<u>Potentiometry</u>: measuring galvanic cell potentials to obtain chemical information (concentration)

Always measure cell potential as; $E_{cell} = E_{working} - E_{ref}\ (+E_j)$

If reference electrode potential is constant--(and E_j)---then can always write expression for E_{cell} being related to analyte ion i--

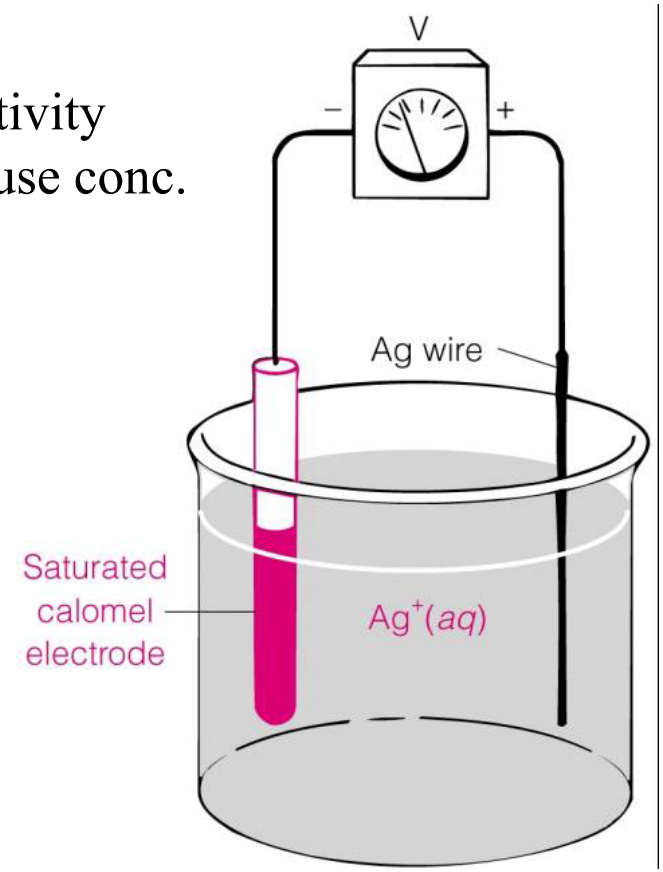
$$E_{cell} = K + (0.0592/z_i)\log(a_i)$$

or [i]

Determining Analyte Concentration from E_{cell}; Another Example--direct potentiometry

- Left: reference electrode
  - S.C.E. @ standard conditions
  - $E=E^0=0.241$ V
- Right: working electrode.
  - $[Ag^+]$ unknown
  - $E^0=0.799$ V
  - $E=0.799 +0.0592*\log([Ag^+])$
- $E_{cell}=E_w-E_{ref}$

really activity
but will use conc.



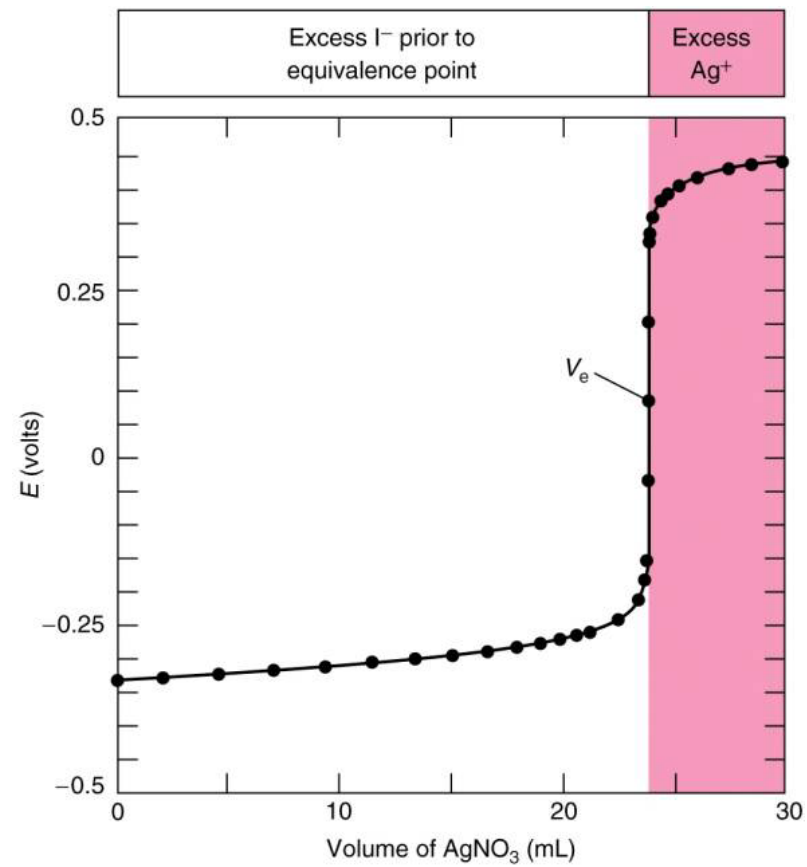
$E_{cell}= (0.799 + 0.0592 \log [Ag^+]) - 0.241$

$E_{cell} = 0.558 + 0.0592 \log [Ag^+]$

Relationship between E_{cell} and $[Ag^+]$---linear as a function of the log $[Ag^+]$ with slope of 59.2 mV/decade!

Potentiometric Titration Curve using Ag^o electrode as working electrode!

- Titration of I^- by Ag^+
- Detect Ag^+ concentration with Ag^+ indicator electrode
  - vs S.C.E.
- $K_{sp}(KI)=8.3x10^{-17}$
- Before V_e: $[I^+]_{excess}$ is known
  - $[Ag^+]=K_{sp}/[I^-]_{excess}$
- At V_e: (all I^- converted to $AgI_{(s)}$
  - $[Ag^+]=(K_{sp})^{0.5}$
- After V_e: $[Ag^+]_{excess}$ is known
  - $[Ag^+]=[Ag^+]_{excess}$



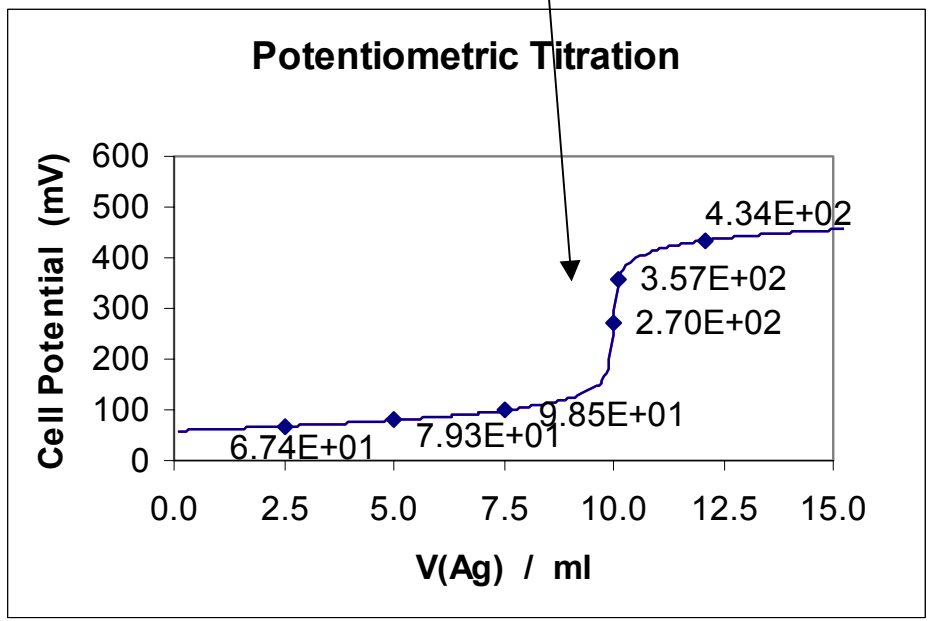
$$E_{cell} = 0.558 + 0.05916 \cdot \log[Ag^+]$$

see sample calculations in ECA text

Ask Yourself 14-A

- Titration of $[Cl^-]$ by Ag^+
- Detect Ag^+ concentration with Ag^+ indicator electrode
  - vs S.C.E.
- $K_{sp}^{KCl} = 1.8 \times 10^{-10}$
- Before V_e:
  - Determine excess $[Cl^-]$
  - $[Ag^+] = K_{sp}/[Cl^-]_{excess}$
- At V_e:
  - $[Ag^+] = (K_{sp})^{0.5}$
- After V_e:
  - $[Ag^+]_{excess}$

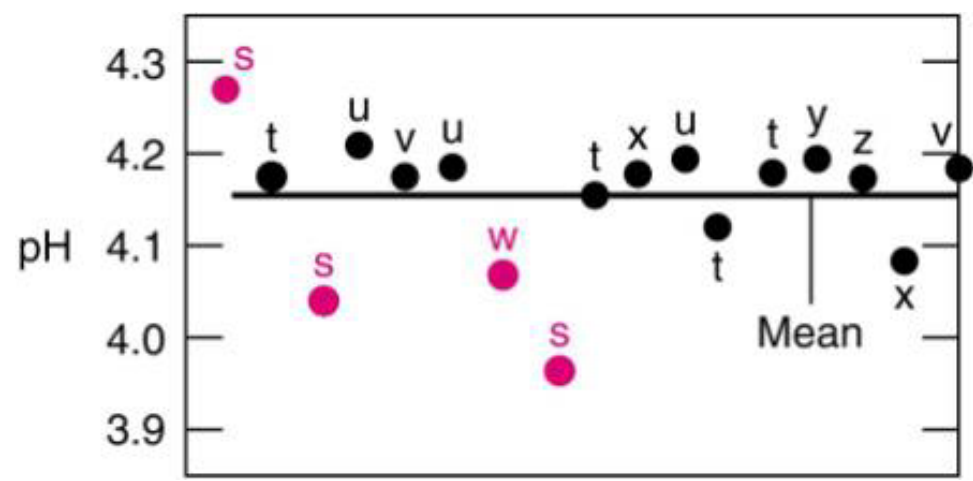
why not as sharp as case with I^- ??



$$E_{cell} = 0.558 + 0.05916 \cdot \log[Ag^+]$$

Why do a titration???
We could measure Cl^- or I^- by <u>direct potentiometry</u>--(E_{cell})--with Ag/AgCl or Ag/AgI electrodes--Yes?

- E_{cell} measurements are prone to lots of error (but still used widely).
- Direct E_{cell} measurements usually accurate to ±1 mV---can be substantial error---4% when slope is 59.2 mV/dec for monovalent ion (also variable E_j values)
- A titration involves multiple measurements
  - Random error, (standard error) decreases as the number of measurements increases
- Endpoint signaled by ΔE, not E
  - This will decrease the significant impact that a systematic error could make

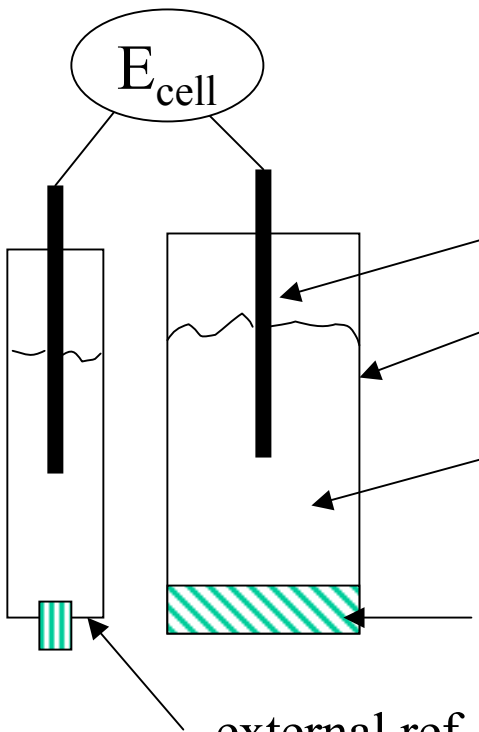


Average pH measured by 17 independent labs, using 9 different types of glass electrodes.

pH electrodes-<u>direct potentiometry</u>

Ion-Selective Membrane Electrodes (ISEs)---most widely used working electrodes for **direct potentiometric measurements**!

Very useful for direct measurements of ions in real world samples (e.g.--blood) due to high selectivity!



Types of Membranes:

-glass

-organic/polymer

-solid crystalline materials

<u>ISE membranes</u>---develop additional membrane potential (E_{mem}) that is related to activity of ions bathing on both sides of the membrane!-this potential is added to potential of cell!

Membrane is capable of participating in equilibrium with selected ions---cause charge separation (e.g., potential) at interface!--In a simplistic view----you can think that the membrane only allows one ion to get inside and move through!!----I.e., kind of like a very selective junction!

if activity of ion is equal on both sides of mem.

$$E_{mem} = (0.0592/z_i) \log (a_i^{sample} / a_i^{int.soln})$$

$E_{mem} = 0$

constant!

charge on selected ion

$$\mathbf{E_{ccll} = (E_{int.ref.} + E_{mem}) - E_{ext.ref} = K + (0.0592/z_i) \log a_i^{sample}}$$

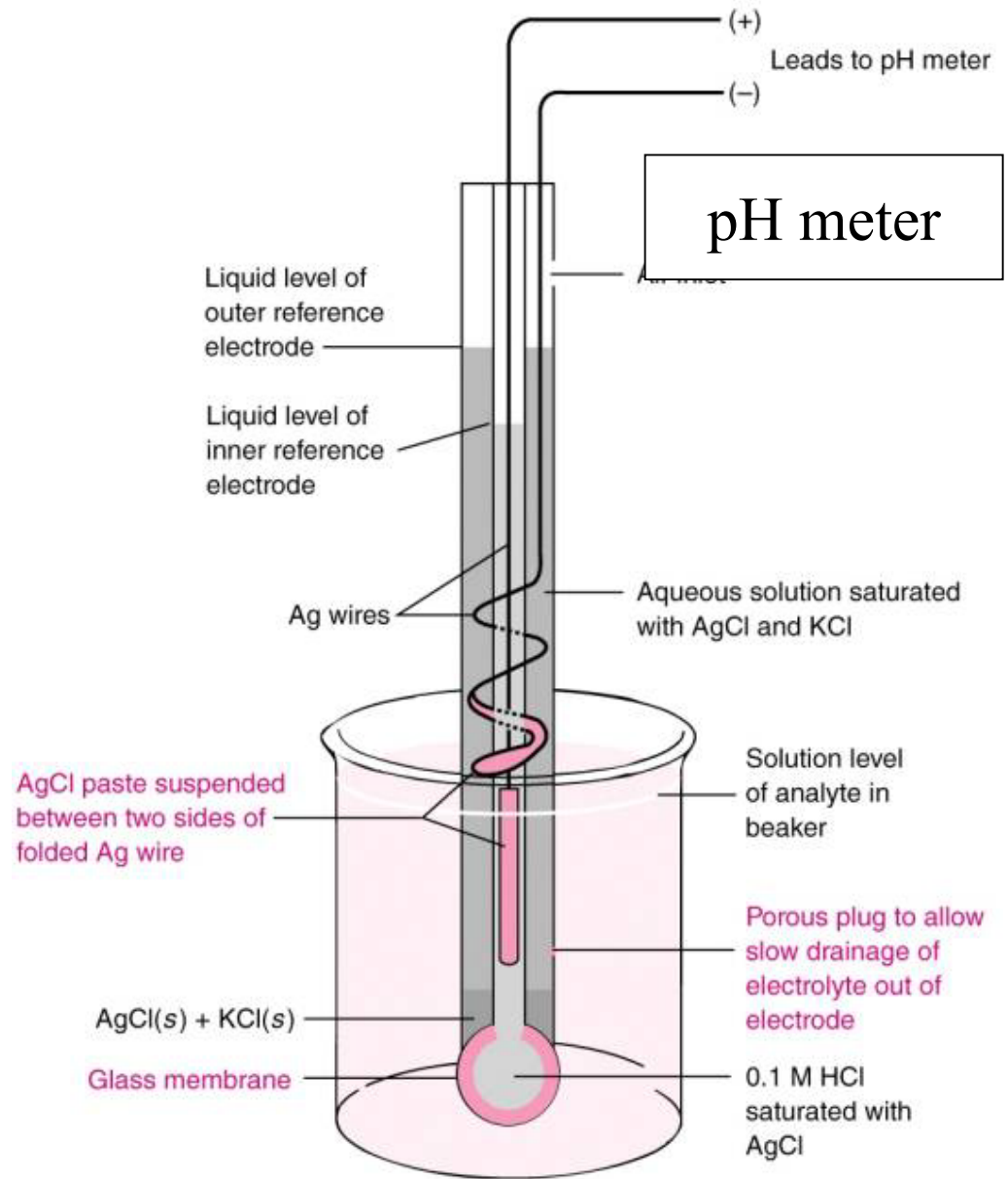
$E_{working}$

usually calibrate electrode with known solutions to determ K and slope ($=0.0592/z_i$)

Glass Membrane pH Electrode-

is a **combination** electrode:

- Contains a inner reference electrode, and an outer (external) reference electrode in one body
- external ref. elect. is separated from the analyte solution by porous membranes (junction)
- internal ref. elect. is separated from sample by glass membrane



Potential from Glass Electrode

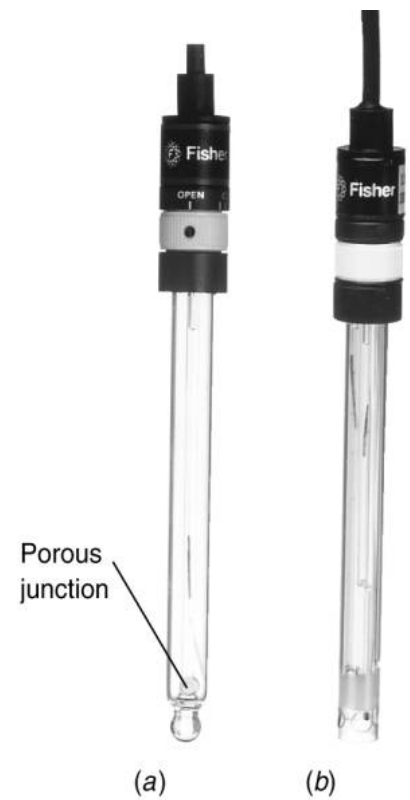
Glass membrane

$$\underbrace{Ag(s) \mid AgCl(s) \mid Cl^-(aq)}_{\text{Outer reference electrode}} \parallel \underbrace{H^+(aq, \text{outside})}_{\text{H}^+\text{ outside glass electrode (analyte solution)}} \vdots \underbrace{H^+(aq, \text{inside})}_{\text{H}^+\text{ inside glass electrode}}, \underbrace{Cl^-(aq) \mid AgCl(s) \mid Ag(s)}_{\text{Inner reference electrode}}$$

pH=1.00

pH=??

- Outer reference electrode contacts the outside analyte solution through a small porous plug (acts like a salt bridge)
- Inner reference electrode contacts the outer solution via thin glass membrane



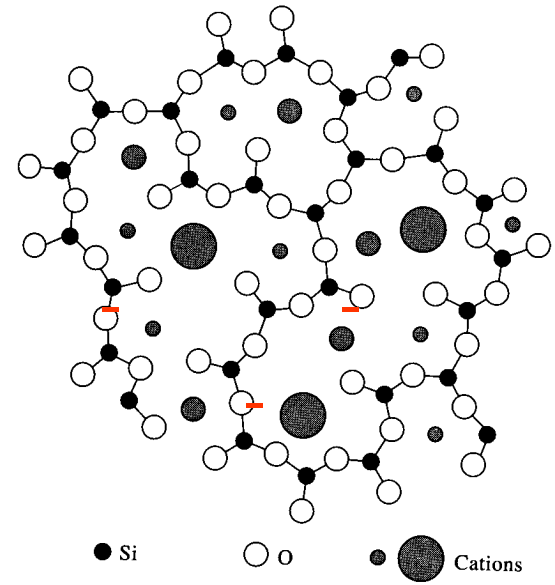
if sample pH is 4.00; what is E_{mem}?

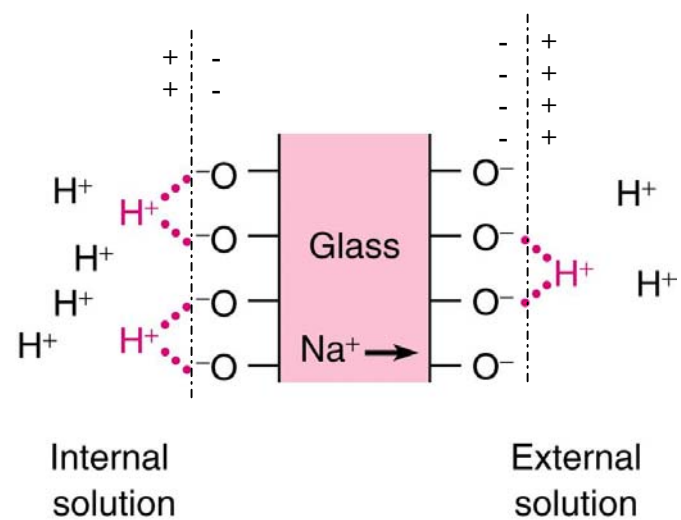
$E_{mem} = (0.0592/1) \log (10^{-4} / 10^{-1}) = -0.1776$ V

Glass Membranes: a Closer Look

- How does $[H^+]$ affect the glass membrane?
- Glass at pH>1 is negatively charged.
- Typically alkali cations, like potassium, sodium, lithium are in the glass to balance the (-) charges-they would carry current through dry glass if current flowed!
- Na^+ is the most mobile and can migrate or diffuse slowly between (-) sites--when current flows (if cell discharged!)

Because movement of ions in dry glass is very slow--resistance of glass membrane is <u>very very</u> high (10 MΩ)





E_{cell} for glass pH electrode

outer electrode $E_{ref} \approx 0.197V$ | glass membrane | inner electrode $E_{ref} \approx 0.281V$

$Ag(s) \mid AgCl(s), [Cl^-]_{sat\ KCl} \parallel [H^+]_{out} \parallel [H^+]_{in}, [Cl-] \mid AgCl(s) \mid Ag(s)$

- Write Nernst equations for reactions at the two reference electrodes:
- External:

  $E_{ref} = E^0 - 0.05916(\log[Cl^-]) = 0.197\ V$

  =3.5 M
- Inner:

  $E_{ref} = E^0 - 0.05916(\log[Cl^-]) = 0.281\ V$

  =0.1M
- $E_{cell} = E_{int.ref} + E_{mem} - E_{ext.ref}$
- $E_{cell} = 0.281 + 0.0592 \log(10^{-7}/10^{-1}) - 0.197$

  $E_{cell} = -0.271\ V$

If pH in sample is 7.00, and pH inside is 1.00 What is cell potential?

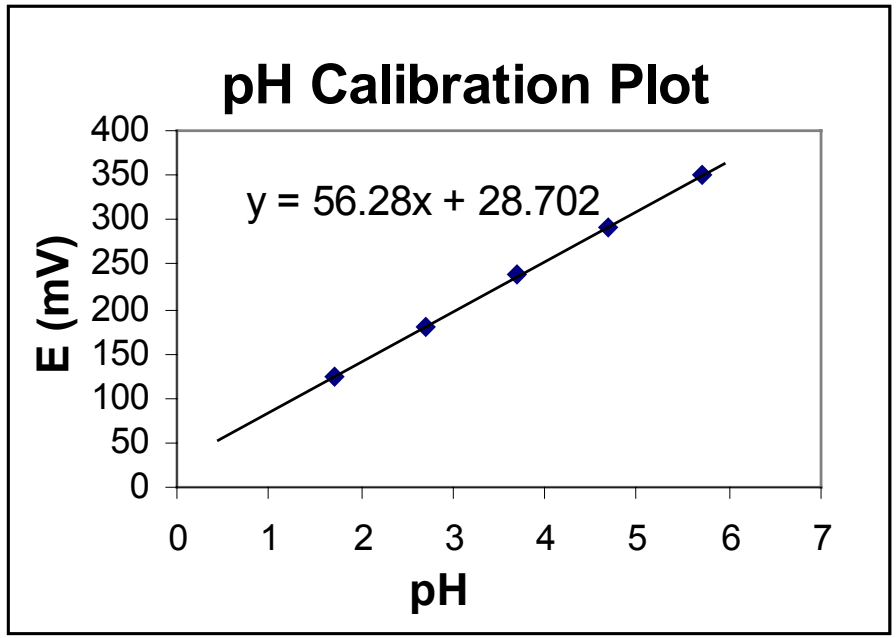
0.1 M

pH Calibration Curves

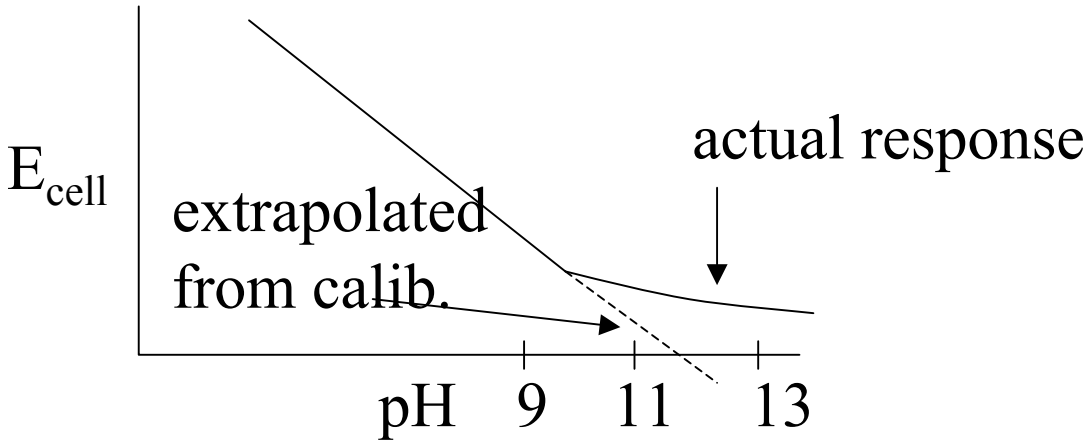
- Example, of pH calibration
- mV (E_{cell}) vs [H^+]
- Slope should equal 0.0592 V
  - 0.0563 V measured
- Intercept is a big variable
  - depends on junction potential and differences in E_{ref} inner and outer electrodes
- Author's recommendation:

  pH meter should be recalibrated every 2 hours.

Typically cabibrate near pH 7.0 and then at either pH 4.0 or pH 10---to determine slope!



Selectivity of glass pH electrode---Alkaline error problem!



a_j = activity of potential interferent ions; z_j -charge on these ions

$$E_{cell} = K' + \frac{0.059}{z_i}\log(a_i + \sum_j k_{i,j}^{pot} a_j^{z_i/z_j})$$

selectivity coefficient!

smaller the k^{pot} value, the more selective the electrode to primary ion i over interferent ions j-

For pH glass electrodes: $k_{H+,Na+}=10^{-10} - 10^{-12}$ depending on composition of glass

at pH 12, $a_i = 10^{-12}$;
if $k_{H+,Na+} = 10^{-10}$
and $a_{Na} = 10^{-2}$
then sodium in sample looks like 10^{-12} H^{+-} ---so
$a_{H}+$ appears to be **2 x 10^{-12}**

e.g.--if solution was pH 12.0, and contained 0.01 M Na^+ ions----if $k_{H,K} = 10^{-10}$, then "apparent pH" would be :

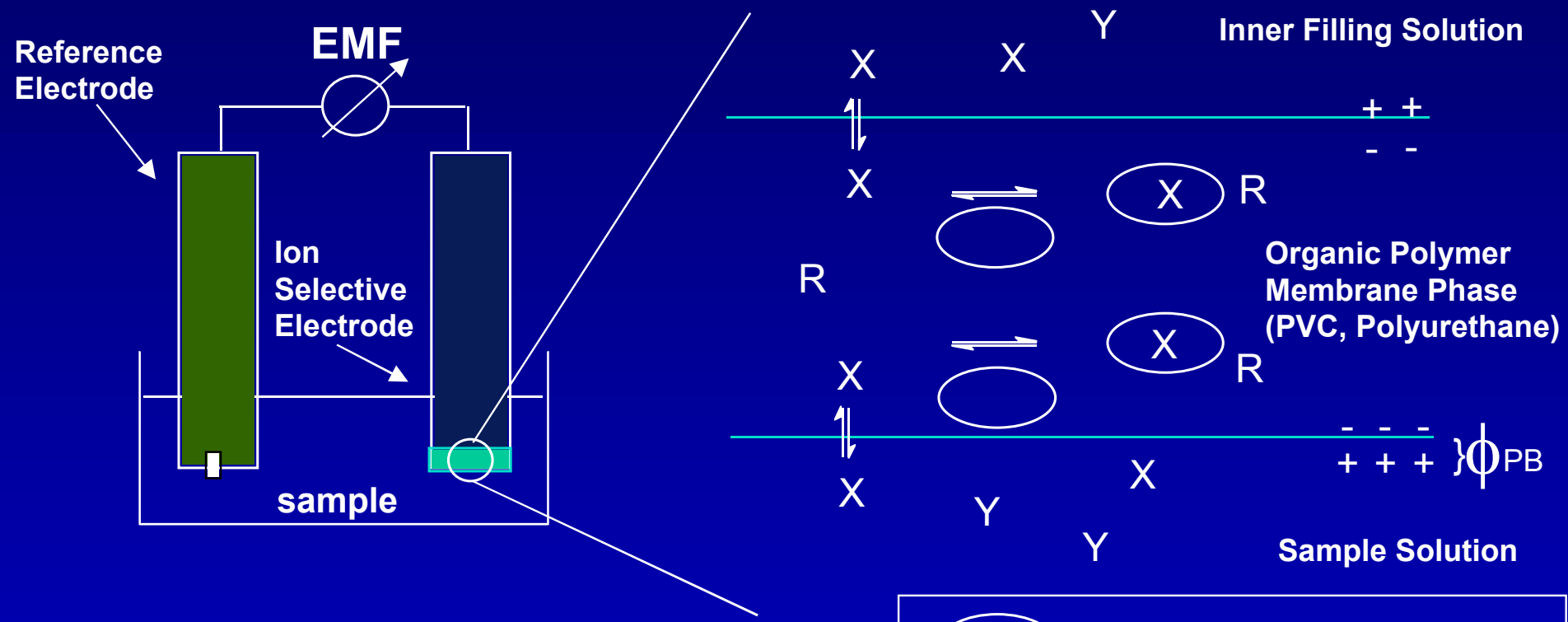
$-\log(a_{H+} + k^{pot}a_j^{1/zj}) = -\log(2 \times 10^{-12}) = 11.7$--not pH 12.0 as expected!

In general---for all ISEs----can estimate error for presence of interferents---if you know selectivity coefficient:

$$\% \text{ error} = \frac{\sum_j k_{i,j}^{pot} a_j^{z_i / z_j}}{a_j} x\ 100$$

Polymer Membrane Ion-Selective Electrodes

Organic Liquid Membrane Electrodes---use Ionophores!



Nicolsky Equation:

$$E_{cell} = K + \frac{59.2}{Z_X} \log \left[a_X + \sum_y k^{pot}_{X,Y} a_Y^{\frac{Z_X}{Z_Y}} \right]$$

= Ionophore

X = analyte ion

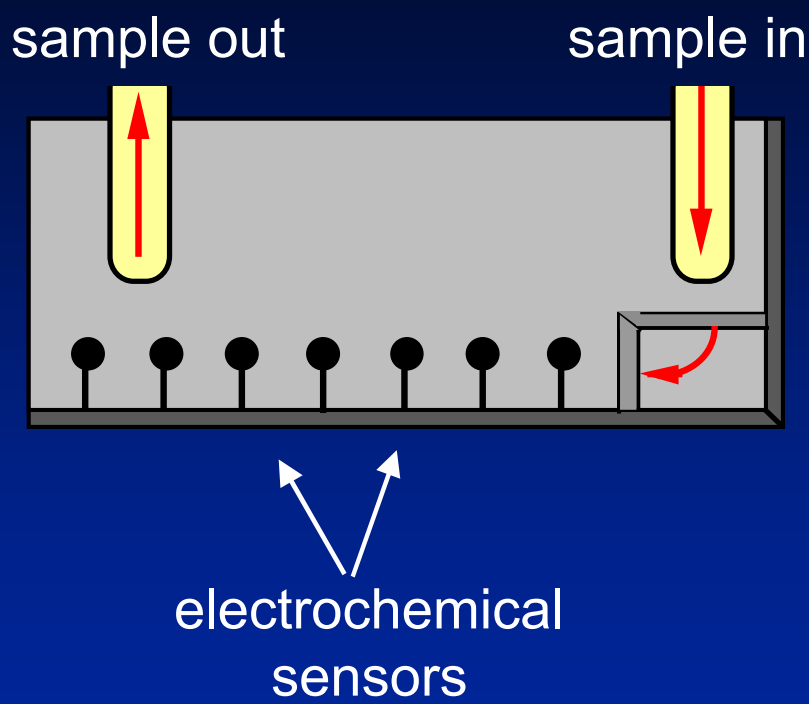
Y = interferent ions

R = lipophilic R^+ or R^+ additives

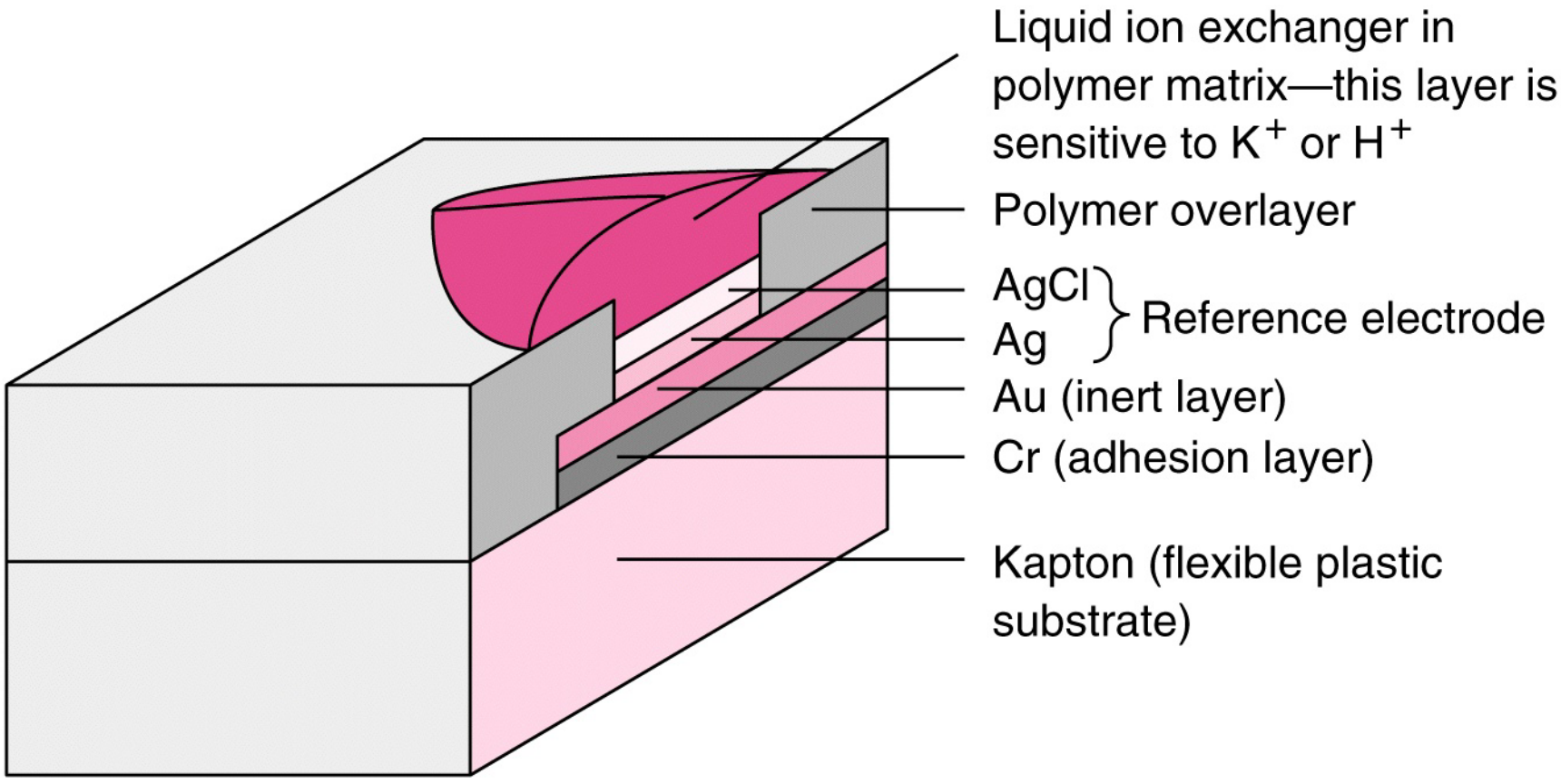
$k^{pot}_{X,Y}$ = selectivity coefficient

Structures of some common ionophores used to make polymer membrane electrodes:

Benchtop Blood Gas/Electrolyte Analyzer

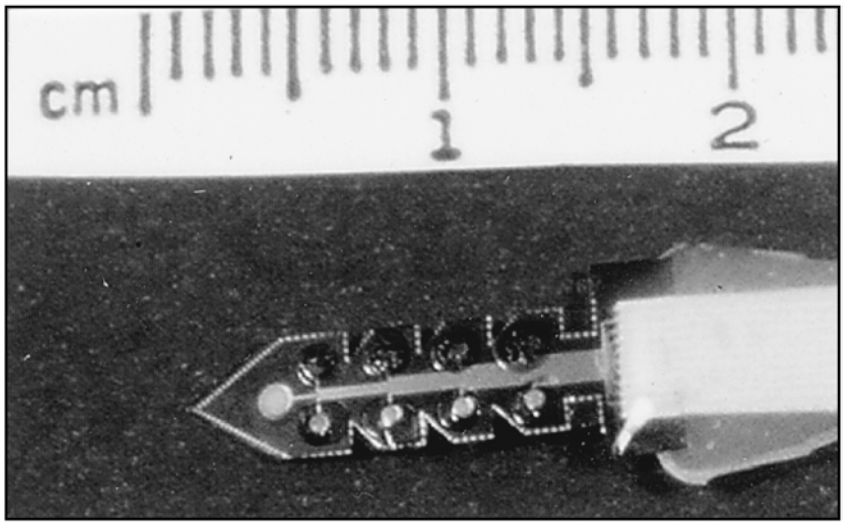


Internal Sensing Cartridge

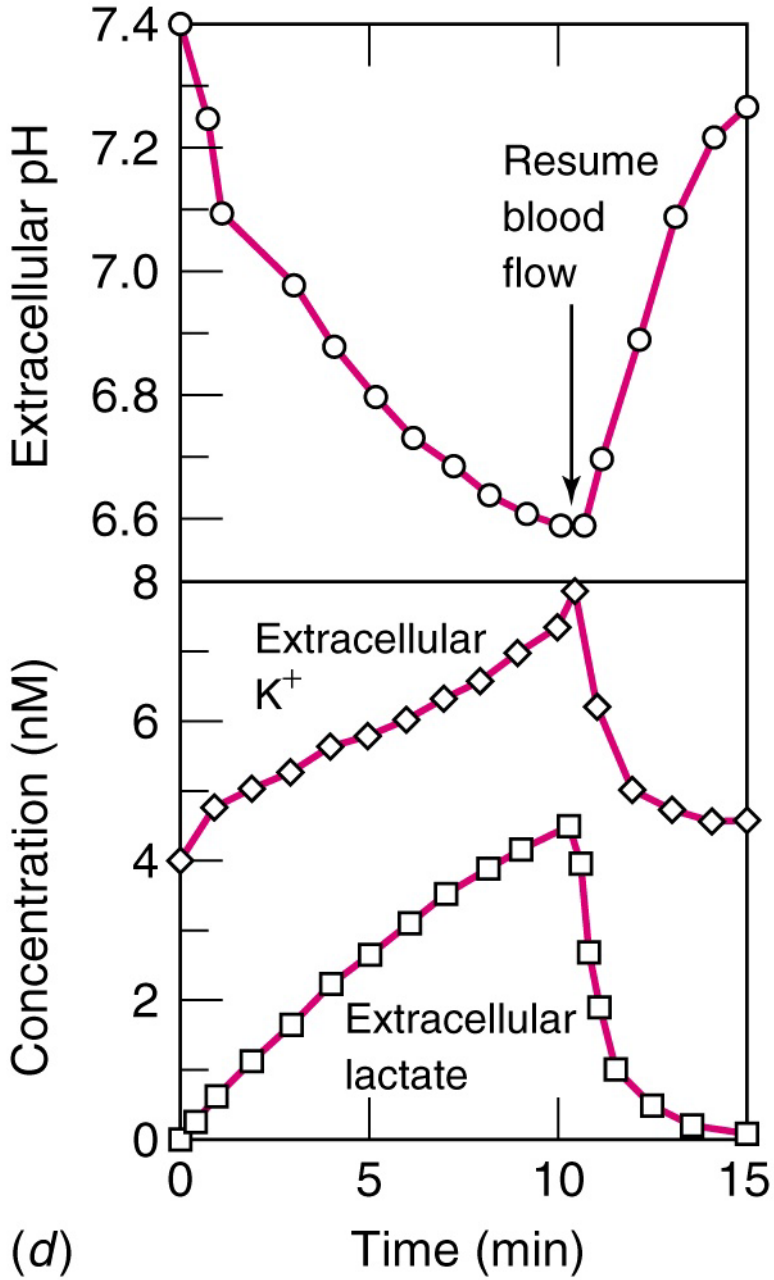

Liquid ion exchanger in polymer matrix—this layer is sensitive to K^+ or H^+
Polymer overlayer
AgCl
Ag
Reference electrode
Au (inert layer)
Cr (adhesion layer)
Kapton (flexible plastic substrate)

a)

ISEs made in miniature form and placed into heart muscle---heart made ischemic by stopping blood flow for period of time!

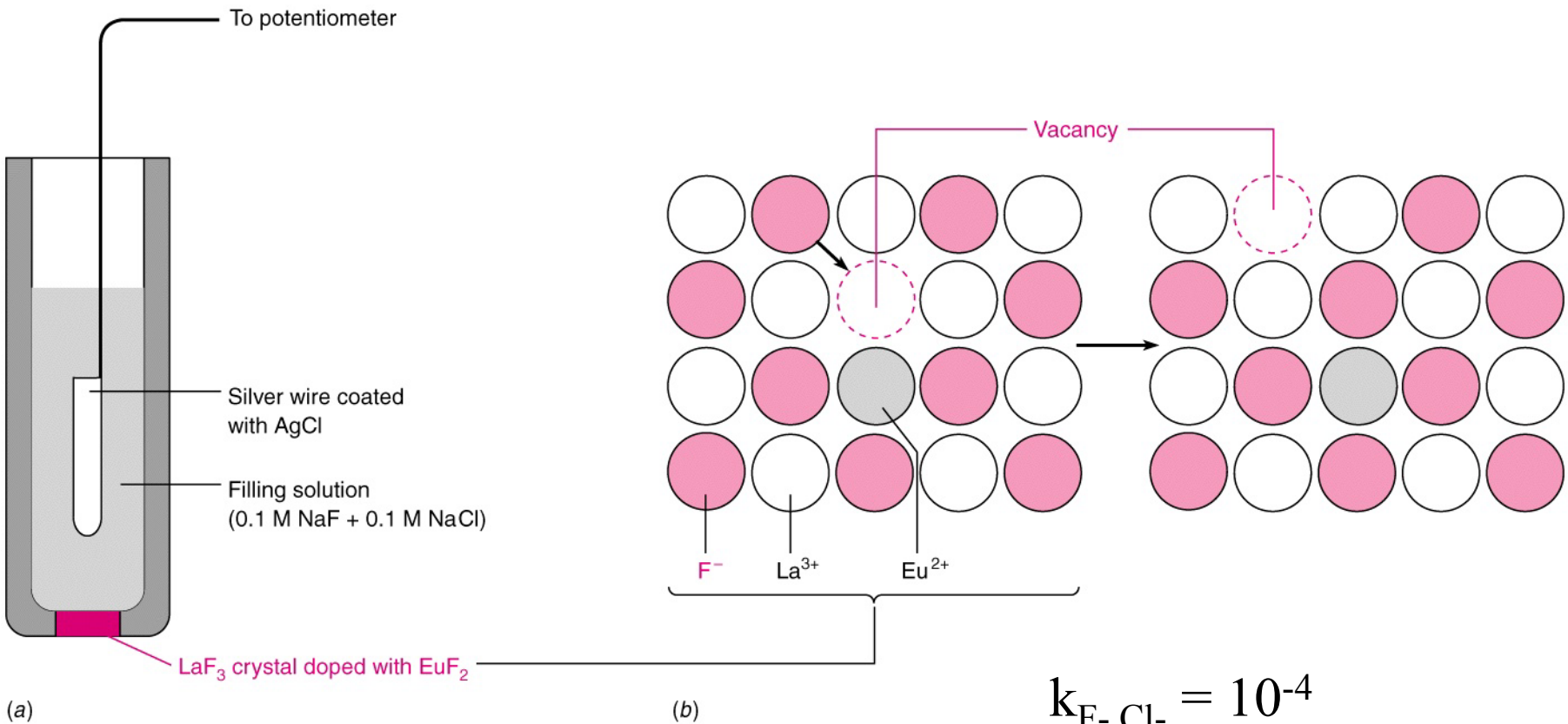


(*b*)



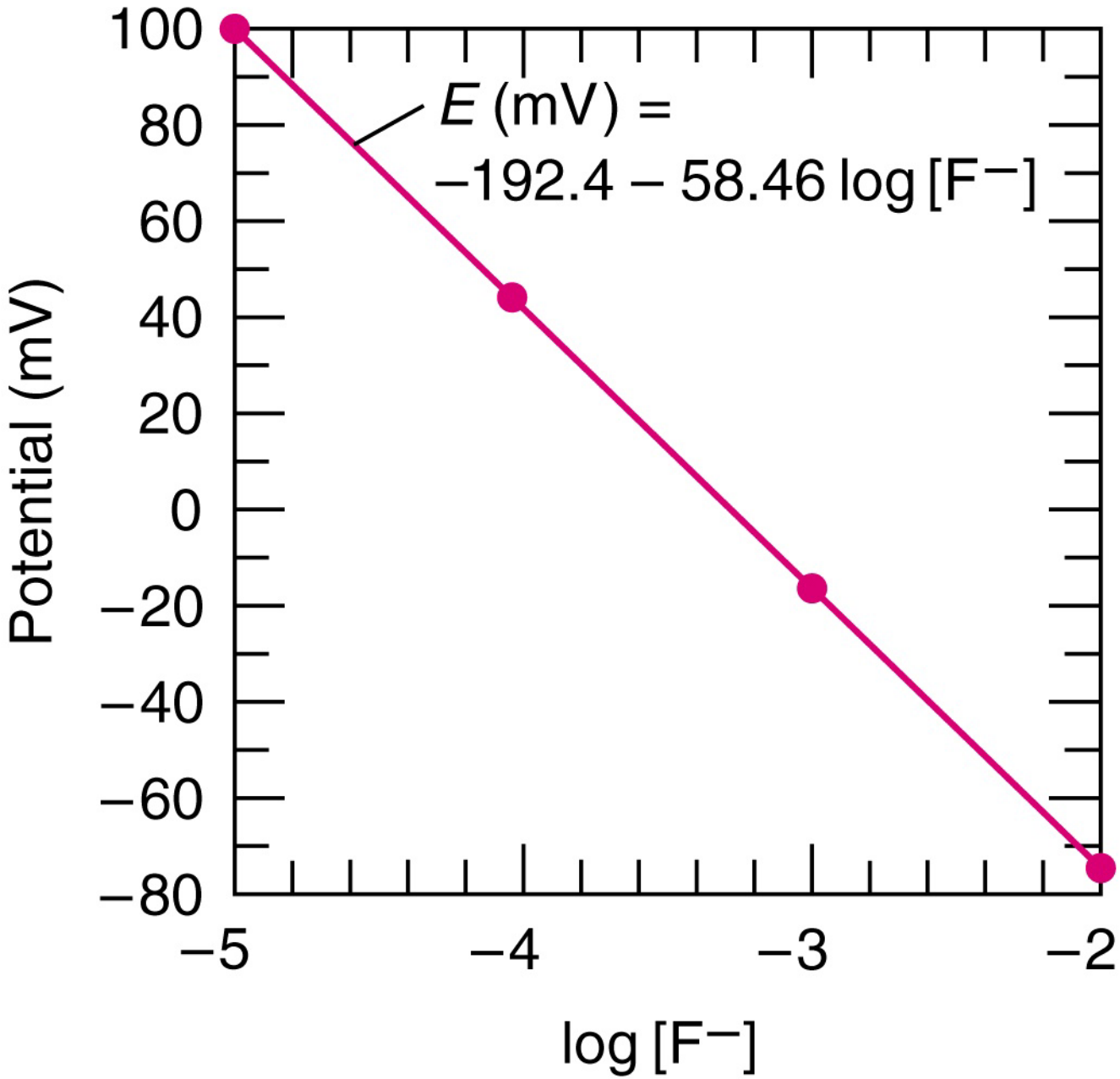
(*d*)

Solid-State Crystal Membrane---Fluoride Electrode---based on LaF_3 crystal as Membrane----used to measure fluoride ion in drinking water!!



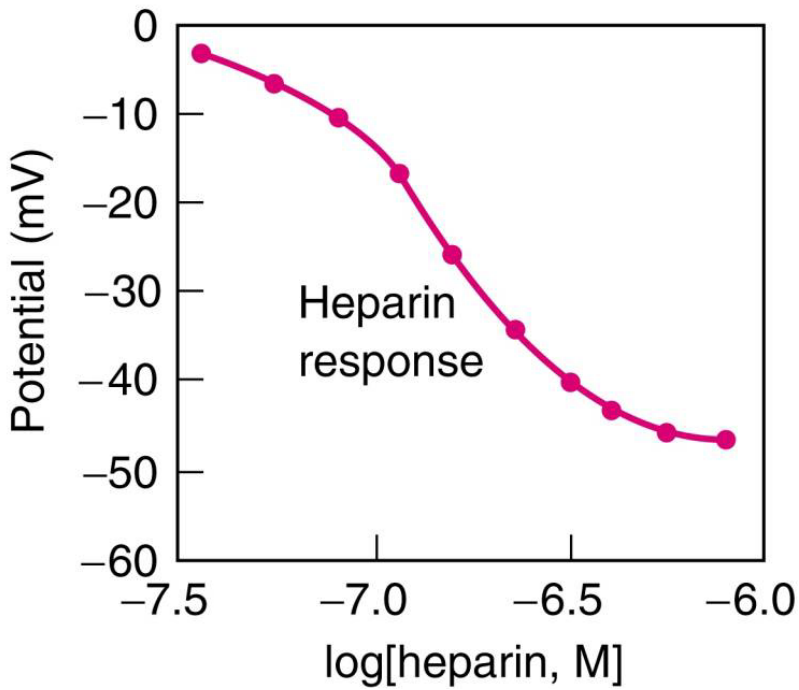
$k_{F-,Cl-} = 10^{-4}$

$$E_{cell} = K - 0.0592 \log a_{F-}^{sample}$$


100
80
60
40
20
0
−20
−40
−60
−80
Potential (mV)
−5
−4
−3
−2
log [F⁻]
E (mV) =
−192.4 − 58.46 log [F⁻]

Other Ion-Selective Electrodes--Polyion Sensors!-

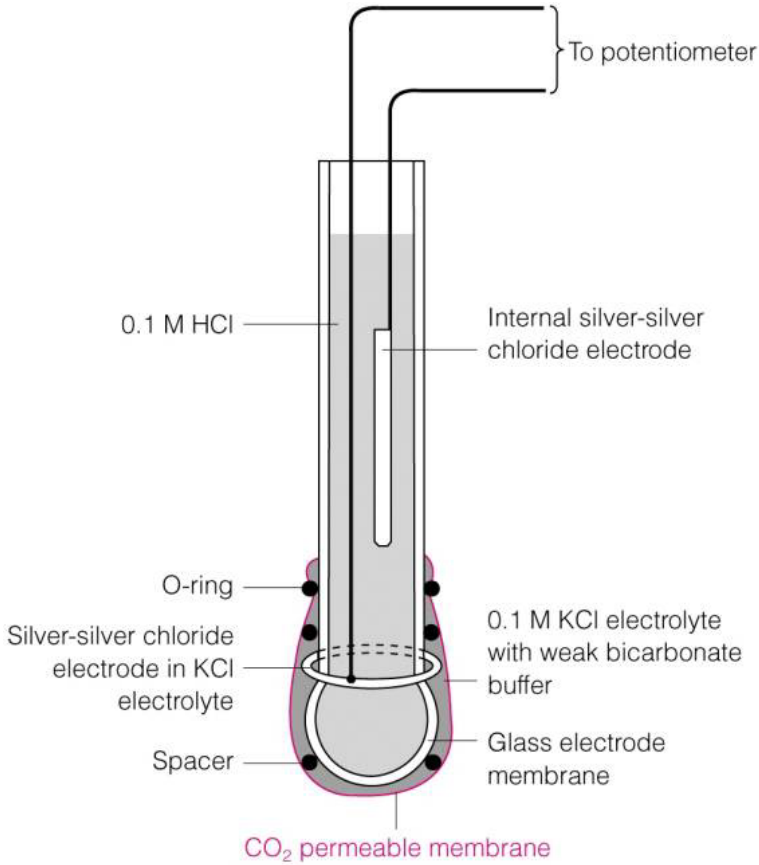
- Example: a heparin sensor
- Heparin is an anti-coagulant drug
  - it prevents blood clotting during surgery
  - Delivery to patient must be very carefully regulated
- Ion-selective membrane
  - Polymer covered with C_n-$N^+R'_3$ ammonium cations
- Heparin is negatively charged, n<=-60
- heparin selectively diffuses into the polymer membrane
- Cl^- or other anions are displaced from the membrane



M.E. Meyerhoff, et al. *Anal. Chem.* **1996,** *68,* 168A.
--U. Mich.

CO_2 Selective Electrode

- This is a modified pH electrode
- Two AgCl|Ag reference electrodes
  - one inside the tube
  - the other is a loop of AgCl coated Ag wire around the tube
- The glass membrane tip is covered with thin polymer membrane, Teflon or rubber
- the plastic membrane will allow CO_2 to diffuse into the "outer" electrode solution
- $CO_2 + H_2O \rightarrow HCO_3^- + H^+$
- The glass membrane adsorbs H^+ and the potential develops



It's really measuring pH