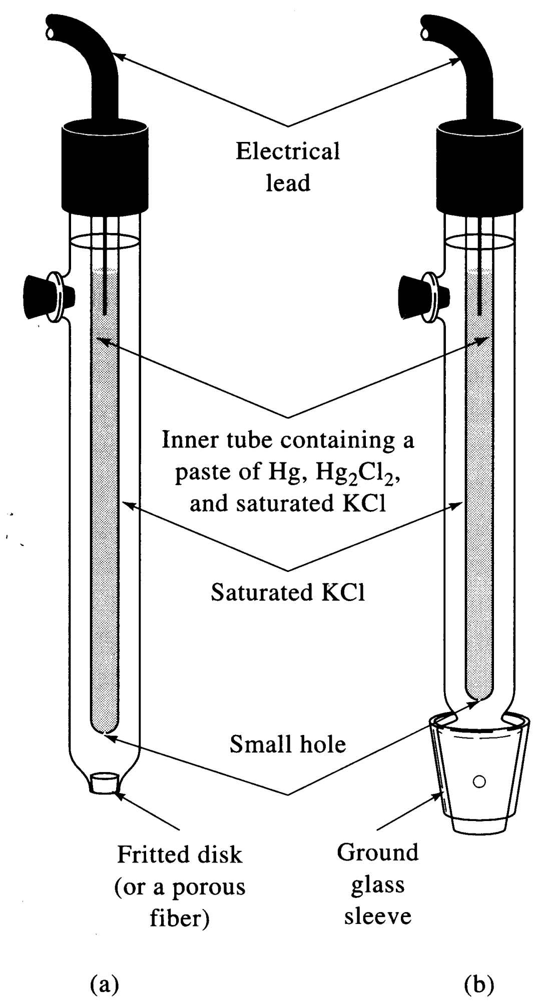
Potentiometry (Chapter 23)

Reference electrodes:

- reversible
- little hysteresis
- follows Nernst equation
- stable potential with time

Saturated Calomel Electrode (SCE):

$$Hg|Hg_2Cl_2(sat'd), KCl(a = x\ M)||...$$



(Fig 23-1)

Half-cell for Calomel Electrode:

$$Hg_2Cl_2(s) + 2e^- \leftrightarrow 2Hg(l) + 2Cl^-$$

Position of equilibrium affected by a_{Cl^-} from KCl so E^0 depends on a_{Cl^-}

Most common saturated calomel electrode SCE ($[Cl^-]$~4.5 M)

Silver/Silver Chloride Electrode:

Similar construction to calomel

- Ag wire coated with AgCl
- solution of KCl sat'd with AgCl

$$Ag|AgCl(sat'd),KCl(a = x\ M)||...$$

$$AgCl(s) + e^- \leftrightarrow Ag(s) + Cl^-$$

Again depends on a_{Cl^-}, but commonly sat'd (~3.5 M)

Potential vs. SHE ↓

TABLE 23-1 Potentials of Reference Electrodes in Aqueous Solutions

Temperature, °C	Electrode Potential (V), vs. SHE				
	0.1 M[c] Calomel[a]	3.5 M[c] Calomel[b]	Saturated[c] Calomel[a]	3.5 M[b,c] Ag/AgCl	Saturated[b,c] Ag/AgCl
10		0.256		0.215	0.214
12	0.3362		0.2528		
15	0.3362	0.254	0.2511	0.212	0.209
20	0.3359	0.252	0.2479	0.208	0.204
25	0.3356	0.250	0.2444	0.205	0.199
30	0.3351	0.248	0.2411	0.201	0.194
35	0.3344	0.246	0.2376	0.197	0.189
38	0.3338		0.2355		
40		0.244		0.193	0.184

[a]Data from: R. G. Bates in *Treatise on Analytical Chemistry,* 2d ed., I. M. Kolthoff and P. J. Elving, Eds., Part I, Vol. 1, p. 793, Wiley: New York, 1978.
[b]Data from: D. T. Sawyer and J. L. Roberts Jr., *Experimental Electrochemistry for Chemists,* p. 42, Wiley: New York, 1974.
[c]"M" and "saturated" refer to the concentration of KCl and *not* Hg_2Cl_2.

Which one?

- Ag/AgCl better for uncontrolled temperature (lower T coefficient)
- Ag reacts with more ions

Precautions in Use:

- Level of liquid inside reference electrode above analyte level to minimize contamination
- Plugging problematic if ion reacts with solution to make solid (e.g. AgCl in Cl^- determination)

Measuring Concentration using Electrodes:

Indicator Electrodes for Ions:

Electrode used with reference electrode to measure potential of unknown solution

- potential proportional to ion activity
- specific (one ion) or selective (several ions)

$$E_{cell} = E_{indicator} - E_{reference}$$

Two general types - metallic and membrane electrodes

Metallic Indicator Electrodes:

Electrodes of the first kind

- respond directly to changing activity of electrode ion

Example: Copper indicator electrode

$$Cu^{2+} + 2e^{-} \leftrightarrow Cu(s)$$

$$K_{eq} = \frac{a_{Cu(s)}}{a_{Cu^{2+}}} = \frac{1}{a_{Cu^{2+}}}$$

$$E_{ind} = E^{0} - \frac{RT}{nF} \log K_{eq}$$

$$E_{ind} = E^{0}_{Cu/Cu^{2+}} - \frac{0.0592}{2} \log \frac{1}{a_{Cu^{2+}}}$$

$$= 0.337\ V - 0.296pCu$$

BUT other ions can be reduced at Cu surface

- those with higher +ve E^0 (better oxidizing agents than Cu)

Ag, Hg, Pd...

In general, electrodes of first kind:

- simple
- not very selective
- some metals easily oxidized (deaerated solutions)
- some metals (Zn, Cd) dissolve in acidic solutions

- Electrodes of the second kind - respond to changes in ion activity through formation of complex

Example: Silver works as halide indicator electrode if coated with silver halide

Silver wire in KCl (sat'd) forms AgCl layer on surface

$$AgCl\,(s) + e^{-} \leftrightarrow Ag(s) + Cl^{-} \quad E^{0} = +0.222\ V$$

$$E_{ind} = +0.222 - \frac{0.0592}{n} \log a_{Cl^{-}}$$

$$= +0.222 + 0.0592pCl$$

- Electrodes of the third kind - respond to changes of different ion than metal electrode

Membrane (or Ion Selective) Electrodes:

Membrane:

- Low solubility - solids, semi-solids and polymers
- Some electrical conductivity - often by doping
- Selectivity - part of membrane binds/reacts with analyte

Two general types - crystalline and non-crystalline membranes

- Non-crystalline membranes:

  Glass - silicate glasses for H^+, Na^+

  Liquid - liquid ion exchanger for Ca^{2+}

  Immobilized liquid - liquid/PVC matrix for Ca^{2+} and NO_3^-

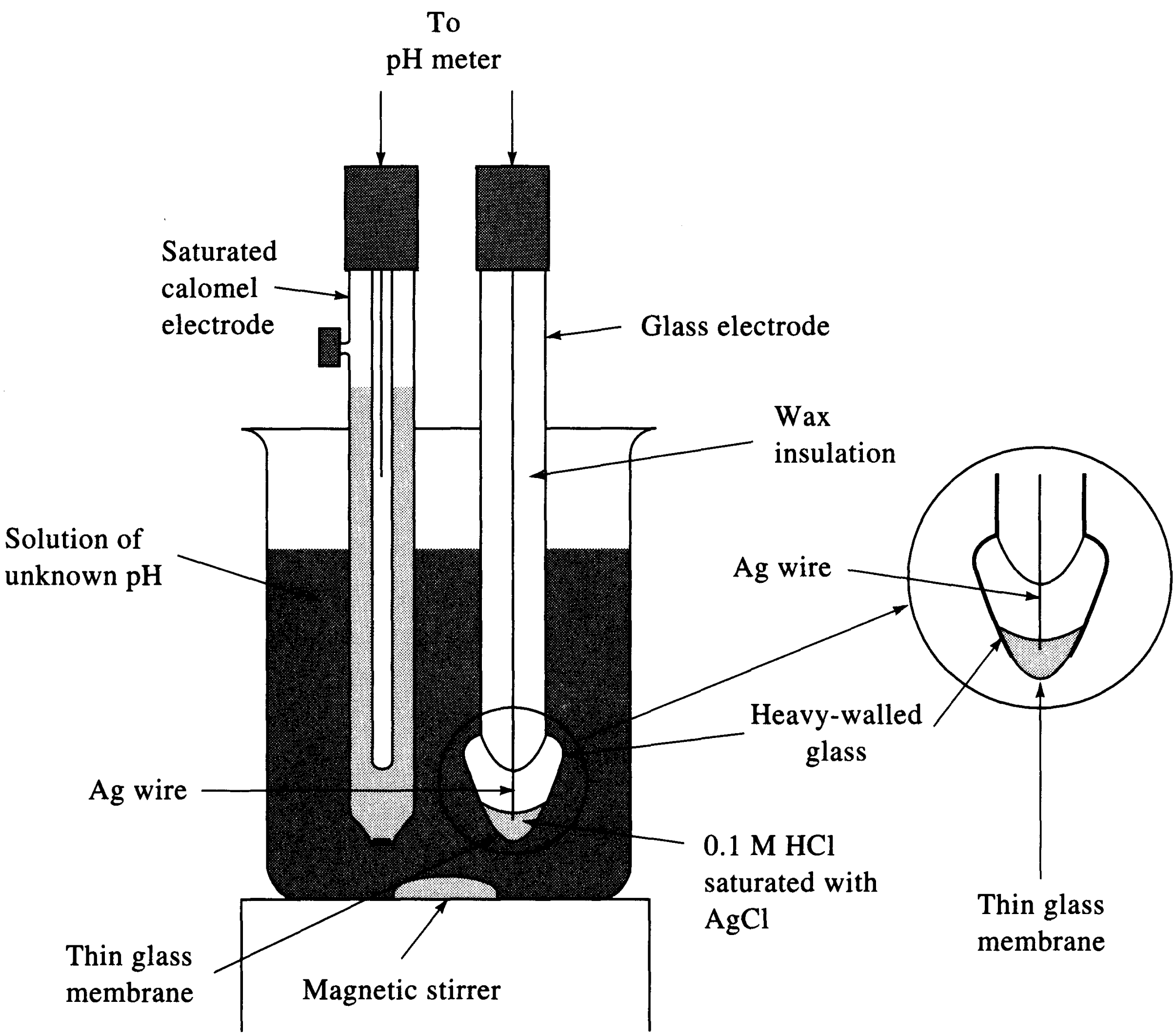
- Crystalline membranes:

  Single crystal - LaF_3 for F^-

  Polycrystalline or mixed crystal - AgS for S^{2-} and Ag^+

Glass Membrane Electrodes:

Fig 23-3



$$\overbrace{\text{SCE}}^{\text{Ref 1}}\|\overbrace{H_3O^+(a=a_1)}^{\text{Analyte}}|\overbrace{\text{Membrane}|H_3O^+(a=a_2),\underbrace{Cl^-(a=1\,M),AgCl(sat'd)|Ag}_{\text{Ref 2}}}^{\text{Glass Electrode}}$$

Combination pIon electrode (ref + ind)

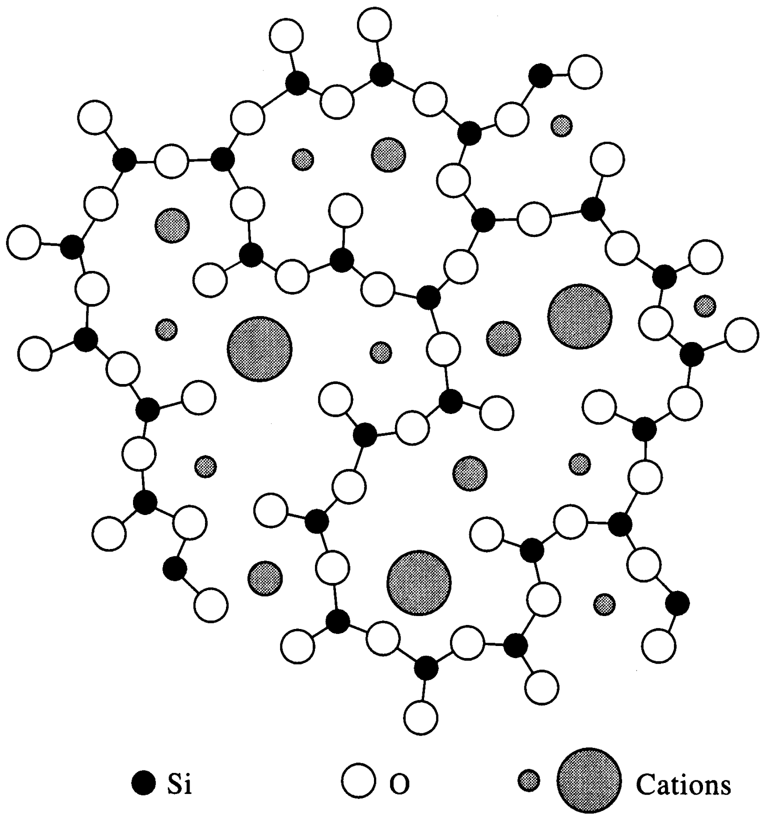
Contains two (reference) electrodes - glass membrane is pH sensitive

Glass Membrane Structure:

SiO_4^{4-} framework with charge balancing cations

- SiO_2 72 %, Na_2O 22 %, CaO 6 %

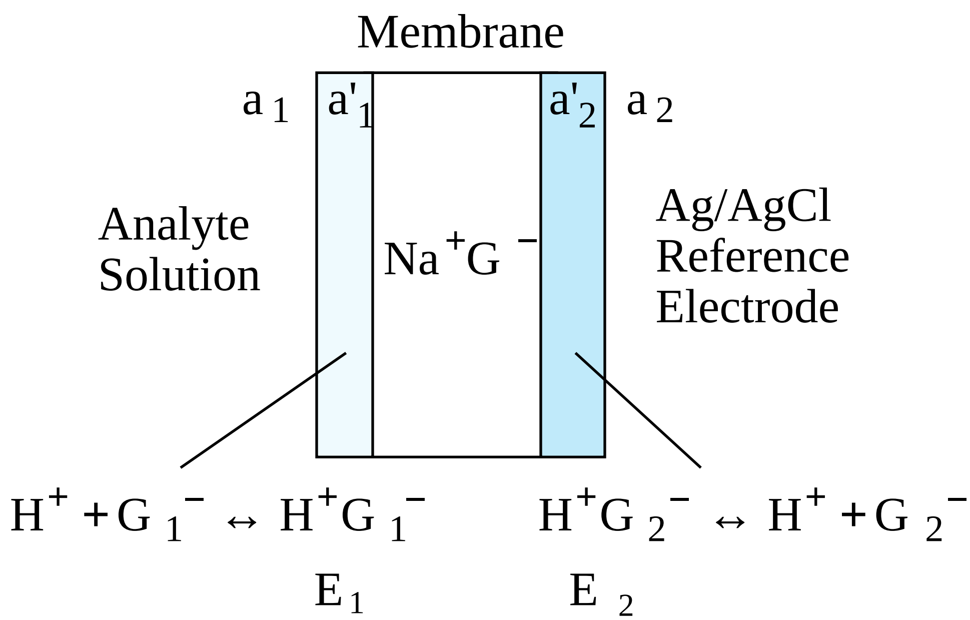
Fig 23-5



In aqueous solution, ion exchange reaction at surface

$$H^+ + Na^+Glass^- \rightleftharpoons H^+Glass^- + Na^+$$

- H^+ carries current near surface
- Na^+ carries current in interior
- Ca^{2+} carries no current (immobile)



Surface where more dissociation occurs becomes negatively charge with respect to other surface

Boundary potential $E_b = E_1 - E_2$

Potential difference determined by

- $E_{ref\ 1}$ - SCE (constant)
- $E_{ref\ 2}$ - Ag/AgCl (constant)
- E_b

Now

$$E_b = E_1 - E_2 = 0.0592 \log \frac{a_1}{a_2}$$

a_1=analyte

a_2=inside ref electrode 2

If a_2 is constant then

$$E_b = L + 0.0592 \log a_1$$
$$= L - 0.0592\ pH$$
$$\text{where } L = -0.0592 \log a_2$$

Since $E_{ref\ 1}$ and E_{ref2} are constant

$$E_{cell} = \text{constant} - 0.0592\ pH$$

Alkaline Error:

At high pH, glass electrode indicates pH less than true value

Low [H^+] means membrane exchanges with alkali metal ions in solution too

$$H^+ + Gl^- \leftrightarrow H^+Gl^- \quad \leftarrow \text{small}$$

$$Na^+ + Gl^- \leftrightarrow Na^+Gl^-$$

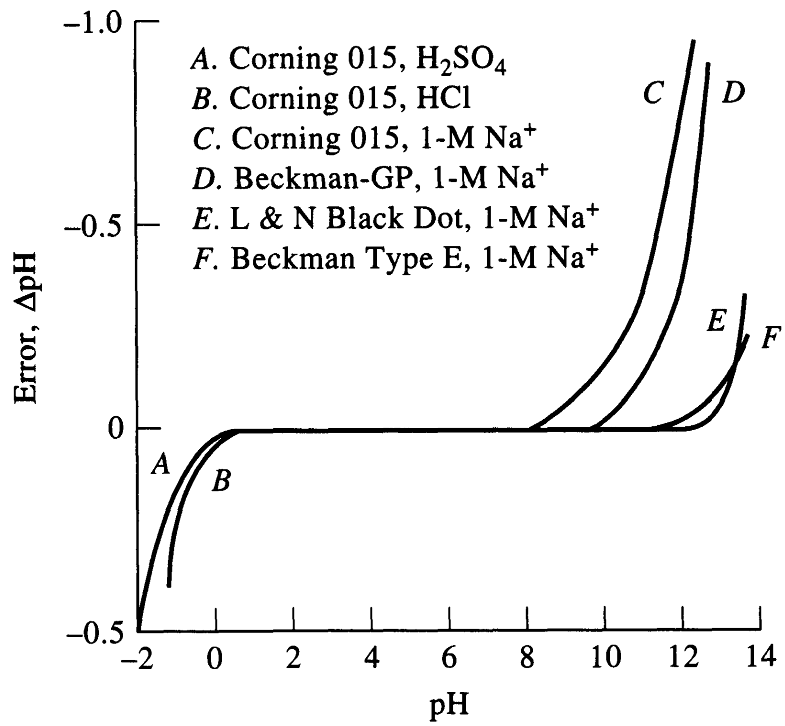


Fig. 23-7

Most accurate 0-10 (0.01-0.03 pH units)

Interference in Glass Membrane Electrodes:

Sensitive to

- H^+
- alkali metal ions

Selectivity coefficients ($k_{X/Y}$) measure sensitivity to other ions

Range between 0 (no interference) to 1 (as sensitive to alkali and hydrogen ions) to >1 (large interference)

$$E_{ind} = \text{constant} - 0.0592 \log(a_{H^+} + k_{Na/H}\, a_{Na^+})$$

selectivity coefficient

Glass Electrodes for Other Ions:

Maximize $k_{H/Na}$ for other ions by modifying glass surface (usually adding Al_2O_3 or B_2O_3)

Possible to make glass membrane electrodes for

Na^+, K^+, NH_4^+, Cs^+, Rb^+, Li^+, Ag^+ …

Crystalline Membrane Electrodes:

- Usually ionic compound
- Single crystal
- Crushed powder, melted and formed
- Sometimes doped (Li^+) to increase conductivity
- Operation similar to glass membrane

$$\underbrace{LaF_2^{\,+}}_{\text{solid}} + \underbrace{F^-}_{\text{analyte}} \leftrightarrow \underbrace{LaF_3}_{\text{solid}}$$

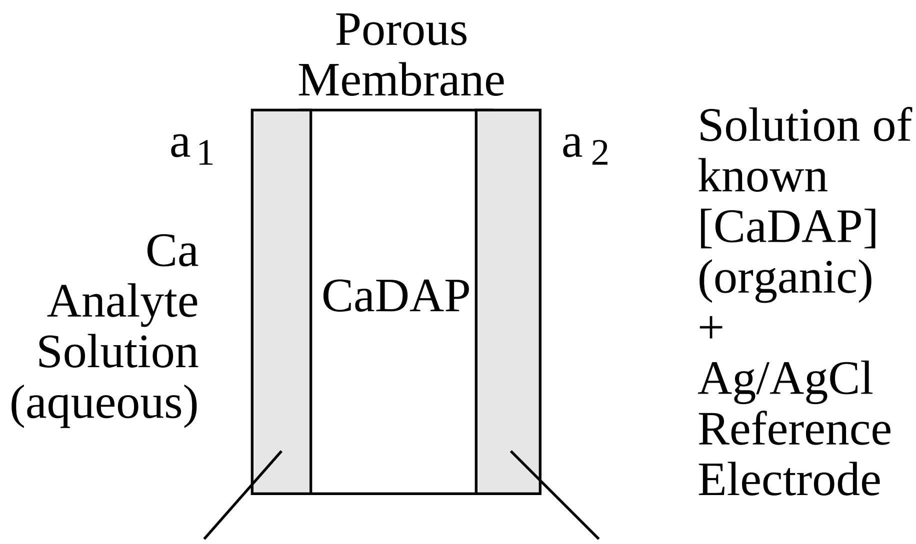
Presence of F^- analyte pushes equilibrium right, reduces +ve charge on electrode surface

$$E_{ind} = L + 0.0592 \log \frac{1}{a_{F^-}}$$
$$= L - 0.0592 \log a_{F^-}$$
$$= L + 0.0592\, pF$$

Liquid Membrane Electrodes:

- Based on potential that develops across two immiscible liquids with different affinities for analyte
- Porous membrane used to separate liquids

Example: Calcium dialkyl phosphate insoluble in water, but binds Ca^{2+} strongly



$$Ca^{2+} + \underbrace{2(RO)_2PO_2^-}_{\text{dialky phosphate}} \leftrightarrow [(RO)_2PO_2]_2Ca$$

$$E_b = E_1 - E_2 = \frac{0.0592}{2}\log\frac{a_1}{a_2}$$

If a_2 is constant

$$E_b = N + \frac{0.0592}{2}\log a_1$$

$$= N - \frac{0.0592}{2}pCa$$

TABLE 23-4 Liquid Membrane Electrodes[a,b]

Analyte Ion	Concentration Range, M	Interferences[c]
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^+

[a]From: *Handbook of Electrode Technology,* pp. 10–13, Appendix, Orion Research: Cambridge, MA, 1982. With permission.
[b]All of the electrodes except the last are of the newer type in which the liquid ion exchanger or neutral carrier is supported in a plastic matrix.
[c]The numbers in front of each ion represent the molar concentration of that ion that gives a 10% error when the analyte concentration is 10^{-3} M.

Molecule Selective Electrodes:

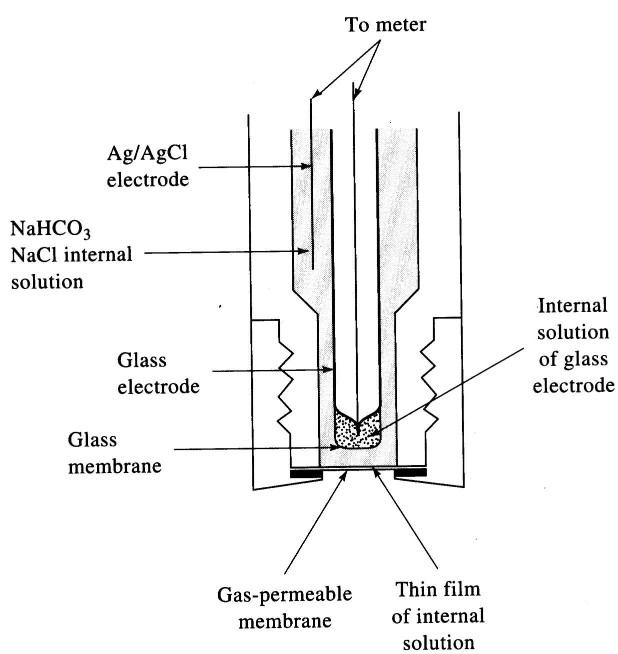
- Gas Sensing Probes
- Biocatalytic Membranes

Gas Sensing Probes:

Simple electrochemical cell with two reference electrodes and gas-permeable PTFE membrane

allows small gas molecules to pass and dissolve into internal solution

Fig 23-11



Analyte not in direct contact with either electrode - dissolved

Mechanism:

$$\underbrace{CO_2(aq/g)}_{\text{analyte}} \leftrightarrow \underbrace{CO_2(g)}_{\text{membrane pores}} \leftrightarrow \underbrace{CO_2(aq)}_{\text{internal solution}}$$

in internal solution

$$CO_2(aq) + H_2O \leftrightarrow H^+ + HCO_3^-$$

can use glass membrane electrode to sense pH!

If we write overall equation

$$\underbrace{CO_2(aq)}_{\text{external analyte}} + H_2O \leftrightarrow \underbrace{H^+ + HCO_3^-}_{\text{internal solution}}$$

$$K_{eq} = \frac{a_{H^+}\, a_{HCO_3^-}}{a_{CO_2}}$$

$$K_{eq} = \frac{K_g}{[CO_2]}$$

activity of neutral unaffected by other ions $a_{CO2}=[CO_2]$

so

$$E_{ind} = L'' - 0.0592 \log \frac{K_g}{[CO_2]}$$

$$= L' + 0.0592 \log [CO_2]$$

Biocatalytic Membrane Electrodes:

Biosensors very important, much research effort

Immobilized enzyme bound to gas permeable membrane

Catalytic enzyme reaction produces small gaseous molecule (H^+, NH_3, CO_2)

Then gas sensing probe measures change in gas concentration in internal solution

- Fast
- Very selective
- Used *in vivo*
- Expensive
- Only few enzymes immobilized
- Immobilization changes activity
- Limited operating conditions (pH, temperature, ionic strength)