Chapter 23 - Potentiometry

- Read: pp. 659-680 Problems: 23-2,4,7,13,14

- Potentiometric methods are based upon measurements of the **potential** of electrochemical cells in the **absence** of appreciable currents (an equilibrium measurement, therefore, the Nernst equation is applicable).

- All equipment is simple: an **indicator** electrode, a **reference** electrode and a **potential measuring device**.

- Billions of these measurements are made annually. Importance in environmental and medical applications. For example, pH, ion selective electrodes, blood gas analysis (O_2, CO_2), etc.

Reference Electrodes

Ideal Properties

1. Reversible and obeys Nerst eq.
2. Stable potential with time.
3. Returns to original position after passage of small currents.
4. Little hysteresis with temperature.

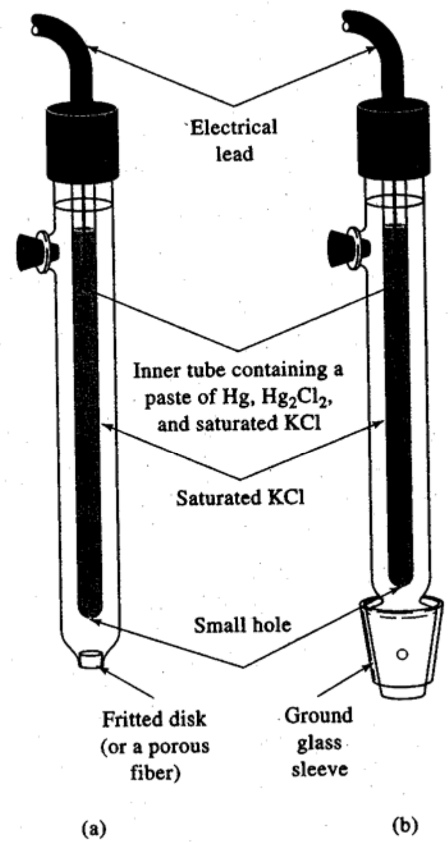


Figure 23-1 Typical commercial calomel reference electrodes.

Hg/Hg_2Cl_2(sat'd),KCl (xM)//
$E^o = 0.244$ V vs. NHE

Ag/AgCl(sat'd),KCl (xM)//
$E^0 = 0.222$ V vs. NHE

Know your redox reactions!!
$AgCl(s) + e^- \leftrightarrow Ag(s) + Cl^-$

Reference is considered the anode!

Types of Metallic Indicator Electrodes

Metallic and Membrane

Electrodes of a First Kind

metallic electrodes in direct equilibrium with the cation derived from the metal.

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

$$E_{ind} = E^o_{Cu} + (0.0592/2)\log[Cu^{+2}]$$

$$E_{ind} = E^o_{Cu} - (0.0592/2)\ p[Cu^{+2}]$$

Electrodes of a Second Kind

metallic electrode that is responsive to the activity of an anion with which its ion forms a precipitate or stable complex ion.

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

$$E_{ind} = E^o_{AgCl} + (0.0592/1)\ \log 1/[Cl^-]$$

$$E_{ind} = E^o_{AgCl} + (0.0592/1)\ p[Cl^-]$$

Remember that inverting the log term changes the sign in front of it.

$pX = -\log X$

Types of Metallic Indicator Electrodes

Electrodes of a Third Kind

A metal electrode, under certain circumstances can be made to respond to a different cation.

$CaY^{-2} \leftrightarrow Ca^{+2} + Y^{-4}$ $K_f = (aCa^{+2} \bullet aY^{-4})/aCaY^{-2}$

Metallic Indicator Electrodes

Pt, Au, Pd (inert metals) are responsive to the activities of the oxidized and reduced forms of the redox couple near the electrode surface.

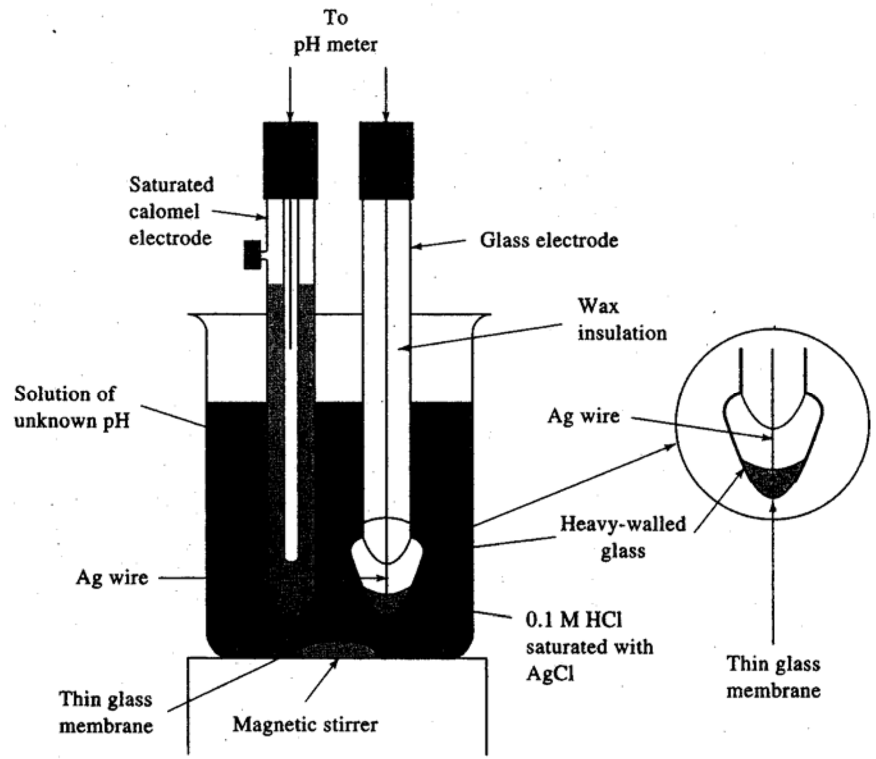
$Ce^{+4} + e^{-} \leftrightarrow Ce^{+3}$ $E = E^{o} + (0.0592/n) \log ([Ce^{+4}]/[Ce^{+3}])$

The pH Electrode – Membrane Electrode

TABLE 23-2 Types of Ion-Selective Membrane Electrodes

A. Crystalline Membrane Electrodes
1. Single crystal
   Example: LaF_3 for F^-
2. Polycrystalline or mixed crystal
   Example: Ag_2S for S^{2-} and Ag^+

B. Noncrystalline Membrane Electrodes
1. Glass
   Examples: silicate glasses for Na^+ and H^+
2. Liquid
   Examples: liquid ion exchangers for Ca^{2+} and neutral carriers for K^+
3. Immobilized liquid in a rigid polymer
   Examples: polyvinyl chloride matrix for Ca^{2+} and NO_3^-



The membranes must have (i) minimal solubility, (ii) be ion conductors and not electrical conductors, and (iii) some selective interaction with the analyte of interest.

Membranes Selectively Separate Charge

Charge separation = potential!

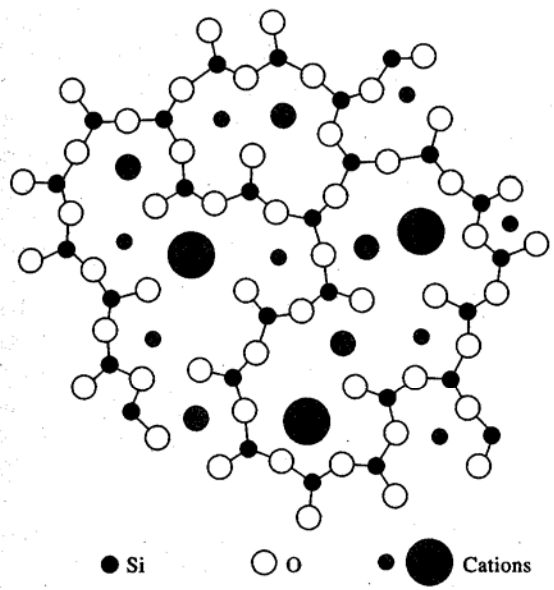
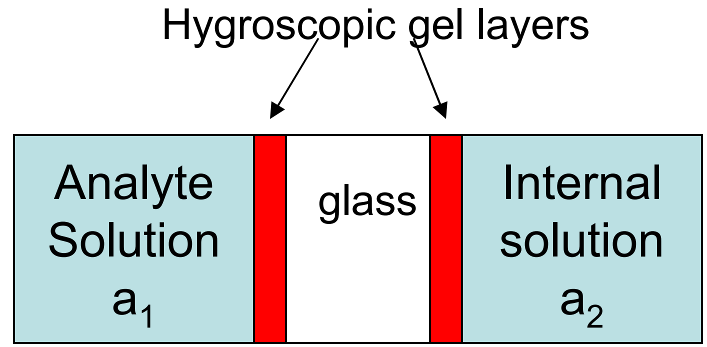


Figure 23-5 Cross-sectional view of a silicate glass structure. In addition to the three Si—O bonds shown, each silicon is bonded to an additional oxygen atom, either above or below the plane of the paper. *(Adapted with permission from G. A. Perley,* Anal. Chem., *1949, 21, 395. Copyright 1949 American Chemical Society.)*



$$E_b = E_1 - E_2 = 0.0592 \log a_1/a_2$$

$$E_b = L' + 0.0592 \log a_1$$
$$= L' - 0.0592\ pH$$

where $L' = -0.0592 \log a_2$

$$H^+_{soln} + Na^+Gl^-_{glass} \leftrightarrow Na^+_{soln} + H^+Gl^-_{glass}$$

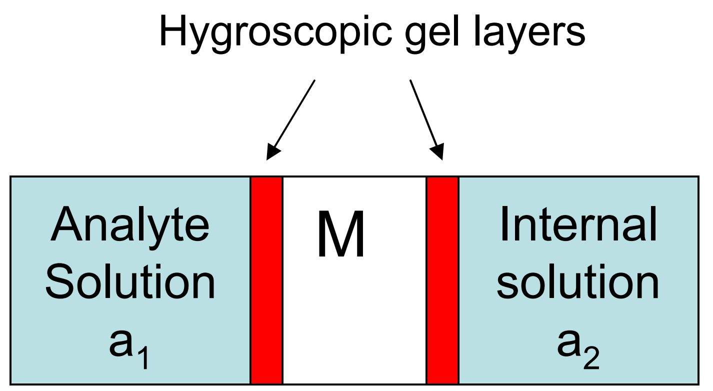
The pH Electrode

- Alkaline error – sensitive to alkali metal ions at pH greater than 12.
- Acid error – at pH less than 0.5, values obtained with the pH electrode are high.
- Dehydration – must keep membrane moist.
- Errors in low ionic strength – varying junction potentials.
- Errors in pH of standard buffer solutions.

Reference Electrode 1//[H_3O^+]=a_1/membrane/[H_3O^+]=a_2//Reference Electrode 2

Boundary potential, E_b, is sensitive to solution pH!

Crystalline Membrane Electrodes



$$LaF_{3\ membrane} \leftrightarrow LaF_2^{+}{}_{membrane} + F^{-}_{soln}$$

$$E_b = E_1 - E_2 = 0.0592 \log a_1/a_2$$

$$E_{ind} = L - 0.0592 \log a_{F-} = L + 0.0592p[F]$$

Crystalline Membrane Electrodes

TABLE 23-3 Commercial Solid-State Electrodes[a]

Analyte Ion	Concentration Range, M	Interferences[b]
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-}

[a]From: *Handbook of Electrode Technology*, pp. 10–13, Appendix, Orion Research: Cambridge, MA, 1982. With permission.

[b]mr: maximum ratio $\left(\frac{c_{interferent}}{c_{analyte}}\right)$ for no interference.

mba: must be absent.

Liquid Membrane Electrodes

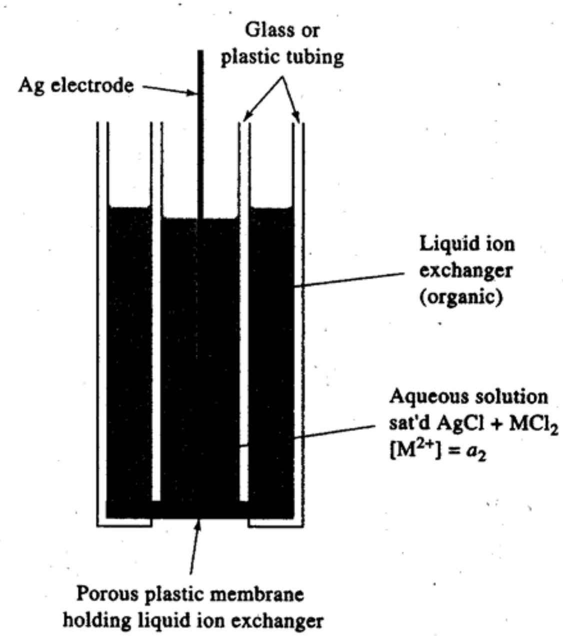


Figure 23-8 Liquid membrane electrode sensitive to M^{2+}.

Ca^{+2}, BF_4^-, NO_3^-, ClO_4^-, K^+

$$[(RO)_2POO]_2Ca \leftrightarrow 2(RO)_2POO^- + Ca^{+2}_{soln}$$

Fill membrane with a compound that selectively binds with the analyte.

$$E_{ind} = L + (0.0592/2) \log a_1$$

(Ca^{+2} is divalent)

$$E_{ind} = L' - (0.0592/2)\, p[Ca]$$

Gas Sensing Electrodes

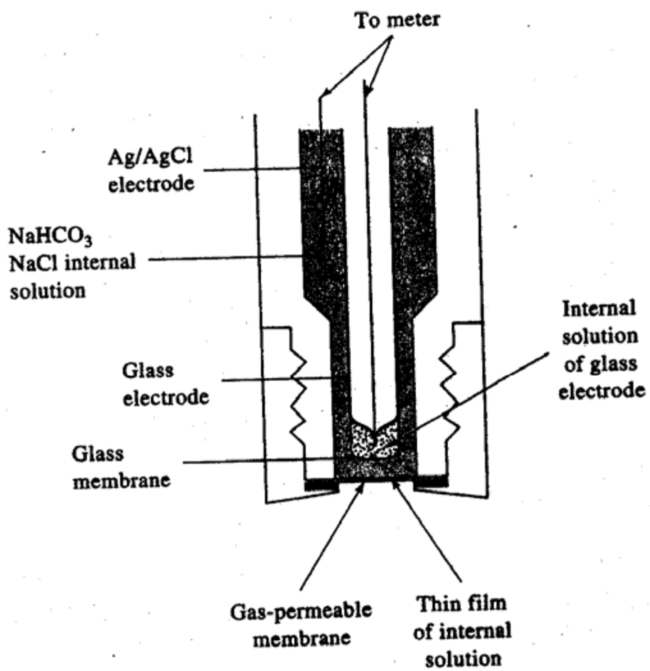


Figure 23-11 Schematic of a gas-sensing probe for carbon dioxide.

$$CO_{2(aq)} + H_2O \leftrightarrow HCO_3^- + H^+$$

TABLE 23-5 Commercial Gas-Sensing Probes

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