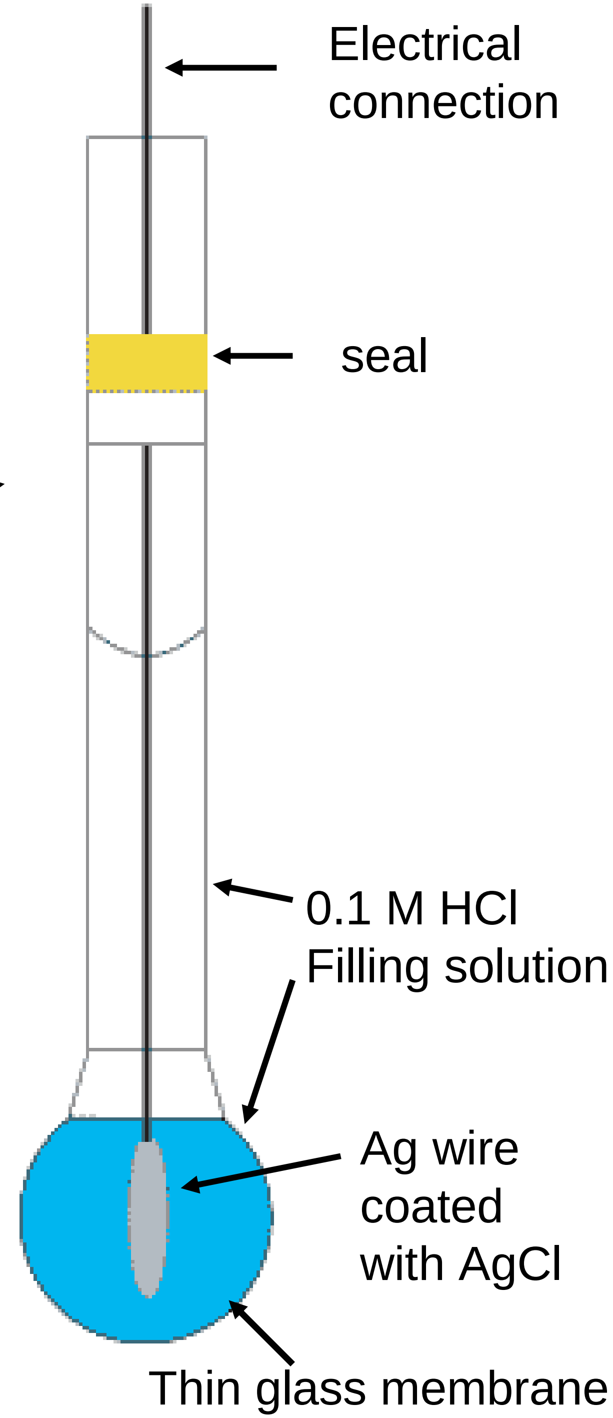
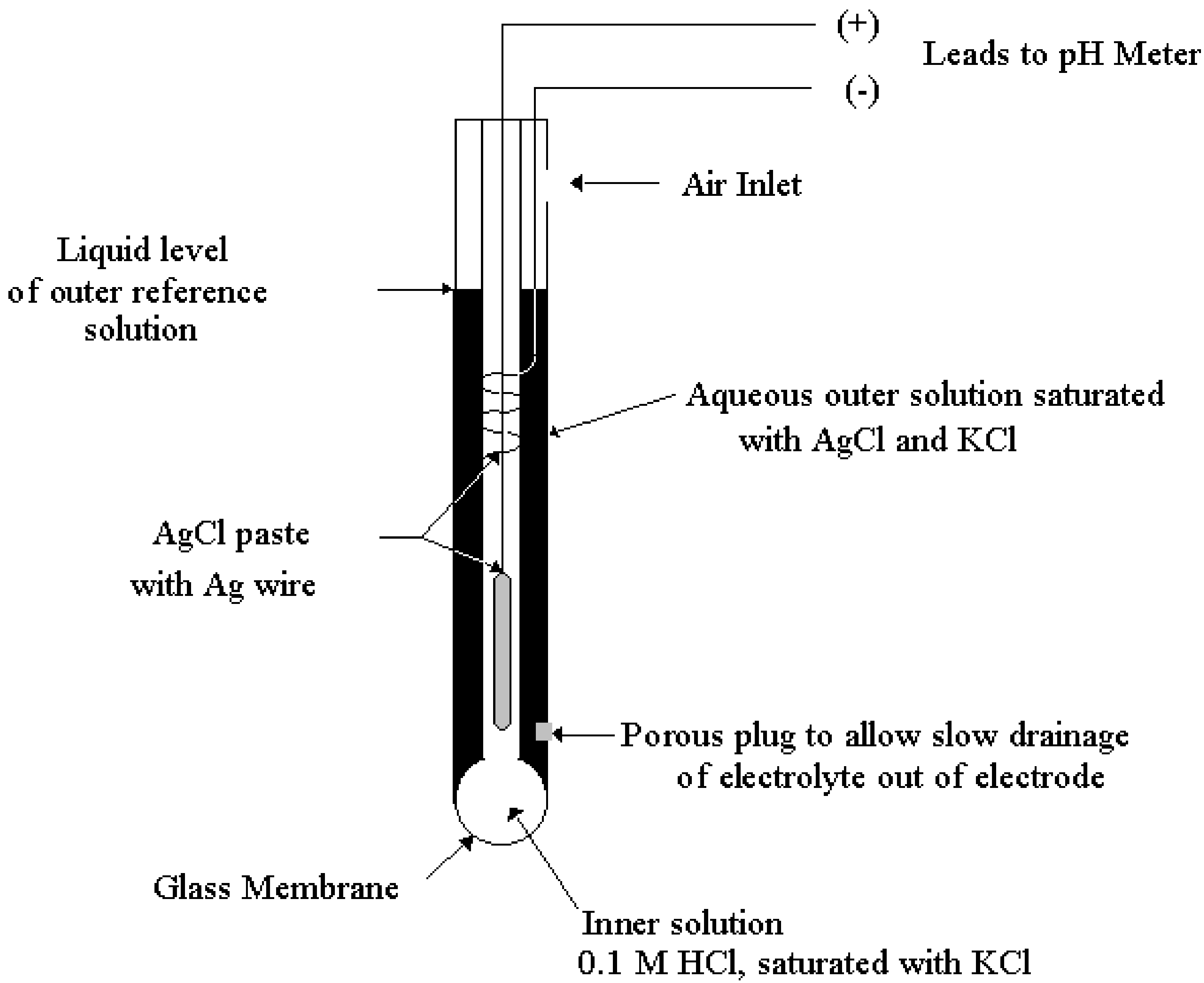
Membrane Electrodes

Several types

- **Glass membrane electrode**
- **Liquid membrane electrode**
- **Solid State membrane electrode**
- **Permeable membrane electrode**

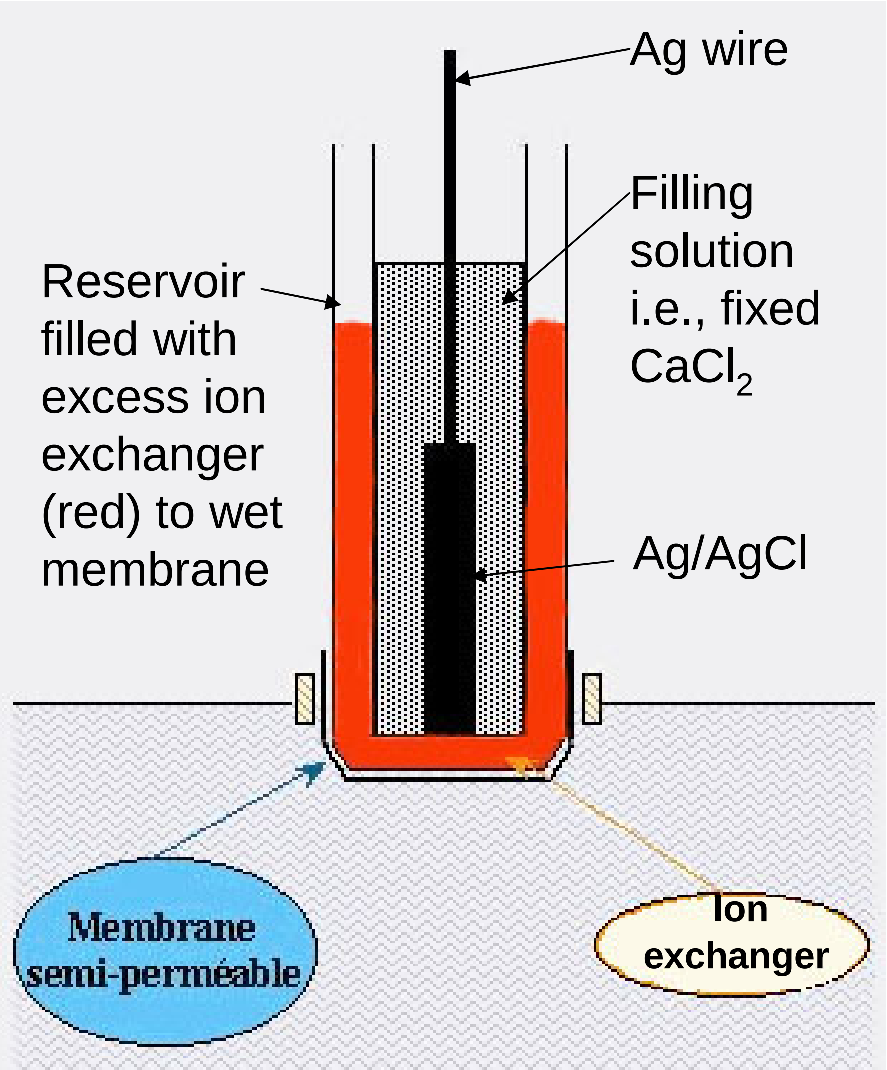


Combination pH Electrode



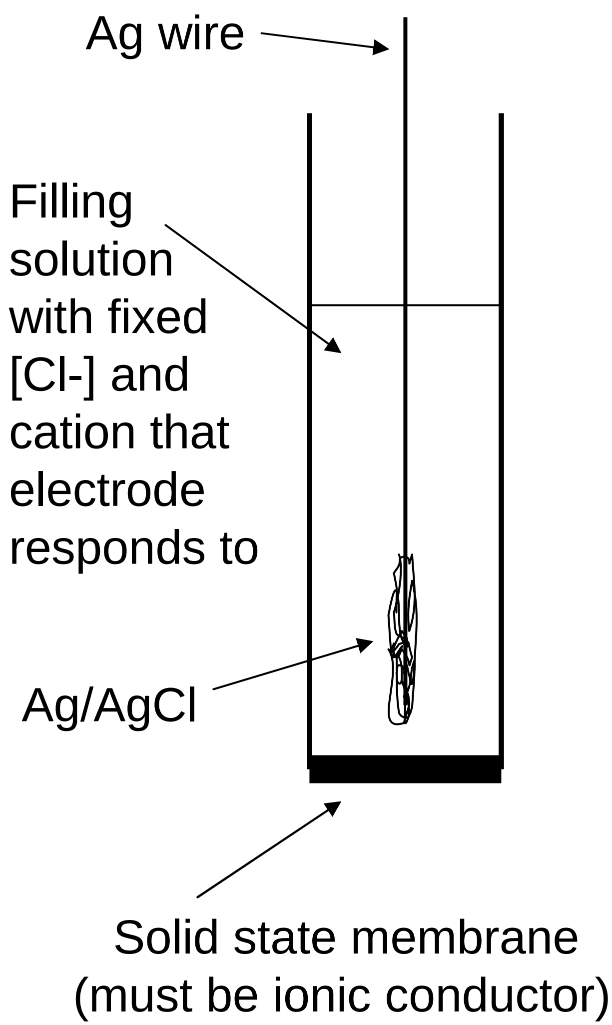
Liquid Membrane Electrodes

- 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

Solid State Membrane Electrodes



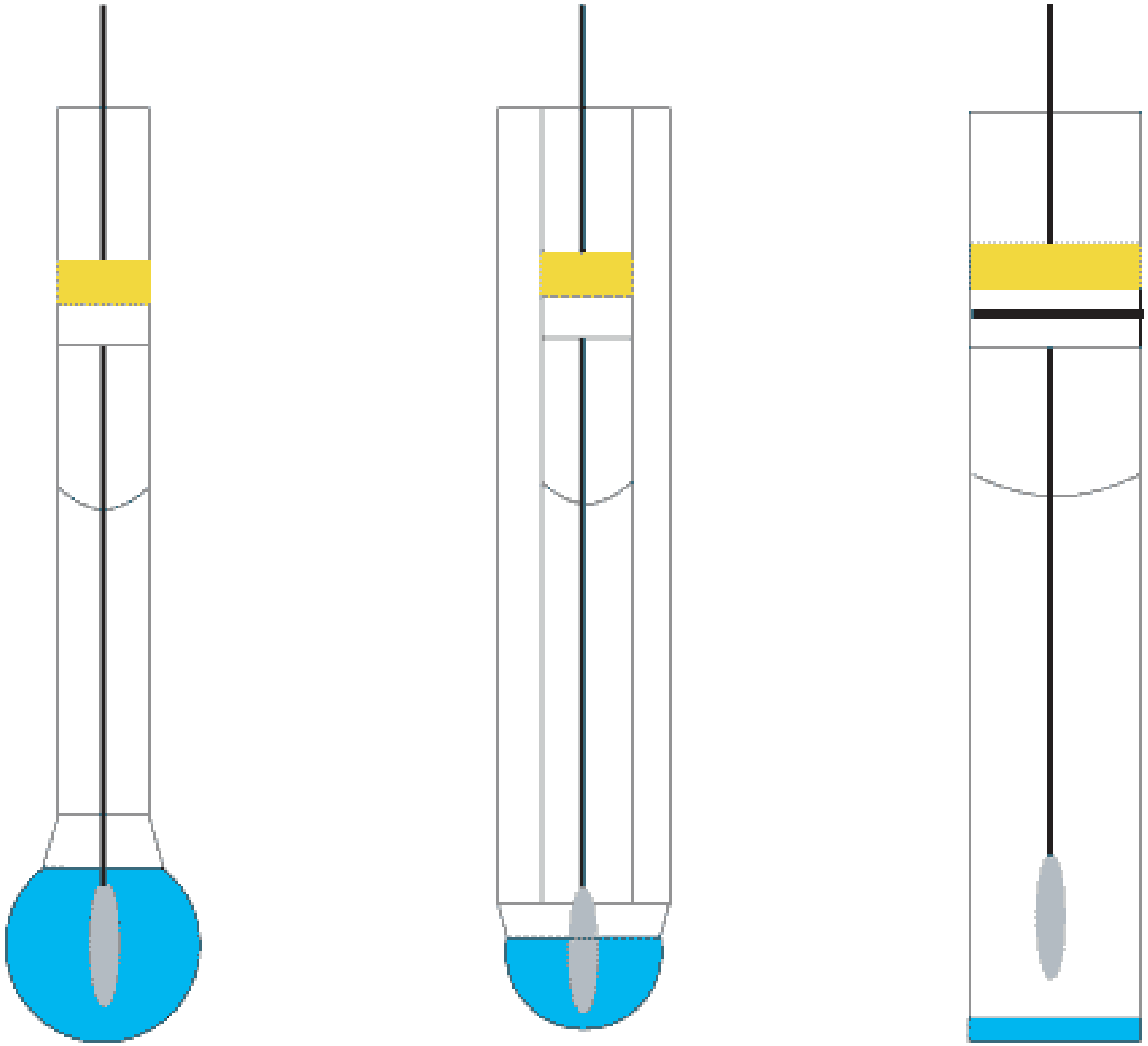
Solid State Membrane Chemistry	
Membrane	Ion Determined
LaF_3	F^-, La^{3+}
AgCl	Ag^+, Cl^-
AgBr	Ag^+, Br^-
AgI	Ag^+, I^-
Ag_2S	Ag^+, S^{2-}
Ag_2S + CuS	Cu^{2+}
Ag_2S + CdS	Cd^{2+}
Ag_2S + PbS	Pb^{2+}

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

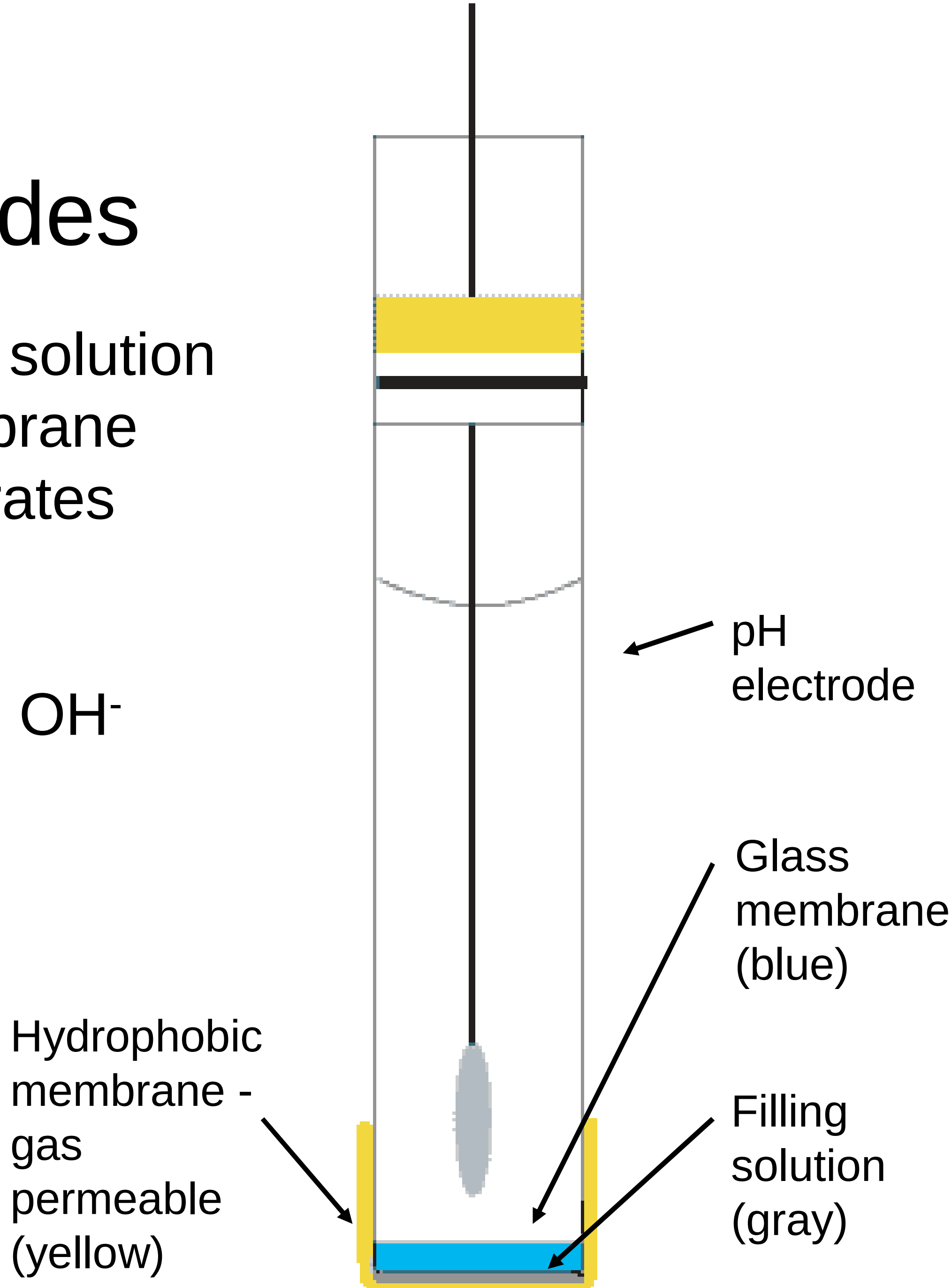
- Electrode immersed in test solution
- NH_3 diffuses through membrane
- NH_3 in test solution equilibrates with NH_3 in filling solution

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

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

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

$$pH = 14 - pOH = pNH_3$$



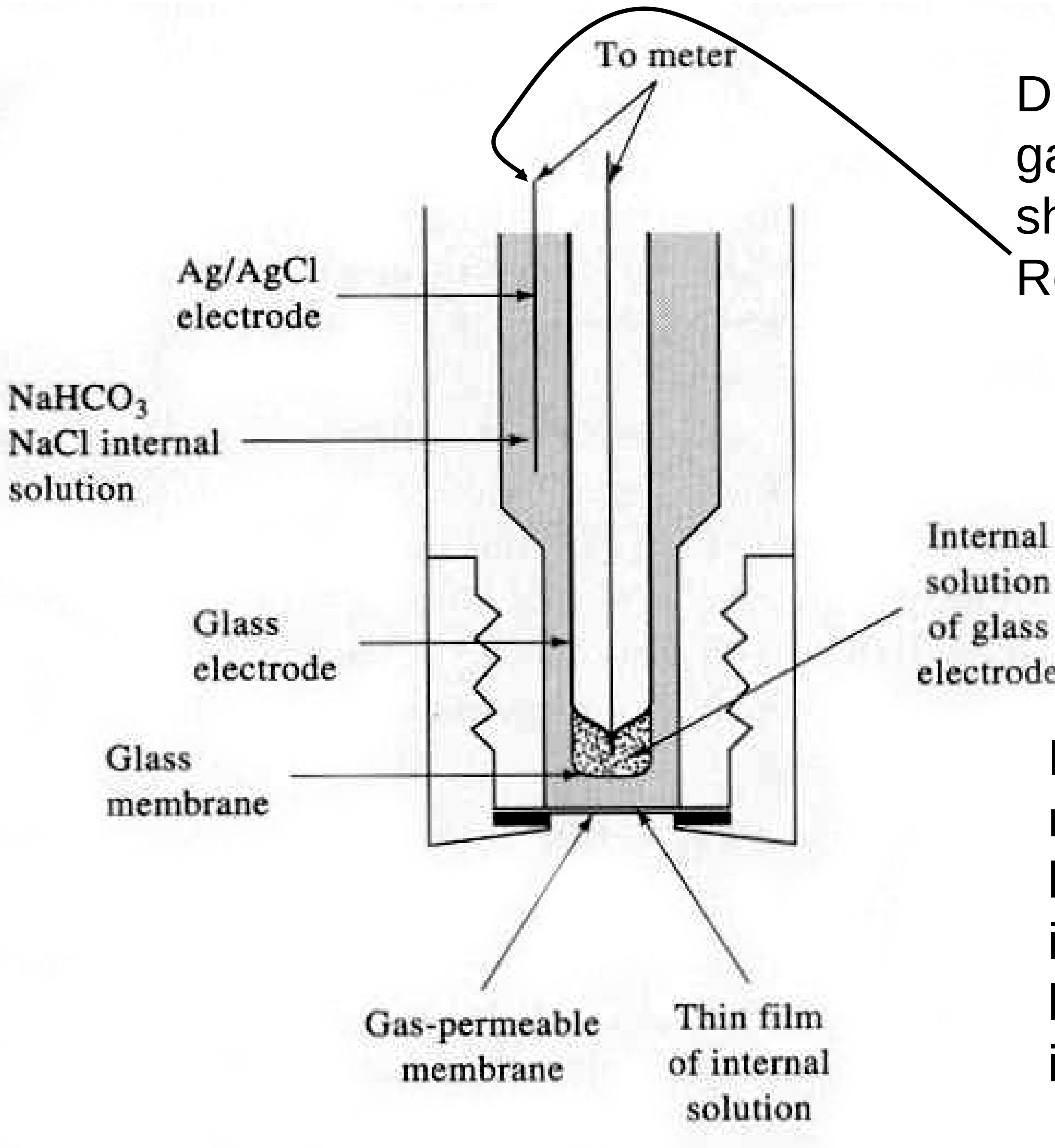


Diagram of CO_2 gas sensing probe showing internal Reference electrode

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

Commercial Gas Sensing Electrodes

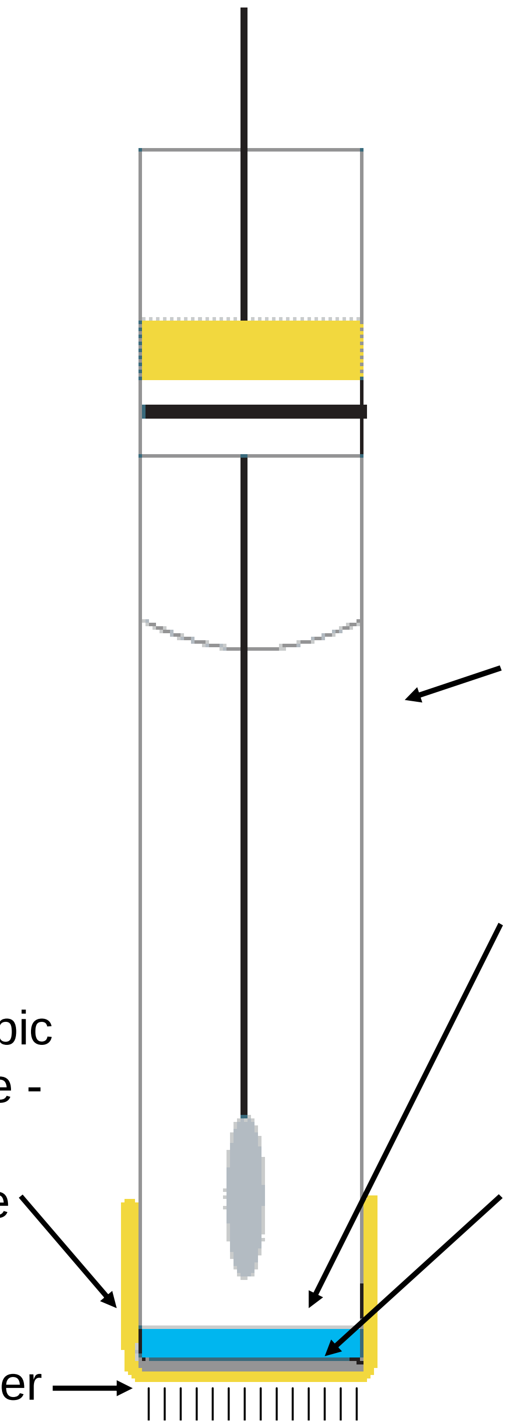
Gas	Equilibrium in Internal Solution	Sensing Electrode
NH_3	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	Glass, pH
CO_2	$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$	Glass, pH
HCN	$HCN \rightleftharpoons H^+ + CN^-$	Ag_2S, pCN
HF	$HF \rightleftharpoons H^+ + F^-$	LaF_3, pF
H_2S	$H_2S \rightleftharpoons 2H^+ + S^{2-}$	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

$$H_2N\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}NH_2 + H_2O \longrightarrow 2\ NH_3 + CO_2$$

- 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



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)

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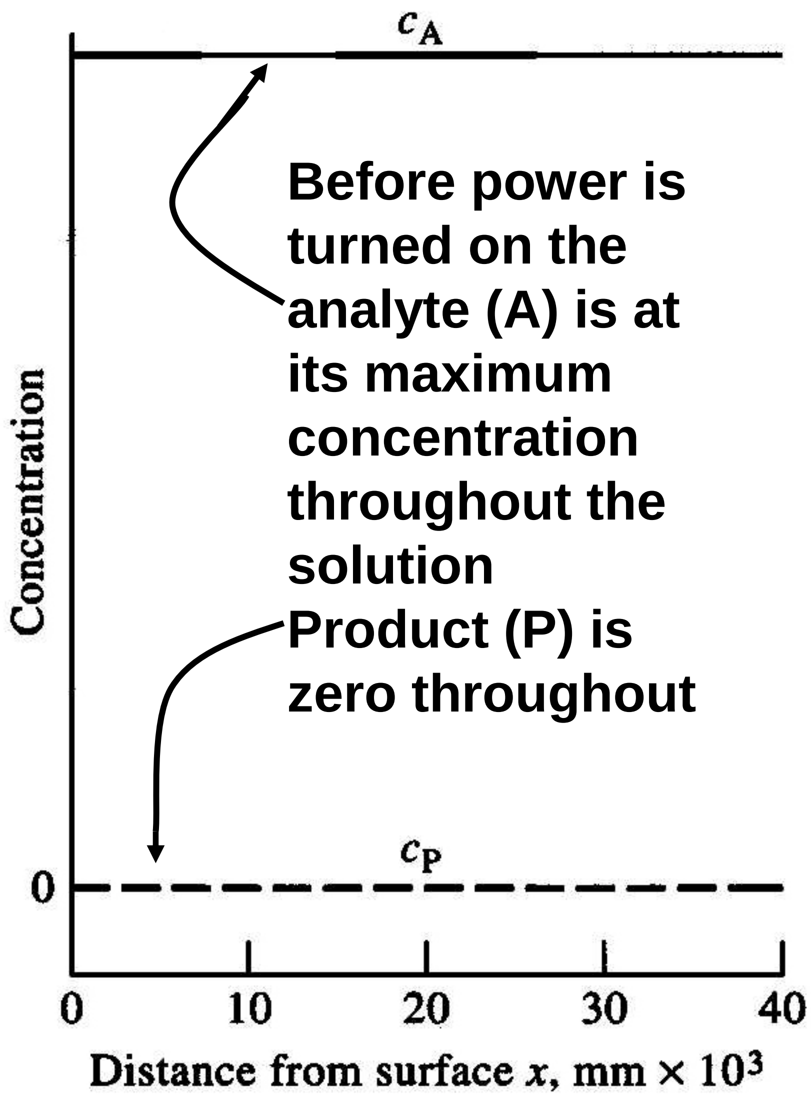
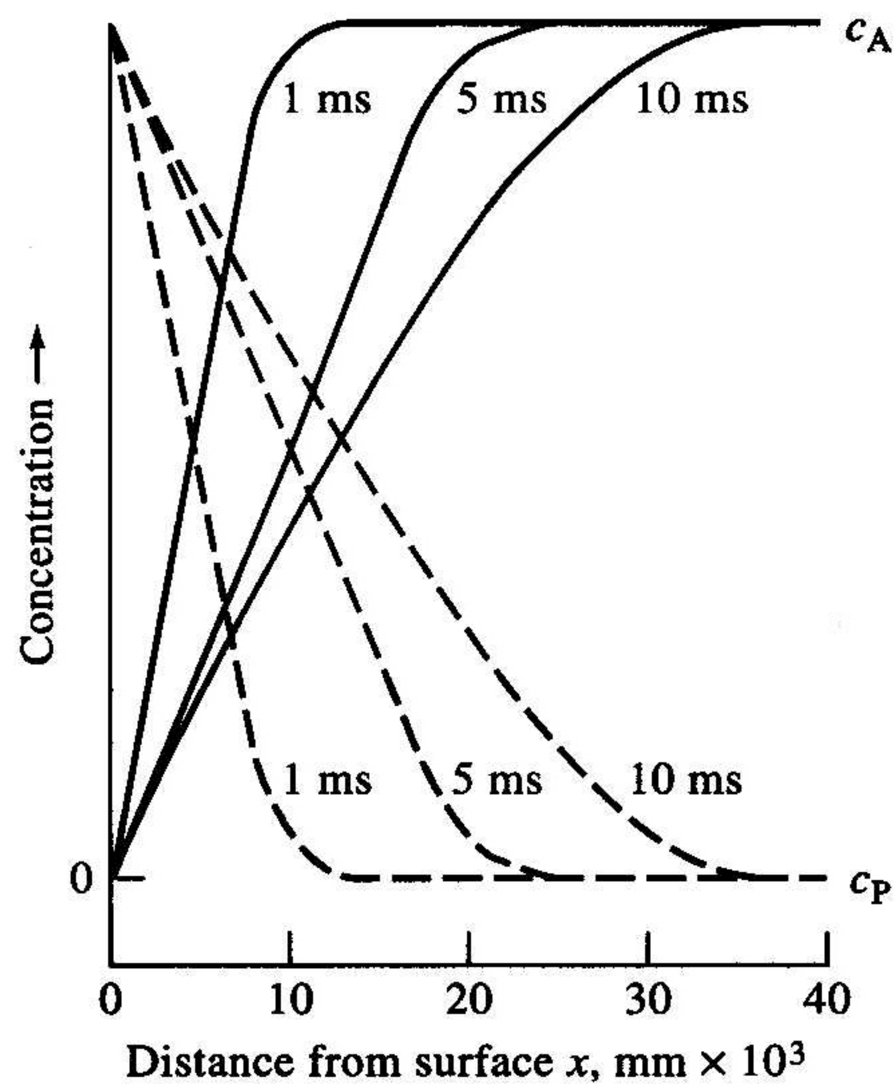
Concentration polarization
Reaction is A + e^- → P





Fick's Laws describe diffusion

1st Law

$$J = -D \frac{\partial C(x,t)}{\partial x}$$

Where

J = flux of material i.e., moles passing a 1 cm^2 plane at point x & time t ($mol/cm^2/sec$)

D = diffusion coefficient (cm^2/sec)

C = concentration

t = time (sec) from when power is turned on

x = distance from electrode surface (cm)