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

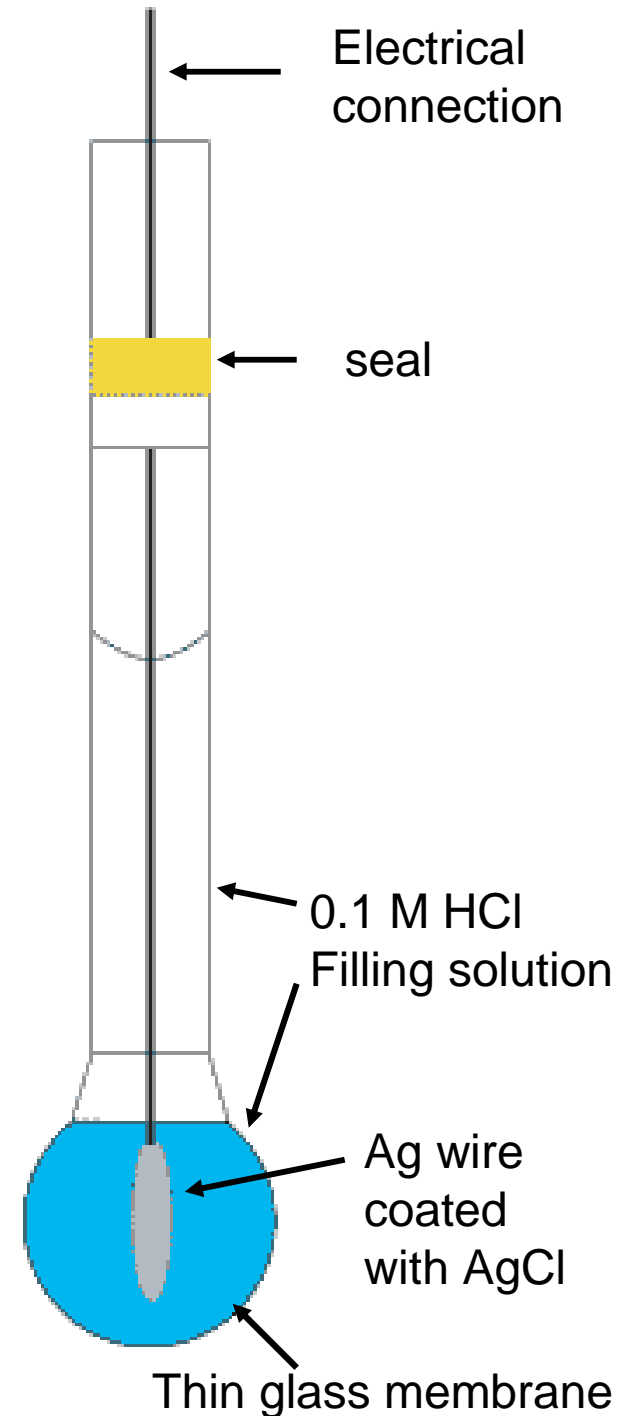 2)   Reference Electrode – chosen so that its potential is independent of solution composition.

Membrane Electrodes

- Several types – Glass membrane electrode

    - Solid State   "   "

    - Liquid Junction "   "

    - Permeable   "   "

- Most important is glass electrode for pH

thin glass membrane

$[H^+] = a_1$ $[H^+] = a_2$ potential develops
across membrane

solution 1   solution 2
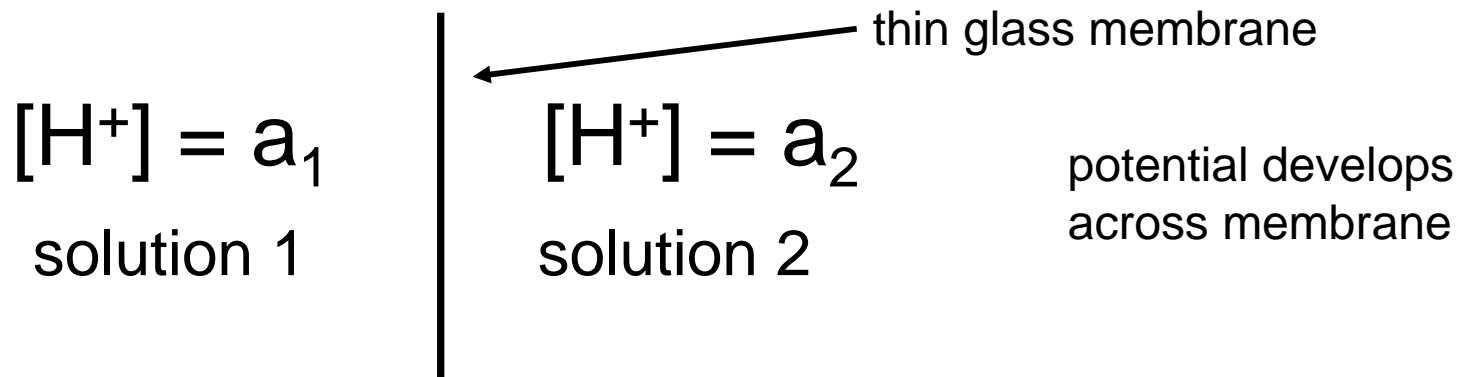
Glass pH Electrode

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

Electrical connection

seal

0.1 M HCl Filling solution

Ag wire coated with AgCl

Thin glass membrane

Errors in pH Measurement 1

- pH measurements are only as good as the buffers used to calibrate

  – Accuracy good to $\pm$0.01 units*

  – Precision may be good to $\pm$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
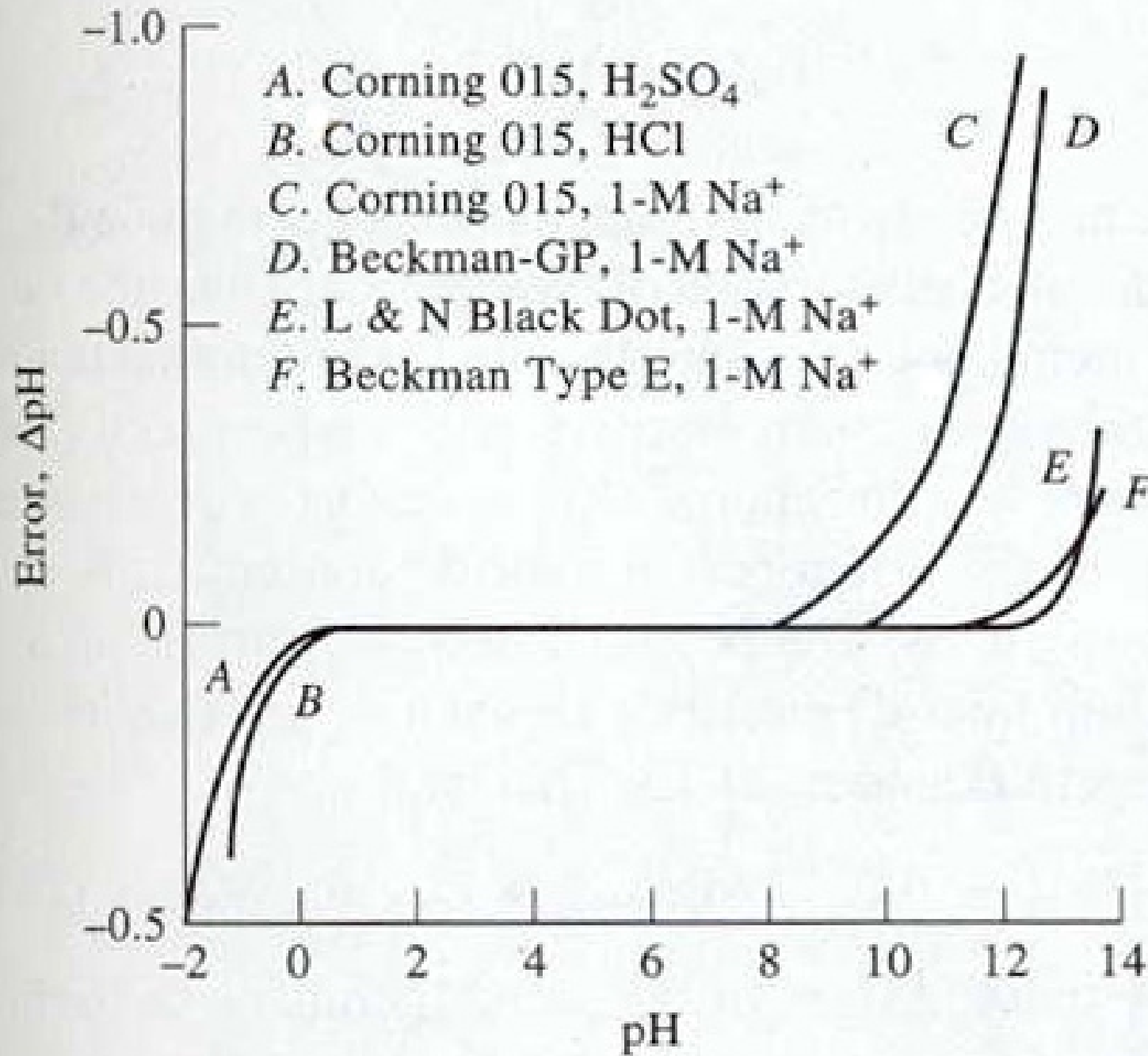
Errors in pH Measurement 2

- 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.

A. Corning 015, H_2SO_4
B. Corning 015, HCl
C. Corning 015, 1-M Na^+
D. Beckman-GP, 1-M Na^+
E. L & N Black Dot, 1-M Na^+
F. Beckman Type E, 1-M Na^+

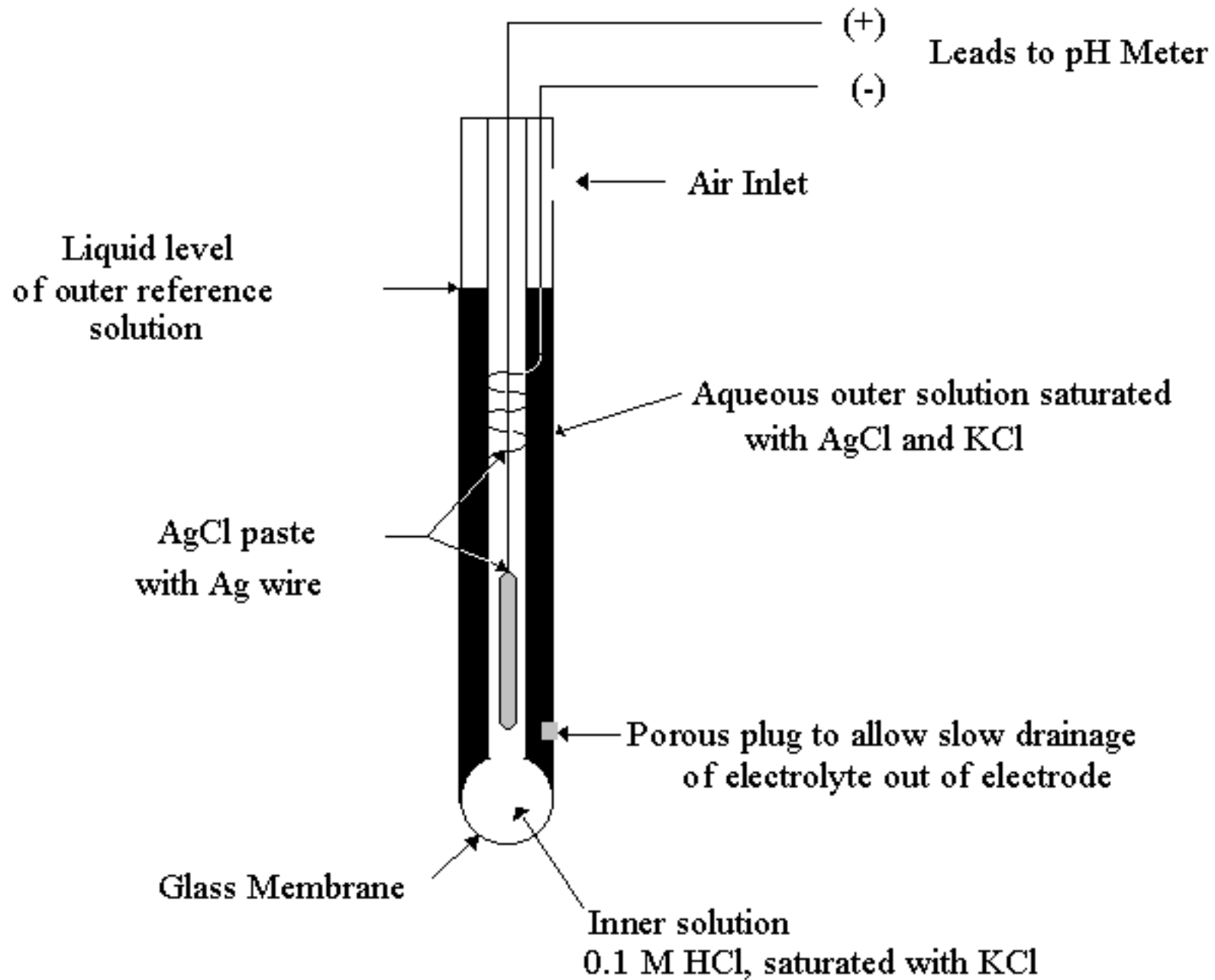Acid and Alkaline error of Some electrodes

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
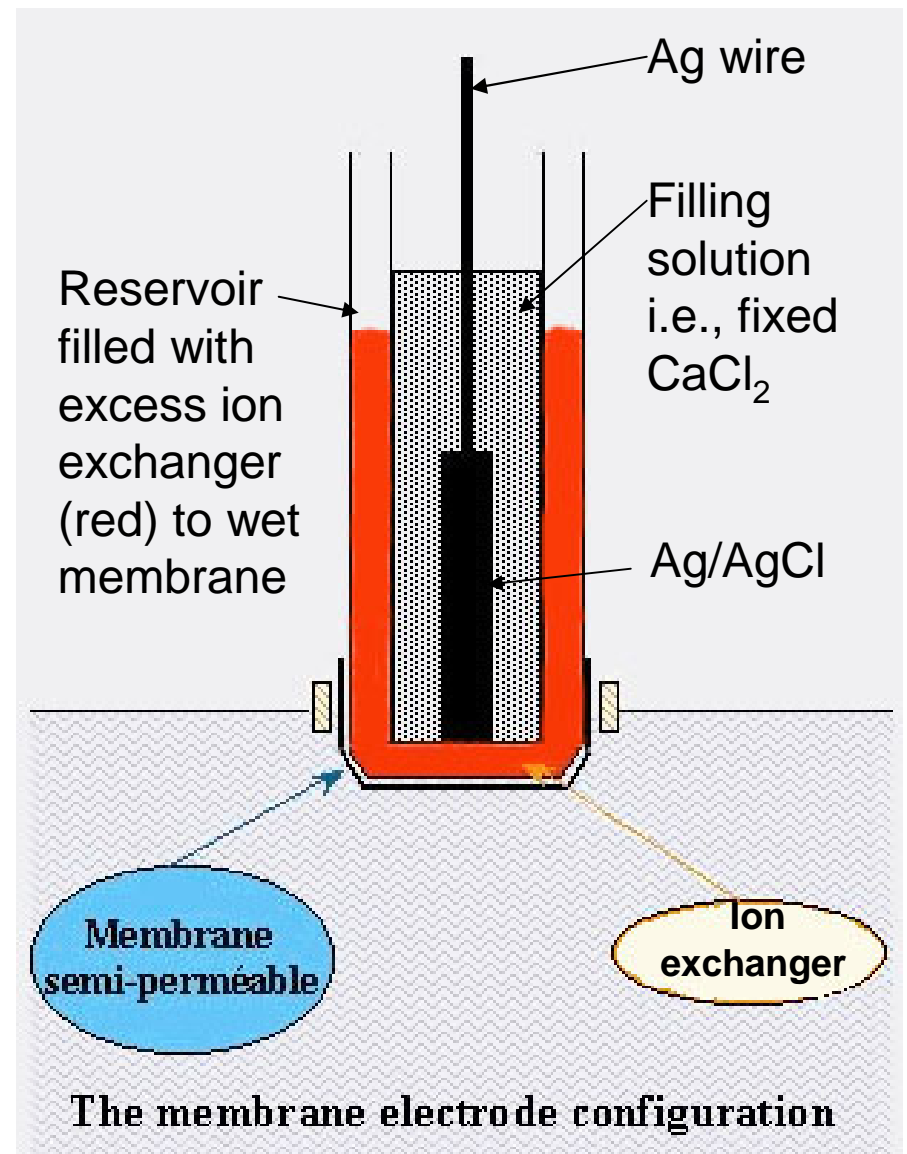
Glass Electrode Summary

- 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

(+)

(-)

Leads to pH Meter

Air Inlet

Liquid level
of outer reference
solution

Aqueous outer solution saturated
with AgCl and KCl

AgCl paste
with Ag wire

Porous plug to allow slow drainage
of electrolyte out of electrode

Glass Membrane

Inner solution
0.1 M HCl, saturated with KCl

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

Ag wire

Filling solution i.e., fixed $CaCl_2$

Reservoir filled with excess ion exchanger (red) to wet membrane

Ag/AgCl

Membrane semi-perméable

Ion exchanger

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 $\rightarrow$ 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

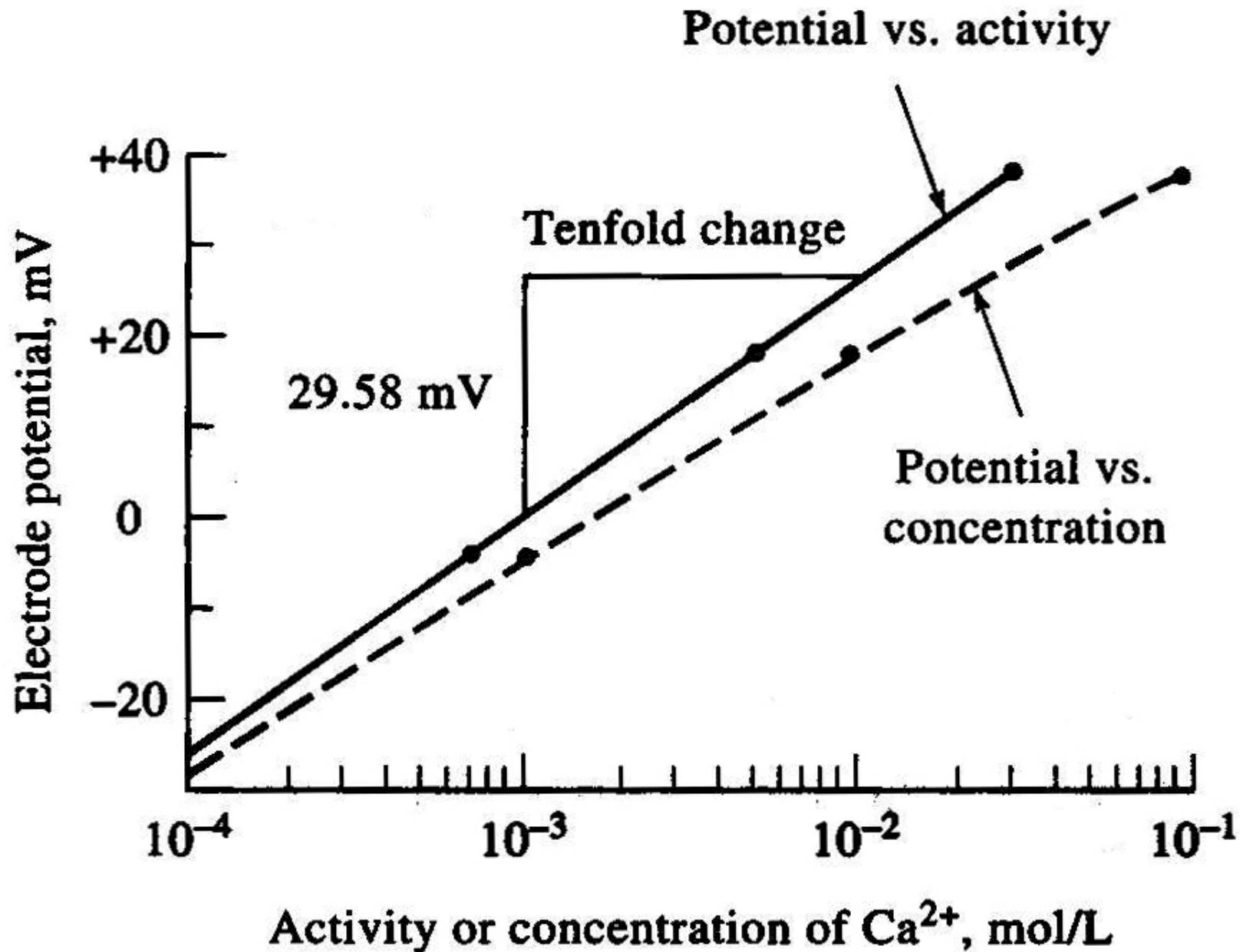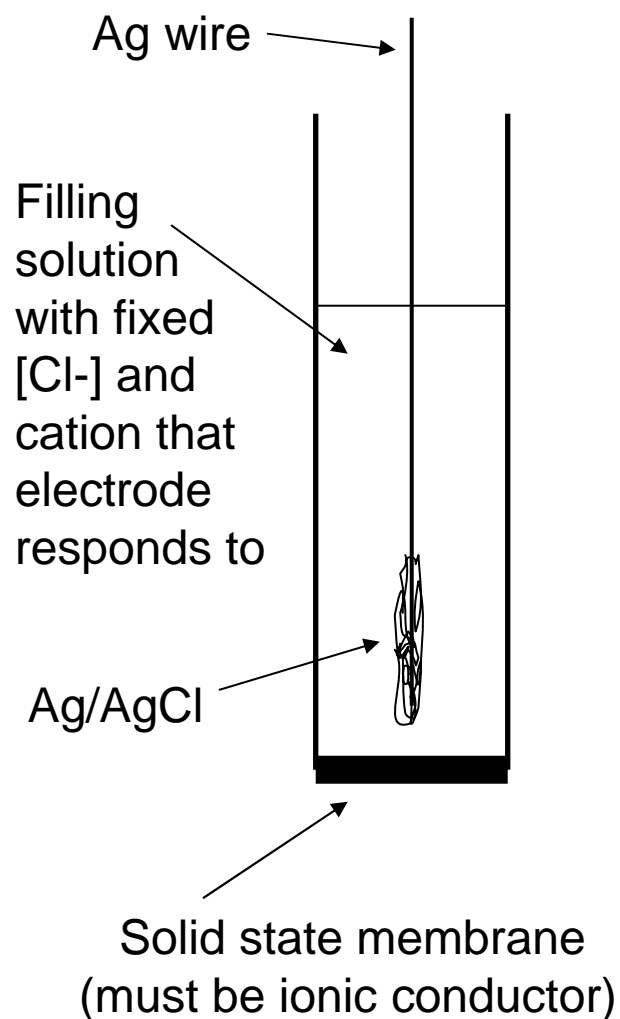# Response of calcium ion liquid membrane electrode

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

Ag wire

Filling solution with fixed [Cl-] and cation that electrode responds to

Ag/AgCl

Solid state membrane
(must be ionic conductor)

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
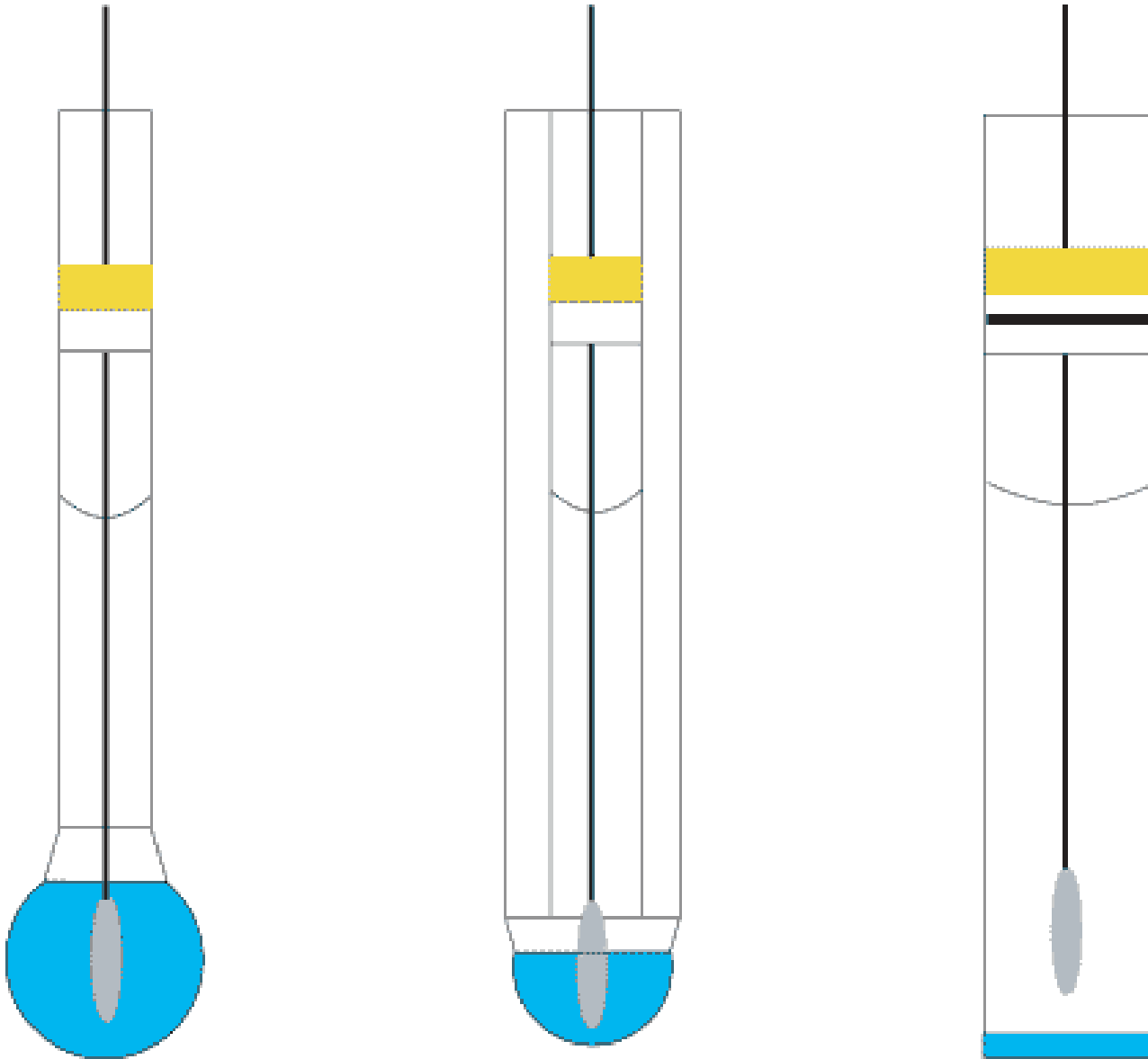
Permeable Membrane Electrodes
Gas Permeable Membrane Electrodes
Gas Sensing Electrodes

- 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

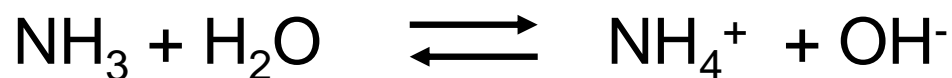$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
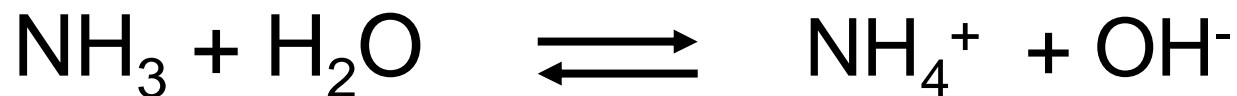
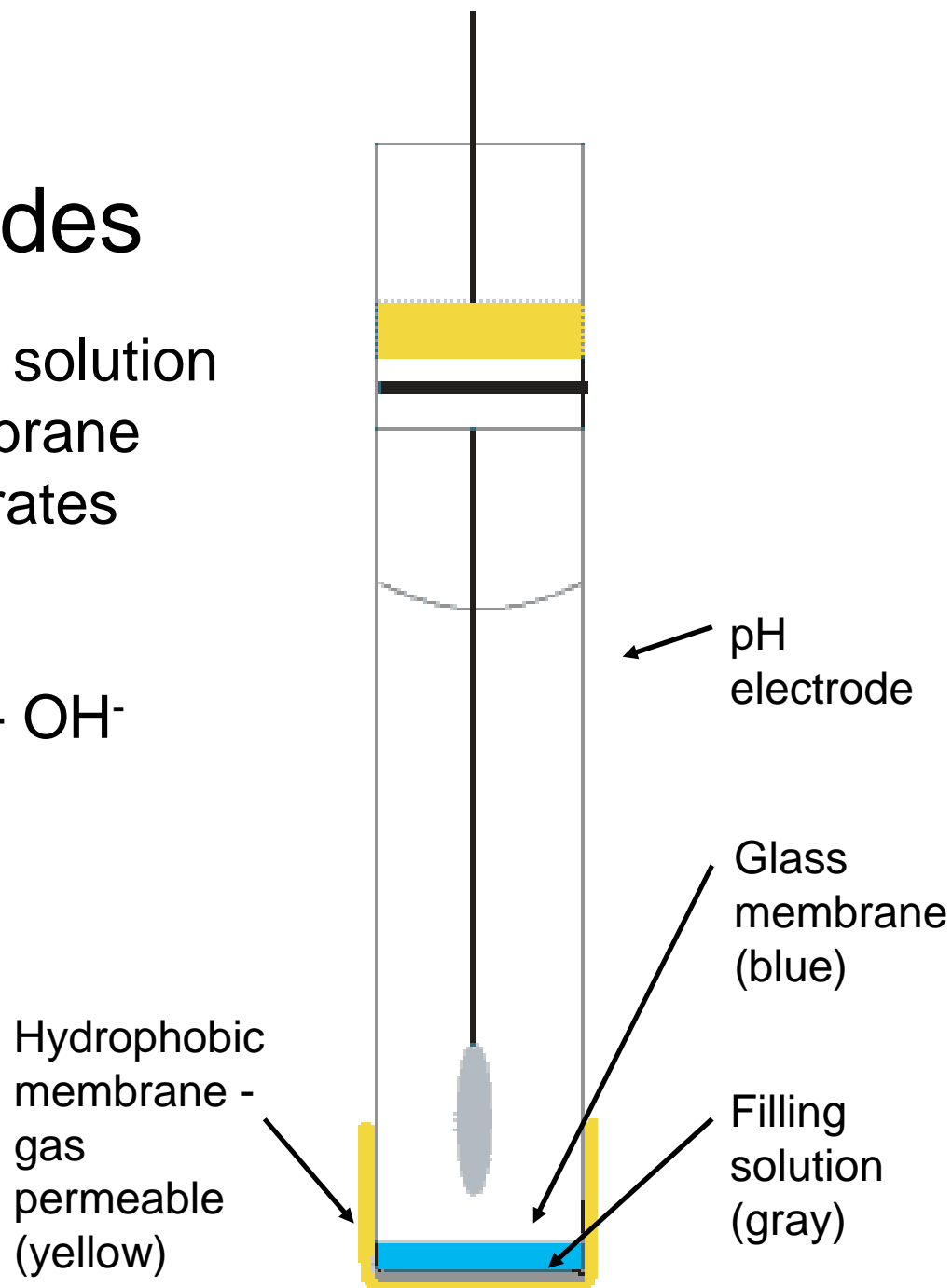# pH Electrode Bulb Styles

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

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

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

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

$$pH = 14 - pOH = pNH_3$$

pH electrode

Glass membrane (blue)

Filling solution (gray)

Hydrophobic membrane - gas permeable (yellow)

To meter
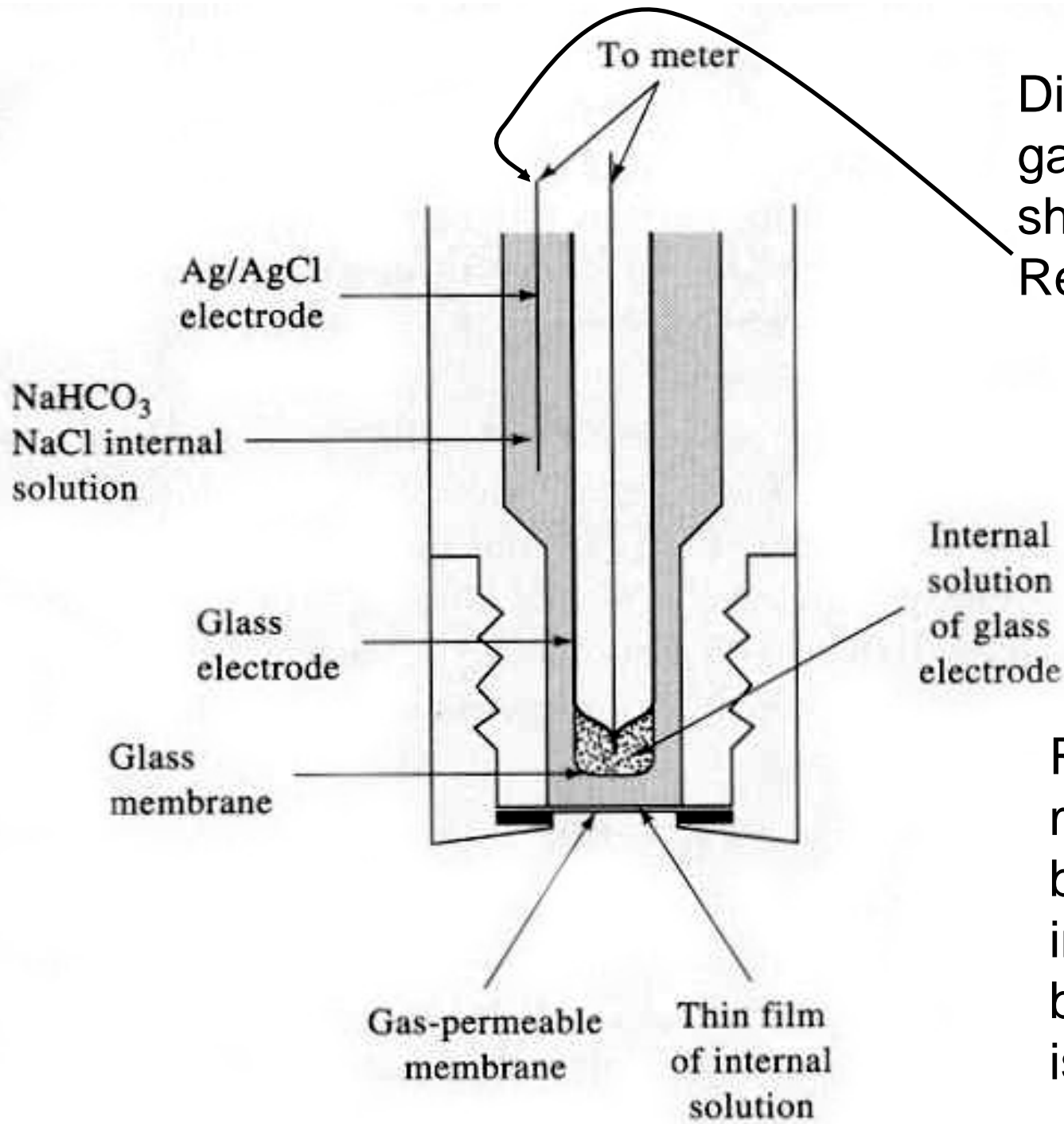
Diagram of CO_2 gas sensing probe showing internal Reference electrode

Ag/AgCl electrode

NaHCO$_3$ NaCl internal solution

Glass electrode

Glass membrane

Internal solution of glass electrode

Gas-permeable membrane

Thin film of internal solution

Reference electrode must be located behind membrane in the filling solution because membrane is hydrophobic

Commercial Gas Sensing Electrodes

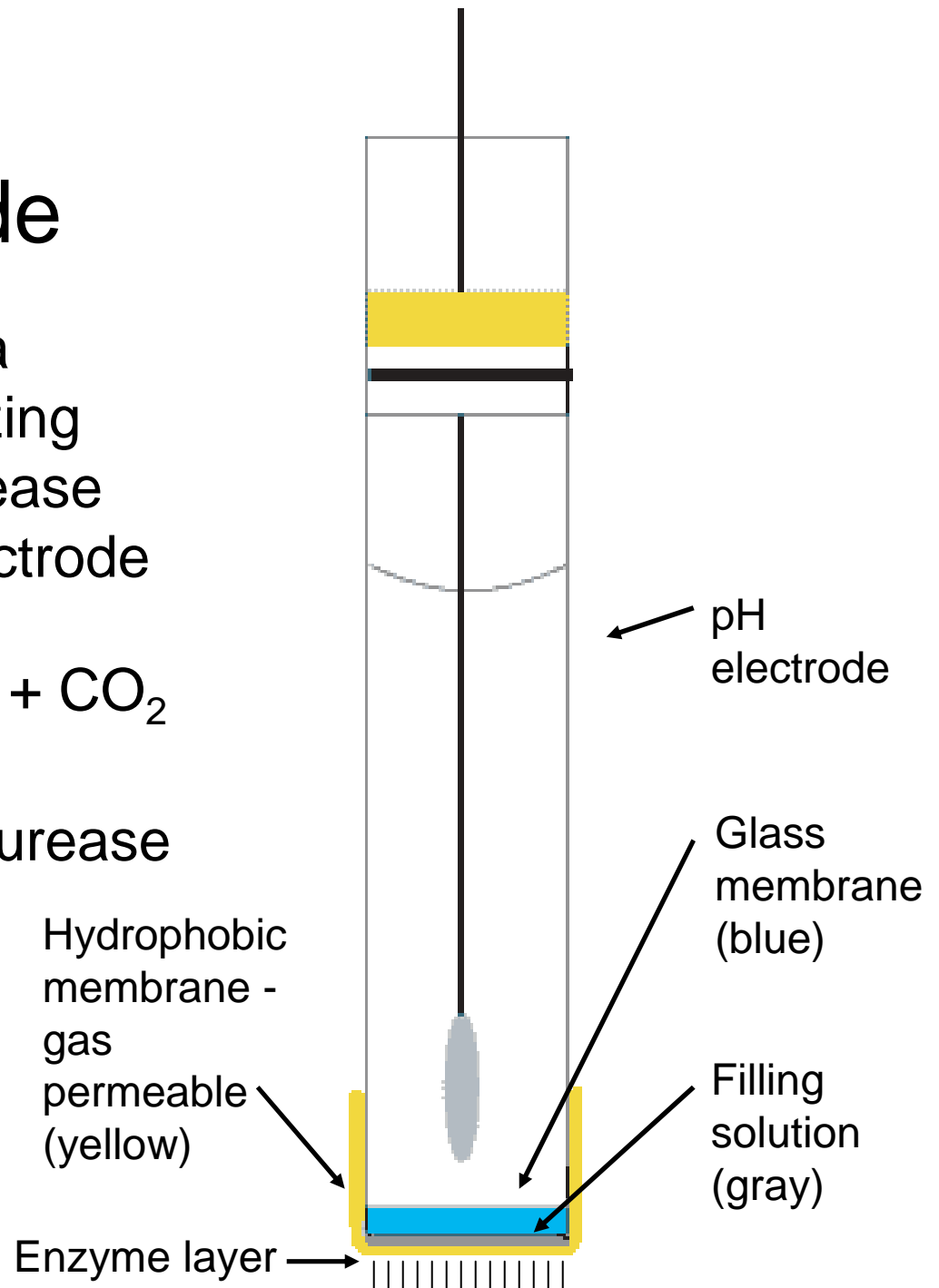| Gas	Equilibrium in Internal Solution	Sensing Electrode
NH_3	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	Glass, pH
CO_2	$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$	Glass, pH
HCN	$HCN \rightleftharpoons H^+ + CN^-$	Ag_2S, pCN
HF	$HF \rightleftharpoons H^+ + F^-$	LaF_3, pF
H_2S	$H_2S \rightleftharpoons 2H^+ + S^{2-}$	Ag_2S, pS
SO_2	$SO_2 + H_2O \rightleftharpoons HSO_3^- + H^+$	Glass, pH
NO_2	$2NO_2 + H_2O \rightleftharpoons NO_2^- + NO_3^- + 2H^+$	Immobilized ion exchange, pNO_3

Enzyme Electrode e.g., Urea Electrode

An electrode sensitive to urea can be prepared by immobilizing a thin layer of the enzyme urease on the surface of the NH_3 electrode

$$H_2N-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O \longrightarrow 2\ NH_3 + CO_2$$
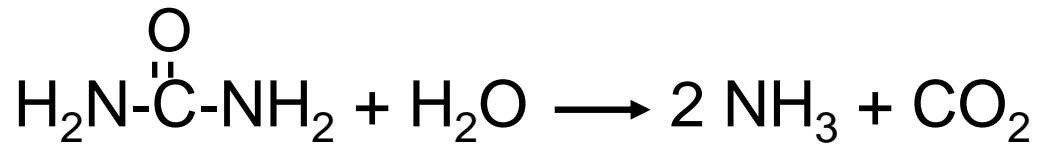
- Urea comes in contact with urease immobilized on the surface
- Urea is broken down to NH_3 & CO_2 in this enzyme layer
- NH_3 diffuses through membrane to give response

pH electrode

Glass membrane (blue)

Filling solution (gray)

Hydrophobic membrane - gas permeable (yellow)

Enzyme layer

Potentiometry - Conclusion

- Electrochemical (galvanic) cell with essentially no current flow

- Requires a solution that is conductive i.e., contains a "supporting electrolyte"

- Laboratory pH/millivolt meters should be capable of measuring $\pm$ 0.1 mV

- This corresponds to 0.4 x n % uncertainty

- Electrodes measure activity not concentration

- Measure "free" or uncomplexed ions not total

Voltammetry

- Methods based on an electrolytic cell
- Apply potential or current to electrochemical cell & concentrations change at electrode surface due to oxidation & reduction reactions
- Can have 2 or 3 electrodes
- Stirred or unstirred solution
- Measure current or voltage

In all electrochemical methods, the rate of oxidation & reduction depend on:

1) rate & means by which soluble species reach electrode surface (mass transport)

2) kinetics of the electron transfer process at electrode surface (electrode kinetics), which depend on:

   a) nature of the reaction

   b) nature of electrode surface

   c) temperature

(we don't have much control over #2)

Mass Transport or Mass Transfer

1) Migration – movement of a charged particle in a potential field – generally bad (important for conductance & electrophoresis)

In most cases migration is undesirable and can be eliminated by adding a 100 fold excess of an inert electrolyte (i.e., electrochemically inert – not oxidized or reduced) Inert electrolyte does the migrating, not the analyte

Mass Transport or Mass Transfer

2) Diffusion – movement due to a concentration gradient. If electrochemical reaction depletes (or produces) some species at the electrode surface, then a concentration gradient develops and the electroactive species will tend to diffuse from the bulk solution to the electrode (or from the electrode out into the bulk solution)