

Chapter 15 Electrodes and Potentiometry

Homework: Due Wednesday, April 12

Problems – 15-1, 15-6, 15-13, 15-21, 15-24, 15-35

Potentiometry

- Potentiometry is the field of electroanalytical chemistry in which potential is measured under the conditions of no current flow.
- The measured potential may be used to determine the concentration of some component of the analyte solution.
- The potential that develops in the *electrochemical cell* is the result of the *free energy change* that would occur if the chemical phenomena were to proceed until the *equilibrium condition* has been satisfied.

$$\Delta G_{\text{rxn}} = -nFE_{\text{rxn}}$$

- The *potential difference* between the cathode electrode potential and the anode electrode potential is the potential of the electrochemical cell.

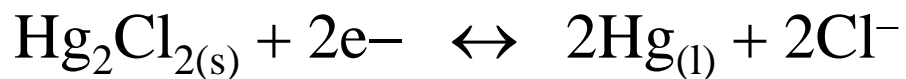
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Reference electrodes

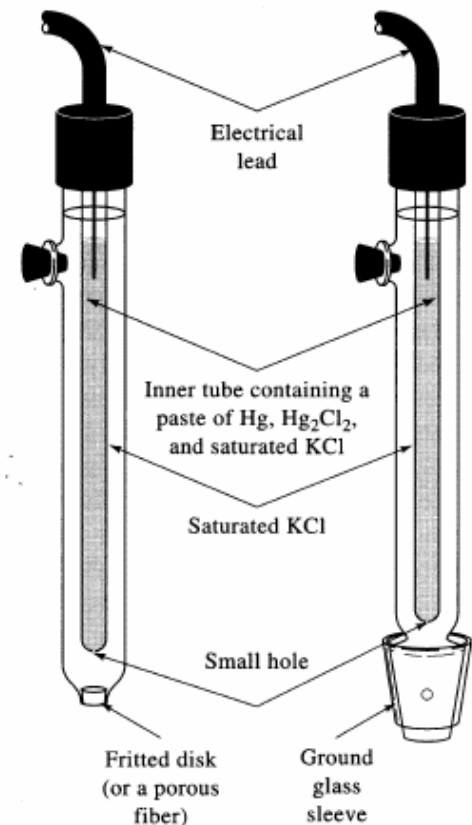
- Used for half of the cell to determine the potential of the analyte of interest.
- Maintains a fixed potential (i.e. reference, stable over time) – in contrast, the indicator electrode responds to the analyte activity
- Follows Nernst equation

Examples of reference electrodes

Saturated Calomel Electrode (SCE):



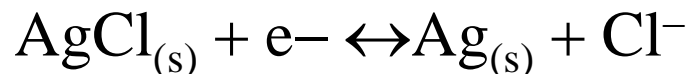
or $\text{Hg}|\text{Hg}_2\text{Cl}_2 \text{ (sat'd, KCl)} || \dots$



Silver/Silver Chloride Electrode:

Similar construction to calomel reference electrode

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



Or $\text{Ag} | \text{AgCl}_{(\text{sat'd, KCl})} || \dots$

Which one should be used– Ag|AgCl or SCE?

- Ag/AgCl better for uncontrolled temperature (lower T coefficient)
- However, 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)

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

^aData 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.

^bData 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 Hg₂Cl₂.

Indicator Electrodes

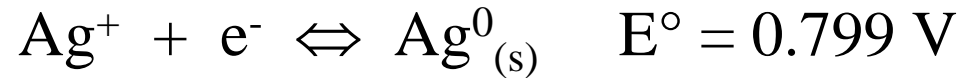
- Two types: metal and membrane indicator electrodes

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

Metal Indicator Electrodes

- These electrodes develop an electric potential in response to a redox reaction at the metal surface.
- These measurements are made against a reference electrode (which has a known, stable potential).
- Typically, Pt or Au are used for the metal indicator electrode as they are inert (do not contribute to the reaction).
- Metal electrodes of the “first kind” respond directly to changing activity of electrode ion – this type of electrode is not selective for a specific analyte.

Example of Metal Indicator Electrode



$$E_+ = 0.799 - 0.05916 \log \left(\frac{1}{[\text{Ag}^+]} \right)$$

$$= 0.799 + 0.05916 \log [\text{Ag}^+]$$

$$E_- = 0.241 \text{ V} \quad (\text{SCE ref.})$$

$$E = E_+ - E_-$$

$$= 0.558 + 0.05916 \log [\text{Ag}^+]$$

The same electrode can be used to measure $[\text{Cl}^-]$ since $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$

$$E = E_+ - E_- = 0.558 + 0.05916 \log \left(\frac{K_{sp}}{[\text{Cl}^-]} \right)$$

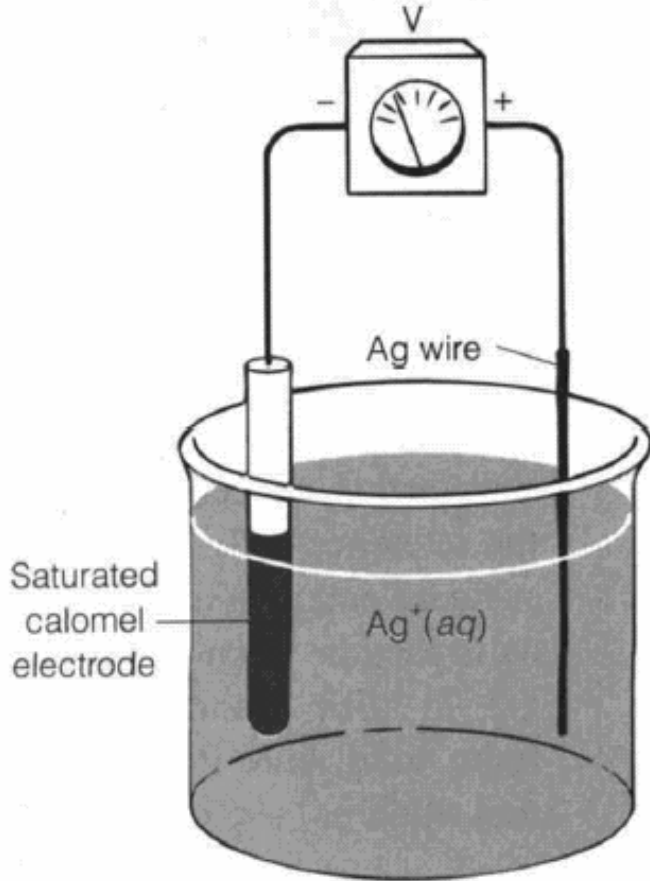


FIGURE 14-1 Use of silver and calomel electrodes to measure the concentration of Ag^+ in a solution.

In general, metal indicator 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 (as seen in example).

Junction Potentials

- Arise because of the differing mobility of different ions in solution
- A charge (potential) develops when one ion moves to an electrode more rapidly than the other ion
- Counteracted by the use of strong electrolytes in solution and/or in the salt-bridge
 - The strong electrolyte helps overcome mobility-induced differences in charge between two cells

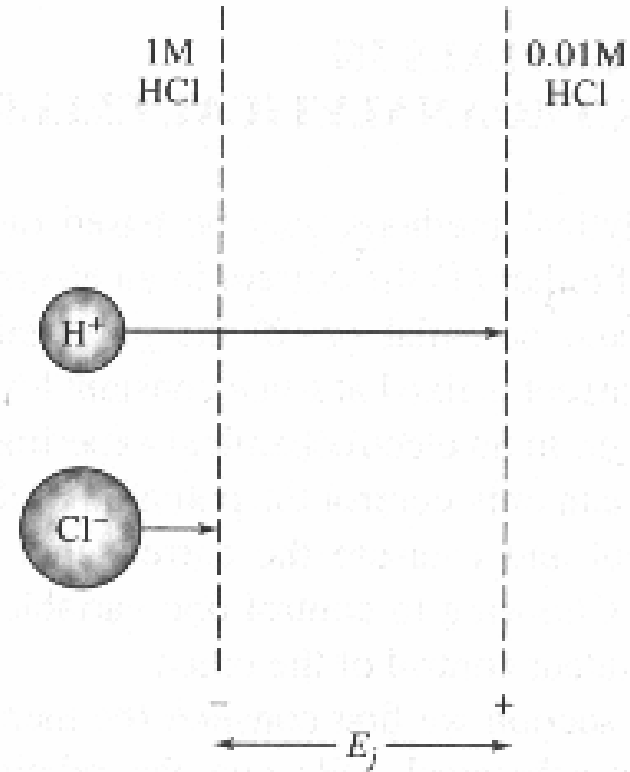


Figure 22-4 Schematic representation of a liquid junction showing the source of the junction potential E_j . The length of the arrows corresponds to the relative mobility of the two ions.

Ion Selective Electrodes

- Physical phenomena which do not involve explicit redox reactions, but whose initial conditions have a non-zero free energy, also will generate a potential.
- An example of this would be ion concentration gradients across a semi-permeable membrane.
- This can also be a potentiometric phenomena, and is the basis of measurements that use *ion-selective electrodes*.

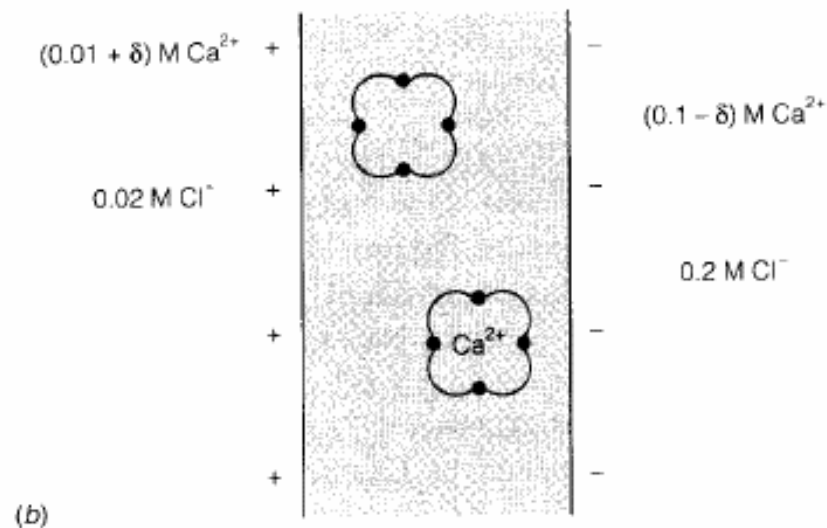
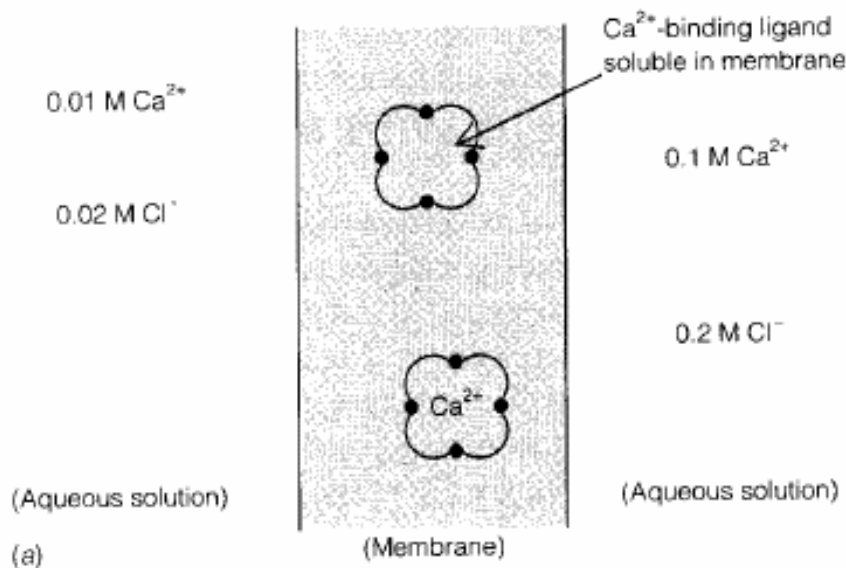
$$E_{\text{mem}} = (\text{constant}) - \frac{RT}{z_i F} \ln(a_i)$$

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
 - Mixed crystal - Ag_2S for S^{2-} and Ag^+



Mechanism of ion-selective electrode:

1. A specific ion crosses the membrane, creating charge imbalance
2. Charge buildup opposes further movement of ion
3. Result: potential difference across membrane is related to difference in concentrations of specific ion on either side

FIGURE 14-5 Mechanism of ion-selective electrode. (a) Initial conditions prior to Ca^{2+} migration across membrane. (b) After δ moles of Ca^{2+} per liter have crossed the membrane, giving the left side a charge of $+2\delta$ mol/L and the right side a charge of -2δ mol/L.

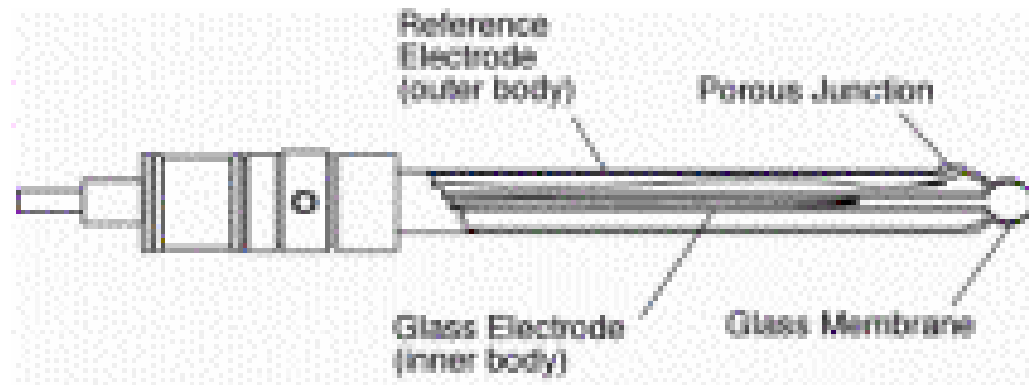
Potential difference across the membrane:

$$E = \frac{0.05916}{n} \log \left(\frac{a_1}{a_2} \right)$$

a_1, a_2 – activities of the ion on both sides of the membrane.

Common ion selective electrode: pH electrode

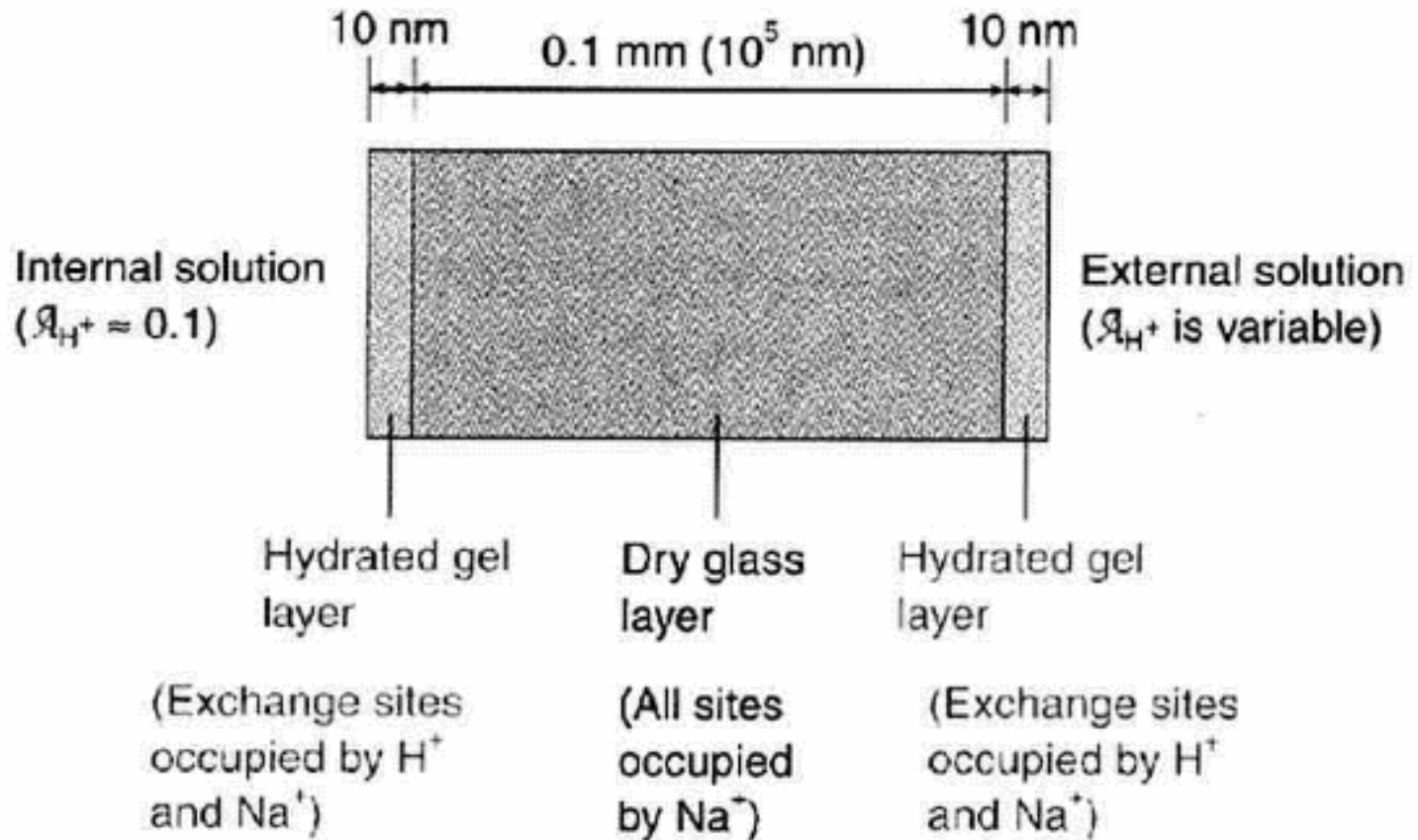
Contains two (reference) electrodes - glass membrane is pH sensitive



Glass Membrane Structure:

SiO₄⁴⁻ framework with charge balancing cations

- SiO₂ 72 %, Na₂O 22 %, CaO 6 %



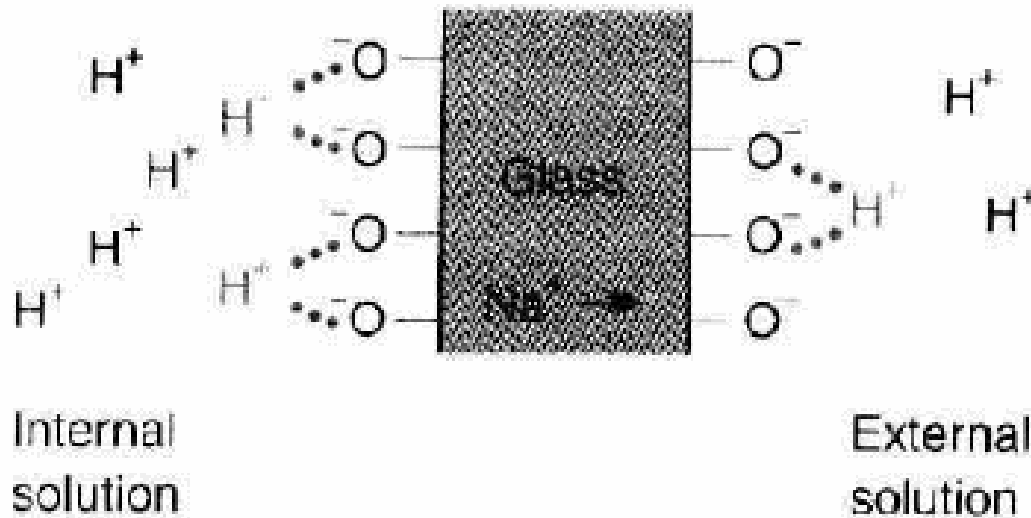


Figure 15-13 Ion-exchange equilibria on the inner and outer surfaces of the glass membrane: H^+ replaces metal cations bound to the negatively charged oxygen atoms. The pH of the internal solution is fixed. As the pH of the external solution (the sample) changes, the electric potential difference across the glass membrane changes.

Alkaline Error:

At high pH, glass electrode indicates pH less than true value
Low $[H^+]$ means membrane exchanges with alkali metal ions in solution also.

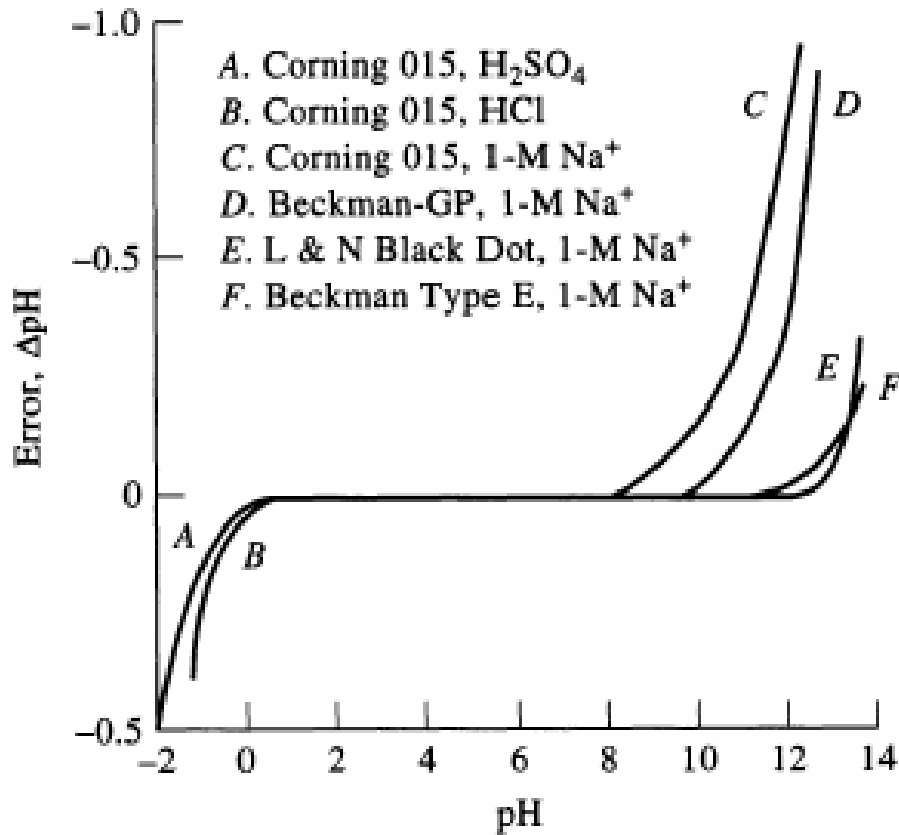


Fig. 23-7