

CHEM.5140 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.

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

Nernst Equation

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

Where

- R = gas constant
- T = absolute temperature
- n = number of electrons in reaction
- F = Faraday's constant
- E = potential
- E° = standard potential
- [Red] = molar concentration of reduced form of species
- [Ox] = molar concentration of oxidized form of species

Reference Electrodes

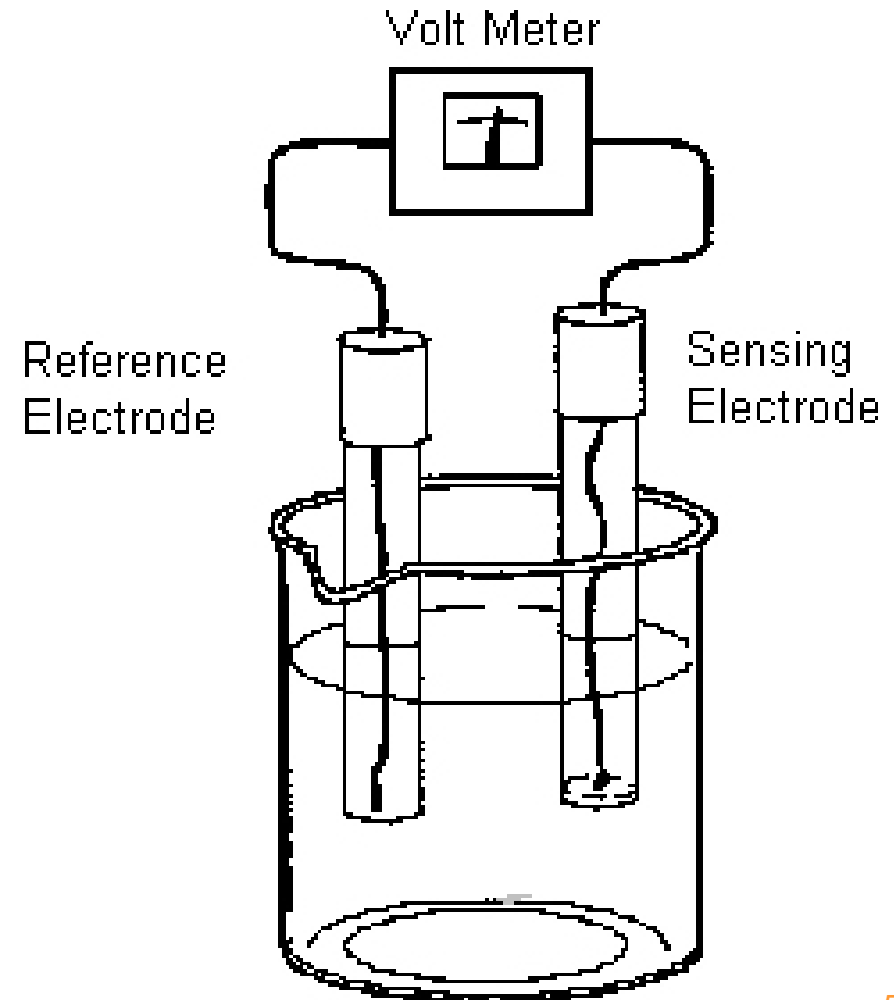
- Normal Hydrogen Electrode (NHE)
- $2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2 \quad E^\circ = 0.000 \text{ v}$

- Saturated Calomel Electrode (SCE)
- $\text{Hg}_2\text{Cl}_2 + 2 \text{e}^- \leftrightarrow 2 \text{Hg} + 2\text{Cl}^- \quad E^\circ = 0.268 \text{ v}$

- Silver/Silver Chloride Electrode (AgCl)
- $\text{AgCl} + \text{e}^- \leftrightarrow \text{Ag} + \text{Cl}^- \quad E^\circ = 0.222 \text{ v}$

Indicator Electrodes

- potential “**indicates**” **activity** of species
- terms Working Electrode or Sensing Electrode are sometimes used
- Coupled to reference and meter as usual



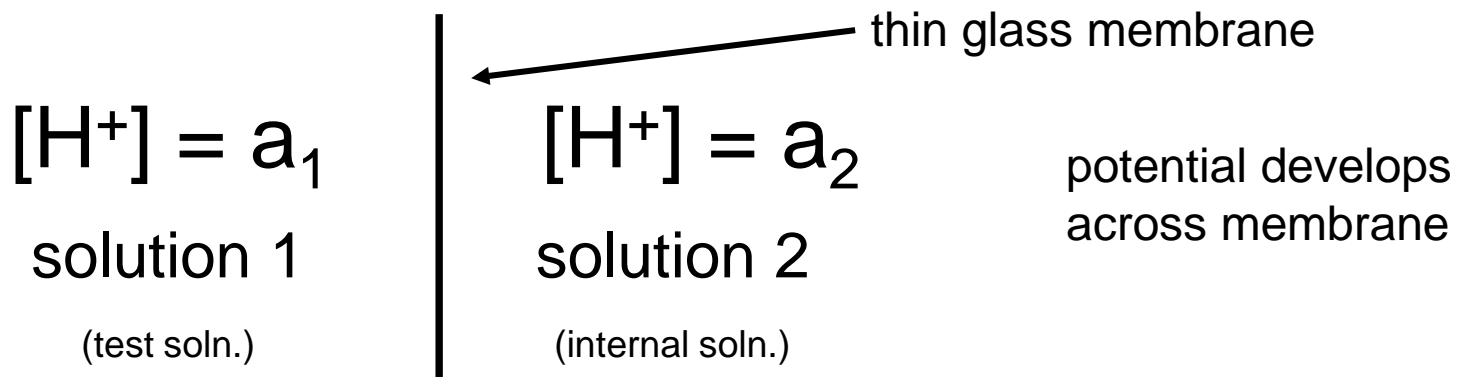
Indicator Electrodes

– Metallic Indicator Electrodes

- 1) Active metals (e.g., Ag, Cu, Hg, Pb, Cd)
can serve as indicators for their own ions
- 2) Active metal in contact with slightly soluble precipitate involving the metal cation –
responds to anion concentration
- 3) Inert Electrodes e.g., Pt or Au (noble metal)

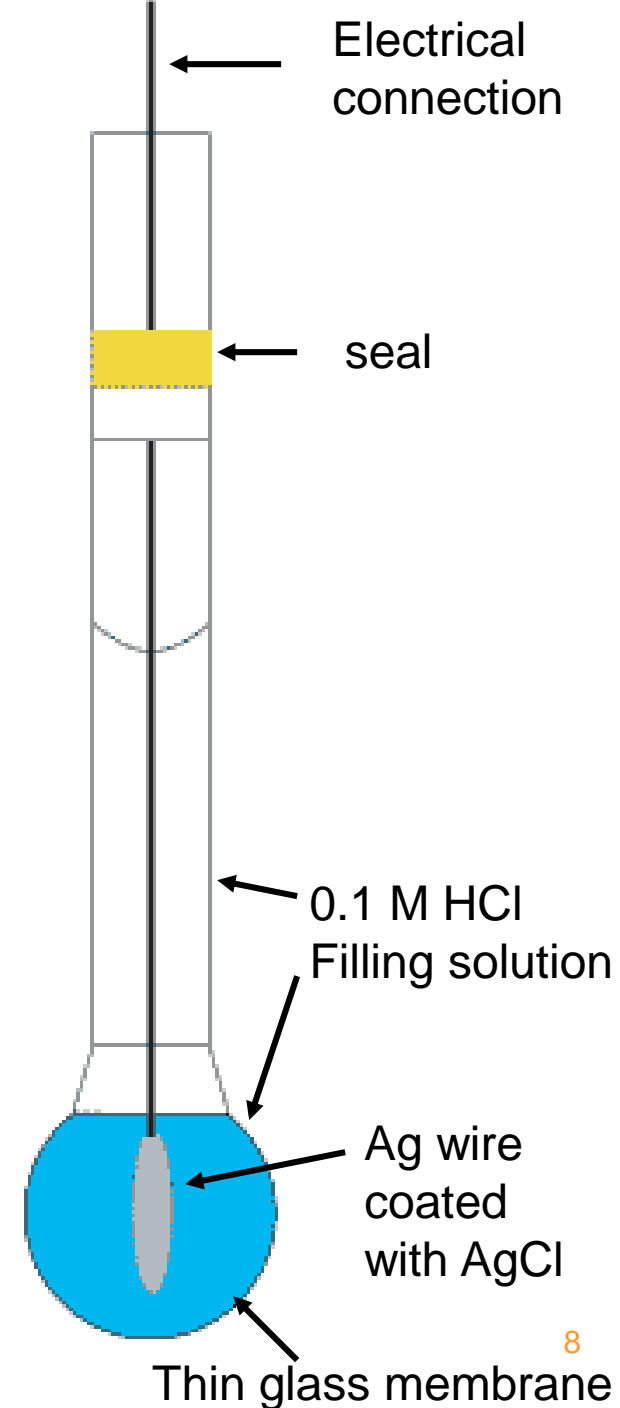
Membrane Electrodes

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



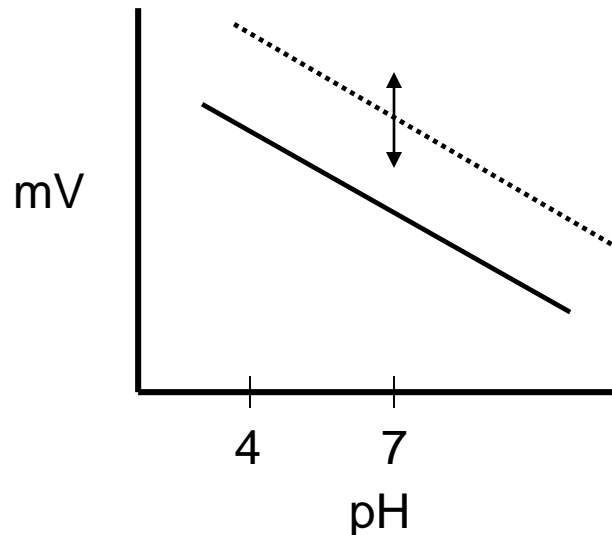
Glass pH Electrode

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



Proper pH Calibration

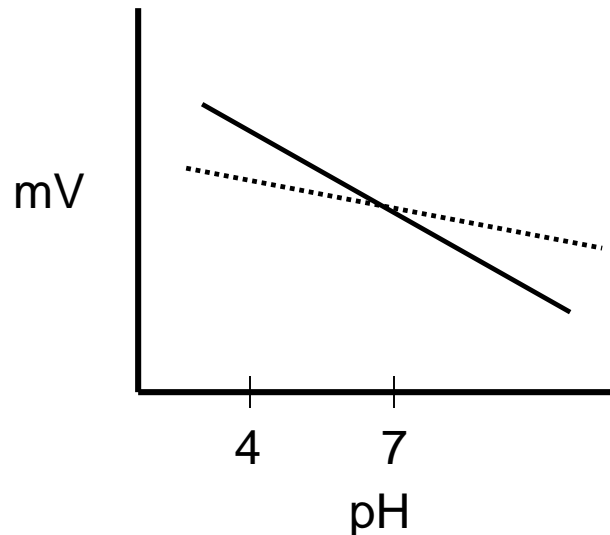
- $E = K' - 0.0591 \text{ pH}$
- Meter measures E vs pH – must calibrate both slope & intercept on meter with buffers
- Meter has two controls – calibrate & slope
- 1st use $\text{pH } 7.00$ buffer to adjust calibrate knob



Calibrate knob raises and lowers the line without changing slope

Proper pH Calibration (cont.)

- 2nd 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

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

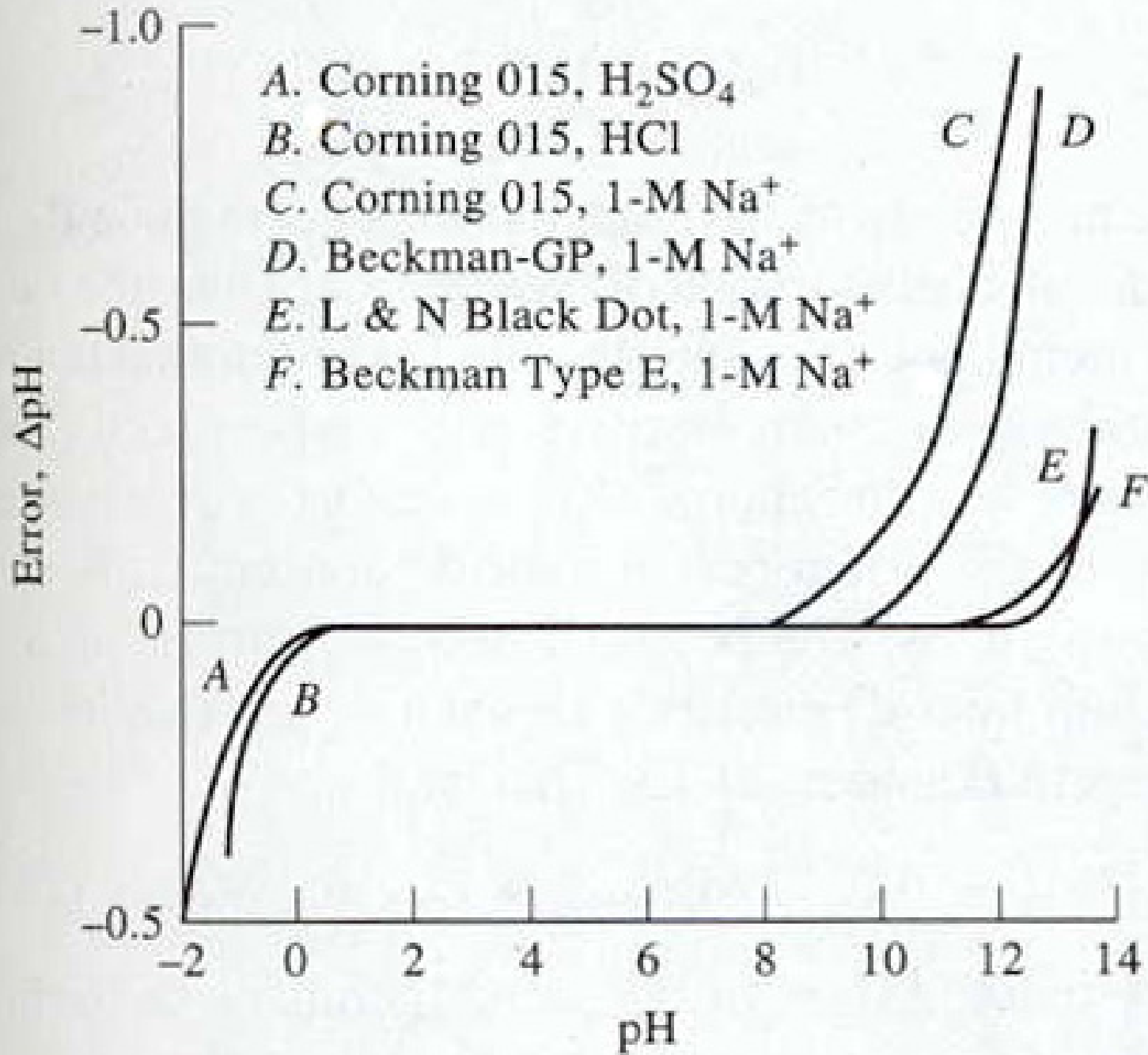
- Asymmetry potential is another non-ideal potential that arises possibly from strain in the glass. When both internal & external H^+ solutions are the same activity, potential should be 0 but it's not

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

- 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, H₂SO₄
- 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

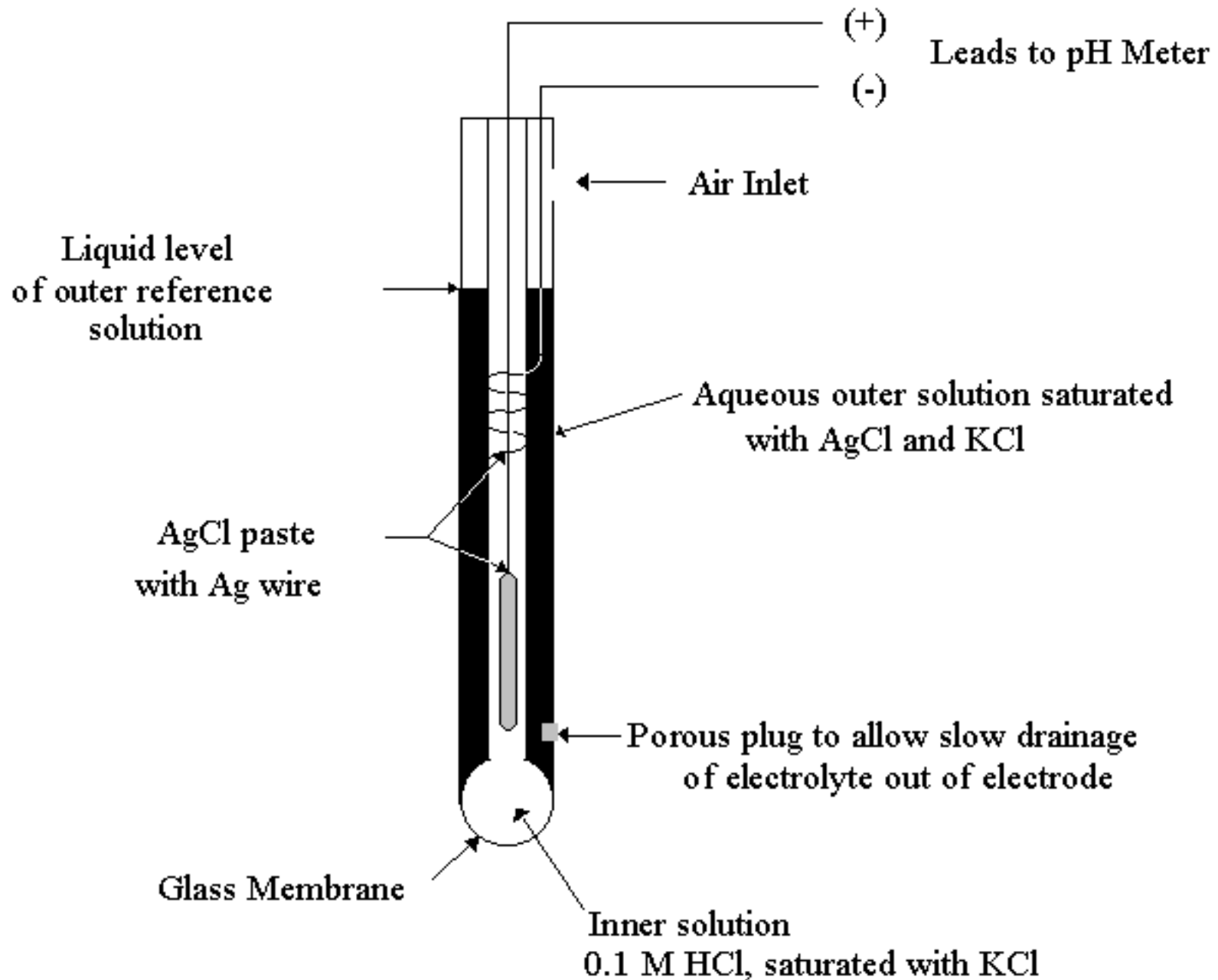
Errors in pH Measurement 4

- 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

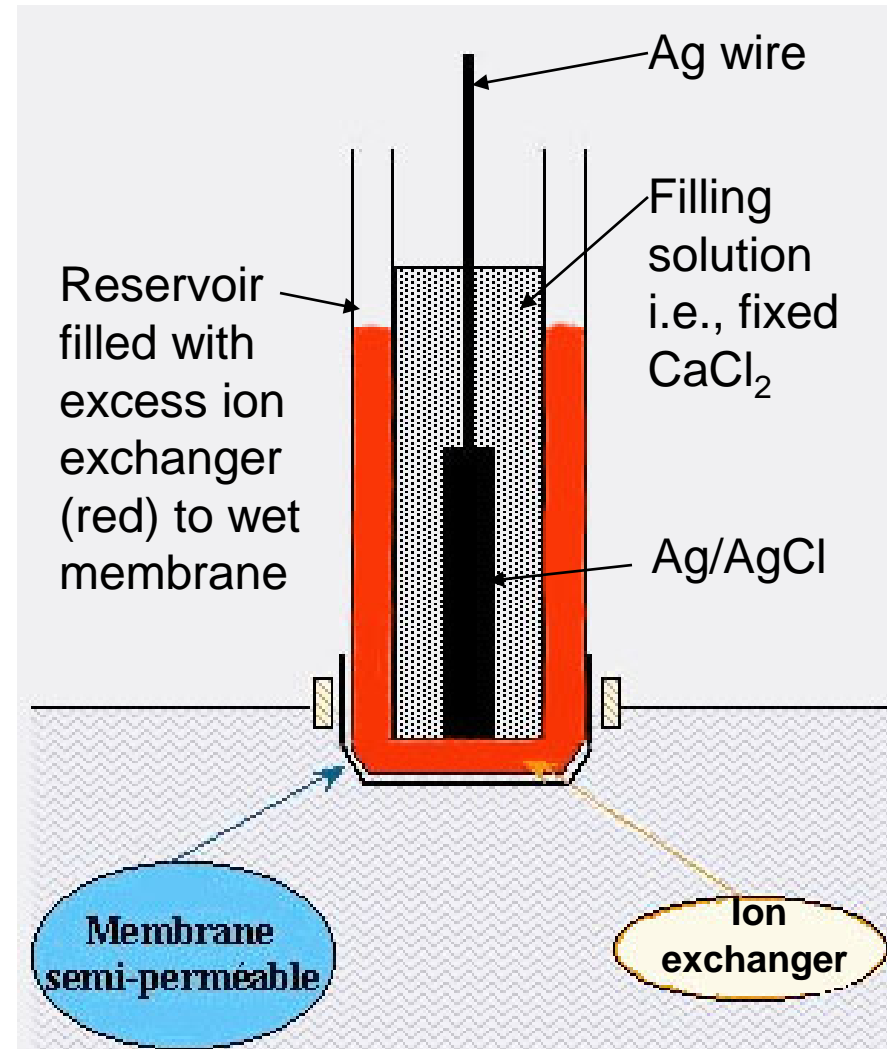
- Glass membrane electrodes are very good indicator electrodes in potentiometry
- Must exercise care in calibration and in maintaining integrity of glass membrane
- Some errors exist & are unavoidable
- Glass electrodes available for Na^+ , K^+ , NH_4^+ , Rb^+ , Cs^+ , Li^+ , Ag^+ (cations only) by varying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

Combination pH Electrode



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 ¹⁹

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

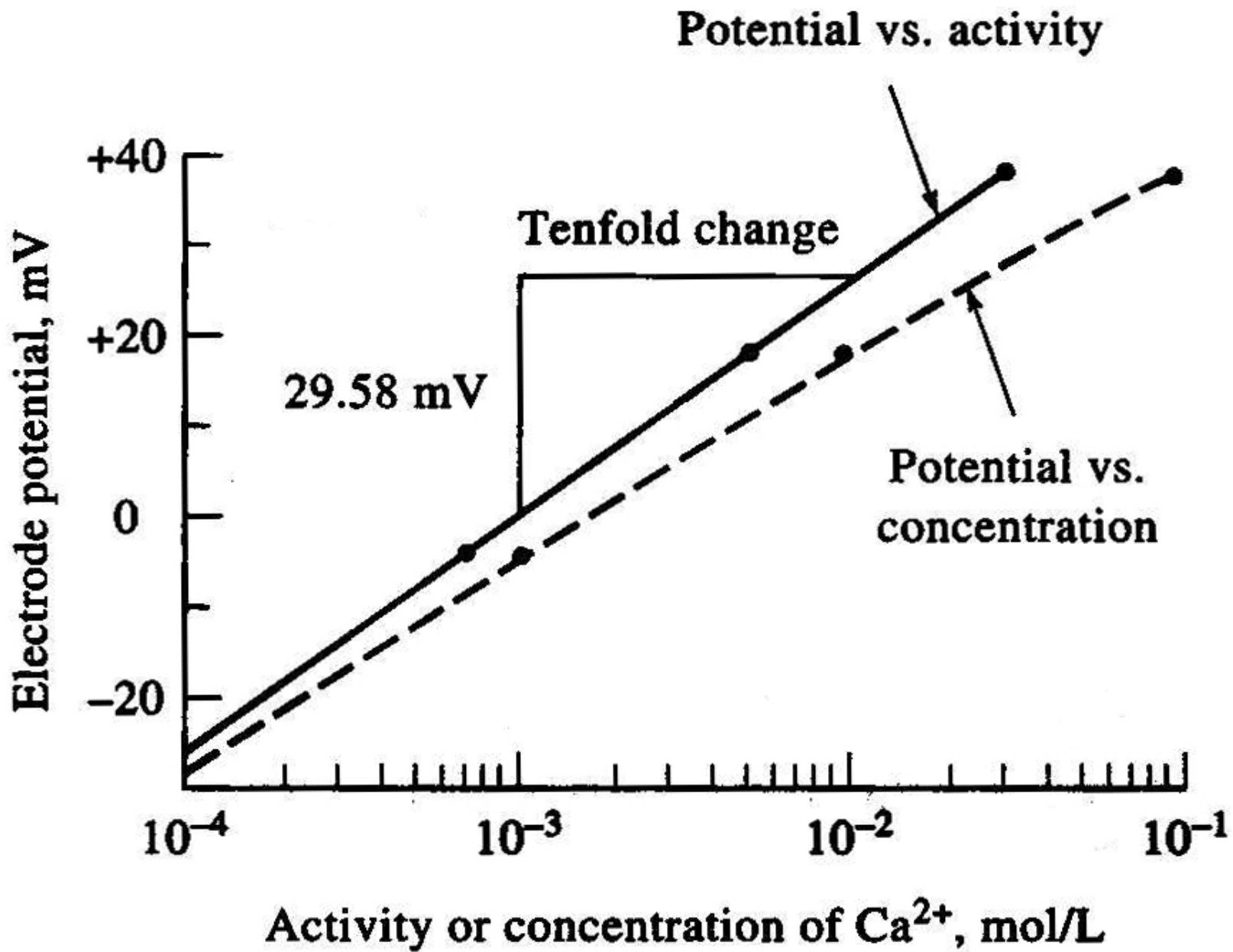
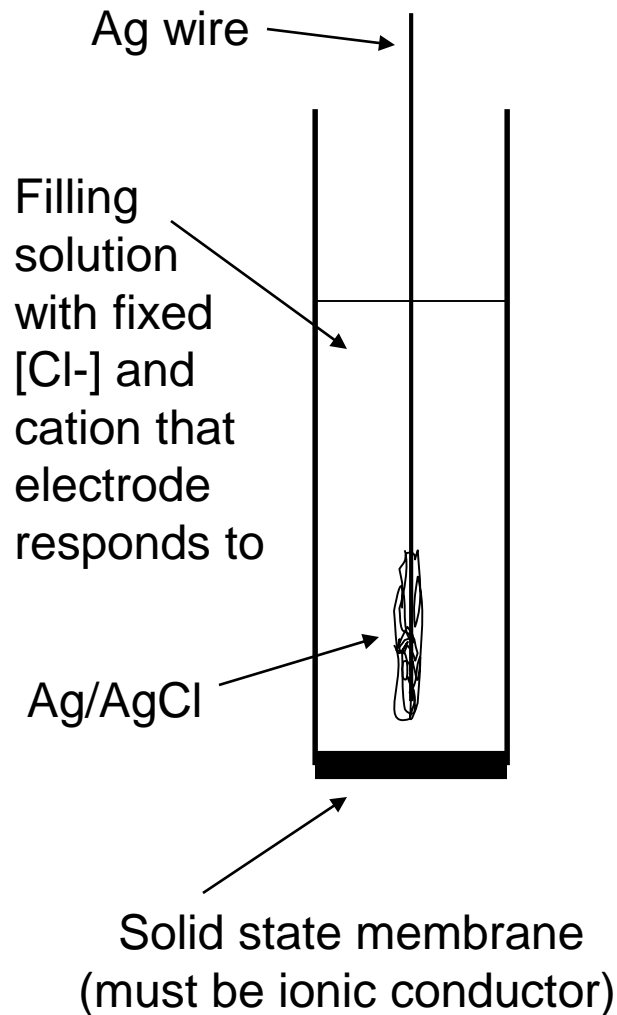


Table of liquid membrane electrodes

Analyte Ion	Concentration Range, M	Interferences
Ca^{2+}	10^0 to 5×10^{-7}	10^{-5}Pb^{2+} ; $4 \times 10^{-3} \text{Hg}^{2+}$, H^+ , $6 \times 10^{-3} \text{Sr}^{2+}$; $2 \times 10^{-2} \text{Fe}^{2+}$; $4 \times 10^{-2} \text{Cu}^{2+}$; $5 \times 10^{-2} \text{Ni}^{2+}$; 0.2NH_3 ; 0.2Na^+ ; 0.3Tris^+ ; 0.3Li^+ ; 0.4K^+ ; 0.7Ba^{2+} ; 1.0Zn^{2+} ; 1.0Mg^{2+}
BF_4^-	10^0 to 7×10^{-6}	$5 \times 10^{-7} \text{ClO}_4^-$; $5 \times 10^{-6} \text{I}^-$; $5 \times 10^{-5} \text{ClO}_3^-$; $5 \times 10^{-4} \text{CN}^-$; 10^{-3}Br^- ; 10^{-3}NO_2^- ; $5 \times 10^{-3} \text{NO}_3^-$; $3 \times 10^{-3} \text{HCO}_3^-$; $5 \times 10^{-2} \text{Cl}^-$; $8 \times 10^{-2} \text{H}_2\text{PO}_4^-$, HPO_4^{2-} , PO_4^{3-} ; 0.2OAc^- ; 0.6F^- ; 1.0SO_4^{2-}
NO_3^-	10^0 to 7×10^{-6}	10^{-7}ClO_4^- ; $5 \times 10^{-6} \text{I}^-$; $5 \times 10^{-5} \text{ClO}_3^-$; 10^{-4}CN^- ; $7 \times 10^{-4} \text{Br}^-$; 10^{-3}HS^- ; 10^{-2}HCO_3^- ; $2 \times 10^{-2} \text{CO}_3^{2-}$; $3 \times 10^{-2} \text{Cl}^-$; $5 \times 10^{-2} \text{H}_2\text{PO}_4^-$, HPO_4^{2-} , PO_4^{3-} ; 0.2OAc^- ; 0.6F^- ; 1.0SO_4^{2-}
ClO_4^-	10^0 to 7×10^{-6}	$2 \times 10^{-3} \text{I}^-$; $2 \times 10^{-2} \text{ClO}_3^-$; $4 \times 10^{-2} \text{CN}^-$, Br^- ; $5 \times 10^{-2} \text{NO}_2^-$, NO_3^- ; 2HCO_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}	$3 \times 10^{-4} \text{Cs}^+$; $6 \times 10^{-3} \text{NH}_4^+$, TI^+ ; 10^{-2}H^+ ; 1.0Ag^+ , Tris^+ ; 2.0Li^+ , Na^+
Water Hardness ($\text{Ca}^{2+} + \text{Mg}^{2+}$)	10^{-3} to 6×10^{-6}	$3 \times 10^{-5} \text{Cu}^{2+}$, Zn^{2+} ; 10^{-4}Ni^{2+} ; $4 \times 10^{-4} \text{Sr}^{2+}$; $6 \times 10^{-5} \text{Fe}^{2+}$; $6 \times 10^{-4} \text{Ba}^{2+}$; $3 \times 10^{-2} \text{Na}^+$; 0.1K^+

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 ₂ O 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 ₂ O 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 ₂ O ₃ ²⁻ ; 20 Cl ⁻ ; 100 OH ⁻ . mba: S ²⁻

mr = maximum ratio of interferent to analyte

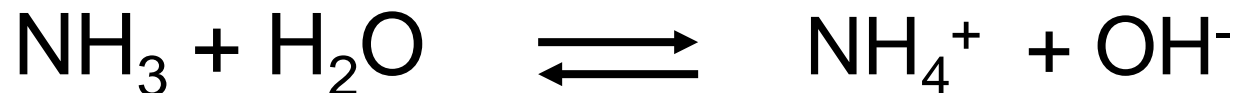
mba = must be absent

Permeable Membrane Electrodes

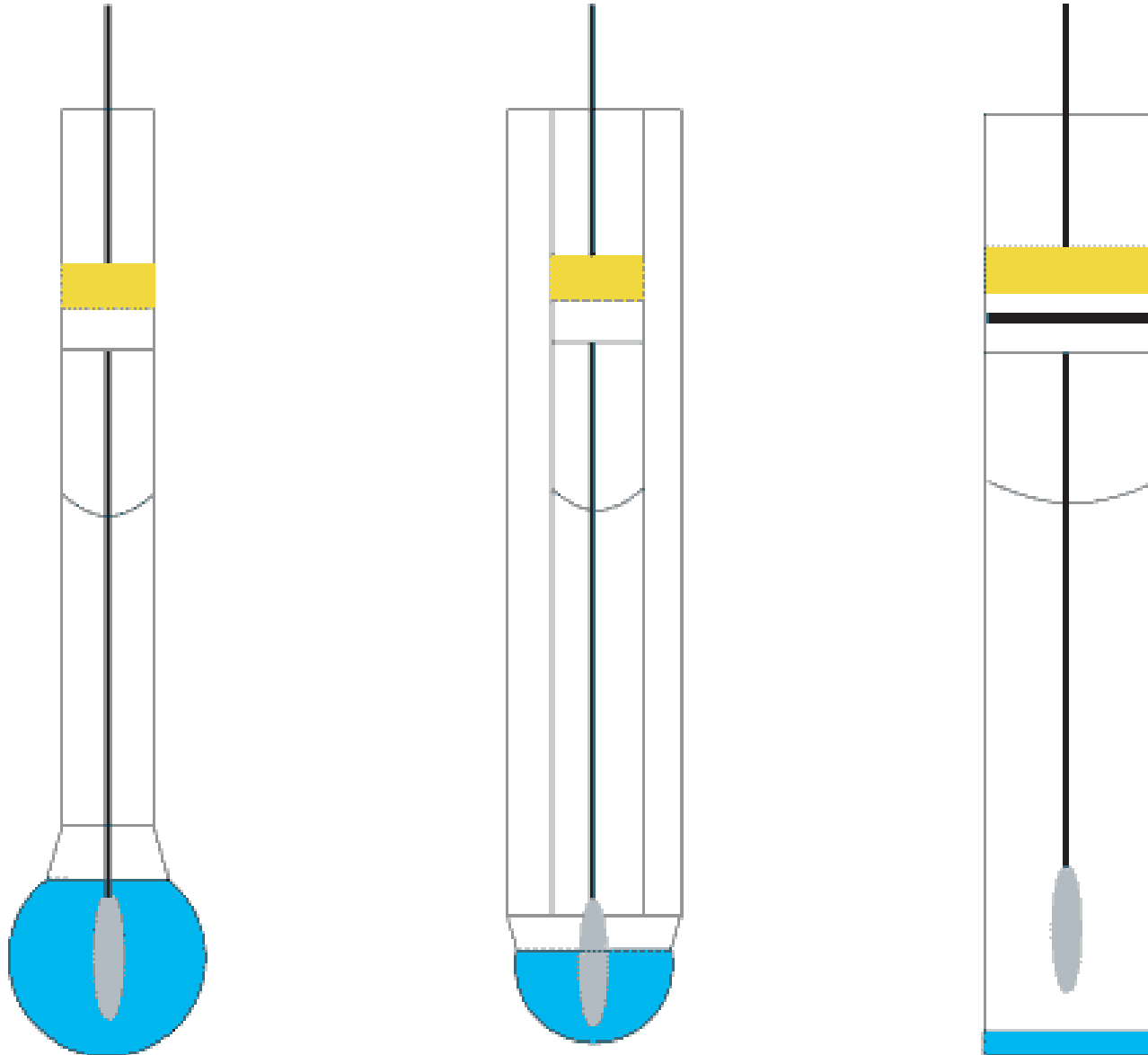
Gas Permeable Membrane Electrodes

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” $[\text{NH}_4^+]$ which responds to changes in $[\text{NH}_3]$ passing membrane according to

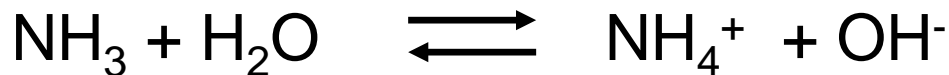


pH Electrode Bulb Styles



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



$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

$$[\text{OH}^-] = \frac{K_b}{[\text{NH}_4^+]} [\text{NH}_3]$$

$$\text{pH} = 14 - \text{pOH} = \text{pNH}_3$$

Hydrophobic membrane - gas permeable (yellow)

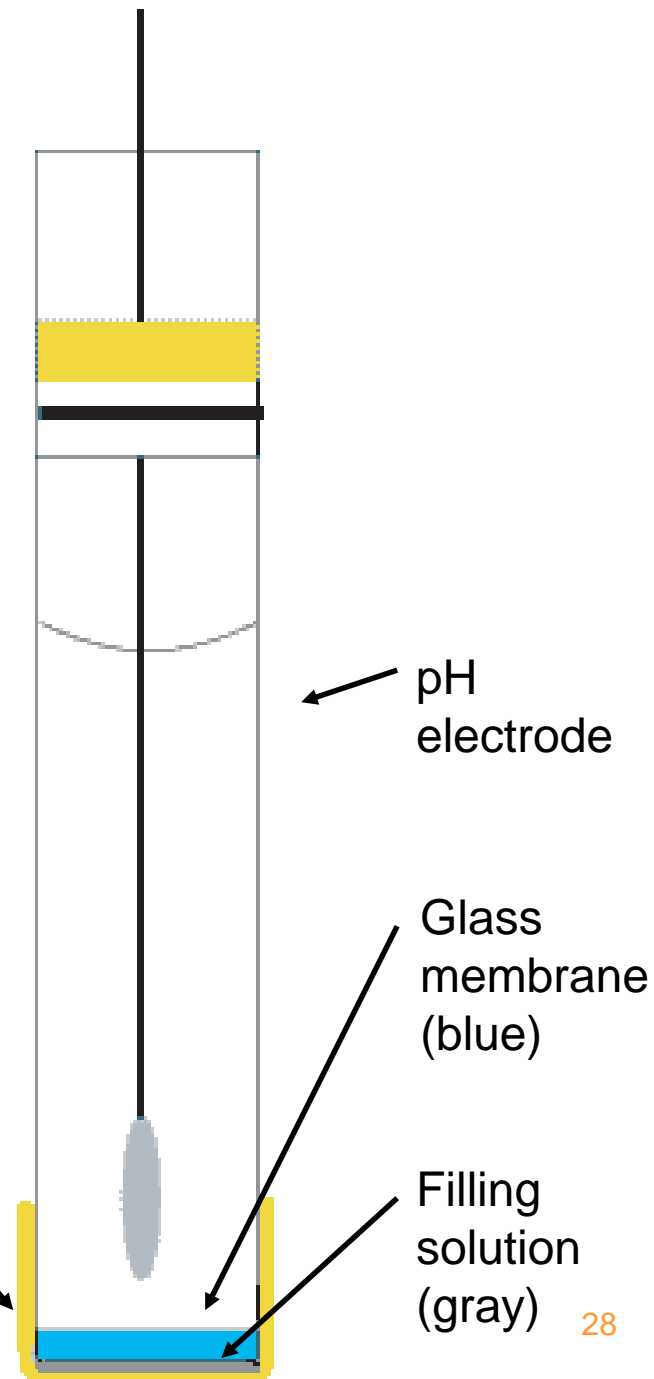
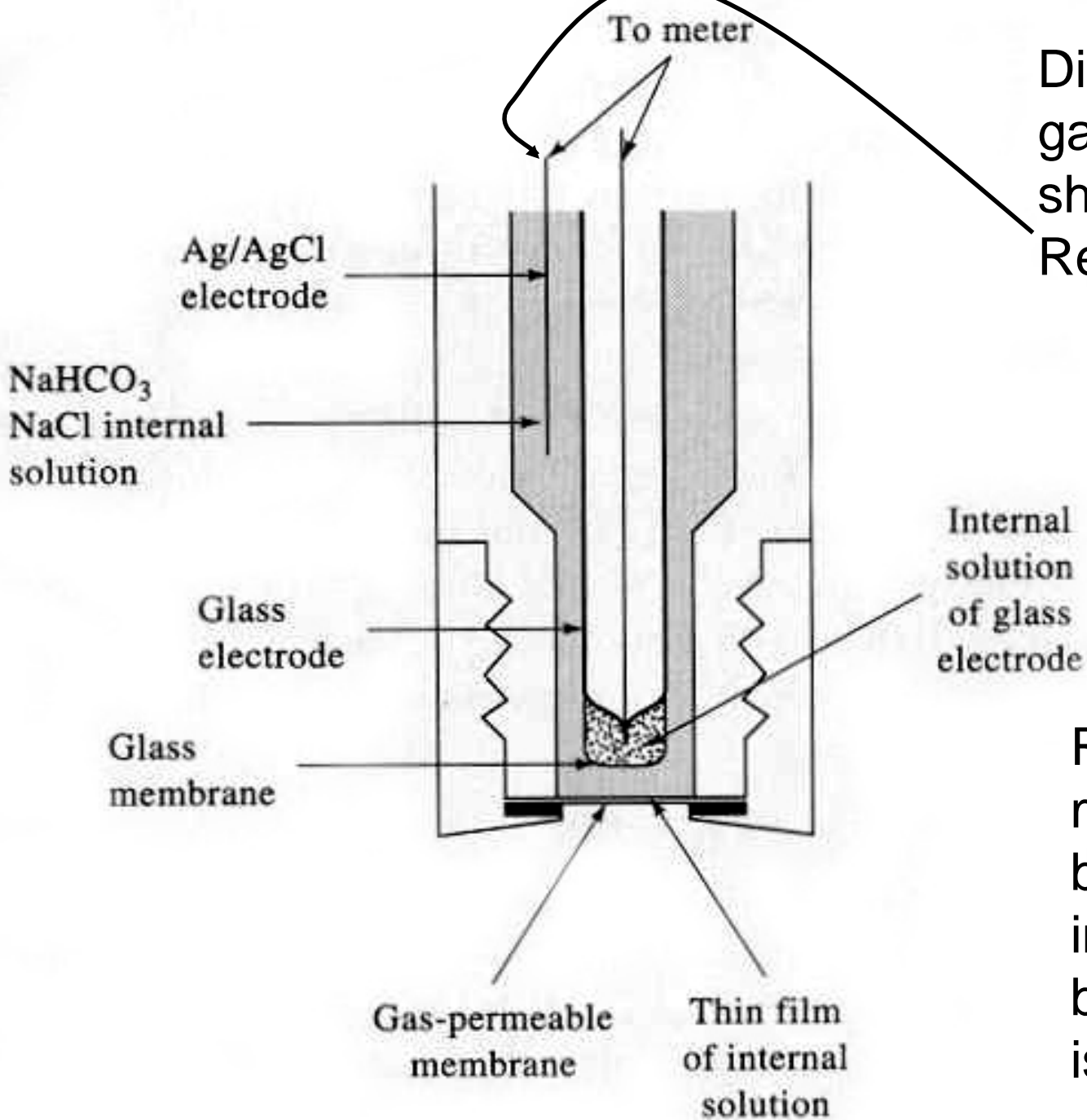


Diagram of CO₂ gas sensing probe showing internal Reference electrode



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

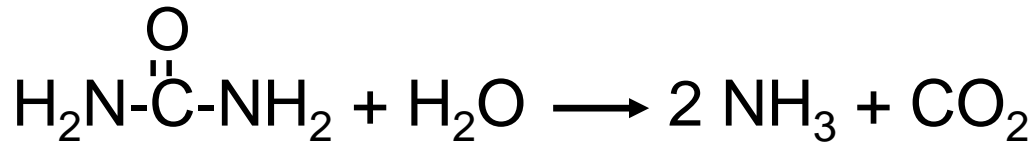
Commercial Gas Sensing Electrodes

Gas	Equilibrium in Internal Solution	Sensing Electrode
NH ₃	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	Glass, pH
CO ₂	$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	Glass, pH
HCN	$\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$	Ag ₂ S, pCN
HF	$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$	LaF ₃ , pF
H ₂ S	$\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$	Ag ₂ S, pS
SO ₂	$\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{H}^+$	Glass, pH
NO ₂	$2\text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2^- + \text{NO}_3^- + 2\text{H}^+$	Immobilized ion exchange, pNO ₃

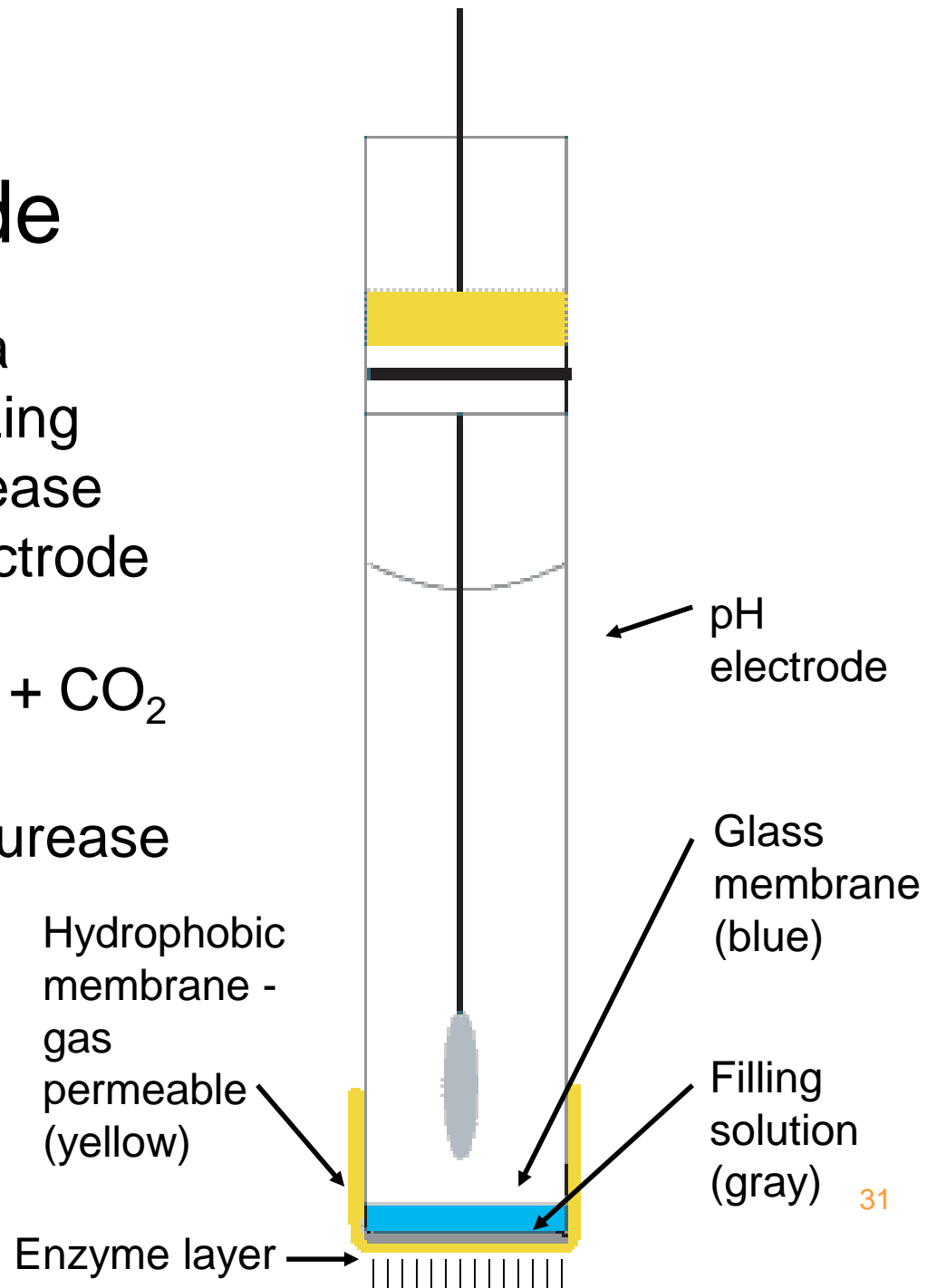
Enzyme Electrode

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



- 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



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 ± 0.1 mV
- This corresponds to $0.4 \times n$ % uncertainty
- Electrodes measure activity not concentration
- Measure “free” or uncomplexed ions not total