

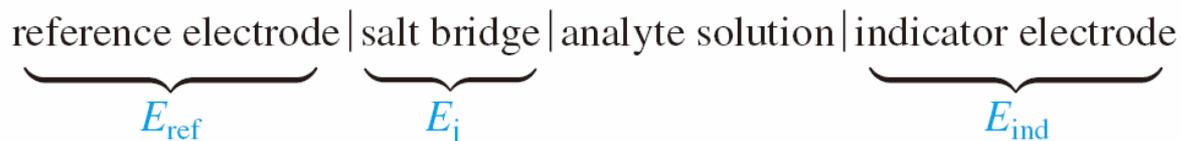
Ch. 23 Potentiometric Methods

Introduction:

1.) *Potentiometric Methods:* based on measurements of the potential of electrochemical cells in the absence of appreciable currents ($i \approx 0$)

2.) *Basic Components:*

- reference electrode: gives reference for potential measurement
- indicator electrode: where species of interest is measured
- salt bridge
- potential measuring device



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

For most electroanalytical methods, the junction potential is small enough to be neglected.

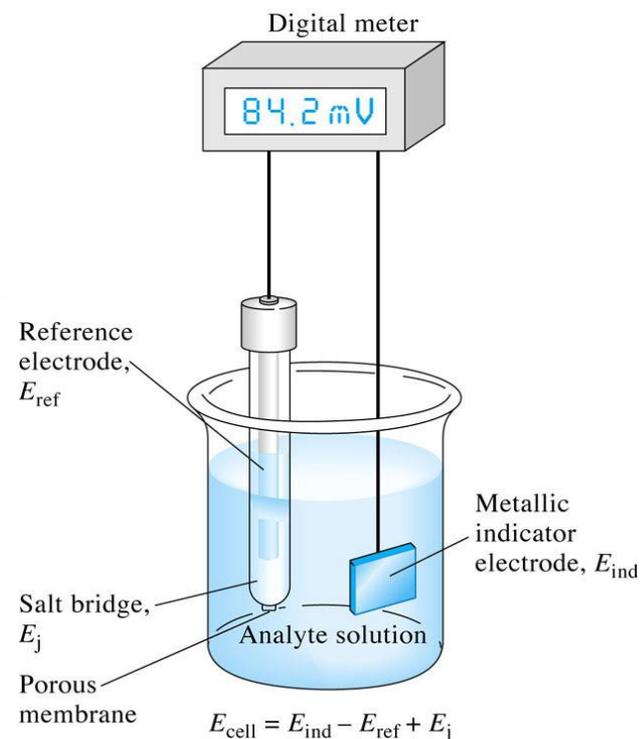


Figure 23.1 A cell for potentiometric determinations

A) Reference Electrodes:

Need one electrode of system to act as a reference against which potential measurements can be made → relative comparison.

Desired Characteristics:

- a) known or fixed potential, E_{ref}
- b) constant response (even when there is a net current in the cell)
- c) insensitive to composition of solution under study
- d) obeys Nernst Equation
- e) reversible
- f) rugged and easy to assemble
- g) Always treated as the left-hand electrode

Common Reference Electrodes used in Potentiometry

- i) Calomel Electrodes (Hg in contact with Hg_2Cl_2 & KCl)
- ii) Silver/Silver Chloride Electrode

A) Reference Electrodes:

1- Saturated Calomel Electrode (SCE)



Note: response is dependent on $[\text{Cl}^-]$, x. Thus, the KCl concentration must be specified in describing the electrode.

- widely used, due to ease of preparation
- equilibration due to temperature change is slow
- leakage of KCl into sample, mercury contamination
 - less common than once they were
 - still preferred for some certain applications

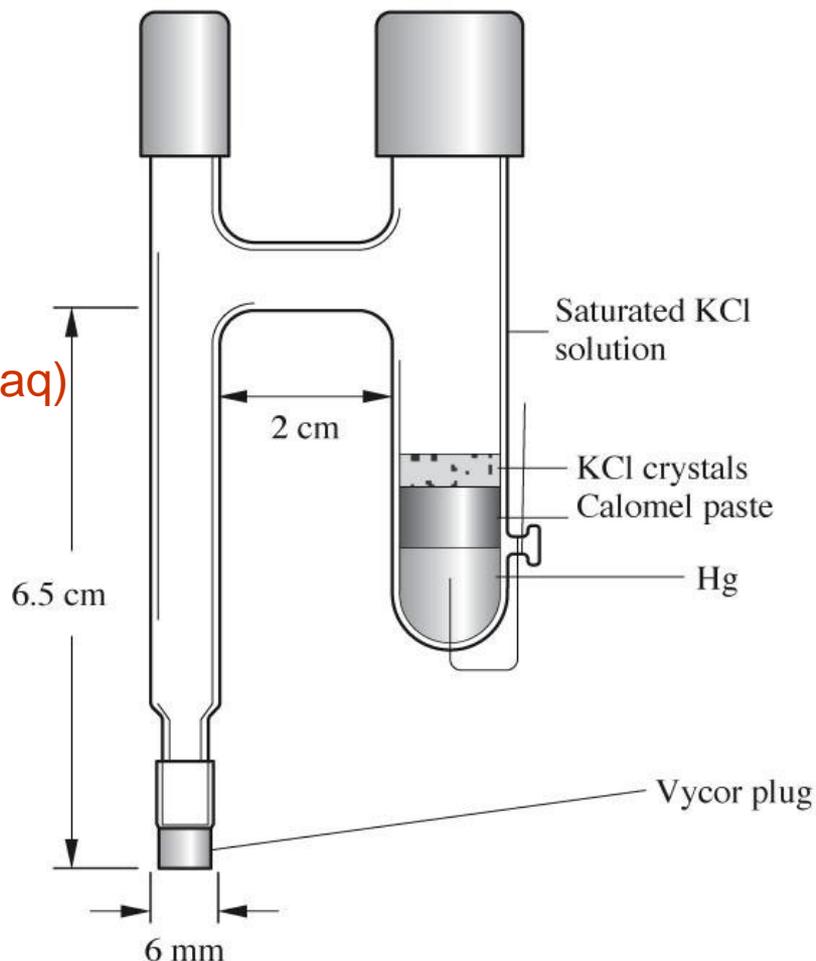


Figure 23.2. A typical SCE

TABLE 23-1 Potentials of Reference Electrodes in Aqueous Solutions

Temperature, °C	Electrode Potential vs. SHE, V				
	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	—	0.184
40	—	0.244	—	0.193	—

- "M" and "saturated" refer to the concentration of KCl and *not* Hg_2Cl_2 .

Table 23-1 lists the composition and the potentials for three common calomel electrodes. Note that each solution is saturated with mercury(I) chloride (calomel) and that the cells differ only with respect to the potassium chloride concentrations.

Temperature coefficient is significantly larger

A) Reference Electrodes:

2- Silver/Silver Chloride Electrode

- most widely used reference electrode system
- Ag electrode immersed in KCl solution saturated with AgCl



Advantage – one advantage over SCE is that Ag/AgCl electrode can be used at temperatures $> 60^\circ\text{C}$

Disadvantage – Ag reacts with more ions,
- plugging of the junction between electrode (Ag) and analyte soln.

- Precautions in the Use of Reference Electrodes

- need to keep level of solution in reference electrode above the level in analyte solution(to prevent rxn of Ag/Hg with analyte)
- need to prevent flow of analyte solution into reference electrode
can result in plugging of electrode at junction → erratic behavior
second salt bridge (non-interfering electrolyte: KNO_3 , NaSO_4)

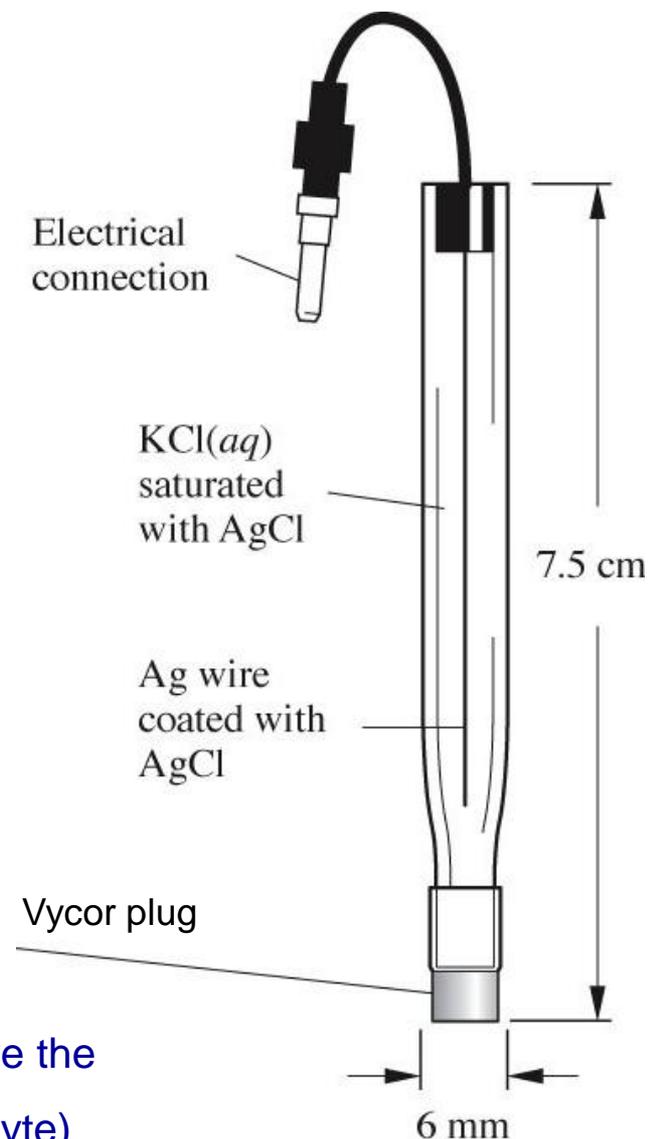


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B) Indicator Electrodes:

- Detects or Responds to Presence of Analyte

Ideal indicator electrode responds *rapidly and reproducibly* to changes in the concentration of an analyte ion (or groups of analyte ions).

Three Common Types:

a) Metallic Indicator Electrodes

Electrodes of the First Kind

Electrodes of the Second Kind

Electrodes of the Third Kind

Metallic Redox Indicators

b) Membrane Indicator Electrodes

Crystalline Membrane Electrodes

Non-crystalline Membrane Electrodes

c) Ion selective Electrode (field effect transistor) ISFET

B) Indicator Electrodes:

Metallic Indicator Electrode (Four Main Types)

a) Metallic Electrodes of the First Kind:

A pure metal electrode that is in direct equilibrium with $X^{n+}(aq) + ne^- \rightleftharpoons X(s)$:

i. Involves single reaction

ii. Detection of cathode derived from the metal used in the electrode

iii. Example: use of copper electrode to detect Cu^{2+} in solution



E_{ind} gives direct measure of Cu^{2+} :

$$E_{ind} = E^{\circ}_{Cu} - (0.0592/2) \log a_{Cu(s)}/a_{Cu^{2+}}$$

since $a_{Cu(s)} = 1$:

$$E_{ind} = E^{\circ}_{Cu} - (0.0592/2) \log 1/a_{Cu^{2+}}$$

or using $pCu = -\log a_{Cu^{2+}}$:

$$E_{ind} = E^{\circ}_{Cu} - (0.0592/2) pCu$$

a) Metallic Electrodes of the First Kind:

Problems

- Electrode of the first kind is not very popular because...
 - metallic indicator electrodes are not very selective and respond not only to their own cations but also to other more easily reduced cations.
 - Many metal electrodes can be used only in neutral or basic solutions because they dissolve in the presence of acids
 - Easily oxidized, can be used only when analyte solutions are deaerated to remove oxygen
 - Certain hard metals (**Fe, Cr, Co, Ni**) do not provide reproducible potentials
- Limited electrodes are:
 - Ag/Ag⁺ and Hg/Hg₂²⁺ in neutral solutions and Cu/Cu²⁺, Zn/Zn²⁺, Cd/Cd²⁺, Bi/Bi³⁺, Tl/Tl⁺, and Pb/Pb²⁺ in deaerated solutions.

B) Indicator Electrodes:

Metallic Indicator Electrode (Four Main Types)

b) Metallic Electrodes of the Second Kind:

Metal electrode respond to the activities of anions that form sparingly soluble precipitates or stable complexes.

i. Example: Detection of Cl^- with Ag electrode



E_{ind} gives direct measure of Cl^- :

$$E_{ind} = E^\circ - (0.0592/1) \log a_{\text{Ag(s)}} a_{\text{Cl}^-} / a_{\text{AgCl(s)}}$$

since $a_{\text{Ag(s)}}$ and $a_{\text{AgCl(s)}} = 1$ & $E^\circ = 0.222 \text{ V}$:

$$E_{ind} = 0.222 - (0.0592/1) \log a_{\text{Cl}^-}$$

B) Indicator Electrodes:

Metallic Indicator Electrode (Four Main Types)

b) Metallic Electrodes of the Second Kind:

ii. Another Example: Detection of EDTA ion (Y^{4-}) with Hg Electrode



E_{ind} responds to $a_{Y^{4-}}$: $E_{ind} = E^{\circ} - (0.0592/2) \log a_{Hg(l)} a_{Y^{4-}}/a_{HgY^{2-}}$

$a_{Hg(l)} = 1$ and $E^{\circ} = 0.21$ V: $E_{ind} = 0.21 - (0.0592/2) \log a_{Y^{4-}}/a_{HgY^{2-}}$

To use this electrode system, it is necessary to introduce a small concentration of HgY_2^- into the analyte solution at the outset. The complex is so stable (for HgY_2^- , $K_f = 6.3 \times 10^{21}$) that its activity remains essentially constant over a wide range of Y^{4-} activities. Therefore, the potential equation can be written in the form

$$E = K - \frac{0.0592}{2} \log a_{Y^{4-}} = \underbrace{K}_{\text{circled}} + \frac{0.0592}{2} pY$$

$$K = 0.21 - \frac{0.0592}{2} \log \frac{1}{a_{HgY^{2-}}}$$

This electrode is useful for locating end points for EDTA titrations.

B) Indicator Electrodes:

Metallic Indicator Electrode (Four Main Types)

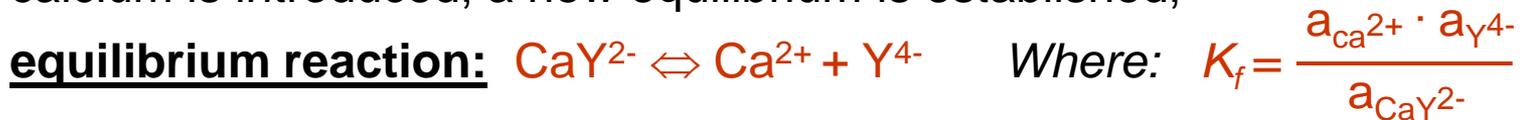
c) Metallic Electrodes of the Third Kind:

- i. Metal electrodes responds to a different cation
- ii. Linked to cation by an intermediate reaction
 - Already saw detection of EDTA by Hg electrode (2nd Kind)
 - Can be made to detect other cations that bind to EDTA → affecting $a_{Y^{4-}}$

Example: A mercury electrode used for the determination of the pCa of calcium containing solutions. As in the previous example, a small concentration of the EDTA complex of Hg(II) is introduced into the solution. The potential of a mercury electrode in this solution is given by

$$E = K - \frac{0.0592}{2} \log a_{Y^{4-}} = K + \frac{0.0592}{2} pY$$

If, in addition, a small volume of a solution containing the EDTA complex of calcium is introduced, a new equilibrium is established,



$$E_{\text{ind}} = K - (0.0592/2) \log. \frac{K_f \cdot a_{\text{CaY}^{2-}}}{a_{\text{Ca}^{2+}}} \qquad a_{\text{Y}^{4-}} = \frac{K_f \cdot a_{\text{CaY}^{2-}}}{a_{\text{Ca}^{2+}}}$$

$$E_{\text{ind}} = K - (0.0592/2) \log. K_f \cdot a_{\text{CaY}^{2-}} - (0.0592/2) \log. \frac{1}{a_{\text{Ca}^{2+}}}$$

If a constant amount of CaY^{2-} is used in the analyte solution and in the solutions for standardization, we may write

$$E_{\text{ind}} = K' - (0.0592/2) \text{pCa.}$$

Where

$$K' = K - (0.0592/2) \log K_f \cdot a_{\text{CaY}^{2-}}$$

Thus, the mercury electrode has become an electrode of the third kind for calcium ion.

B) Indicator Electrodes:

Metallic Indicator Electrode (Four Main Types)

d) Metallic Redox Indicators

i. Electrodes made from inert metals (Pt, Au, Pd) often serve as indicator electrodes for oxidation-reduction systems.

ii. Electrode acts as e^- source/sink for electrons transferred from a redox system in the solution

Example: Detection of Ce^{3+} with Pt electrode



E_{ind} responds to Ce^{4+} : $E_{ind} = E^{\circ} - (0.0592/1) \log a_{Ce^{3+}}/a_{Ce^{4+}}$

Thus, a platinum electrode can serve as the indicator electrode in a titration in which Ce(IV) serves as the standard reagent.

Problems:

- electron-transfer processes at inert electrodes are frequently not reversible
- do not respond predictably to $\frac{1}{2}$ reactions in tables

Membrane Indicator Electrodes

- Electrodes based on determination of cations or anions by the selective adsorption of these ions to a membrane surface
- Often called Ion Selective Electrodes (ISE) or Ion Electrodes, because the data obtained from them are usually presented as p-functions, (pH, pCa, pNO₃)
- The general mechanism by which an ion selective potential develops in these devices depends on the *nature of the membrane* and is entirely different from the source of potential in metallic indicator electrodes.
- We have seen that the potential of a *metallic electrode* arises from the tendency of an *oxidation-reduction reaction to occur at an electrode surface*.
- In membrane electrodes, in contrast, the observed potential is a kind of *junction potential that develops across a membrane* that separates the analyte solution from a reference solution.

Desired properties of ISE's

* *minimal solubility*

- membrane will not dissolve in solution during measurement
- Many membranes are formed from large molecules or molecular aggregates: silica glasses, polymeric resin, low solubility inorganic compounds (AgX) can be used as membranes

* *need some electrical conductivity*

- Generally, this conduction takes the form of migration of singly charged ions within the membrane.

* *selective reactivity with the analyte*

Three types of binding are encountered: ion-exchange, crystallization and complexation. The former two are the more common, and we will largely focus on these types of bindings.

Membrane Indicator Electrodes

a) pH Electrode

i. most common example of an ISE

♣ based on use of glass membrane that preferentially binds H^+

ii. Typical pH electrode system is shown

♣ Two reference electrodes here

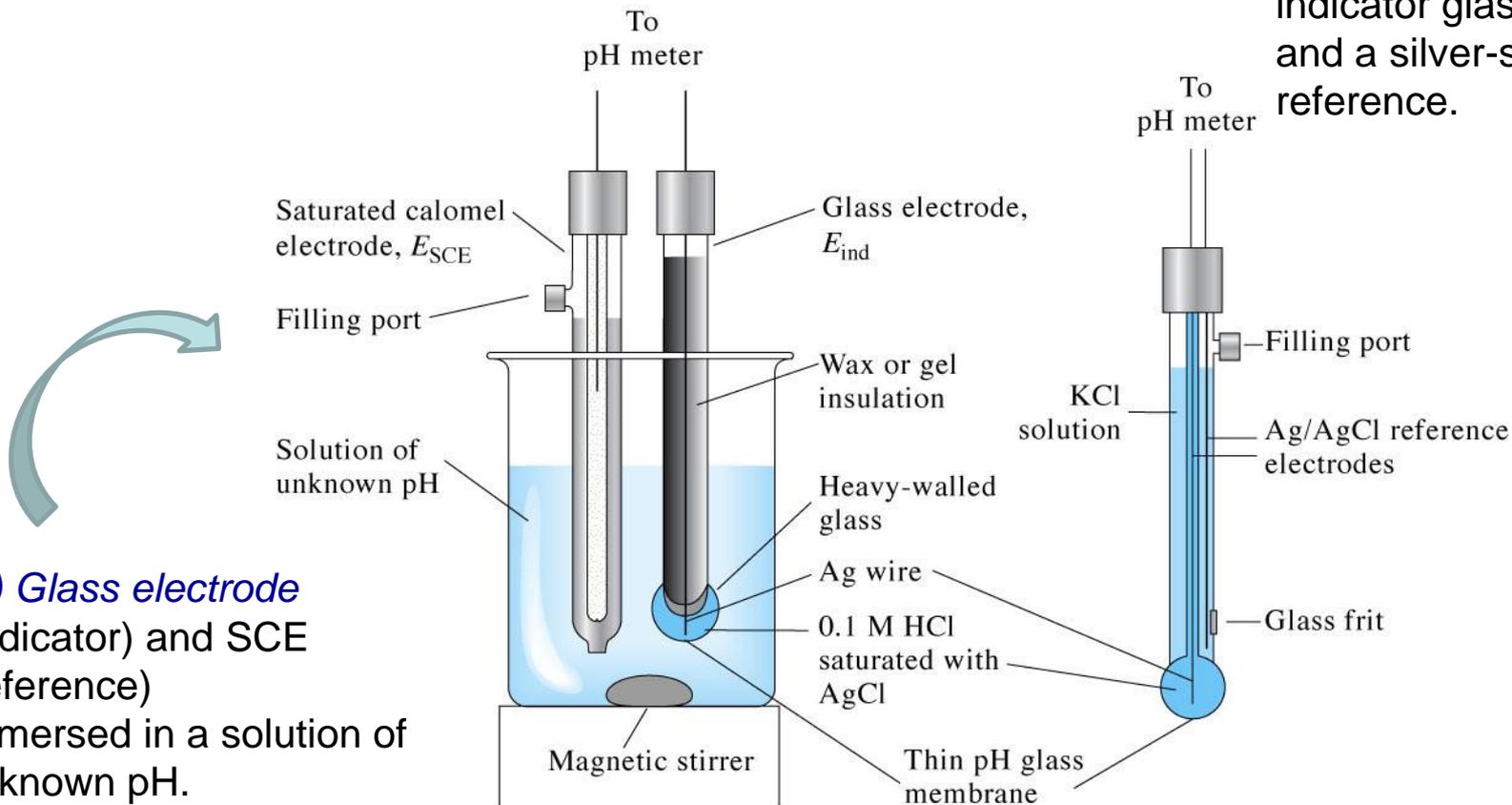
♣ one SCE- outside of membrane

♣ one Ag/AgCl - inside membrane

♣ pH sensing element is glass tip of Ag/AgCl electrode

(b) *Combination probe*

consisting of both an indicator glass electrode and a silver-silver chloride reference.



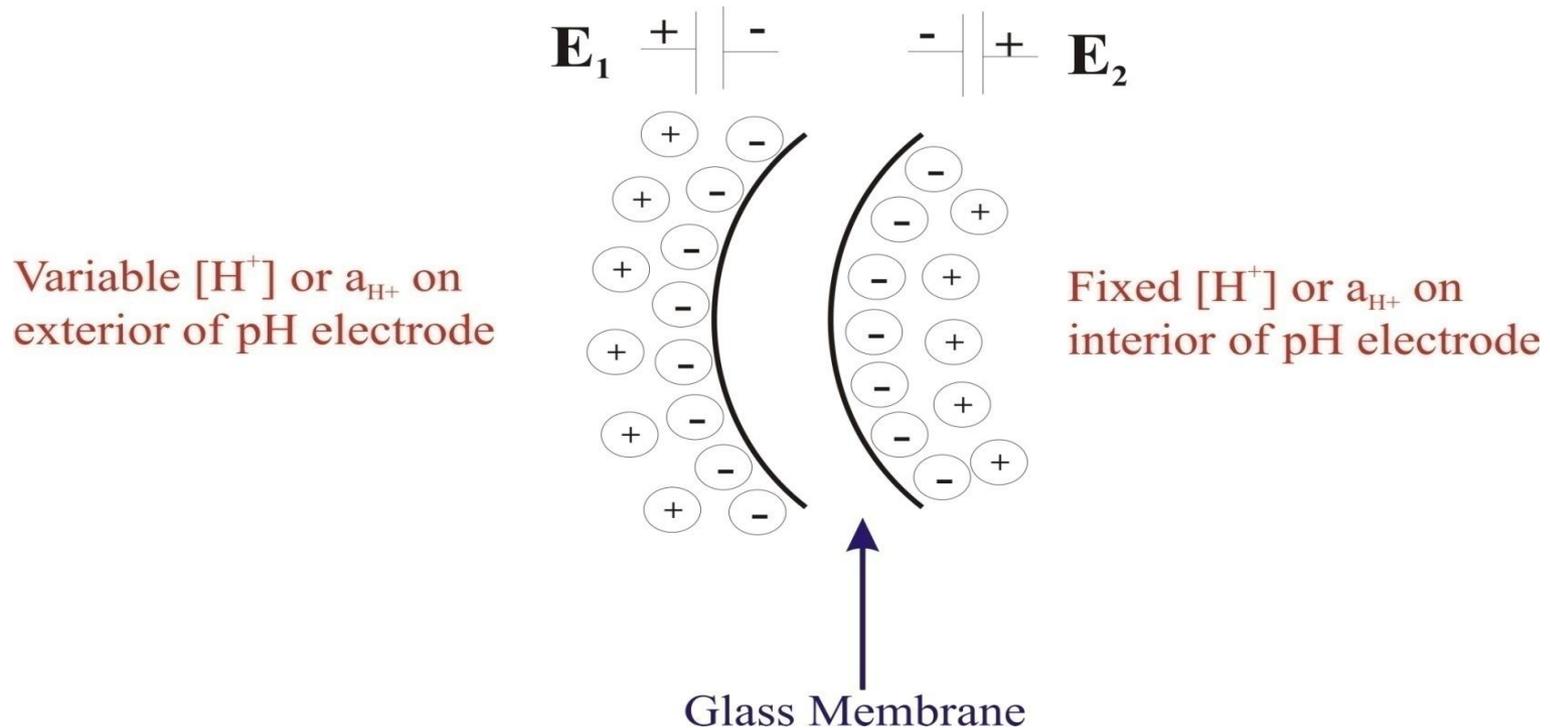
(a) *Glass electrode* (indicator) and SCE (reference)

immersed in a solution of unknown pH.

pH is determined by formation of boundary potential across glass membrane

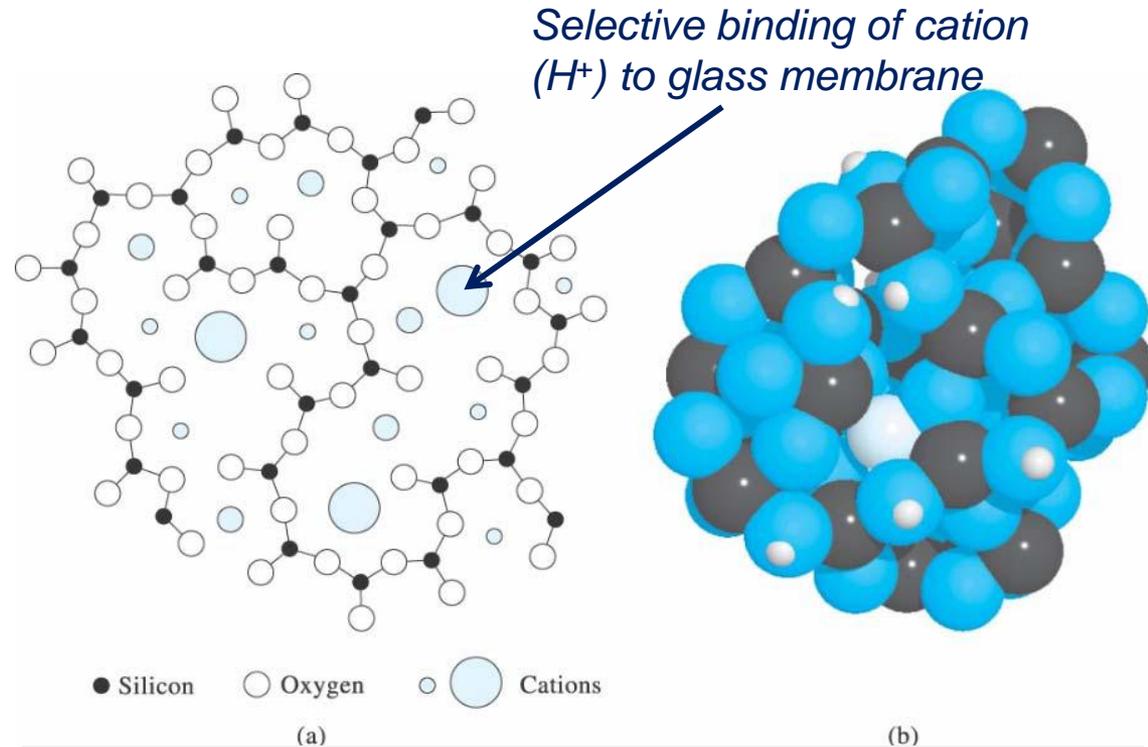
Whenever there is a charge imbalance across any material, there is an electrical potential across the material:

- the concentration of protons inside the membrane is constant, and the concentration outside is determined by the concentration, or activity, of the protons in the analyte solution.
- This concentration difference produces the potential difference that we measure with a pH meter.
- At each membrane-solvent interface, a small local potential develops due to the preferential adsorption of H^+ onto the glass surface.



The Composition and Structure of Glass Membranes

- Glass composition affects the sensitivity of membranes to protons and other cations
- Corning 015 glass, which has been widely used for membranes, consists of approximately 22% Na₂O, 6% CaO, and 72% SiO₂. This membrane is specific in its response toward hydrogen ions up to a pH of about 9. At higher pH values, however, the glass becomes somewhat responsive to sodium, as well as to other singly charged cations
- Other glass formulations are now in use in which sodium and calcium ions are replaced to various degrees by barium and lithium ions. These membranes have superior selectivity at high pH.

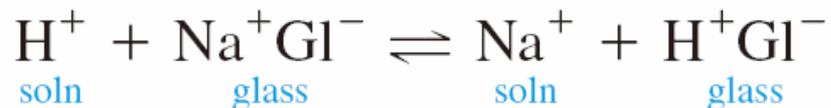


Cross-sectional view of a silicate glass membrane structure. Each silicon atom is shown as being bonded to three oxygen atoms in the plane of the paper. In addition, each is bonded to another oxygen above or below the plane. Thus, the glass consists of an infinite three-dimensional network of SiO₂ groups in which each silicon is bonded to four oxygens and each oxygen is shared by two silicons. Within the interstices of this structure are sufficient cations to balance the negative charge of the silicate groups. Singly charged cations, such as sodium and lithium, are mobile in the lattice and are responsible for electrical conduction within the membrane.

The Hygroscopicity of Glass Membranes

- The surface of a glass membrane must be hydrated before it will function as a pH electrode.
- Nonhygroscopic glasses show no pH function. Even hygroscopic glasses lose their pH sensitivity after dehydration by storage over a desiccant.
- The effect is reversible, however, and the response of a glass electrode can be restored by soaking it in water.

The hydration of a pH-sensitive glass membrane involves an ion-exchange reaction between singly charged cations in the interstices of the glass lattice and protons from the solution:



The equilibrium constant for this process is so large that the surface of a hydrated glass membrane ordinarily consists entirely of silicic acid (H +Gl-) groups.

Electrical Conduction across Glass Membranes

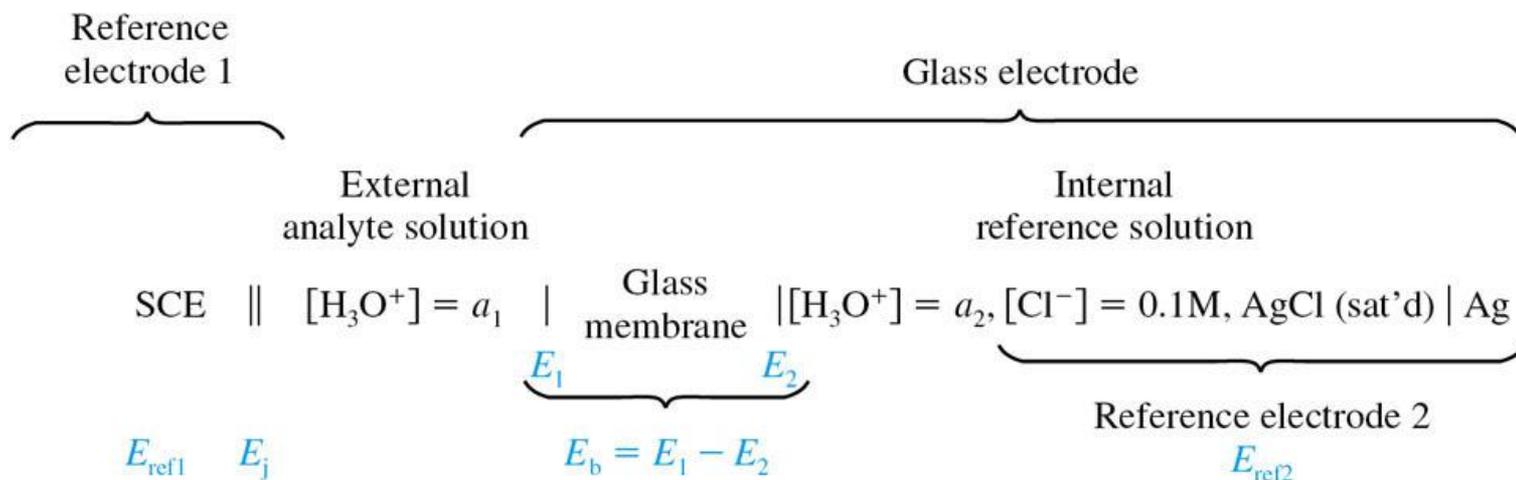
To serve as an indicator for cations, a glass membrane must conduct electricity. Conduction within the hydrated gel layer involves the movement of hydrogen ions. Sodium ions are the charge carriers in the dry interior of the membrane.

Conduction across the solution-gel interfaces occurs by the reactions



Cell Potentials

- The potentials of the two reference electrodes
 - depend on the electrochemical characteristics of their respective redox couples
- The potential across the glass membrane:
 - depends on the physicochemical characteristics of the glass and its response to ionic concentrations on both sides of the membrane

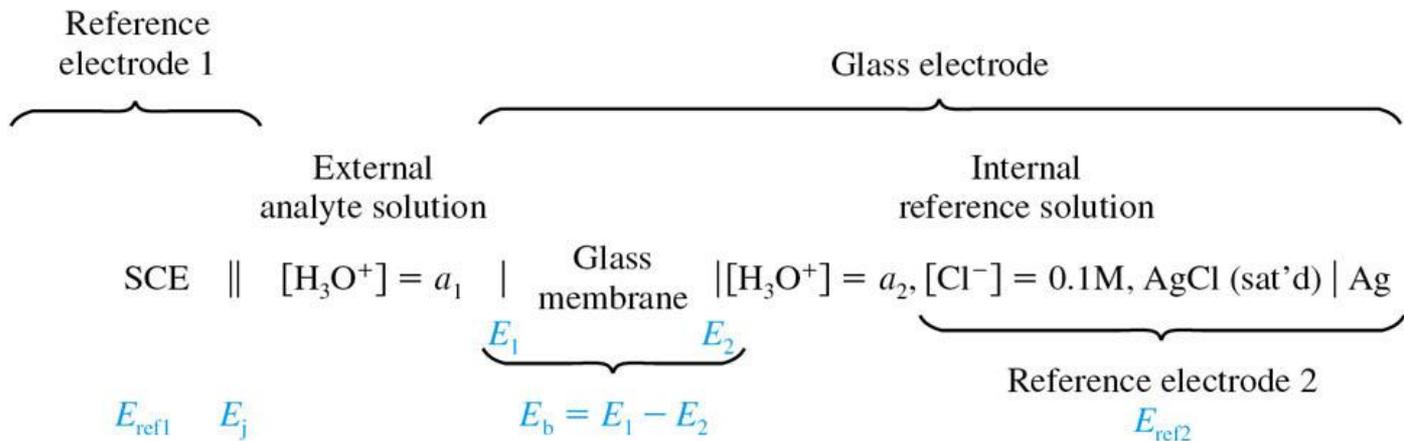


- 4 potentials:

- $E_{\text{Ag,AgCl}}$ and E_{SCE} , are reference electrode potentials that are constant.
- A 3rd potential is the junction potential E_j across the salt bridge that separates the calomel electrode from the analyte solution.
- The 4th and most important potential is the *boundary potential*, E_b , which varies with the pH of the analyte solution.

pH is determined by formation of boundary potential across glass membrane

Boundary Potential



The boundary potential is determined by potentials, E_1 and E_2 , which appear at the two surfaces of the glass membrane from the reactions:



- where subscript 1 refers to the interface between the exterior of the glass and the analyte solution and subscript 2 refers to the interface between the internal solution and the interior of the glass.
- These two reactions cause the two glass surfaces to be negatively charged with respect to the solutions with which they are in contact.

Boundary Potential

- The resulting difference in potential between the two surfaces of the glass is the boundary potential, which is related to the activities of hydrogen ion in each of the solutions by the Nernst-like equation:

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

– where a_1 is the activity of the analyte solution and a_2 is that of the internal solution.

- For a glass pH electrode, the hydrogen ion activity of the internal solution is held constant:

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

– with $L' = -0.0592 \log a_2$

The boundary potential is then a measure of the hydrogen ion activity of the external solution (a_1)

The Asymmetry Potential

- When identical solutions are placed on the two sides of a glass membrane, the boundary potential should in principle be zero (see Figure 23-6b). In fact, however we frequently encounter a small asymmetry potential that changes gradually with time due to slight imperfections in the membrane
- The sources of the asymmetry potential are obscure but undoubtedly include such causes as differences in strain on the two surfaces of the membrane created during manufacture, mechanical abrasion on the outer surface during use, and chemical etching of the outer surface.
 - To eliminate the bias caused by the asymmetry potential, all membrane electrodes must be calibrated against one or more standard analyte solutions.
 - Such calibrations should be carried out at least daily, and more often when the electrode receives heavy use.

The Glass Electrode Potential

- The potential of a glass indicator electrode E_{ind} has three components:
 - the boundary potential
 - the potential of the internal Ag/AgCl reference electrode
 - the small asymmetry potential which changes slowly with time

$$E_{ind} = E_b + E_{Ag/AgCl} + E_{asy}$$

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

$$E_{ind} = L' + 0.0592 \log a_1 + E_{Ag/AgCl} + E_{asy}$$

$$E_{ind} = L + 0.0592 \log a_1 = L - 0.0592 \text{ pH}$$

where L is a combination of the three constant terms

$$L = L' + E_{Ag/AgCl} + E_{asy}$$

Alkali Error

In basic solutions, glass electrodes respond to the concentration of not only hydrogen ion but alkali metal ions.

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

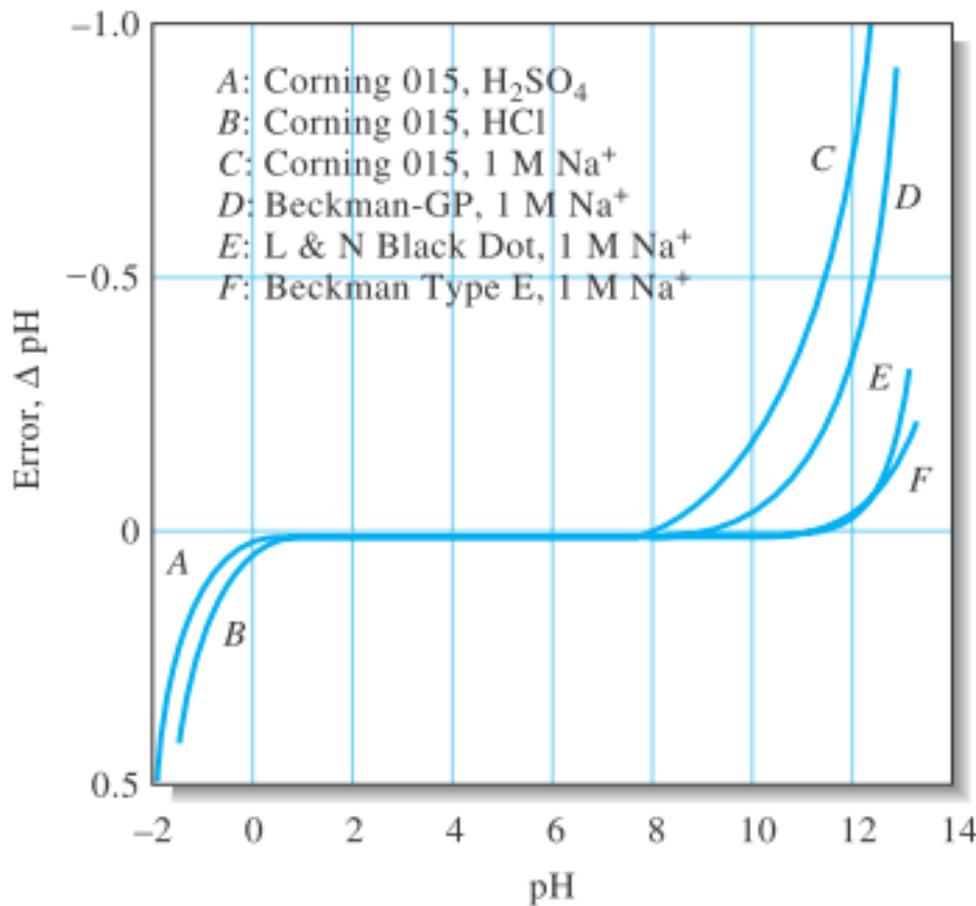
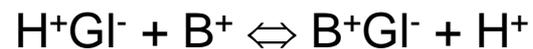


Figure 21-11 Acid and alkaline errors for selected glass electrodes at 25°C.

The alkaline error can be satisfactorily explained by assuming an exchange equilibrium between the hydrogen ions on the glass surface and the cations in solution.



where B⁺ represents some singly charged cation, such as sodium ion. In this case, the activity of the sodium ions relative to that of the hydrogen ions becomes so large that the electrode responds to both species.

Most significant when [H⁺] or a_{H⁺} is low (high pH) - usually pH ≈ 11-12

Selectivity Coefficient

The effect of an alkali metal ion on the potential across a membrane can be accounted for by inserting an additional term called the selectivity coefficient ($k_{H,B}$), which is a measure of the response of an ion-selective electrode to other ions.

$$E_b = L' + 0.0592 \log (a_1 + k_{H,B}b_1)$$

Selectivity coefficients range from zero (no interference) to values greater than unity.

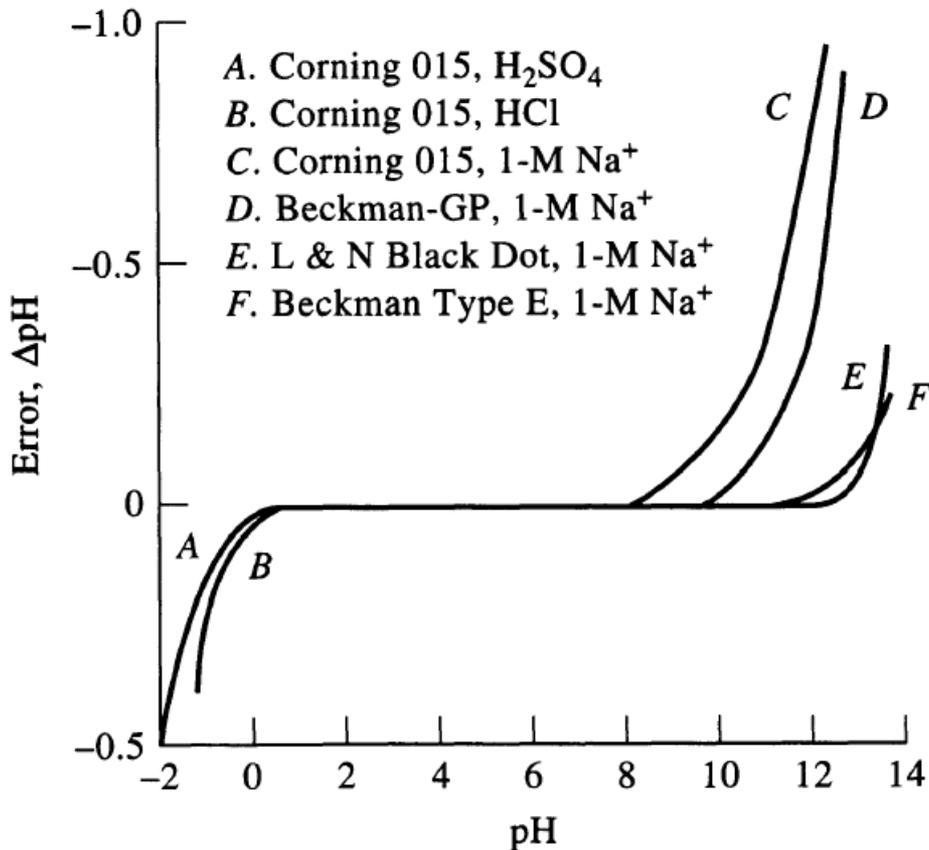
- A selectivity coefficient of unity means the electrode responds equally to the analyte ion and the interfering ion.
- If an electrode for ion A responds 20 times more strongly to ion B than to ion A, then $k_{A,H}$ has a value of 20.
- If the response of the electrode to ion C is 0.001 of its response to A (a much more desirable situation), $k_{A,C}$ is 0.001

Acid Error

The typical glass electrode exhibits an error, opposite in sign to the alkaline error, in solution of pH less than about 0.5.

➤ The negative error ($\text{pH}_{\text{read}} - \text{pH}_{\text{true}}$) indicates that pH readings tend to be too high in this region

② Exact cause not known



Glass Electrodes for Other Cations

To eliminate the alkaline error in glass electrodes, several other glass electrodes have been developed using different compositions that include Al_2O_3 or B_2O_3 . This enhances binding for ions other than H^+

Glass electrodes that permit the direct potentiometric measurement of such singly charged species as Na^+ , K^+ , NH_4^+ , Rb^+ , Cs^+ , Li^+ , and Ag^+ have been developed.

23D-5 Crystalline Membrane Electrode

- The most important type of crystalline membranes is manufactured from an *ionic compound* or a homogeneous mixture of ionic compounds.
- In some instances the membrane is cut from a *single crystal*; in others, disks are formed from the *finely ground crystalline solid by high pressures or by casting from a melt*.
- Typical membranes have a diameter of about 10 mm and a thickness of 1 or 2 mm.
- To form an electrode, a membrane is sealed to the end of a tube made from a chemically inert plastic such as Teflon or polyvinyl chloride (PVC).

Conductivity of Crystalline Membranes

Most ionic crystals are insulators and do not have sufficient electrical conductivity at room temperature to be used as membrane electrodes. Those that are conductive are characterized by having a small singly charged ion that is mobile in the solid phase.

Examples are

- fluoride ion in certain rare earth fluorides,
- silver ion in silver halides and sulfides, and
- copper(I) ion in copper(I) sulfide.

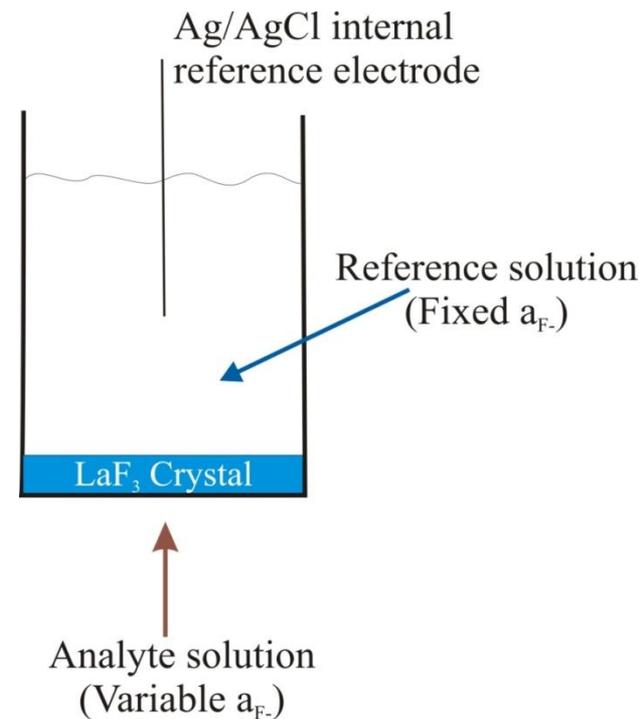
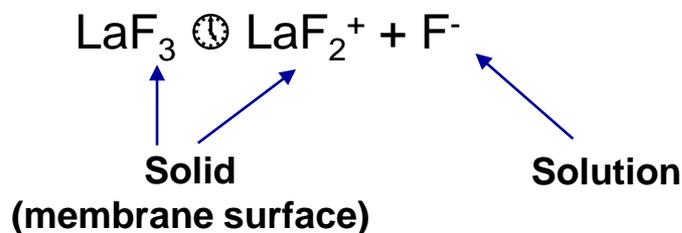
TABLE 21-3

Characteristics of Solid-State Crystalline Electrodes*		
Analyte Ion	Concentration Range, M	Major Interferences
Br ⁻	10 ⁰ to 5 × 10 ⁻⁶	CN ⁻ , I ⁻ , S ²⁻
Cd ²⁺	10 ⁻¹ to 1 × 10 ⁻⁷	Fe ²⁺ , Pb ²⁺ , Hg ²⁺ , Ag ⁺ , Cu ²⁺
Cl ⁻	10 ⁰ to 5 × 10 ⁻⁵	CN ⁻ , I ⁻ , Br ⁻ , S ²⁻ , OH ⁻ , NH ₃
Cu ²⁺	10 ⁻¹ to 1 × 10 ⁻⁸	Hg ²⁺ , Ag ⁺ , Cd ²⁺
CN ⁻	10 ⁻² to 1 × 10 ⁻⁶	S ²⁻ , I ⁻
F ⁻	Sat'd to 1 × 10 ⁻⁶	OH ⁻
I ⁻	10 ⁰ to 5 × 10 ⁻⁸	CN ⁻
Pb ²⁺	10 ⁻¹ to 1 × 10 ⁻⁶	Hg ²⁺ , Ag ⁺ , Cu ²⁺
Ag ⁺ /S ²⁻	Ag ⁺ : 10 ⁰ to 1 × 10 ⁻⁷ S ²⁻ : 10 ⁰ to 1 × 10 ⁻⁷	Hg ²⁺
SCN ⁻	10 ⁰ to 5 × 10 ⁻⁶	I ⁻ , Br ⁻ , CN ⁻ , S ²⁻

*From *Orion Guide to Ion Analysis*, Boston, MA: Thermo Orion, 1992.

Fluoride Electrode

- ✓ LaF_3 crystal doped with EuF_2
- ✓ mechanism similar to pH electrode with potential developing at two interfaces of the membrane from the reaction



$$\begin{aligned}
 E_{\text{ind}} &= L + 0.0592 \log \frac{1}{a_{\text{F}^-}} \\
 &= L - 0.0592 \log a_{\text{F}^-} \\
 &= L + 0.0592 \text{pF}
 \end{aligned}$$

⑧ the side of the membrane with the lower a_{F^-} becomes positive relative to the other surface:

- Commercial lanthanum fluoride electrodes are available from several sources., rugged Most are rugged, 0 and 80°C.
- The response is linear down to 10^{-6} M (0.02 ppm), where the solubility of lanthanum fluoride begins to contribute to the concentration of fluoride ion in the analyte soln.
- The only ion that interferes directly with fluoride measurements is hydroxide ion; this interf. e becomes serious at $\text{pH} > 8$. At $\text{pH} < 5$, hydrogen ions also interf. in total fluoride determinations.
- Under these conditions, undissociated hydrogen fluoride forms, and the electrode does not respond to this species.

Electrodes Based on Silver Salts

- Membranes prepared from single crystals or pressed disks of the various silver halides are selective toward silver and halide ions.
- Their behavior is generally far from ideal, however, because of low conductivity, low mechanical strength, and a tendency to develop high photoelectric potentials.
- These disadvantages are minimized if the silver salts are mixed with crystalline silver sulfide in an approximately 1:1 molar ratio. Homogeneous mixtures are formed from equimolar solutions of sulfide and halide ions by precipitation with silver nitrate.
- After washing and drying, the product is shaped into disks under a pressure of about 10' pounds per square inch.
- The resulting disk exhibits good electrical conductivity because of the mobility of the silver ion in the sulfide matrix.
- Membranes constructed either from silver sulfide or from a mixture of silver sulfide and another silver salt are useful for the determination of both sulfide and silver ions.
- Toward silver ions, the electrical response is similar to a metal electrode of the first kind (although the mechanism of activity is totally different).
- The electrical response of a silver sulfide membrane to sulfide ions is similar to that of an electrode of the second kind.
- When the membrane is immersed in the analyte solution, a minuscule amount of silver sulfide dissolves and quickly saturates the film of liquid adjacent to the electrode. The solubility, and thus the silver ion concentration, however, depends on the sulfide concentration of the analyte.
- Crystalline membranes are also available that consist of a homogeneous mixture of silver sulfide with sulfides of copper(U), lead, or cadmium. Toward these divalent cations, electrodes from these materials have electrical responses similar to electrodes of the third kind.
- Note that these divalent sulfides, by themselves, are not conductors and thus do not exhibit ion-selective activity..

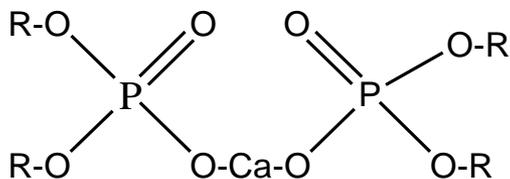
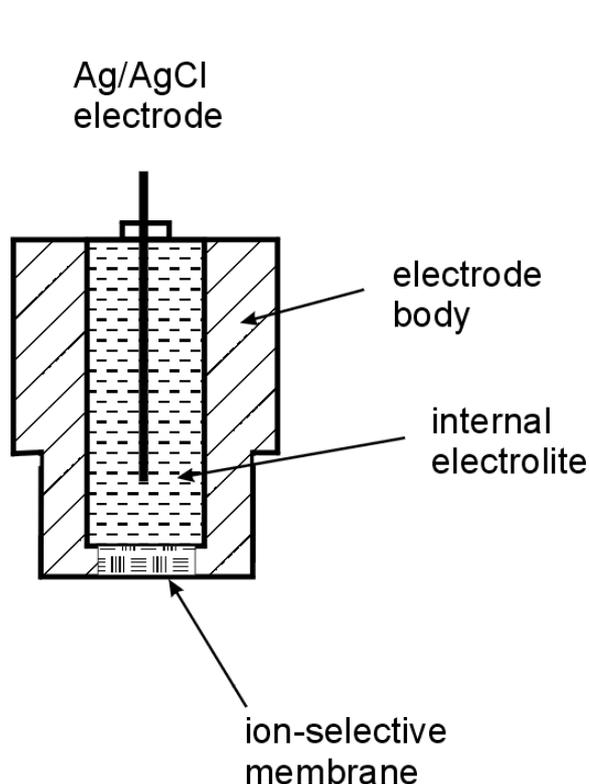
23D-6 Liquid Membrane Electrode

Liquid membranes are formed from immiscible liquids that selectively bond certain ions. Membranes of this type are particularly important because they permit the direct potentiometric determination of the activities of several polyvalent cations and of certain singly charged anions and cations as well

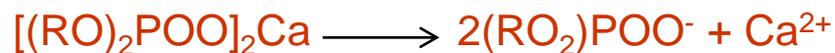
② “Membrane” usually consists of organic liquid (not soluble in sample) held by porous disk between aqueous reference solution and aqueous sample solution.

② Membrane has ability to selectively bind ions of interest

Example: Calcium dialkyl phosphate Liquid membrane electrodes



At solution/membrane interfaces:



Organic
(membrane)

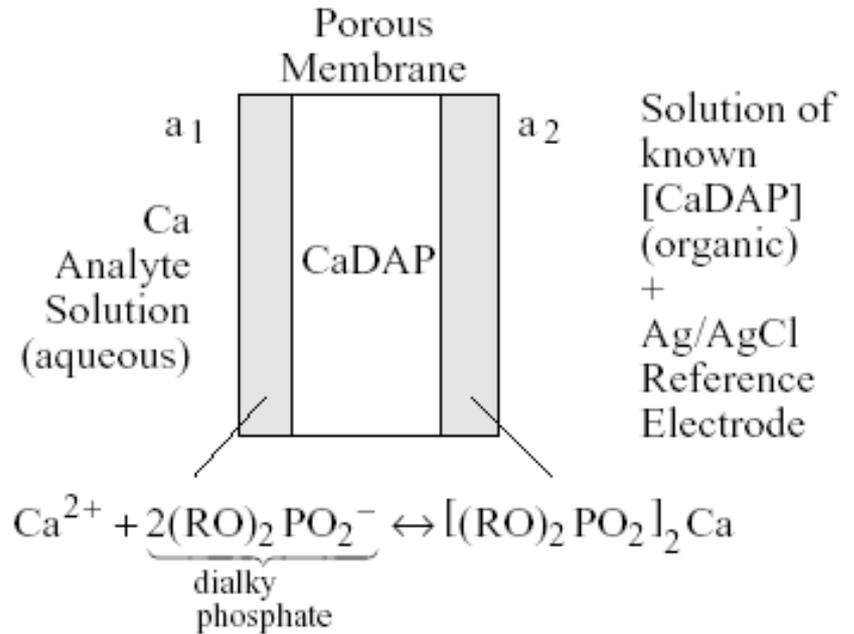
Organic
(membrane surface)

Solution
(aqueous sample)

⑧ the side of the membrane with the lower $a_{\text{Ca}^{2+}}$ becomes negative relative to the other surface:

Liquid membrane electrodes

- Based on potential that develops across two immiscible liquids with different affinities for analyte
- Porous membrane used to separate liquids
- Selectively bond certain ions
 - Activities of different cations
- Calcium dialkyl phosphate insoluble in water, but binds Ca^{2+} strongly
- The active substances in liquid membranes are of three kinds:
 - (1) cation exchangers;
 - (2) anion exchangers;and
 - (3) neutral macrocyclic compounds, which selectively complex certain cations.



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

If a_2 is constant

$$\begin{aligned}
 E_b &= N + \frac{0.0592}{2} \log a_1 \\
 &= N - \frac{0.0592}{2} \text{pCa}
 \end{aligned}$$

Liquid Membrane Electrode

- ② Can design Liquid Membrane Electrodes for either cations or anions
- cations → use cation exchangers in membrane
 - anions → use anion exchangers in membrane

Analyte Ion	Concentration Range, M	Interferences ^c
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}	$3 \times 10^{-4} \text{Cs}^+$; $6 \times 10^{-3} \text{NH}_4^+$, Tl^+ ; 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^+

- **Ion-Sensitive Field Effect Transistors (ISFETs)**

- The field effect transistor, or the metal oxide field effect transistor (MOSFET), is a tiny solid-state semiconductor device that is widely used in computers and other electronic circuits as a switch to control current flow in circuits.
- Its drawback is its pronounced sensitivity to ionic surface impurities.

Since 1970 much has been accomplished in exploiting the sensitivity of MOSFETs to surface ionic impurities for the selective potentiometric determination of various ions. These studies have led to the development of a number of different *ion-selective field-effect transistors (ISFETs)*. *The*

- ISFETs offer significant advantages over membrane electrodes including ruggedness, small size, inertness toward harsh environments, rapid response, and low electrical impedance.

23-F Molecular Selective Electrodes

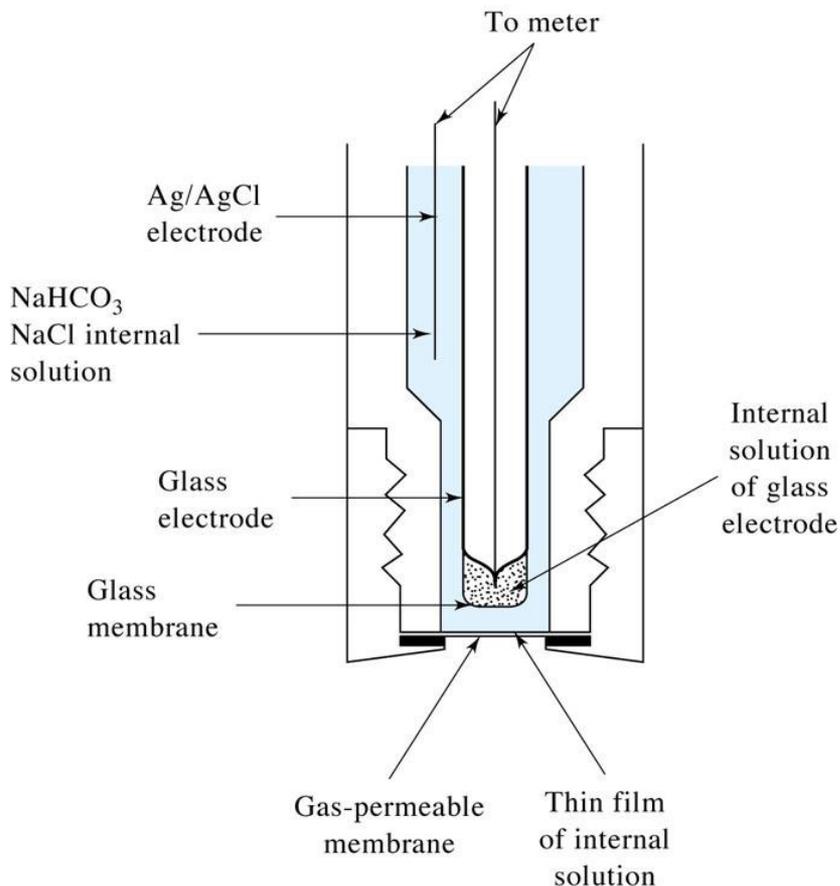
i. Electrodes designed for the detection of molecules instead of ions

ii. Gas sensing electrodes (or gas-sensing probes)

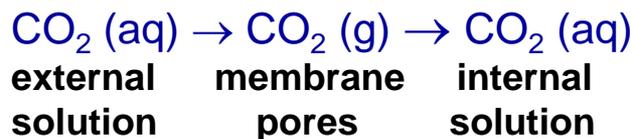
② Typically based on ISE surrounded by electrolyte solution

- activity of ion measured is affected by dissolved gas
- gas enters interior solution from sample by passing through a gas permeable membrane

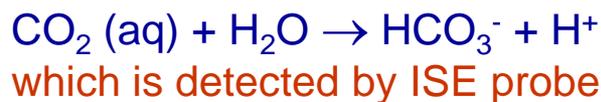
O_2 , NH_3/NH_4^+ , and $CO_2/HCO_3^-/CO_3^{2-}$



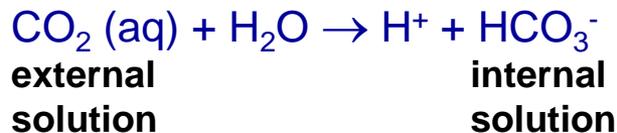
Gas effuses through membrane:



In internal solution, pH changes:



Overall reaction:



$$E_{\text{ind}} = L' + 0.0592 \log [CO_2]_{\text{ext}}$$

iii. Enzyme electrodes (or Biocatalytic Membrane Electrodes)

② General approach is to use an immobilized enzyme

- enzyme converts a given molecular analyte into a species that can be measured electrochemically

✱ enzyme substrate

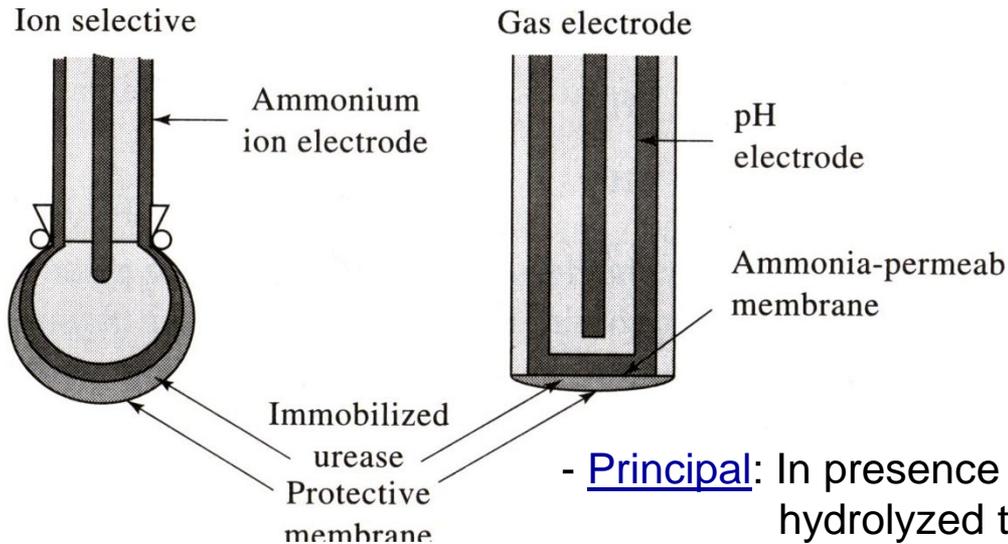
- Examples:

H^+ → pH electrode

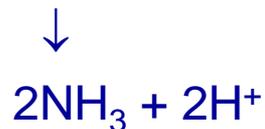
CO_2 → CO_2 gas sensing electrode

NH_4^+ → NH_4^+ ISE

② Example – Urea Enzyme Electrode



- Principal: In presence of enzyme *urease*, urea $(NH_4)_2CO$ is hydrolyzed to give NH_3 and H^+



Monitor amount of NH_3 produced using NH_3 gas sensing electrode

23 G Instruments for measuring cell potential

- Most cells containing a membrane electrode have very high electrical resistance. 100 M Ω or more,
- In order to measure potentials of such high-resistance circuits accurately, it is necessary that the voltmeter have an electrical resistance that is several orders of magnitude greater than the resistance of the cell being measured. (at least 10^{12} Ω .)
- If the meter resistance is too low, current is drawn from the cell, which has the effect of lowering its output potential (IR drop), thus creating a negative loading error.

Example: The true potential of a glass-calomel electrode system is 0.800 V; Its internal resistance is 20 M Ω . What would be the relative error in the measured potential if the measuring device has a resistance of 100 M Ω

From Ohm's law, we may write $E_s = IR_s + IR_m$

I is the current in this circuit consisting of the cell and the measuring device . The current is then given by

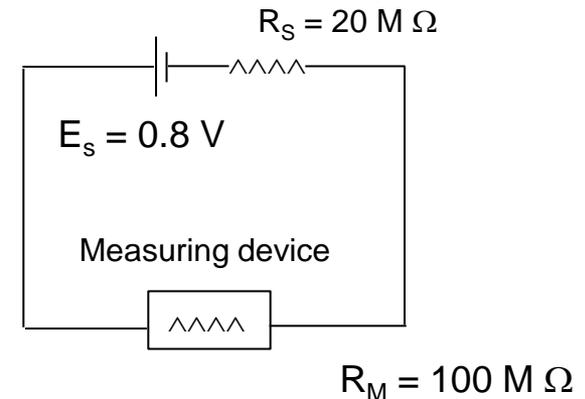
$$I = 0.8 / (20+100) \times 10^6 \Omega = 6.67 \times 10^{-9} \text{ A}$$

The potential drop across the measuring device

$$E_m = (6.67 \times 10^{-9} \text{ A}) \times (100 \times 10^6 \Omega) = 0.667 \text{ V}$$

$$\text{Relative error: } (0.667 \text{ V} - 0.8 \text{ V}) / 0.8 \text{ V} \times 100\% = -17 \%$$

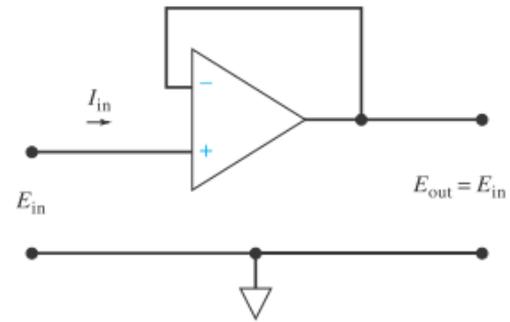
We can easily show that to reduce the loading error to 1%, the resistance of the voltage measuring device must be about 100 times greater than the cell resistance; for a relative error of 0.1%, the resistance must be 1000 times greater.



Numerous high-resistance, direct-reading digital voltmeters with internal resistances of $>10^{11}$ ohms called pH meters or plan meters or ion meters are available.

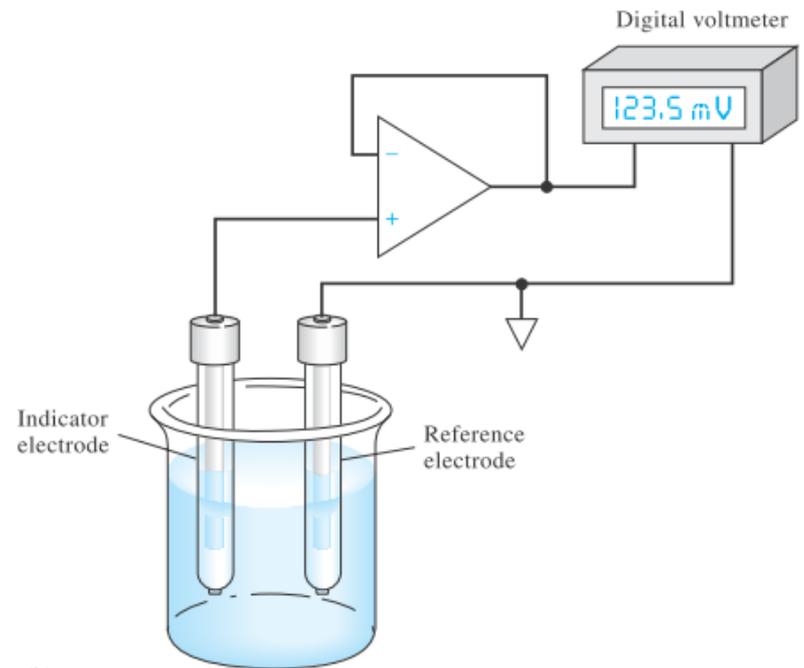


Figure 21-16 Photo of a typical benchtop pH meter. (Courtesy of Mettler Toledo, Inc., Columbus, OH.)



(a)

Figure 21F-7 (a) A voltage-follower operational



(b)

amplifier. (b) Typical arrangement for potentiometric measurements with a

23-H Direct potentiometric measurements

Direct potentiometric measurements provide a rapid and convenient method for determining the activity of a variety of cations and anions.

The technique requires only a comparison of the potential developed in a cell containing the indicator electrode in the analyte solution with its potential when immersed in one or more standard solutions of known analyte concentration.

23-H1 Equations Governing Direct Potentiometry

For direct potentiometric measurements, the potential of a cell can then be expressed in terms of the potentials developed by the indicator electrode, the reference electrode, and a junction potential,

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

For the cation X^{n+} at 25°C, the electrode response takes the general Nernstian form

$$E_{\text{ind}} = L - \frac{0.0592}{n} pX = L + \frac{0.0592}{n} \log a_X$$

Substitution and rearrangement leads to

The constant terms can be combined to give a new constant K,

For an anion A-

When the two equations are solved for E_{cell} , we find that for cations

and anions

$$pX = -\log a_x = -\left[\frac{E_{cell} - (E_j - E_{ref} + L)}{0.0592/2} \right]$$

$$pX = -\log a_x = -\frac{(E_{cell} - K)}{0.0592/n} = -\frac{n(E_{cell} - K)}{0.0592}$$

$$pA = \frac{(E_{cell} - K)}{0.0592/n} = \frac{n(E_{cell} - K)}{0.0592}$$

$$E_{cell} = K - \frac{0.0592}{n} pX$$

$$E_{cell} = K + \frac{0.0592}{n} pA$$

23H-2 The Electrode-Calibration Method

The electrode-calibration method is also referred to as the method of external standards.

The electrode-calibration method offers the advantages of simplicity, speed, and applicability to the continuous monitoring of pX or pA.

However, there is an inherent error (of the order of ≥ 1 mV) in the electrode calibration method that results from the assumption that K remains constant after calibration.

The magnitude of the error can be obtained as:

$$-\log_{10} e \frac{da_x}{a_x} = -0.434 \frac{da_x}{a_x} = -\frac{dK}{0.0592/n}$$

$$\text{Percent relative error} = \frac{\Delta a_x}{a_x} \times 100\% = 38.9n\Delta K \times 100\%$$

Activity vs Concentration

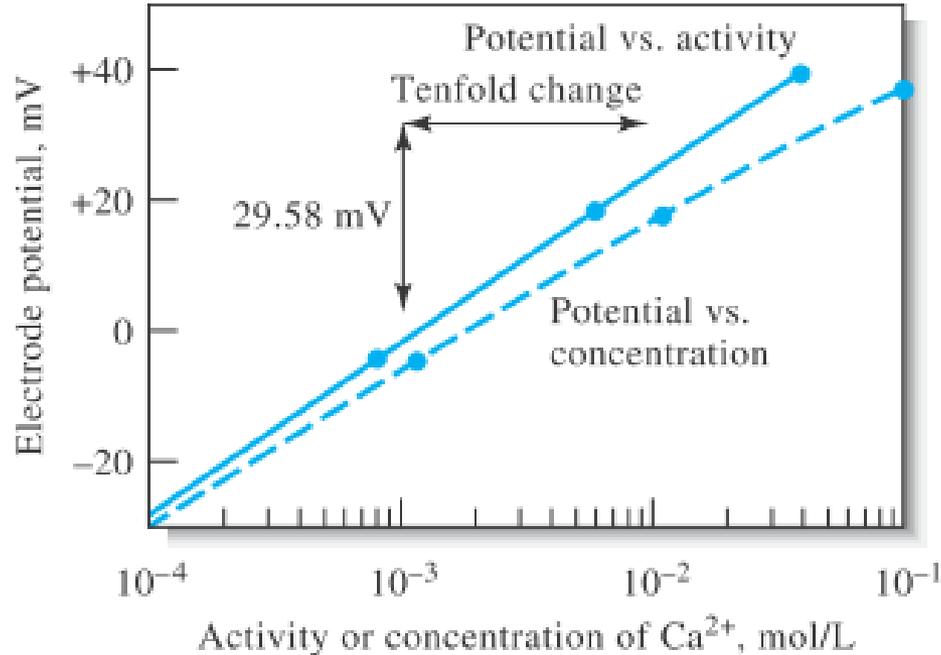


Figure 21-17 Response of a liquid-membrane electrode to variations in the concentration and activity of calcium ion.

The nonlinearity is due to the increase in ionic strength—and the consequent decrease in the activity of calcium ion—with increasing electrolyte concentration.

EXAMPLE 21-1

A cell consisting of a saturated calomel electrode and a lead ion electrode developed a potential of -0.4706 V when immersed in 50.00 mL of a sample. A 5.00 -mL addition of standard 0.02000 M lead solution caused the potential to shift to -0.4490 V. Calculate the molar concentration of lead in the sample.

Solution

We shall assume that the activity of Pb^{2+} is approximately equal to $[\text{Pb}^{2+}]$ and apply Equation 21-21. Thus,

$$\text{pPb} = -\log [\text{Pb}^{2+}] = -\frac{E'_{\text{cell}} - K}{0.0592/2}$$

where E'_{cell} is the initial measured potential (-0.4706 V).

After the standard solution is added, the potential becomes E''_{cell} (-0.4490 V), and

$$-\log \frac{50.00 \times [\text{Pb}^{2+}] + 5.00 \times 0.0200}{50.00 + 5.00} = -\frac{E''_{\text{cell}} - K}{0.0592/2}$$

$$-\log(0.9091[\text{Pb}^{2+}] + 1.818 \times 10^{-3}) = -\frac{E''_{\text{cell}} - K}{0.0592/2}$$

Subtracting this equation from the first leads to

$$\begin{aligned} -\log \frac{[\text{Pb}^{2+}]}{0.09091[\text{Pb}^{2+}] + 1.818 \times 10^{-3}} &= \frac{2(E''_{\text{cell}} - E'_{\text{cell}})}{0.0592} \\ &= \frac{2[-0.4490 - (-0.4706)]}{0.0592} \\ &= 0.7297 \end{aligned}$$

$$\frac{[\text{Pb}^{2+}]}{0.09091[\text{Pb}^{2+}] + 1.818 \times 10^{-3}} = \text{antilog}(-0.7297) = 0.1863$$

$$[\text{Pb}^{2+}] = 3.45 \times 10^{-4} \text{ M}$$

Potentiometric pH Measurement with the Glass Electrode

The glass/calomel electrode system is a remarkably versatile tool for the measurement of pH under many conditions.

However, there are distinct limitations to the electrode:

1. The alkaline error
2. The acid error
3. Dehydration
4. Errors in low ionic strength solutions
5. Variation in junction potential
6. Error in the pH of the standard buffer
7. Errors resulting from temperature changes

The operational definition of pH:

➤ The operational definition of pH, endorsed by the National Institute of Standards and Technology (NIST) and IUPAC, is based on the direct calibration of the meter with carefully prescribed standard buffers followed by potentiometric determination of the pH of unknown solutions.

$$\text{pH}_s = \frac{E_s - K}{0.0592}$$

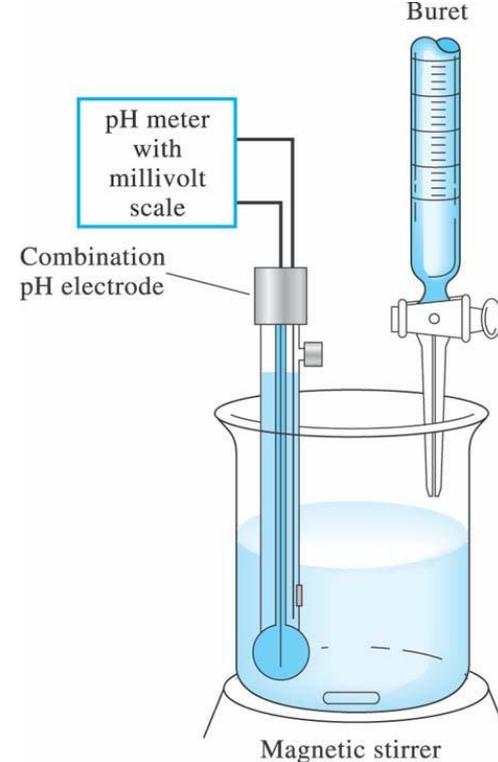
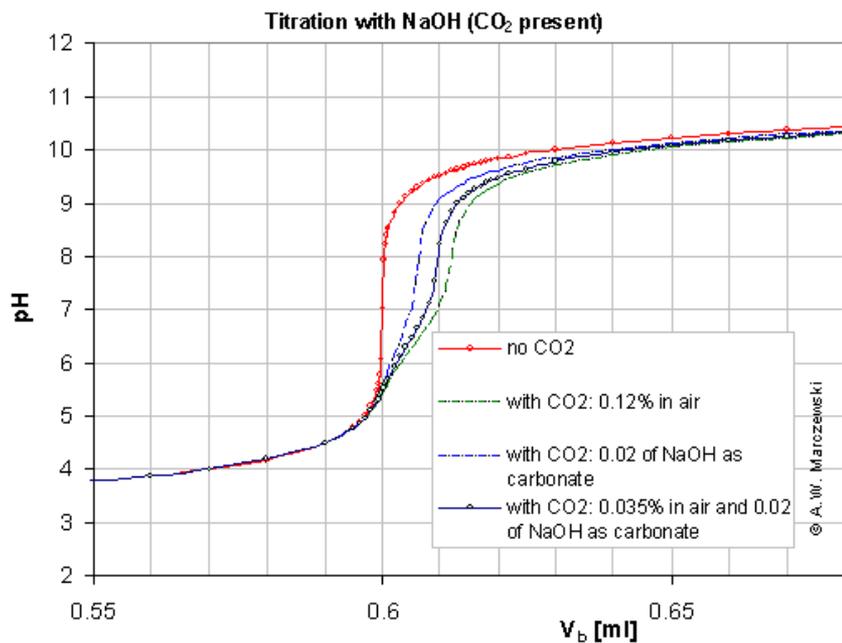
where E_s is the cell potential when the electrodes are immersed in the buffer. If the cell potential is E_u when the electrodes are immersed in a solution of unknown pH, we have

$$\text{pH}_u = \frac{E_u - K}{0.0592}$$

$$\text{pH}_u = \text{pH}_s - \frac{(E_u - E_s)}{0.0592}$$

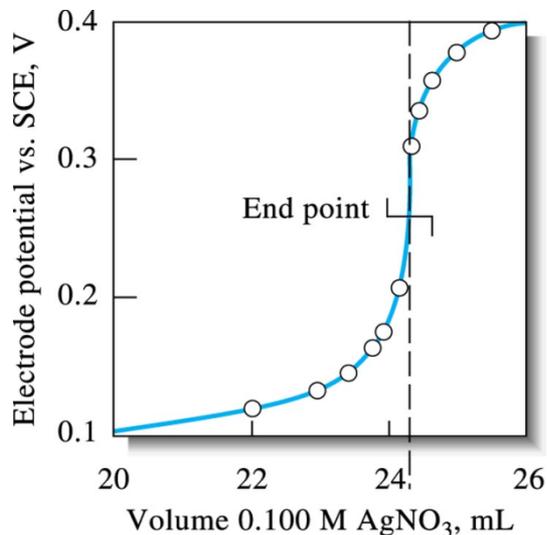
Potentiometric titrations

- Potentiometric titrations are not dependent on measuring absolute values of E_{cell} .
- Potentiometric titration results depend most heavily on having a titrant of accurately known concentration.



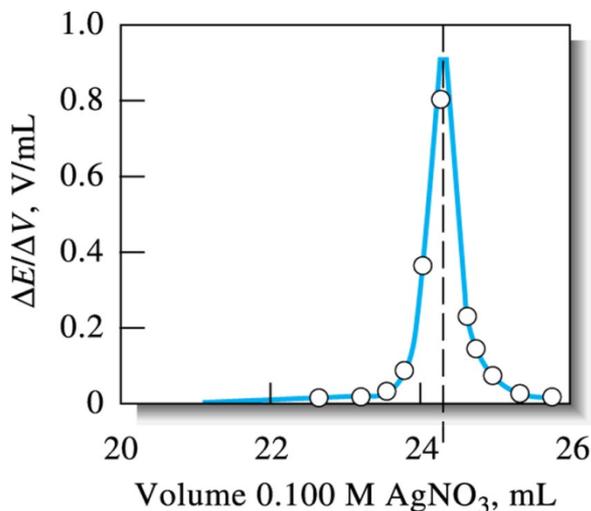
Detecting the End Point

- A direct plot of potential as a function of reagent volume
 - the inflection point in the steeply rising portion of the curve, and take it as the end point.



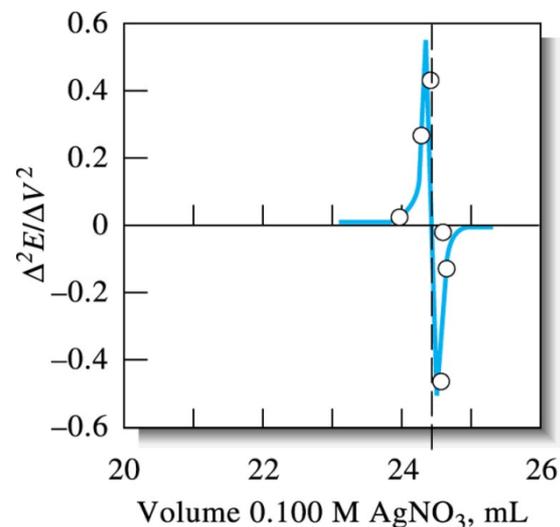
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- Calculate the change in potential per unit volume of titrant (i.e., $\Delta E/\Delta V$)
 - If the titration curve is symmetrical, the point of maximum slope coincides with the equivalence point.



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- Calculate the second derivative for the data changes sign at the point of inflection
 - This change is used as the analytical signal in some automatic titrators.



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Complex-Formation Titrations

- Both metallic and membrane electrodes have been used to detect end points in potentiometric titrations involving complex formation:
 - Mercury electrodes are useful for EDTA titrations of cations that form complexes that are less stable than HgY^{2-}

Neutralization Titrations

- An approximate numerical value for the dissociation constant of a weak acid or base can be estimated from potentiometric titration curves.

- At half-titration point: $[HA] \approx [A^-]$

- Therefore:
$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = [H_3O^+]$$

$$pK_a = pH$$

– It is important to note that the use of concentrations instead of activities may cause the value of K_a differ from its published value by a factor of 2 or more.

- A more correct form:

$$\begin{aligned} K_a &= \frac{a_{H_3O^+} a_{A^-}}{a_{HA}} = \frac{a_{H_3O^+} \gamma_{A^-} [A^-]}{\gamma_{HA} [HA]} \\ &= \frac{a_{H_3O^+} \gamma_{A^-}}{\gamma_{HA}} \end{aligned}$$

EXAMPLE:

• To determine K_1 and K_2 for H_3PO_4 from titration data, careful pH measurements are made after 0.5 and 1.5 mol of base are added for each mole of acid. It is then assumed that the hydrogen ion activities computed from these data are identical to the desired dissociation constants. Calculate the relative error incurred by the assumption if the ionic strength is 0.1 at the time of each measurement.

$$\text{Since } K_a(\text{exptl}) = a_{H_3O^+} = K \left(\frac{\gamma_{HA}}{\gamma_{A^-}} \right)$$

– the activity coefficient for

- H_3PO_4 is ca. 1

- $H_2PO_4^-$ is ca. 0.78

- HPO_4^{2-} is ca. 0.36

• Therefore:

$$K_1(\text{exptl}) = 7.11 \times 10^{-3} \left(\frac{1.00}{0.78} \right) = 9.1 \times 10^{-3}$$

$$\text{error} = \frac{9.1 \times 10^{-3} - 7.11 \times 10^{-3}}{7.11 \times 10^{-3}} \times 100\% = 28\%$$

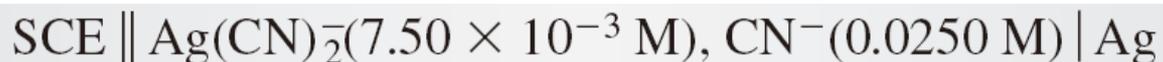
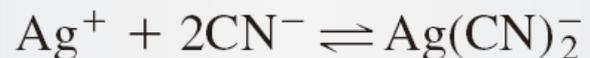
$$K_2(\text{exptl}) = 6.34 \times 10^{-8} \left(\frac{0.78}{0.36} \right) = 1.37 \times 10^{-7}$$

$$\text{error} = \frac{1.37 \times 10^{-7} - 6.34 \times 10^{-8}}{6.34 \times 10^{-8}} \times 100\% = 116\%$$

Potentiometric Determination of Equilibrium Constants

- Numerical values for solubility-product constants, dissociation constants, and formation constants are conveniently evaluated through the measurement of cell potentials.

EXAMPLE: Calculate the formation constant K_f for $\text{Ag}(\text{CN})_2^-$:



if the cell develops a potential of -0.625 V .



$$-0.625 = E_{\text{right}} - E_{\text{left}} = E_{\text{Ag}^+} - 0.244$$

$$E_{\text{Ag}^+} = -0.625 + 0.244 = -0.381 \text{ V}$$

$$-0.381 = 0.799 - \frac{0.0592}{1} \log \frac{1}{[\text{Ag}^+]}$$

$$[\text{Ag}^+] = 1.2 \times 10^{-20}$$

$$\begin{aligned} K_f &= \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2} = \frac{7.50 \times 10^{-3}}{(1.2 \times 10^{-20})(2.5 \times 10^{-2})^2} \\ &= 1.0 \times 10^{21} \approx 1 \times 10^{21} \end{aligned}$$

EXAMPLE:

- Calculate the dissociation constant K_{HP} for the weak acid HP if the cell develops

SCE || HP(0.010 M), NaP(0.040 M) | Pt, H₂ (1.00 atm) a potential of -0.591 V.

The diagram for this cell indicates that the saturated calomel electrode is the left-hand electrode. Thus,

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{right}} - 0.244 = -0.591 \text{ V}$$

$$E_{\text{right}} = -0.591 + 0.244 = -0.347 \text{ V}$$

We then apply the Nernst equation for the hydrogen electrode to find that

$$\begin{aligned} -0.347 &= 0.000 - \frac{0.0592}{2} \log \frac{1.00}{[\text{H}_3\text{O}^+]^2} \\ &= 0.000 - \frac{2 \times 0.0592}{2} \log[\text{H}_3\text{O}^+] \end{aligned}$$

$$\log[\text{H}_3\text{O}^+] = \frac{-0.347 - 0.000}{0.0592} = -5.86$$

$$[\text{H}_3\text{O}^+] = 1.38 \times 10^{-6}$$

$$K_{HP} = \frac{[\text{H}_3\text{O}^+][\text{P}^-]}{HP} = \frac{(1.38 \times 10^{-6})(0.040)}{0.010} = 5.5 \times 10^{-6}$$