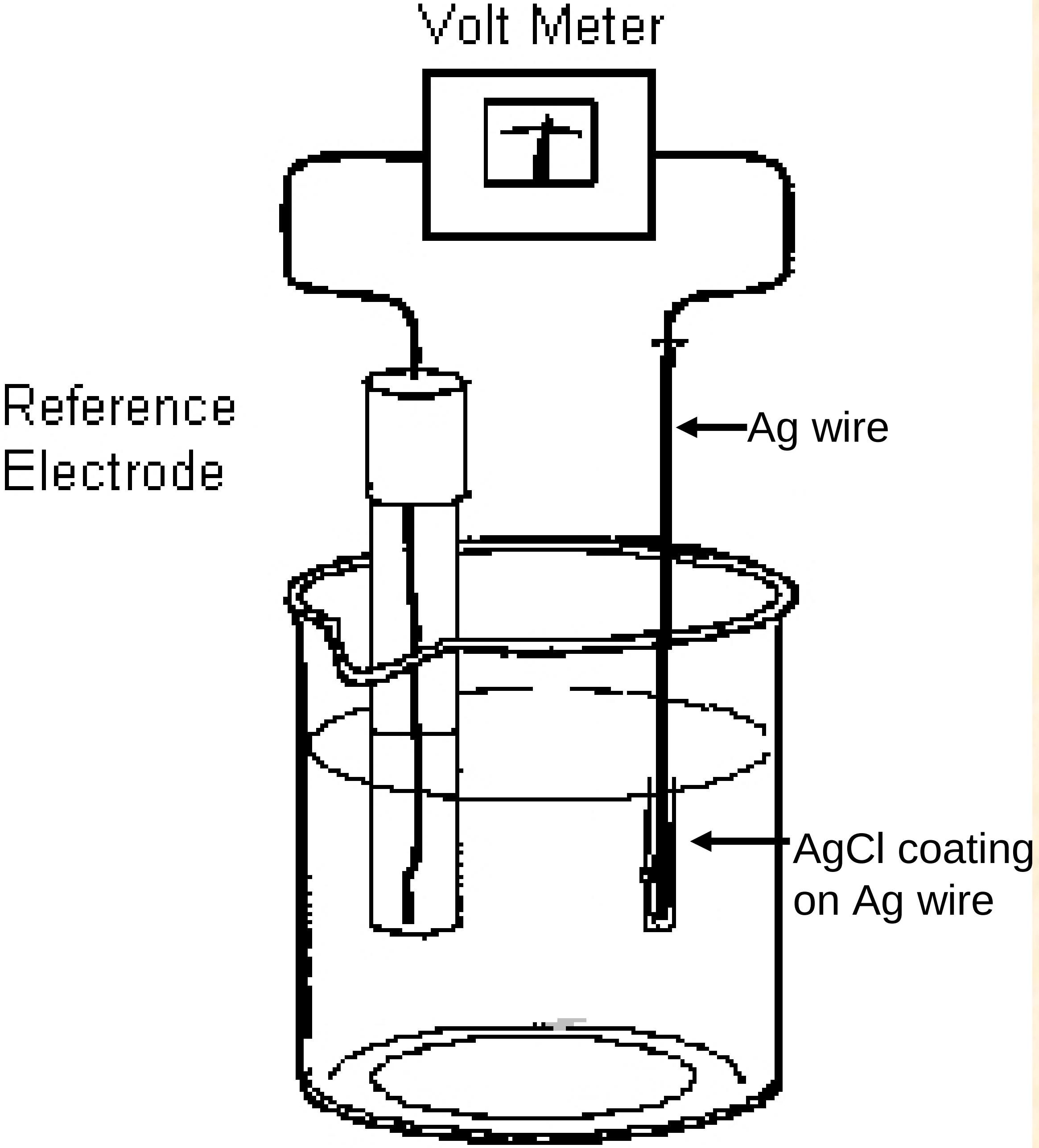
- Metallic Indicator Electrodes

  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)

$$AgCl + e^- \leftrightarrow Ag + Cl^- \quad E^o = 0.222\ v$$



Silver/Silver Chloride Electrode to measure Cl^- ions

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

For the Silver/Silver Chloride system

$$AgCl + e^- \leftarrow\rightarrow Ag + Cl^- \quad E^o = 0.222\ v$$

The Nernst equation becomes

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

Electrode potential is directly proportional to the concentration (activity)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

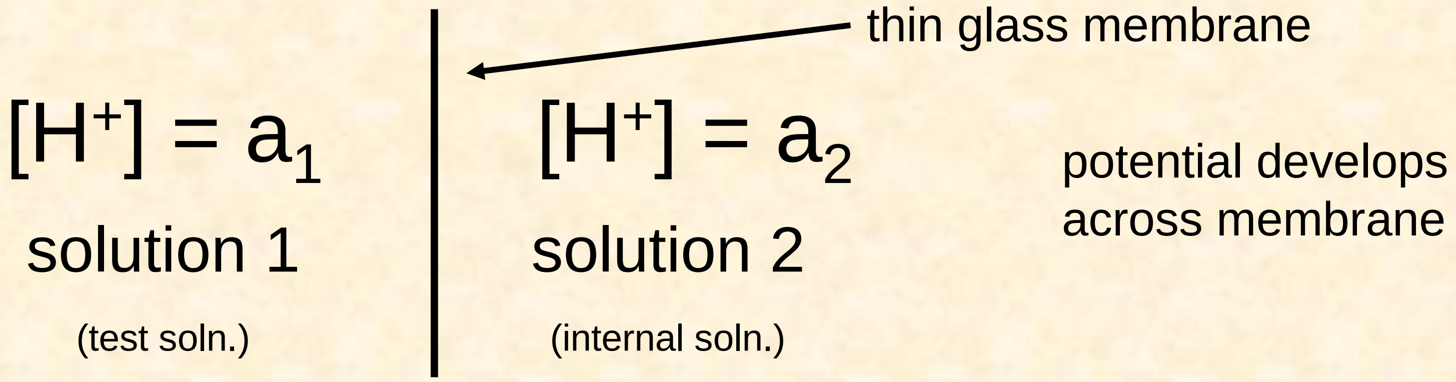
- Several types – Glass membrane electrode

  - Solid State “ “

  - Liquid Junction “ “

  -Permeable “ “

- Most important is glass electrode for pH



thin glass membrane

$[H^+] = a_1$

solution 1

(test soln.)

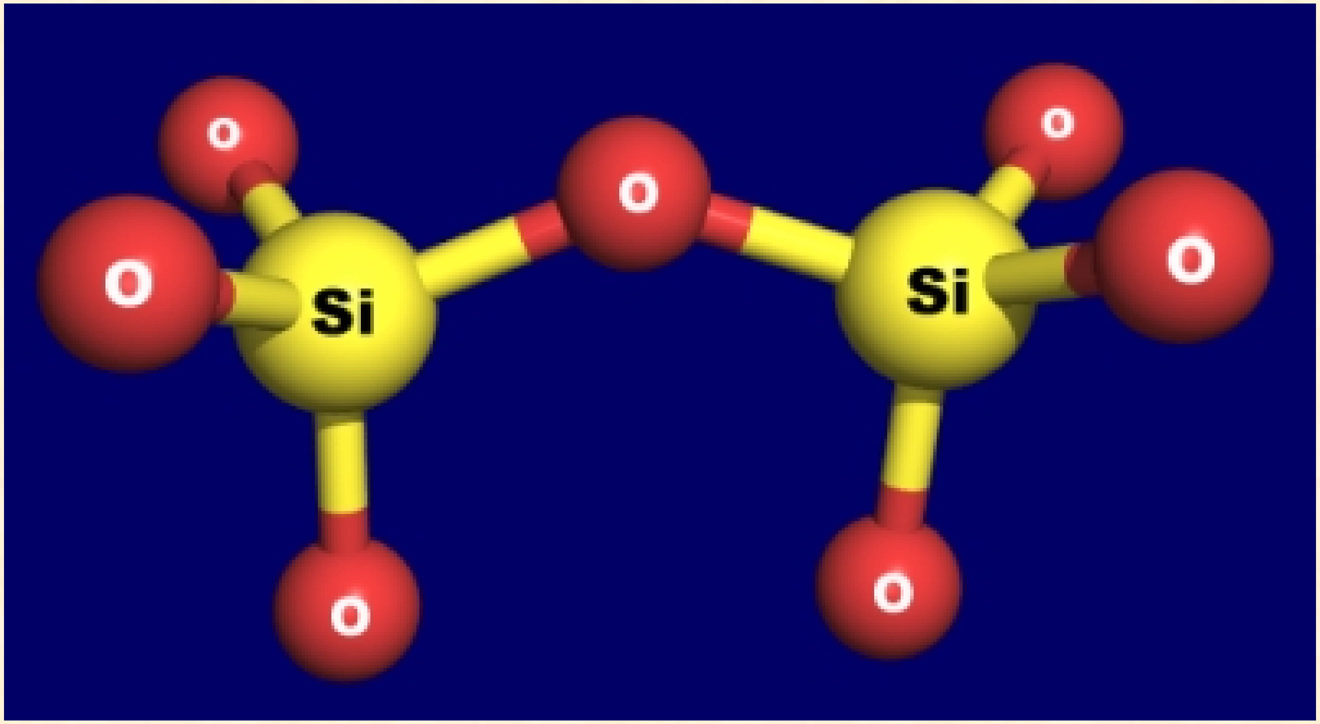
$[H^+] = a_2$

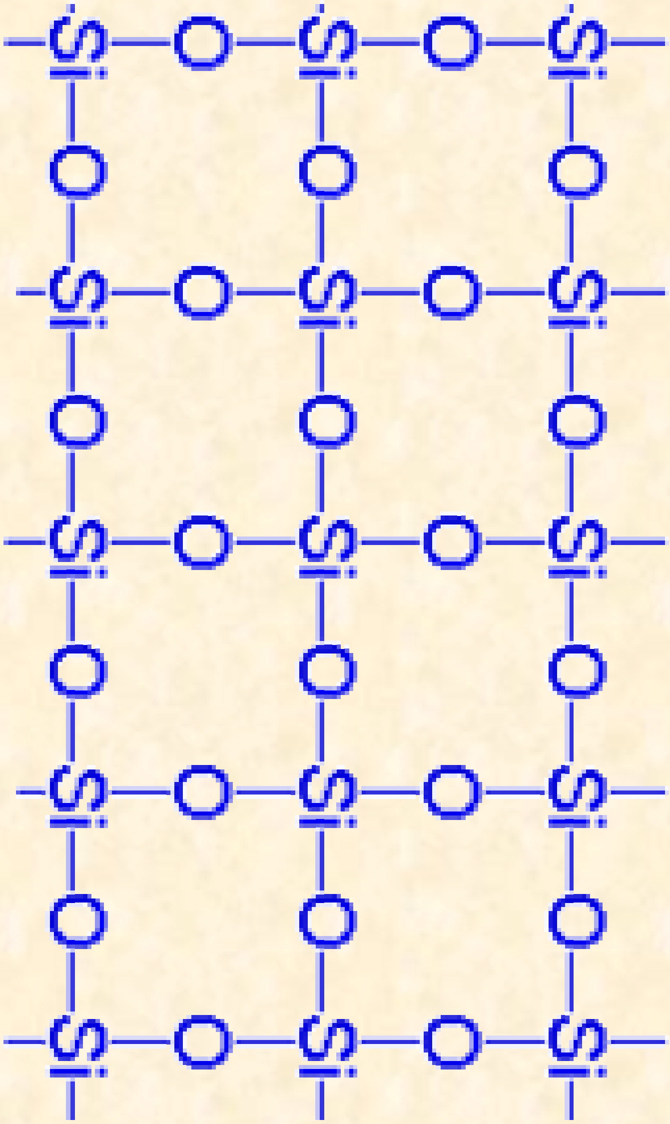
solution 2

(internal soln.)

potential develops
across membrane

Glass is SiO_2





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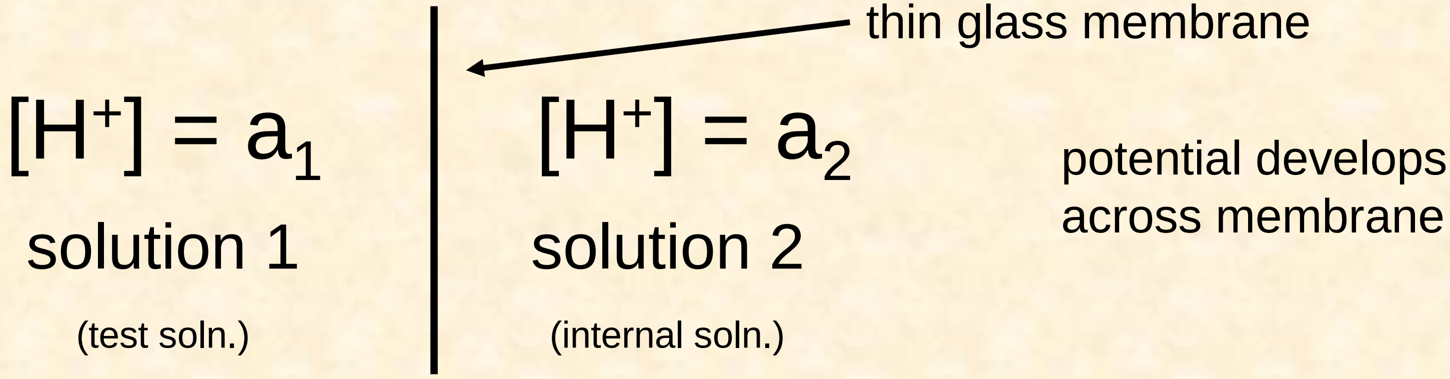

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Glass Membrane Electrode for pH

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

where K is constant at fixed temp

In Glass Electrode, a_2 is fixed at 0.1 M HCl

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

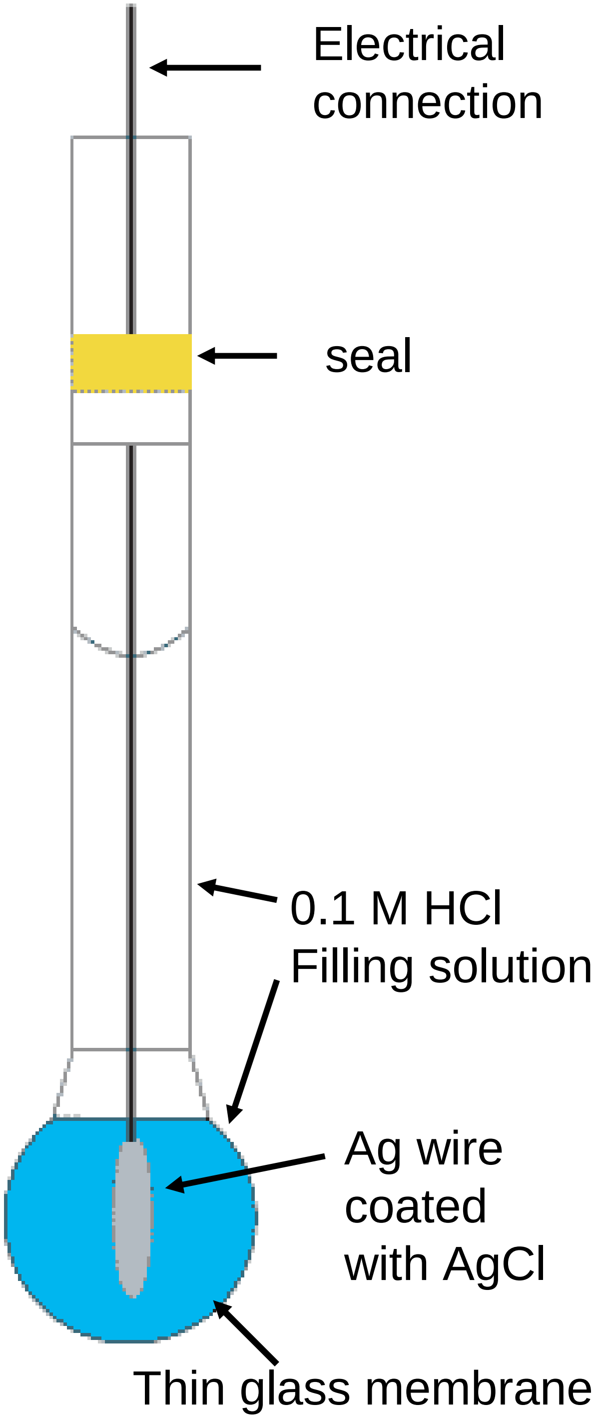
K' new constant that includes a_2

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

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

Glass pH Electrode

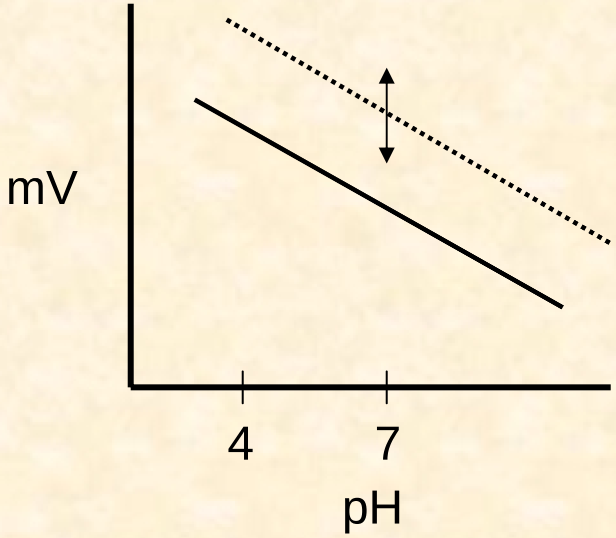
- $E = K' - 0.0591 \ \text{pH}$
- Combine with reference electrode and meter
- Half cell voltage proportional to pH
- Nernstian slope
- Intercept is K', no E^o
- Calibrate with buffers




6.888
MV
STD
BY
pH/.01
REL MV
pH/.001
CALIB
TEMP°C
% SLOPE
ORION RESEARCH
model 701 A / digital IONALYZER
9116

Proper pH Calibration

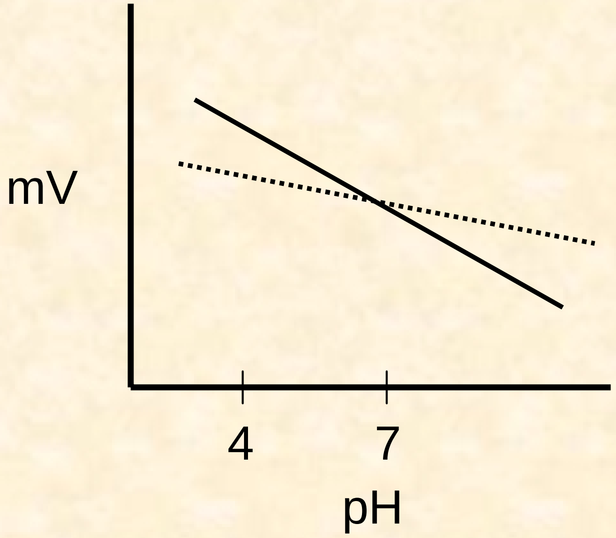
- $E = K' - 0.0591\ \mathrm{pH}$
- Meter measures E vs pH – must calibrate both slope & intercept on meter with buffers
- Meter has two controls – calibrate & slope
- 1st use pH 7.00 buffer to adjust calibrate knob



Calibrate knob raises
and lowers the line
without changing slope

Proper pH Calibration (cont.)

- 2^{nd} 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)

$$\underbrace{Ag_{(s)}\,|\,AgCl_{(s)}\,|\,Cl^-_{(aq)}}_{\text{reference electrode}}\,\|\,\underset{\text{test soln}}{H^+_{unk}}\,\|\,\underbrace{HCl(0.1M)\,|\,AgCl_{(sat'd)}\,|\,Ag_{(s)}}_{\text{glass electrode}}$$

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

* Unless using special buffers, temp. control & a Faraday cage

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 activity, potential should be 0 but it’s not

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

- Temperature of electrodes, calibration buffers and sample solutions must be the same primarily because of T in Nernst Eq. ATC probes are available for many meters

Errors in pH Measurement 3

- Alkaline Error or Sodium Error occurs when pH is very high (e.g., 12) because Na^+ concentration is high (from NaOH used to raise pH) and H^+ is very low. Electrode responds slightly to Na^+ & gives a lower reading than actual pH. This is related to the concept of selectivity coefficients where the electrode responds to many ions but is most selective for H^+. Problem occurs because Na^+ is 10 orders of magnitude higher than H^+ in the solution.