Electrodes and Potentiometry

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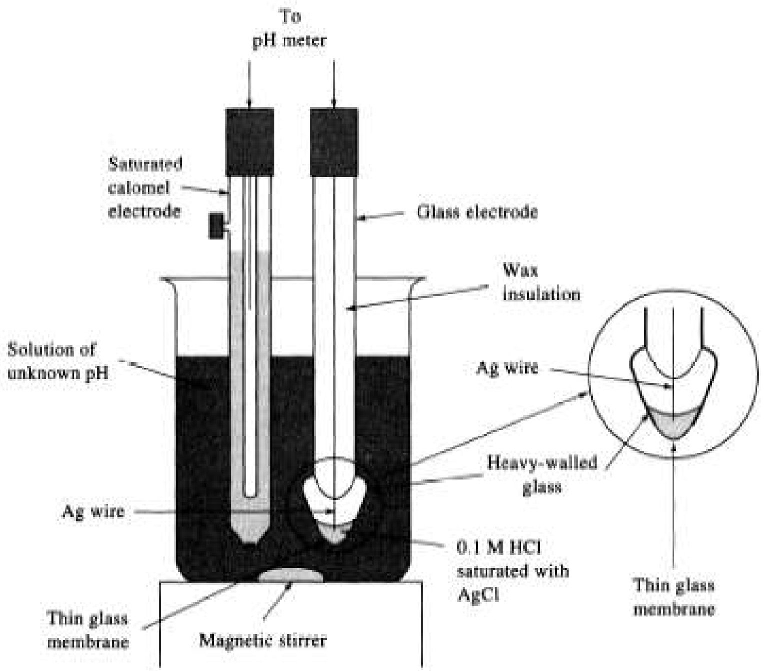
Electrodes and Potentiometry

Introduction

1.) Potentiometry

- Use of Electrodes to Measure Voltages that Provide Chemical Information
  - **Various electrodes have been designed to respond selectively to specific analytes**

- Use a Galvanic Cell
  - **Unknown solution becomes a ½-cell**
  - **Add Electrode that transfers/accepts electrons from unknown analyte**
  - **Connect unknown solution by salt bridge to second ½-cell at fixed composition and potential**



- Indicator Electrode: electrode that responds to analyte and donates/accepts electrons

- Reference Electrode: second ½ cell at a constant potential

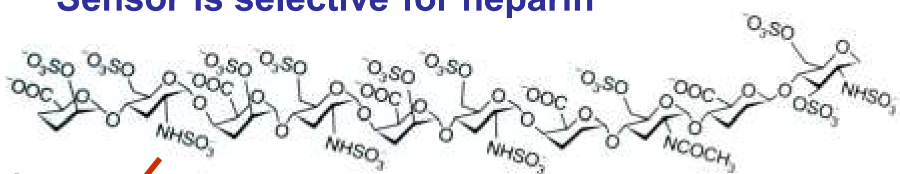
- Cell voltage is difference between the indicator and reference electrode

Electrodes and Potentiometry

Introduction

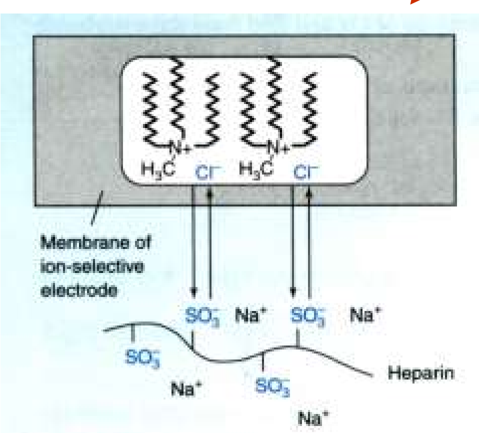
2.) Example

- A Heparin Sensor
  - **Voltage response is proportional to heparin concentration in blood**
  - **Sensor is selective for heparin**

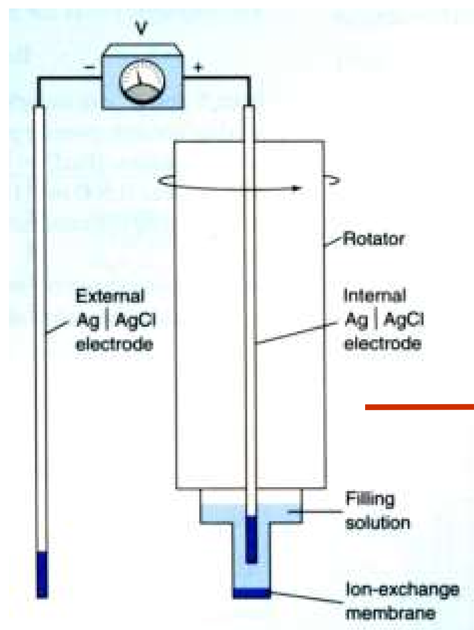


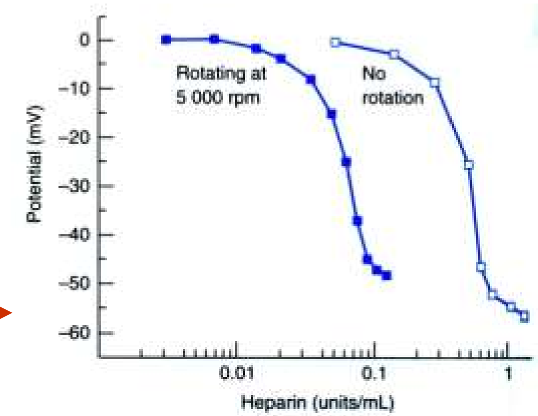
heparin

Negatively charged heparin binds selectively to positively charged membrane.



Binding generates potential difference.





Potential is proportional to [heparin]

Electrodes and Potentiometry

Reference Electrodes

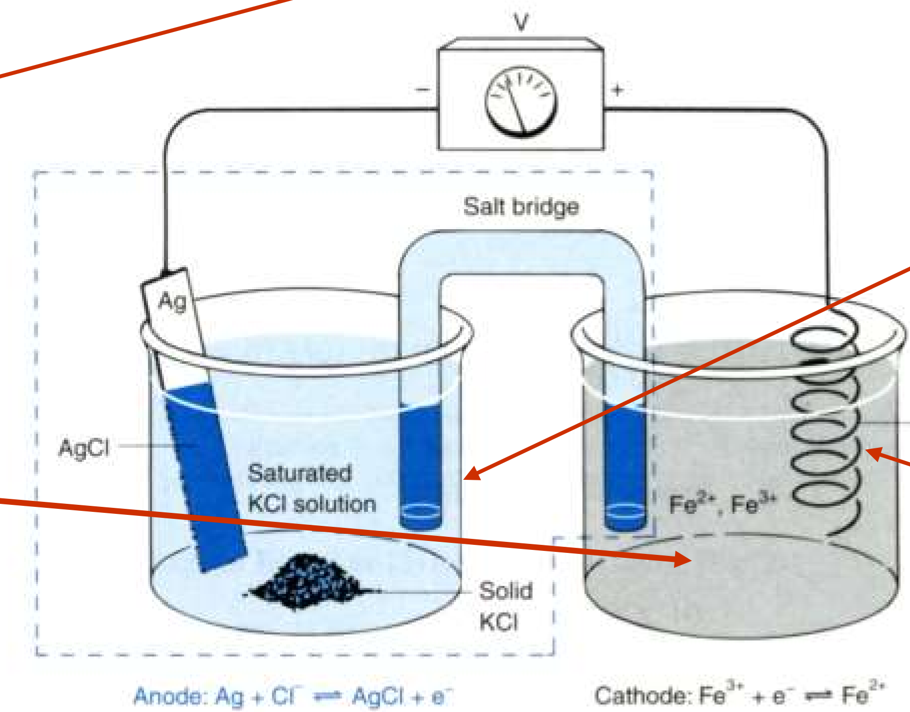
1.) Overview

- Potential change only dependent on one ½ cell concentrations
- *Reference electrode* is fixed or saturated → doesn't change!

$$E_{cell} = \left\{ 0.771 - \frac{0.05916}{1} \log \boxed{\left(\frac{[Fe^{2+}]}{[Fe^{3+}]} \right)} \right\} - \boxed{\left\{ 0.222 - 0.05916 \log [Cl^{-}] \right\}}$$

Potential of the cell only depends on $[Fe^{2+}]$ & $[Fe^{3+}]$

Reference electrode, $[Cl^{-}]$ is constant



Unknown solution of $[Fe^{2+}]$ & $[Fe^{3+}]$

Pt wire is indicator electrode whose potential responds to $[Fe^{2+}]/[Fe^{3+}]$

Electrodes and Potentiometry

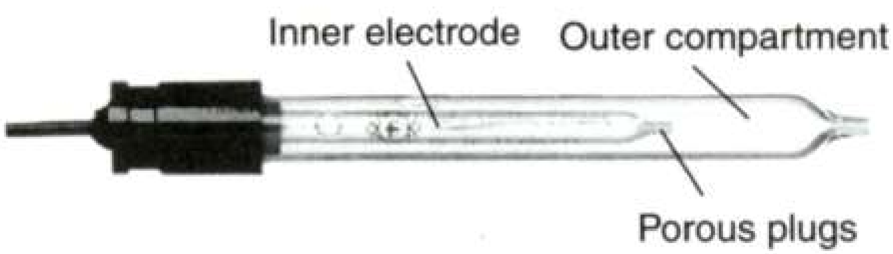
Reference Electrodes

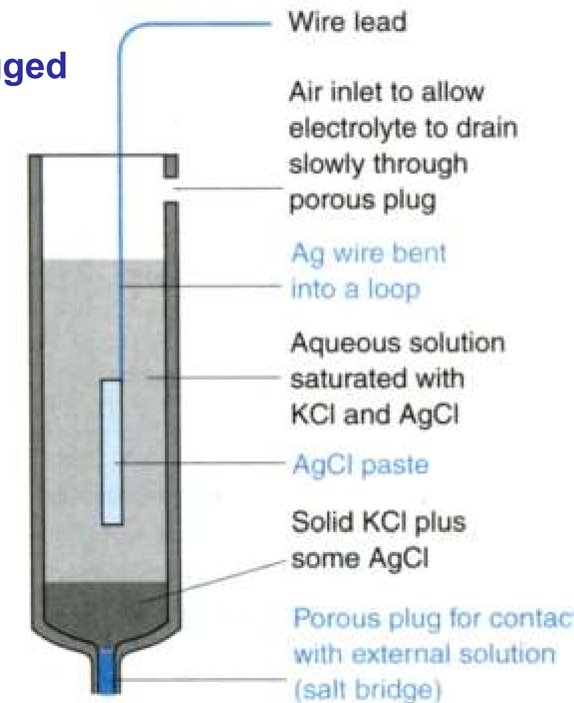
2.) Silver-Silver Chloride Reference Electrode

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^- \quad E^o = +0.222\ V$$

Activity of Cl^- not 1 → $E_{(sat,KCl)} = +0.197\ V$

- Convenient
  - **Common problem is porous plug becomes clogged**





Electrodes and Potentiometry

Reference Electrodes

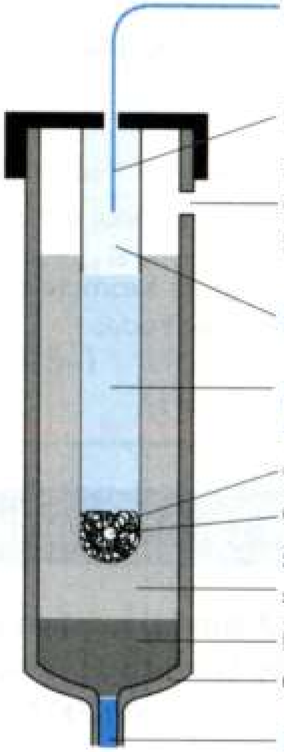
3.) Saturated Calomel Reference Electrode (S.C.E)

$$HgCl(s) + 2e^- \rightleftharpoons 2Hg(l) + Cl^- \quad E^o = +0.268\ V$$

Activity of Cl^- not 1 → $E_{(sat,KCl)} = +0.241\ V$

- Saturated KCl maintains constant [Cl^-] even with some evaporation

- Standard hydrogen electrodes are cumbersome
  - **Requires H_2 gas and freshly prepared Pt surface**



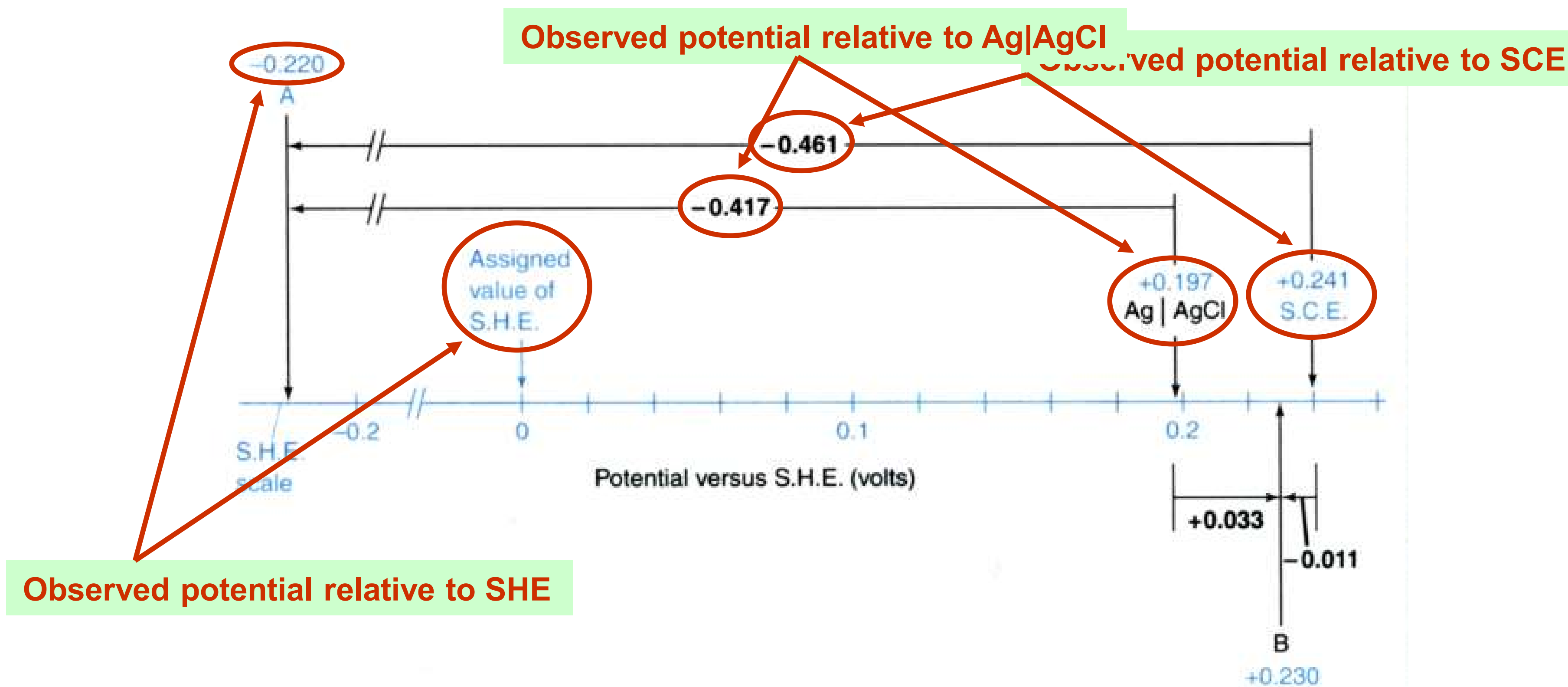
Electrodes and Potentiometry

Reference Electrodes

4.) Observed Voltage is Reference Electrode Dependant

- The observed potential depends on the choice of reference electrode
  - **Silver-silver chloride and calomel have different potentials**

- Use Reference Scale to convert between Reference Electrodes



Electrodes and Potentiometry

Junction Potential

1.) Occurs Whenever Dissimilar Electrolyte Solutions are in Contact

- Develops at solution interface (salt bridge)
- Small potential (few millivolts)
- *Junction potential puts a fundamental limitation on the accuracy of direct potentiometric measurements*
  - **Don't know contribution to the measured voltage**

Different ion mobility results in separation in charge

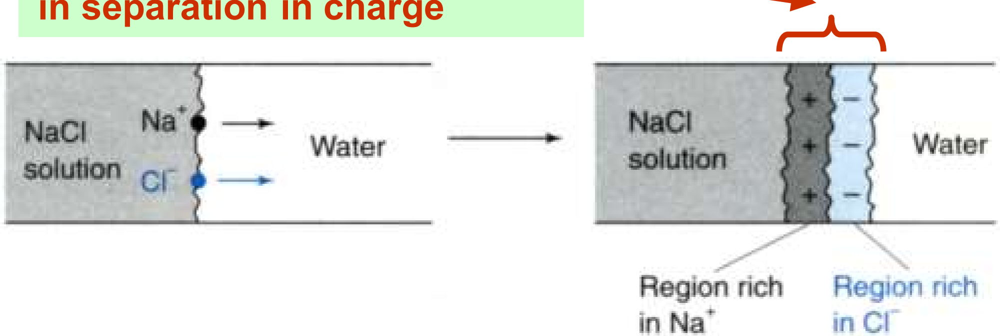


Table 15-2 Liquid junction potentials at 25°C

Junction	Potential (mV)
0.1 M NaCl | 0.1 M KCl	−6.4
0.1 M NaCl | 3.5 M KCl	−0.2
1 M NaCl | 3.5 M KCl	−1.9
0.1 M HCl | 0.1 M KCl	+27
0.1 M HCl | 3.5 M KCl	+3.1

Again, an electric potential is generated by a separation of charge

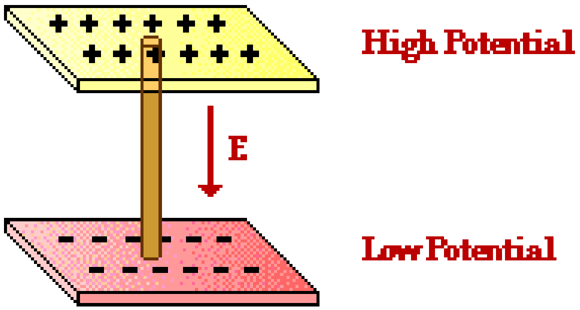
Electrodes and Potentiometry

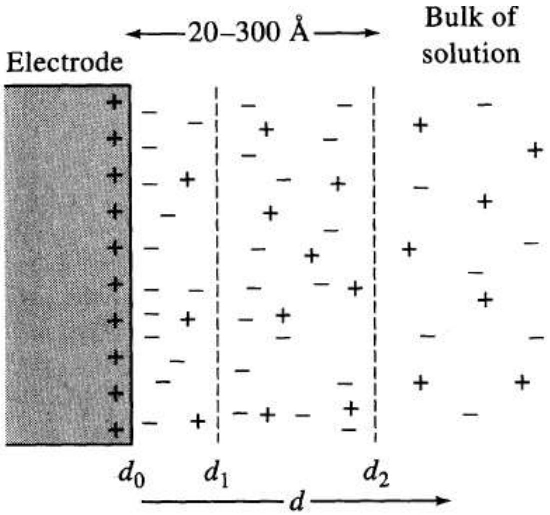
Indicator Electrodes

1.) Two Broad Classes of Indicator Electrodes

- Metal Electrodes
  - **Develop an electric potential in response to a redox reaction at the metal surface**

- Ion-selective Electrodes
  - **Selectively bind one type of ion to a membrane to generate an electric potential**





Remember an electric potential is generated by a separation of charge

Electrodes and Potentiometry

Indicator Electrodes

2.) Metal Electrodes

- Platinum
  - **Most common metal indicator electrode**
  - **Inert: does not participate in many chemical reactions**
  - **Simply used to transmit electrons**
- Other electrodes include Gold and Carbon
- Metals (Ag, Cu, Zn, Cd, Hg) can be used to monitor their aqueous ions
  - **Most metals are not useable**
  - **Equilibrium not readily established at the metal surface**

$$M^{n+} + e^- \rightleftharpoons M(s)$$

Example:

½ Reaction at Ag indicator electrode: $Ag^+ + e^- \rightleftharpoons Ag(s)$ **E_+^o = +799 V**

½ Reaction at Calomel reference electrode: $HgCl(s) + 2e^- \rightleftharpoons 2Hg(l) + Cl^-$ **$E_{(sat,KCl)}$ = +0.241 V**

Cell Potential from Nernst Equation:
$$E_{cell} = E_+ - E_- = \underbrace{\left\{0.799 - \frac{0.05916}{1} \log\left(\frac{1}{[Ag^+]}\right)\right\}}_{\text{Potential of Ag indicator electrode}} - \{0.241\}$$

Cell voltage changes as a function of [Ag$^+$]

Electrodes and Potentiometry

Indicator Electrodes

3.) Example

- A 10.0 mL solution of 0.0500 M AgNO3 was titrated with 0.0250M NaBr in the cell:

S.C.E. || titration solution | Ag(s)

Find the cell voltage for 10.0 mL of titrant

Electrodes and Potentiometry

Indicator Electrodes

4.) Ion-Selective Electrodes

- Responds Selectively to <u>*one*</u> ion
  - **Contains a thin membrane capable of only binding the desired ion**
- Does not involve a redox process

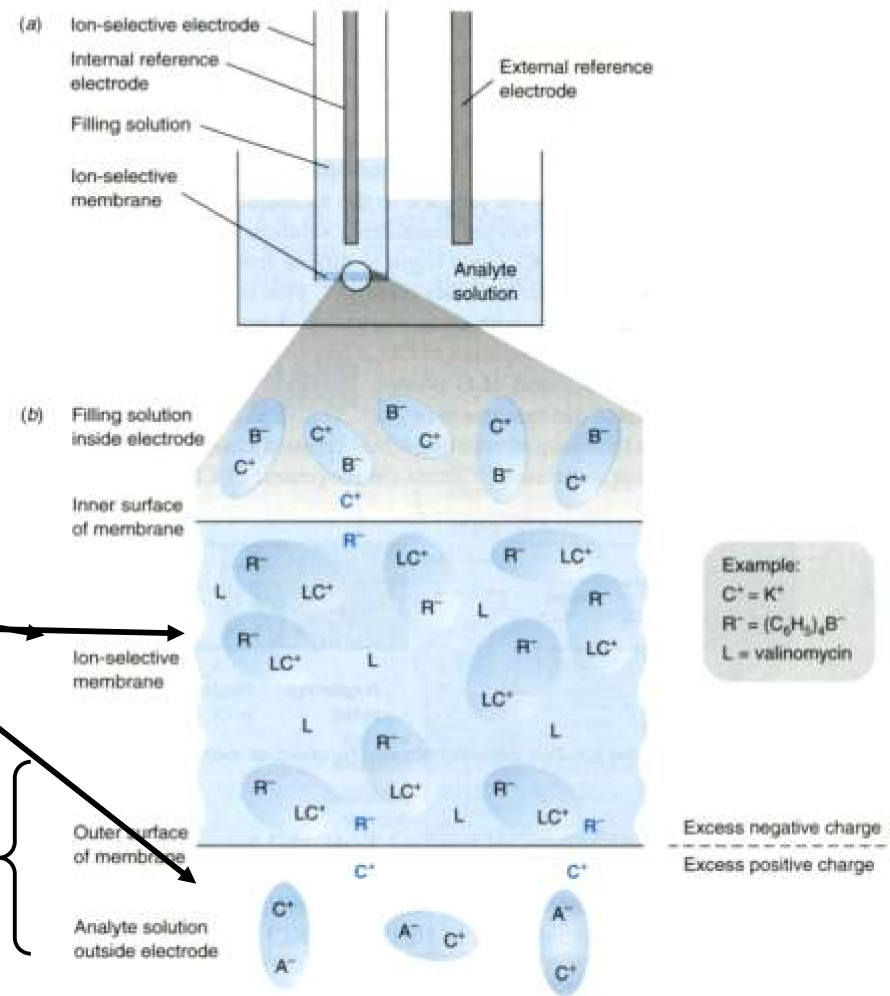
Membrane contains a ligand (L) that specifically and tightly binds analyte of interest (C^+)

The counter-ions (R^-,A^-) can't cross the membrane and/or have low solubility in membrane or analyte solution

C^+ diffuses across the membrane due to C^+ concentration gradient resulting in charge difference across membrane

A difference in the concentration of exists across the outer membrane.

Potential across outer membrane depends on [C+] in analyte solution



Remember an electric potential is generated by a separation of charge

Electrodes and Potentiometry

Indicator Electrodes

4.) Ion-Selective Electrodes

- Responds Selectively to <u>*one*</u> ion
  - **Contains a thin membrane capable of only binding the desired ion**
- Does not involve a redox process

C$^+$ diffuses across the membrane due to concentration gradient resulting in charge difference across membrane

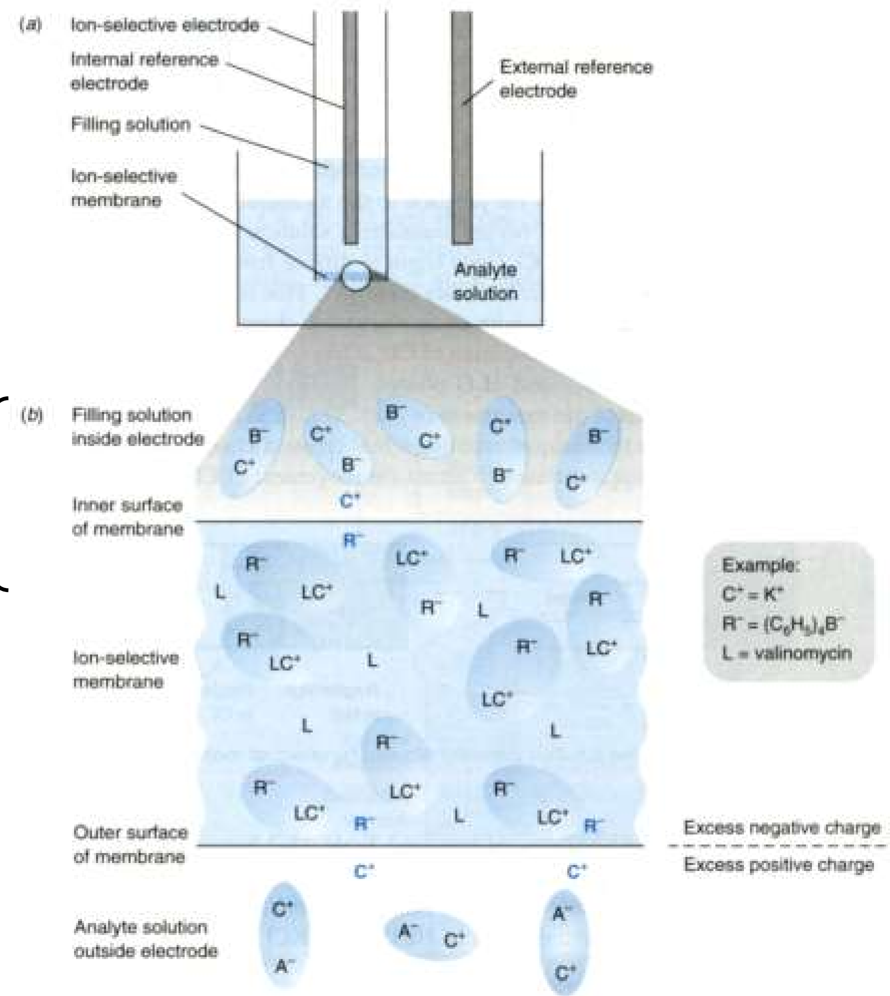
A difference in the concentration of C$^+$ exists across the inner membrane.

Potential across inner membrane depends on [C$^+$] in filling solution, which is a known constant

Electrode potential is determined by the potential difference between the inner and outer membranes:

$$E = E_{outer} - E_{inner}$$

where E_{inner} is a constant and E_{outer} depends on the concentration of C$^+$ in analyte solution



Remember an electric potential is generated by a separation of charge

Electrodes and Potentiometry

Indicator Electrodes

4.) Ion-Selective Electrodes

- Responds Selectively to *one* ion
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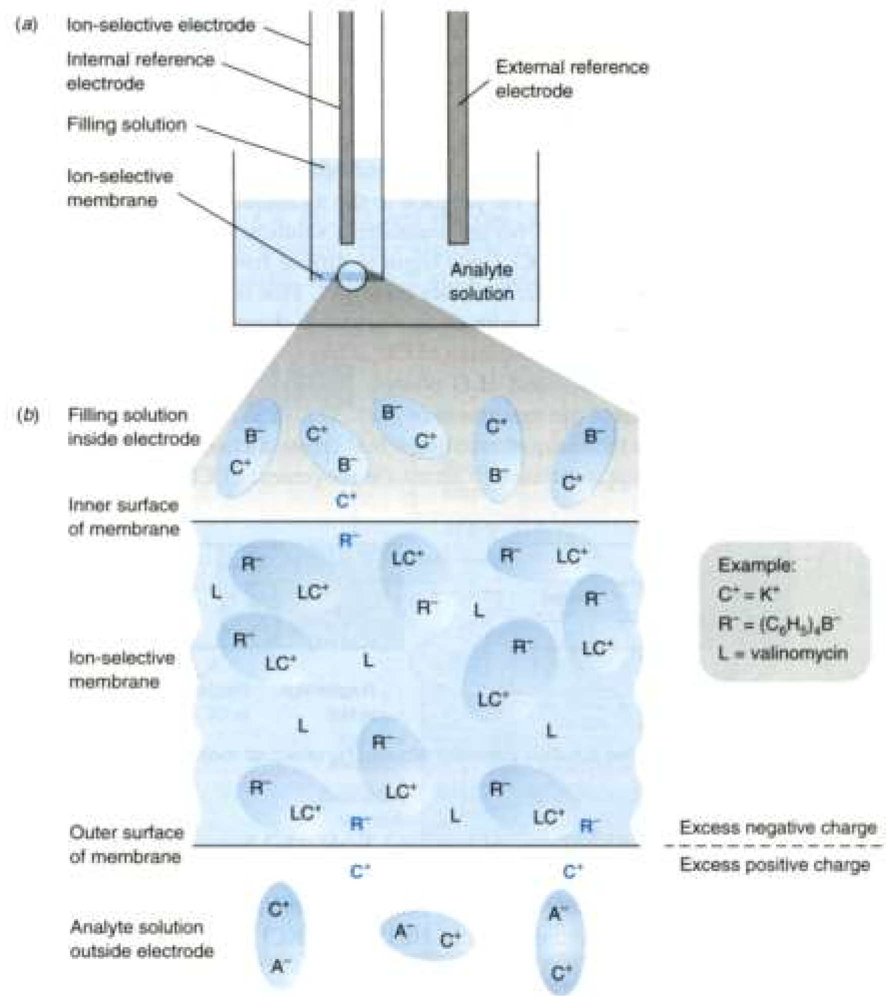


Electrode Potential is defined as:

$$E = \text{constant} + \frac{0.05916}{n} \log[C^+]$$

where $[C^+]$ is actually the activity of the analyte and *n* is the charge of the analyte

Electrodes and Potentiometry

pH Electrodes

1.) pH Measurement with a Glass Electrode

- Glass electrode is most common ion-selective electrode
- Combination electrode incorporates both glass and reference electrode in one body

Ag(*s*)|AgCl(*s*)|Cl$^-$(*aq*)||H$^+$(*aq*,outside) ⋮ H$^+$(*aq*,inside),Cl$^-$(*aq*)|AgCl(*s*)|Ag(*s*)

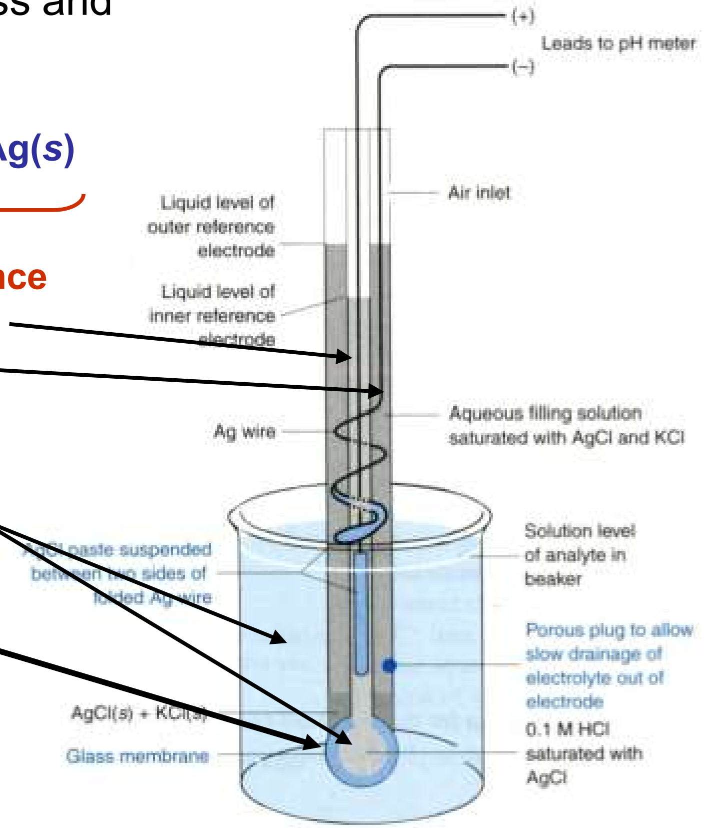
Outer reference electrode

[H$^+$] outside (analyte solution)

[H$^+$] inside

Inner reference electrode

Glass membrane Selectively binds H$^+$



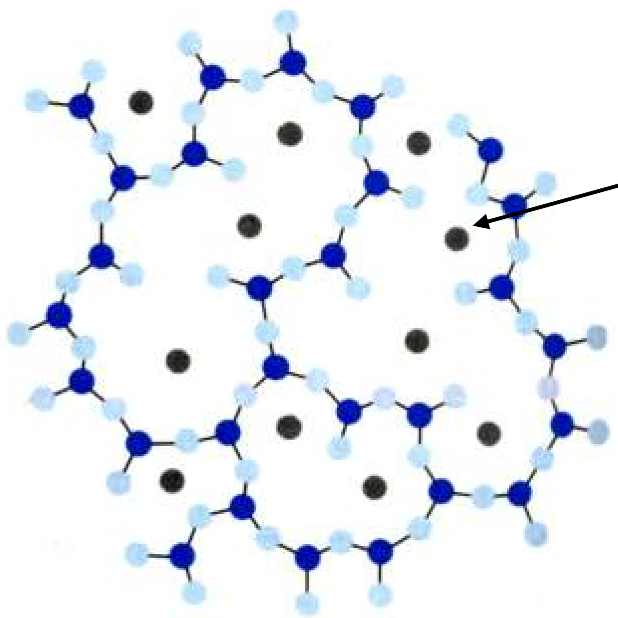
Electric potential is generated by [H$^+$] difference across glass membrane

Electrodes and Potentiometry

pH Electrodes

2.) Glass Membrane

- Irregular structure of silicate lattice



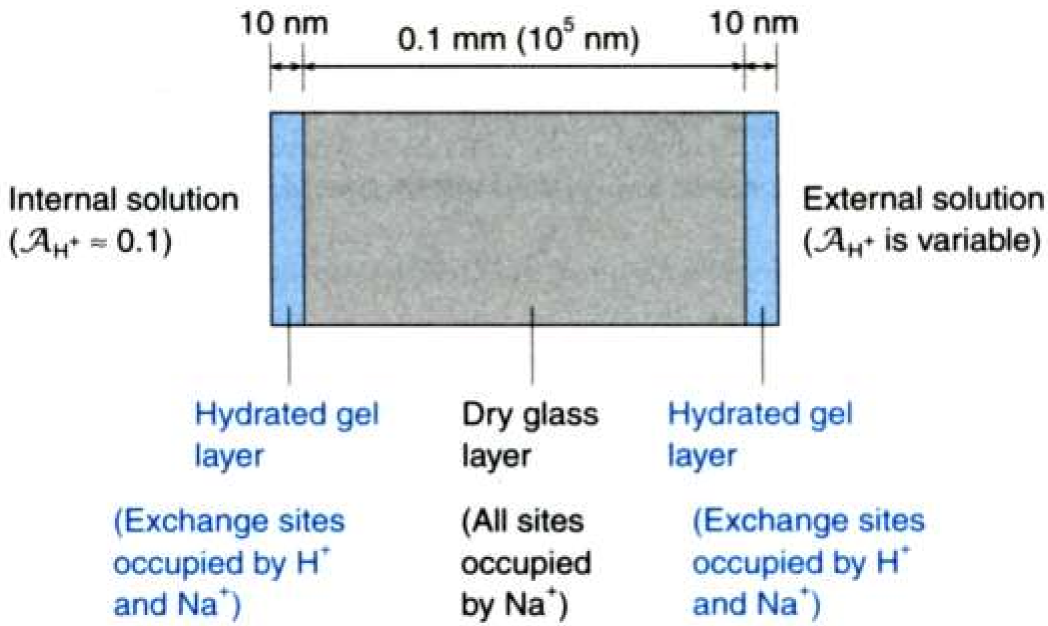
Cations (Na^+) bind oxygen in SiO_4 structure

Electrodes and Potentiometry

pH Electrodes

2.) Glass Membrane

- Two surfaces of glass "swell" as they absorb water
  - **Surfaces are in contact with [H^+]**

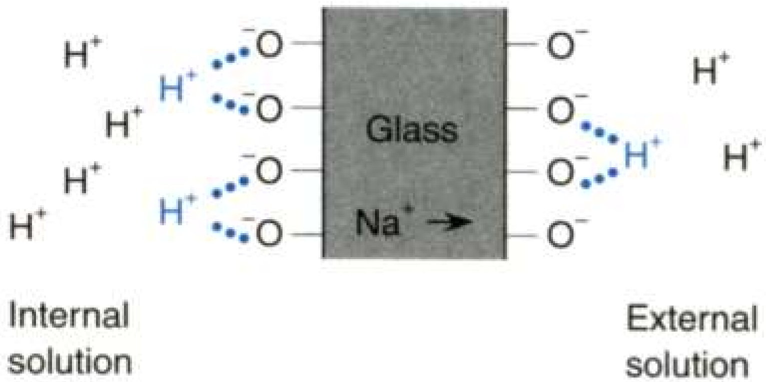


Electrodes and Potentiometry

pH Electrodes

2.) Glass Membrane

- H^+ diffuse into glass membrane and replace Na^+ in hydrated gel region
  - **Ion-exchange equilibrium**
  - **Selective for H^+ because H^+ is only ion that binds significantly to the hydrated gel layer**



Charge is slowly carried by migration of Na+ across glass membrane

$$E = \text{constant} - \beta(0.05916)\,p\text{H}$$

Potential is determined by external [H+]

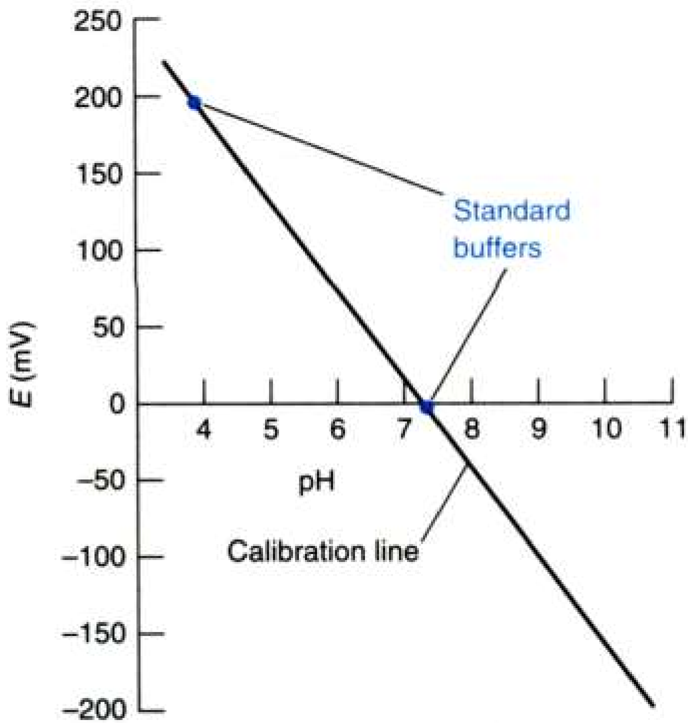
Constant and b are measured when electrode is calibrated with solution of known pH

Electrodes and Potentiometry

pH Electrodes

3.) Calibration

- A pH electrode should be calibrated with two or more standard buffers before use.
- pH of the unknown should lie within the range of the standard buffers



Measured voltage is correlated with a pH, which is then used to measure an unknown.

Electrodes and Potentiometry

pH Electrodes

4.) Errors in pH Measurements

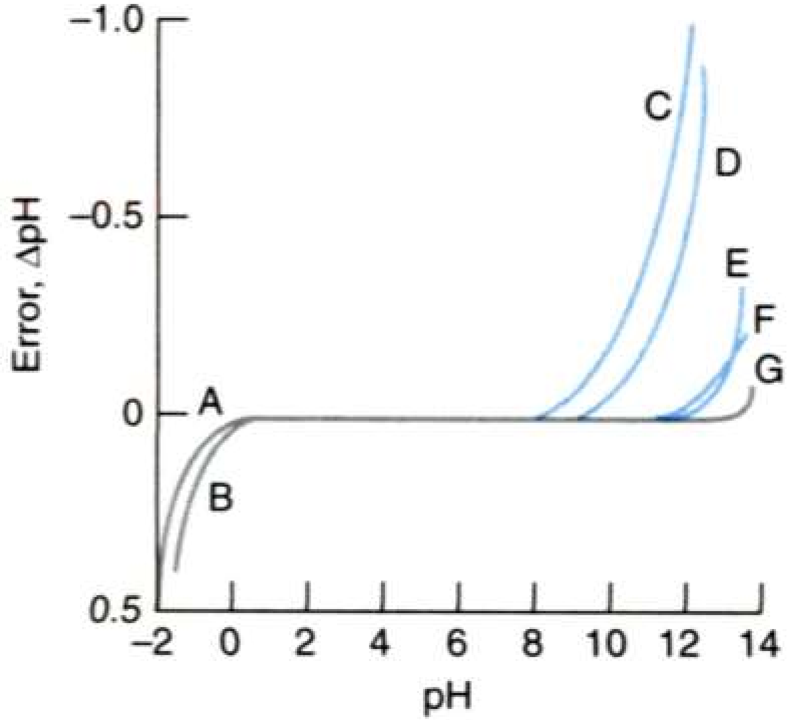
- Standards
  - **pH measurements cannot be more accurate than standards (±0.01)**
- Junction potential
  - **If ionic strengths differ between analyte and standard buffer, junction potential will differ resulting in an error of ±0.01**
- Junction Potential Drift
  - **Caused by slow changes in [KCl] and [AgCl]→ *re-calibrate*!**
- Sodium Error
  - **At very low [H^+], electrode responds to Na^+ and the apparent pH is lower than the true pH**
- Acid Error
  - **At high [H^+], the measured pH is higher than actual pH, glass is saturated**
- Equilibration Time
  - **Takes ~30s to minutes for electrode to equilibrate with solution**
- Hydration of glass
  - **A dry electrode will not respond to H^+ correctly**
- Temperature
  - **Calibration needs to be done at same temperature of measurement**
- Cleaning
  - **Contaminates on probe will cause reading to drift until properly cleaned or equilibrated with analyte solution**

Electrodes and Potentiometry

pH Electrodes

4.) Errors in pH Measurements

- pH measurements are accurate to ± 0.02 pH units



Larger errors occur at high and low pH readings

Electrodes and Potentiometry

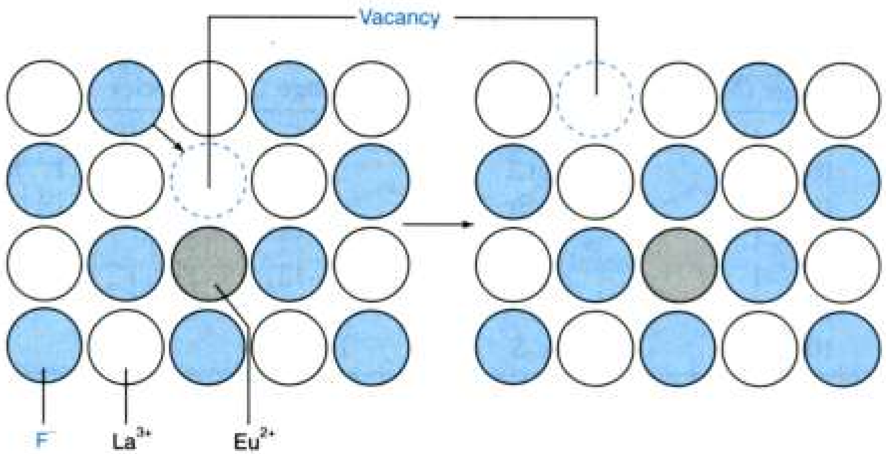
Other Ion-Selective Electrodes

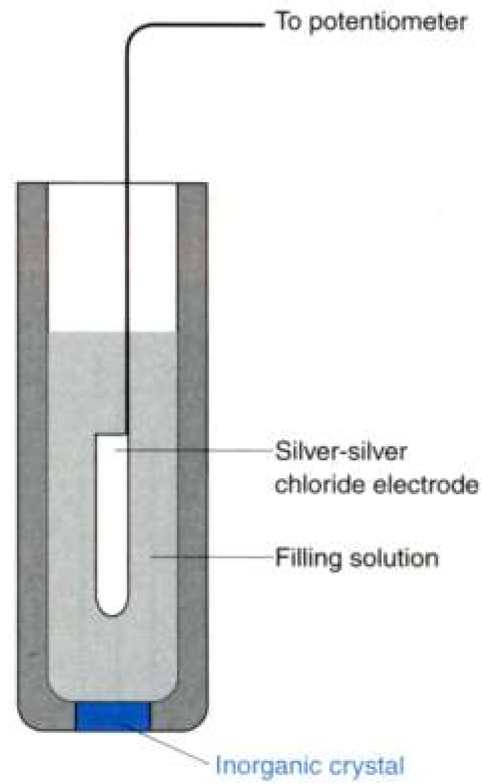
1.) Solid-State Electrode

- Based on an inorganic crystal
  - **Fluoride electrode: LaF_3 crystal doped with Eu^{2+}**

$$E = \text{constant} - \beta(0.05916)\, p\mathrm{F}^-$$

F^- migrates across crystal by "jumping" into crystal vacancies caused by Eu^{2+}





Potential caused by charge imbalance from migrating ion across membrane

Electrodes and Potentiometry

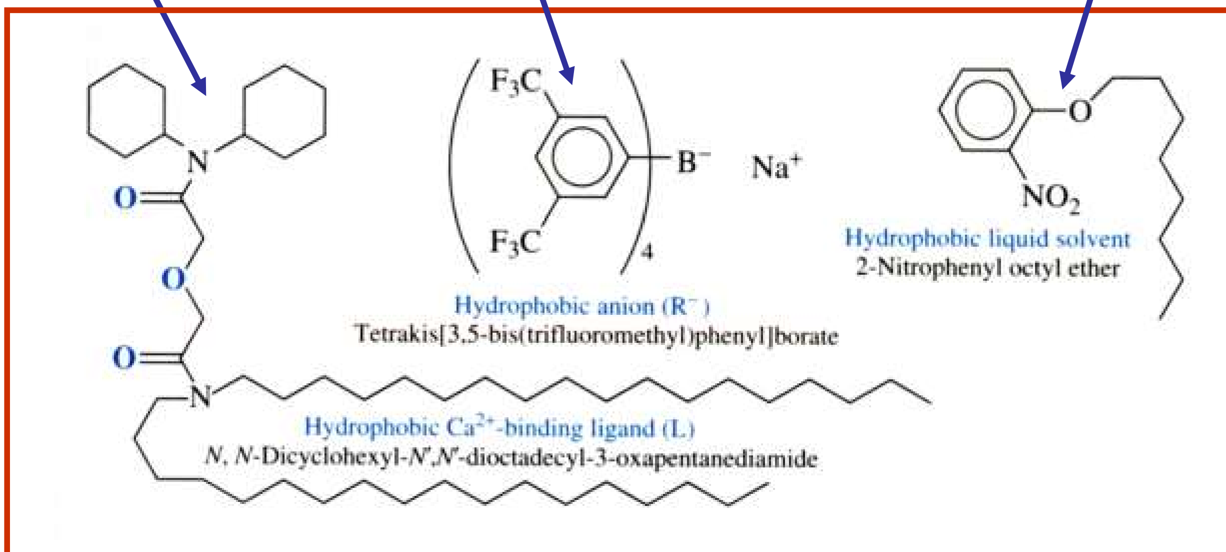
Other Ion-Selective Electrodes

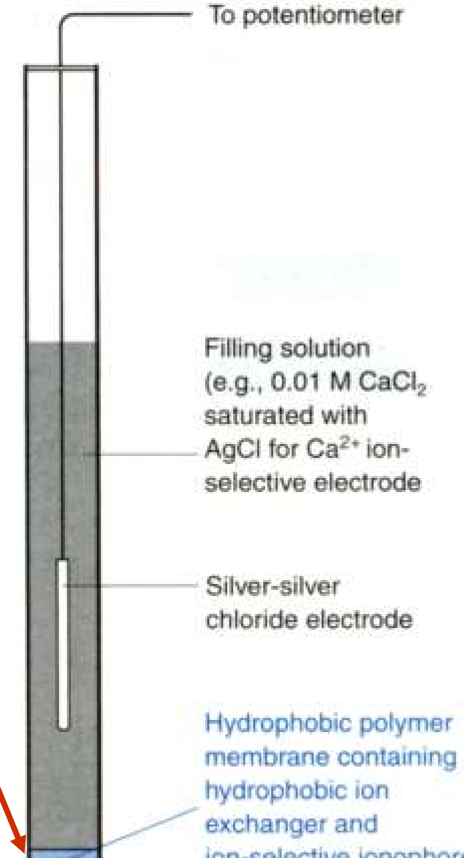
2.) Liquid-Based Ion-Selective Electrodes

- Similar to solid-state electrode
  - **Hydrophobic membrane impregnated with hydrophobic ion exchanger**
  - **Hydrophobic ion exchanger selective for analyte ion**

$$E = \text{constant} + \beta\left(\frac{0.05916}{2}\right) pCa^{2+}$$

Binds Ca^{+2} **Hydrophobic counter-ion** **Hydrophobic solvent**

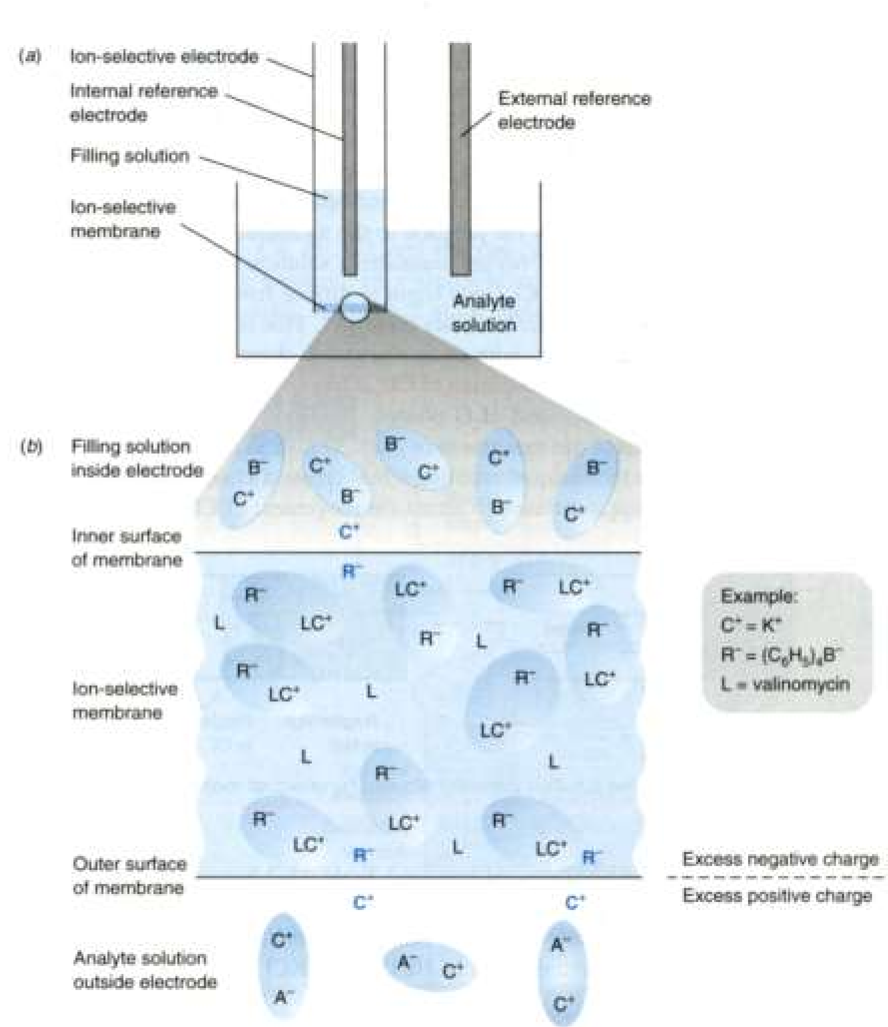




Electrodes and Potentiometry

Other Ion-Selective Electrodes

2.) Liquid-Based Ion-Selective Electrodes



Remember: **ion-selective electrodes create a potential from a charge imbalance caused by analyte ion migration across membrane**

Electrodes and Potentiometry

Other Ion-Selective Electrodes

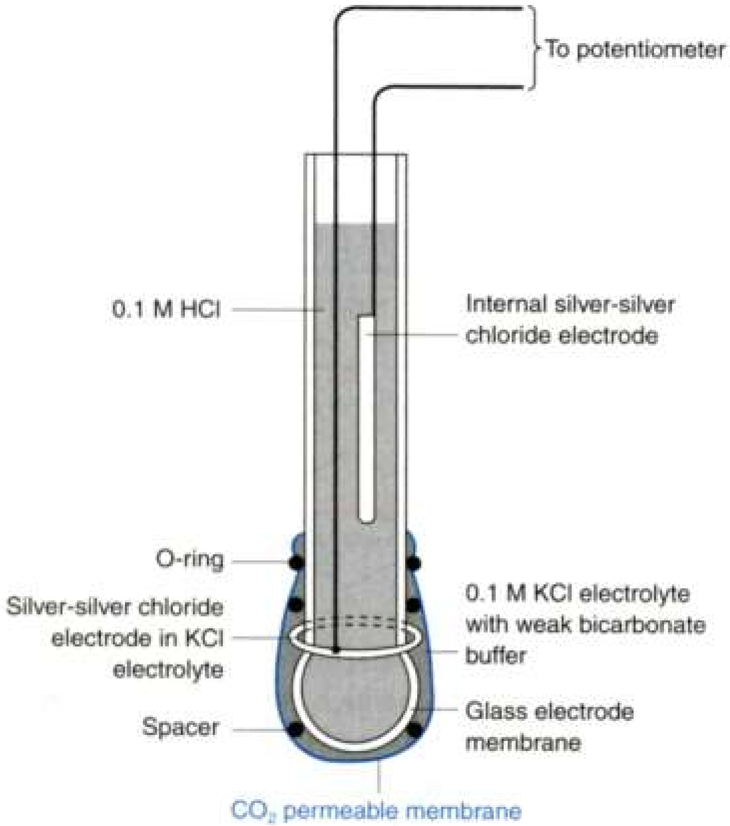
3.) Compound Electrodes

- Conventional electrode surrounded by a membrane that isolates or generates the analyte to which the electrode responds

pH electrode surrounded by membrane permeable to CO_2.

As CO_2 passes through membrane and dissolves in solution, pH changes.

pH change is an indirect measure of CO_2 concentration

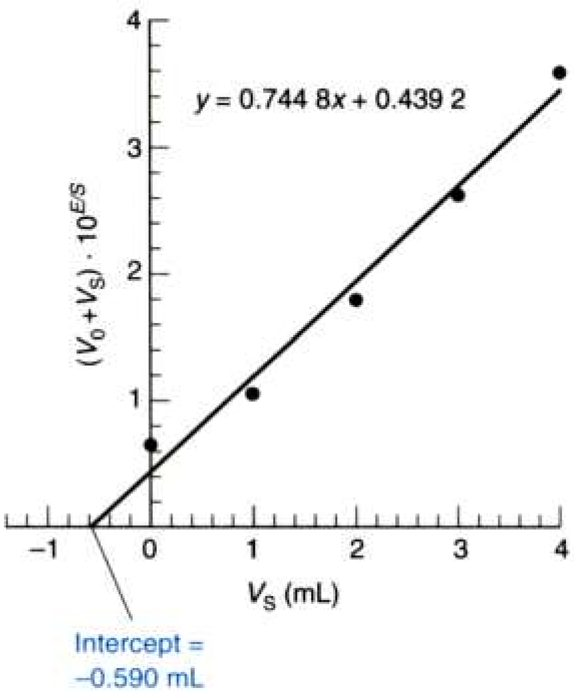


Electrodes and Potentiometry

Other Ion-Selective Electrodes

4.) Standard Addition

- Corrects for analyte dissolved in complex or unknown matrix
  - **Blood, urine, biomass, etc**
- Procedure:
  1. **Measure potential for unknown analyte solution**
  2. **Add small (known) volume of a standard**
  3. **Measure new potential**
  4. **Repeat and graph data**



$$\underbrace{(V_o+V_s)10^{E/S}}_{y} = \underbrace{10^{k/S}V_oc_x}_{b} + \underbrace{10^{k/S}c_s}_{m}\underbrace{V_s}_{x}$$

where:

V_o is the initial volume
V_s is the added volume
E is the measured potential
c_x is the unknown concentration
c_s is the standard concentration
s is a constant (βRT/*n*F)ln10

Electrodes and Potentiometry

Other Ion-Selective Electrodes

4.) Standard Addition

- Corrects for analyte dissolved in complex or unknown matrix
  - **Blood, urine, biomass, etc**
- Procedure:
  5. **x-intercept yields the unknown (c_x) concentration**

Only unknown

$$x - \text{intercept} = -\frac{b}{m} = \frac{V_o \boxed{c_x}}{c_s}$$