Membrane Electrodes

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

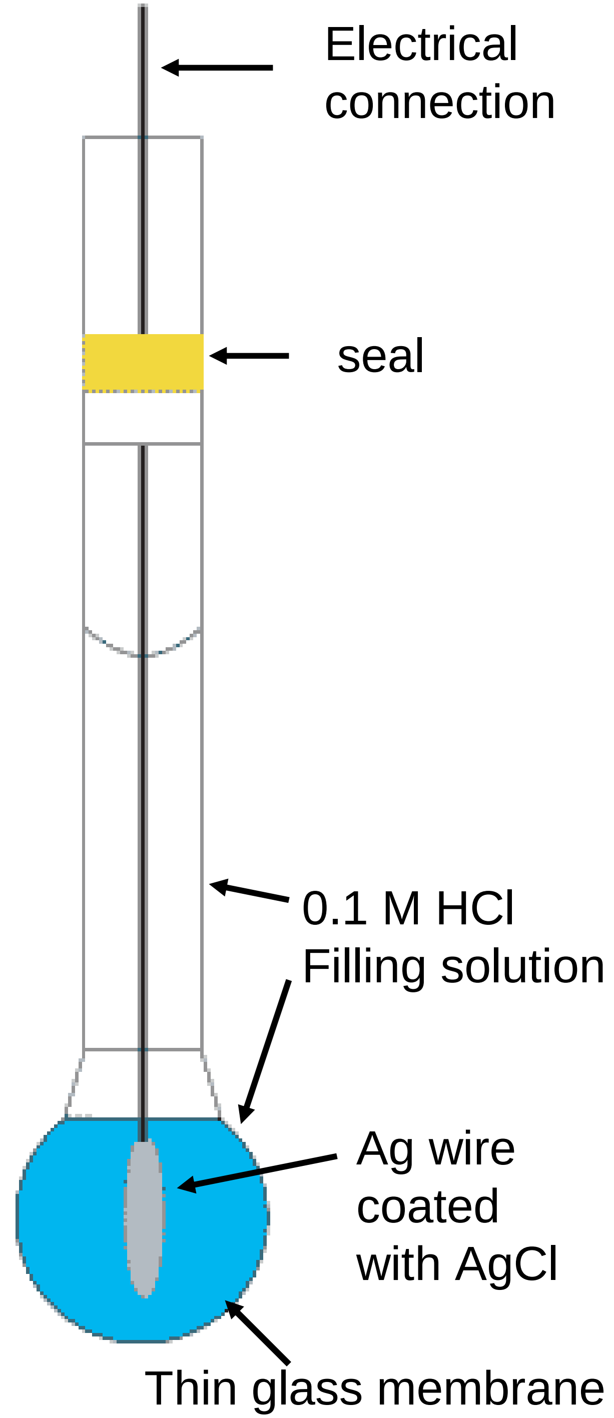
thin glass membrane

$[H^+] = a_1$ | $[H^+] = a_2$
solution 1 | solution 2

potential develops across membrane

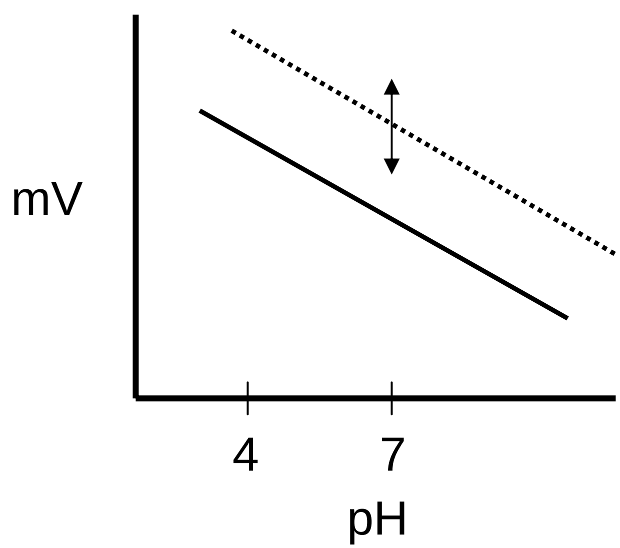
Glass pH Electrode

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



Proper pH Calibration

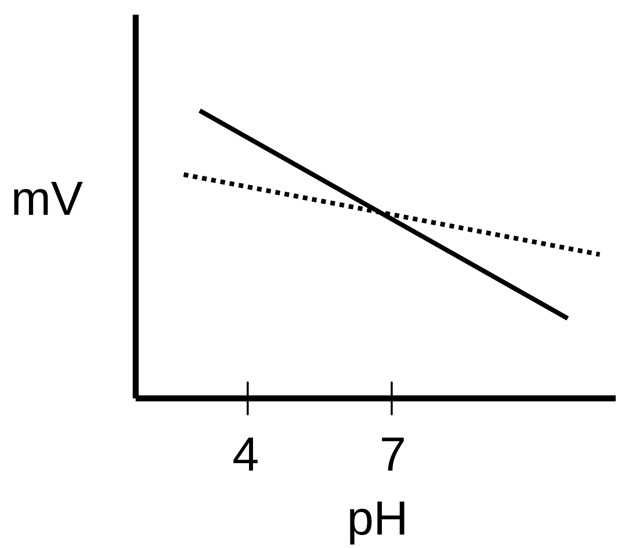
- $E = K' - 0.0591\ pH$
- Meter measures E vs pH – must calibrate both slope & intercept on meter with buffers
- Meter has two controls – calibrate & slope
- 1st use pH 7.00 buffer to adjust calibrate knob



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 $\underline{+}$0.01 units*
  - Precision may be good to $\underline{+}$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

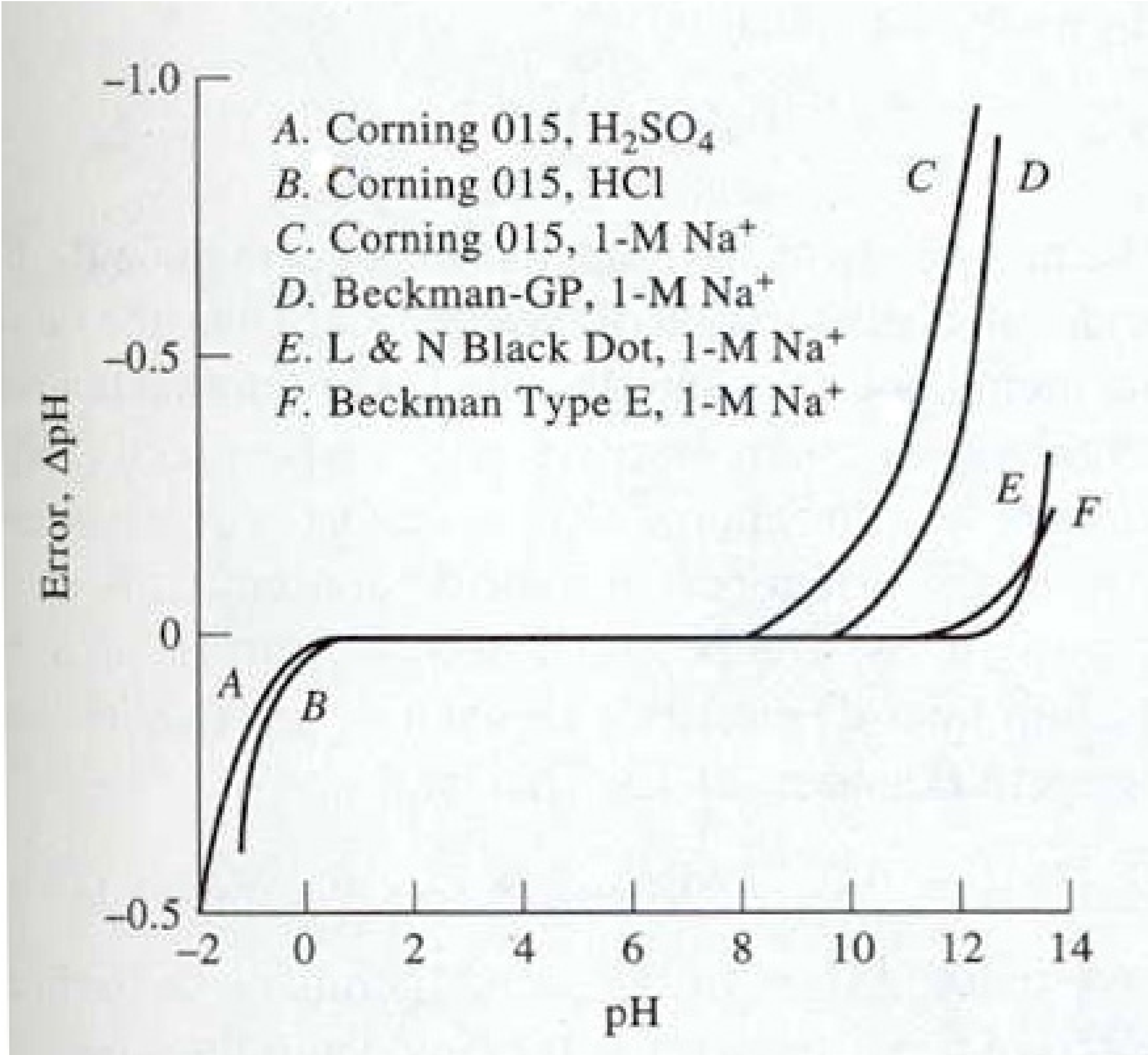
- Asymmetry potential is another non-ideal potential that arises possibly from strain in the glass. When both internal & external H^+ solutions are the same activity, potential should be 0 but it's not

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

- 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.



Acid and Alkaline error of Some electrodes

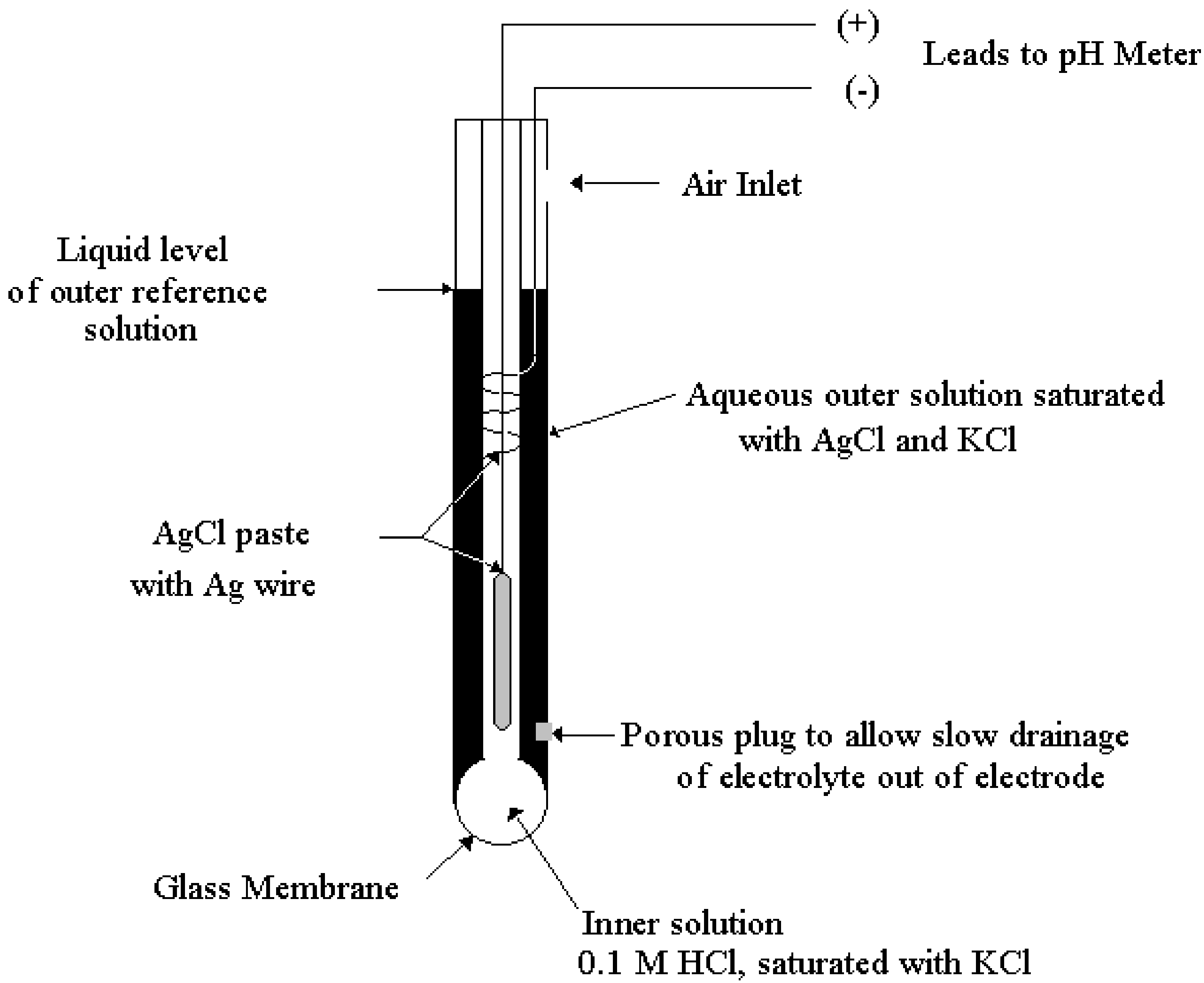
Errors in pH Measurement 4

- Acid Error – electrode reads slightly higher than the actual pH in very acidic solutions (not well understood)
- Response Time – related to activity for all potentiometric electrodes & is fast at high activity (concentration) & slow at low conc.
- Hydration of Glass Surface – glass electrodes must be kept hydrated for good measurement & must be rehydrated for 24 hrs if it dries out – will cause noisy readings

Glass Electrode Summary

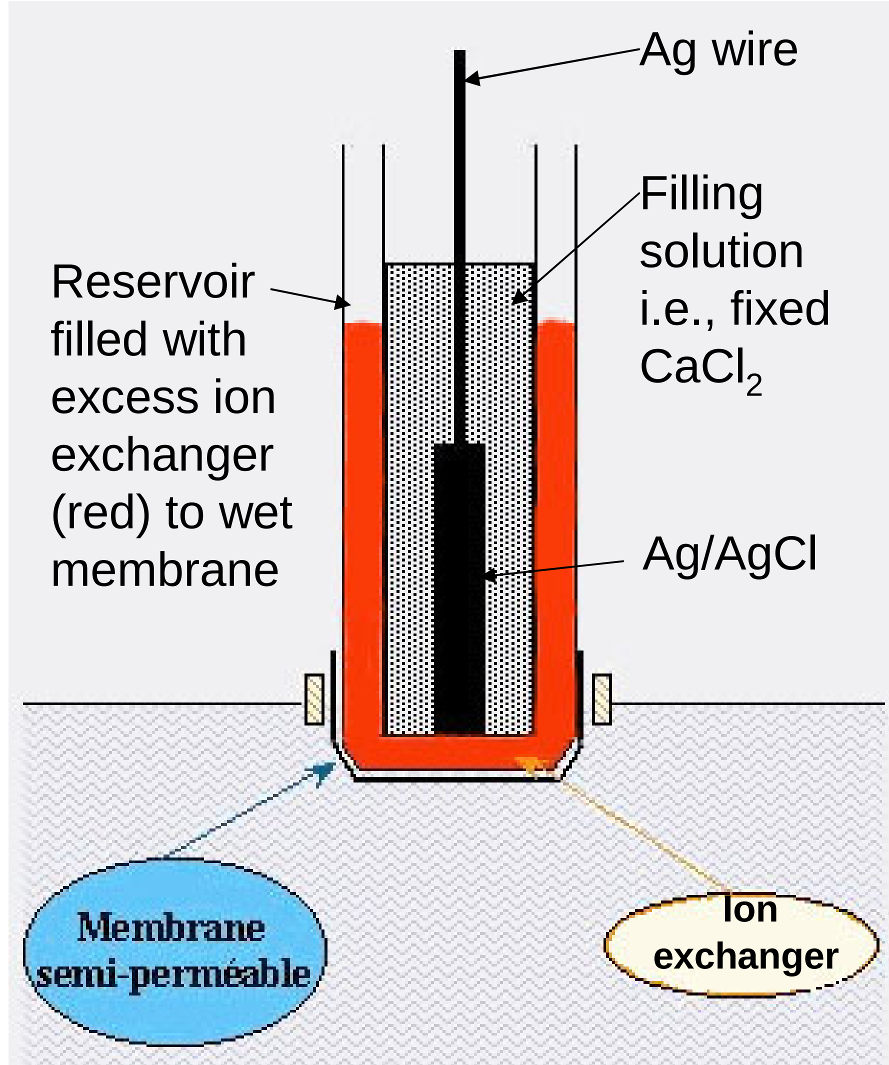
- Glass membrane electrodes are very good indicator electrodes in potentiometry
- Must exercise care in calibration and in maintaining integrity of glass membrane
- Some errors exist & are unavoidable
- Glass electrodes available for Na^+, K^+, NH_4^+, Rb^+, Cs^+, Li^+, Ag^+ (cations only) by varying glass composition
- Combination electrodes combine pH & ref.

Combination pH Electrode



Liquid Membrane Electrodes

- Calcium Electrode is good example
- Liquid ion exchanger – water immiscible organic compound with phosphate groups selective for Ca^{2+} in a hydrophobic membrane



The membrane electrode configuration

Liquid Membrane Electrodes

- Principle of Ca^{2+} electrode is the same as for glass electrode, however, since Ca^{2+} is divalent n = 2 → Nernstian slope = 29.5 mV per 10 fold change in concentration
- Detection limit for Ca^{2+} is approx. 10^{-5} M
- Selectivity is:
  - Independent of pH from 5.5 to 11
  - 50 times better for Ca^{2+} than for Mg^{2+}
  - 1000 times better for Ca^{2+} than Na^{+} or K^{+}
- Other liquid membrane electrodes available

Response of calcium ion liquid membrane electrode

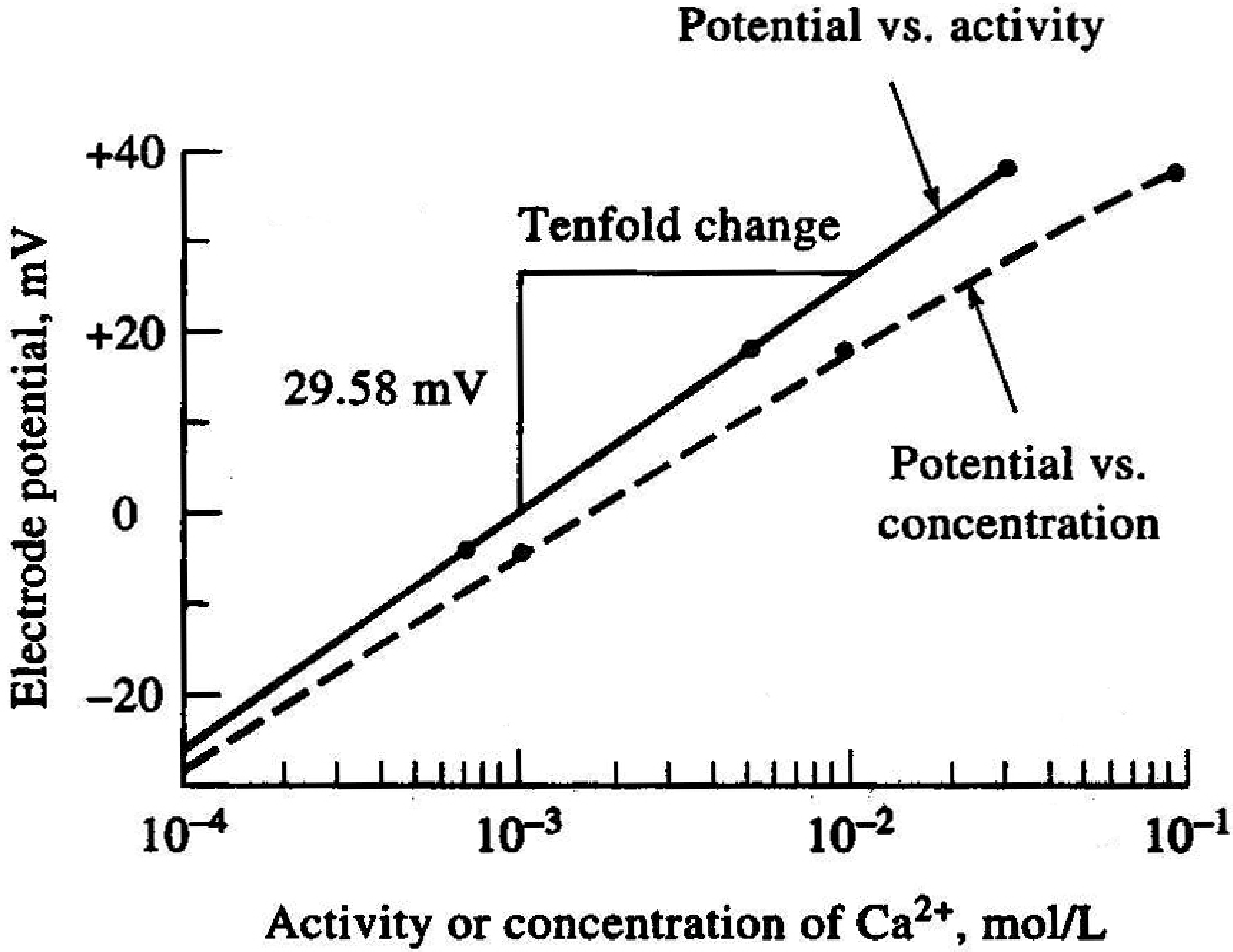
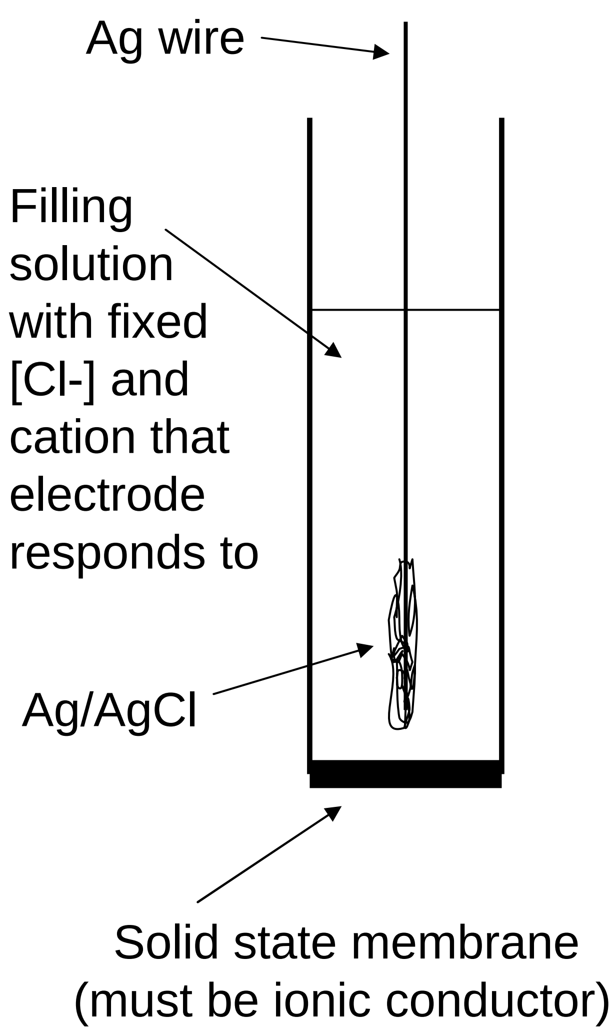


Table of liquid membrane electrodes

Analyte Ion	Concentration Range, M	Interferences
Ca^{2+}	10^{0} to 5×10^{-7}	10^{-5} Pb^{2+}; 4×10^{-3} Hg^{2+}, H^{+}, 6×10^{-3} Sr^{2+}; 2×10^{-2} Fe^{2+}; 4×10^{-2} Cu^{2+}; 5×10^{-2} Ni^{2+}; 0.2 NH_3; 0.2 Na^{+}; 0.3 $Tris^{+}$; 0.3 Li^{+}; 0.4 K^{+}; 0.7 Ba^{2+}; 1.0 Zn^{2+}; 1.0 Mg^{2+}
BF_4^-	10^{0} to 7×10^{-6}	5×10^{-7} ClO_4^-; 5×10^{-6} I^-; 5×10^{-5} ClO_3^-; 5×10^{-4} CN^-; 10^{-3} Br^-; 10^{-3} NO_2^-; 5×10^{-3} NO_3^-; 3×10^{-3} HCO_3^-; 5×10^{-2} Cl^-; 8×10^{-2} $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}; 0.2 OAc^-; 0.6 F^-; 1.0 SO_4^{2-}
NO_3^-	10^{0} to 7×10^{-6}	10^{-7} ClO_4^-; 5×10^{-6} I^-; 5×10^{-5} ClO_3^-; 10^{-4} CN^-; 7×10^{-4} Br^-; 10^{-3} HS^-; 10^{-2} HCO_3^-; 2×10^{-2} CO_3^{2-}; 3×10^{-2} Cl^-; 5×10^{-2} $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}; 0.2 OAc^-; 0.6 F^-; 1.0 SO_4^{2-}
ClO_4^-	10^{0} to 7×10^{-6}	2×10^{-3} I^-; 2×10^{-2} ClO_3^-; 4×10^{-2} CN^-, Br^-; 5×10^{-2} NO_2^-, NO_3^-; 2 HCO_3^-, CO_3^{2-}, Cl^-, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, OAc^-, F^-, SO_4^{2-}
K^+	10^{0} to 10^{-6}	3×10^{-4} Cs^+; 6×10^{-3} NH_4^+, Tl^+; 10^{-2} H^+; 1.0 Ag^+, $Tris^+$; 2.0 Li^+, Na^+
Water Hardness (Ca^{2+} + Mg^{2+})	10^{-3} to 6×10^{-6}	3×10^{-5} Cu^{2+}, Zn^{2+}; 10^{-4} Ni^{2+}; 4×10^{-4} Sr^{2+}; 6×10^{-5} Fe^{2+}; 6×10^{-4} Ba^{2+}; 3×10^{-2} Na^+; 0.1 K^+

Solid State Membrane Electrodes



Solid State Membrane Chemistry	
Membrane	Ion Determined
LaF_3	F^-, La^{3+}
AgCl	Ag^+, Cl^-
AgBr	Ag^+, Br^-
AgI	Ag^+, I^-
Ag_2S	Ag^+, S^{2-}
Ag_2S + CuS	Cu^{2+}
Ag_2S + CdS	Cd^{2+}
Ag_2S + PbS	Pb^{2+}

Solid State Membrane Electrodes

- Detection limits depend on solubility of the solid state membrane
- K_{sp} for AgCl = approx. 10^{-10}
- Therefore solubility is 10^{-5} M or membrane starts to produce ions of interest in solution
- Mixed crystals improve this somewhat but it is still a limitation
- Interferences or poisoning by high affinity ions
- Can polish electrodes to remove fouling
- Selectivity coefficient = electrode response ratio

Commercially Available Solid State Ion Selective Electrodes (ISEs)

Analyte Ion	Concentration Range, M	Interferences
Br^-	10^0 to 5×10^{-6}	mr: 8×10^{-5} CN^-; 2×10^{-4} I^-; 2 NH_3; 400 Cl^-; 3×10^4 OH^-. mba: S^{2-}
Cd^{2+}	10^{-1} to 10^{-7}	Fe^{2+} + Pb^{2+} may interfere. mba: Hg^{2+}, Ag^+, Cu^{2+}
Cl^-	10^0 to 5×10^{-5}	mr: 2×10^{-7} CN^-; 5×10^{-7} I^-; 3×10^{-3} Br^-; 10^{-2} $S_2O_3^{2-}$; 0.12 NH_3; 80 OH^-. mba: S^{2-}
Cu^{2+}	10^{-1} to 10^{-8}	high levels Fe^{2+}, Cd^{2+}, Br^-, Cl^-. mba: Hg^{2+}, Ag^+, Cu^+
CN^-	10^{-2} to 10^{-6}	mr: 10^{-1} I^-; 5×10^3 Br^-; 10^6 Cl^-. mba: S^{2-}
F^-	sat'd to 10^{-6}	0.1 M OH^- gives <10% interference when $[F^-] = 10^{-3}$ M
I^-	10^0 to 5×10^{-8}	mr: 0.4 CN^-; 5×10^3 Br^-; 10^5 $S_2O_3^{2-}$; 10^6 Cl^-
Pb^{2+}	10^{-1} to 10^{-6}	mba: Hg^{2+}, Ag^+, Cu^{2+}
Ag^+/S^{2-}	10^0 to 10^{-7} Ag^+ 10^0 to 10^{-7} S^{2-}	Hg^{2+} must be less than 10^{-7} M
SCN^-	10^0 to 5×10^{-6}	mr: 10^{-6} I^-; 3×10^{-3} Br^-; 7×10^{-3} CN^-; 0.13 $S_2O_3^{2-}$; 20 Cl^-; 100 OH^-. mba: S^{2-}

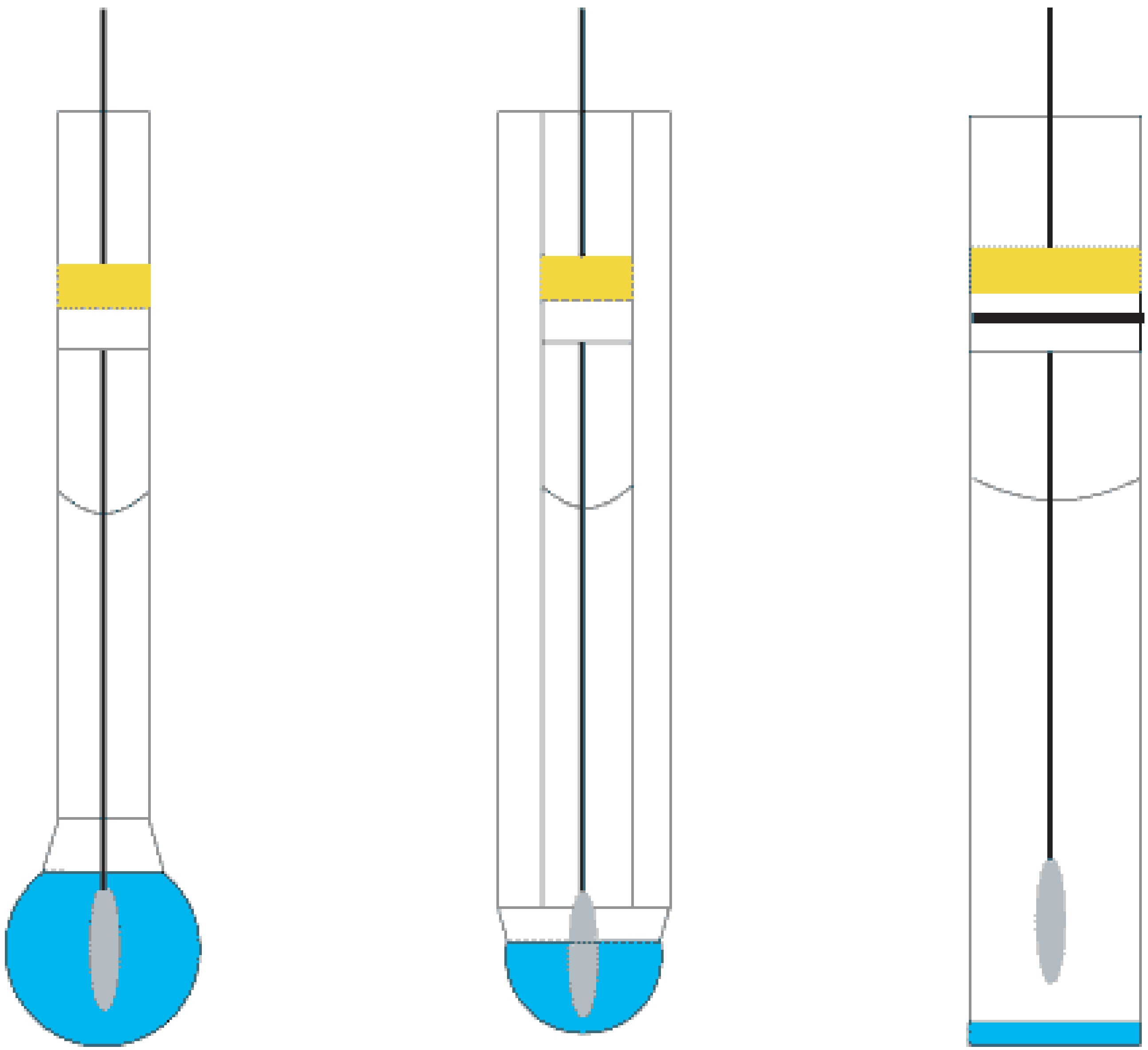
mr = maximum ratio of interferent to analyte
mba = must be absent

Permeable Membrane Electrodes
Gas Permeable Membrane Electrodes
Gas Sensing Electrodes

- Membrane that is permeable to a gas (e.g., NH_3) is the key component of electrode
- Membrane is part of a small chamber which encloses a filling solution with a pH electrode housed inside
- Filling solution has “fixed” $[NH_4^+]$ which responds to changes in $[NH_3]$ passing membrane according to

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

pH Electrode Bulb Styles



Gas Permeable Membrane Electrodes

- Electrode immersed in test solution
- NH_3 diffuses through membrane
- NH_3 in test solution equilibrates with NH_3 in filling solution

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$[OH^-] = \frac{K_b}{[NH_4^+]}[NH_3]$$

$$pH = 14 - pOH = pNH_3$$