CHAPTER 21

Potentiometry

Lecture 7

Potentiometric Measurements

- Including:
  - a reference electrode, an indicator electrode, and a potential-measuring device
- Based on measuring the potential of electrochemical cells without drawing appreciable current.
- Used to
  - locate end points in titrations.
  - Determine ion concentrations with ion-selective membrane electrodes
  - Measure the pH
  - determine thermodynamic equilibrium constants such as K_a, K_b, and K_{sp}.

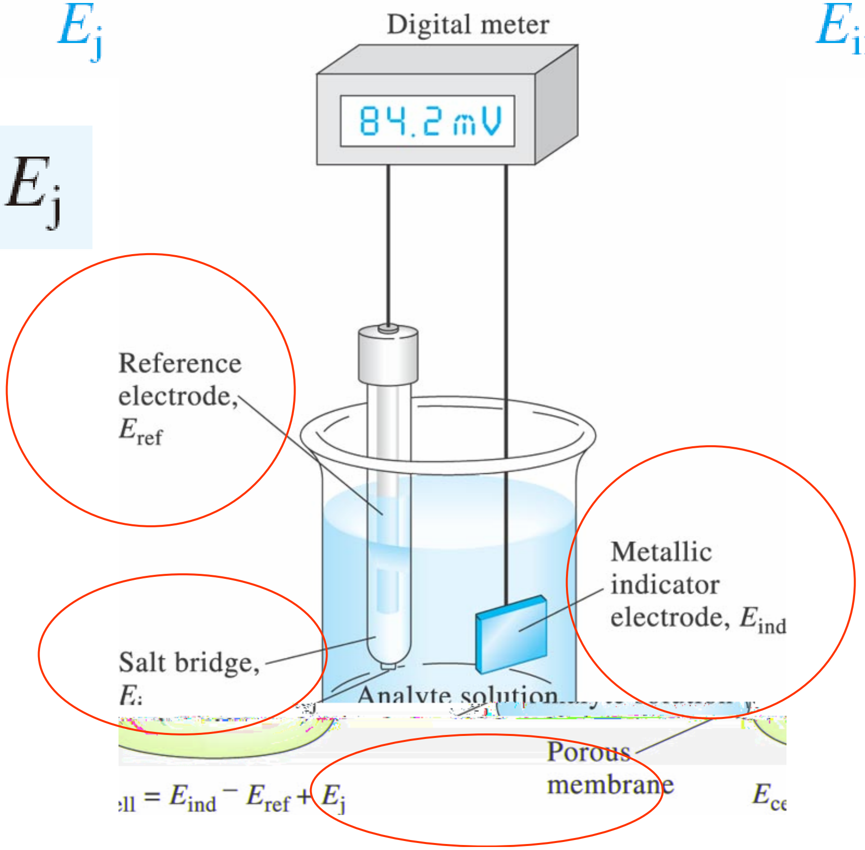
General Principles

- A typical cell for potentiometric analysis:

$$\underbrace{\text{reference electrode}}_{E_{\text{ref}}} \,|\, \underbrace{\text{salt bridge}}_{E_{\text{j}}} \,|\, \text{analyte solution} \,|\, \underbrace{\text{indicator electrode}}_{E_{\text{ind}}}$$

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

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



Potentiometric Analysis

- Reference electrode
  - A half-cell with an accurately known electrode potential, E_{ref}, that is independent of the concentration of the analyte or any other ions in the solution
  - Always treated as the left-hand electrode
- Indicator electrode
  - which is immersed in a solution of the analyte, develops a potential, E_{ind}, that depends on the activity of the analyte.
  - Is selective in its response
- Salt bridge
  - Preventing components of the analyte solution from mixing with those of the reference electrode
  - A potential develops across the liquid junctions at each end of the salt bridge.
  - Potassium chloride is a nearly ideal electrolyte for the salt bridge because the mobilities of the K^+ion and the Cl^- ion are nearly equal.

Reference Electrodes

- Ideal reference electrode
  - has a potential that is accurately known, constant and completely insensitive to the composition of the analyte solution.
- Calomel reference electrodes:

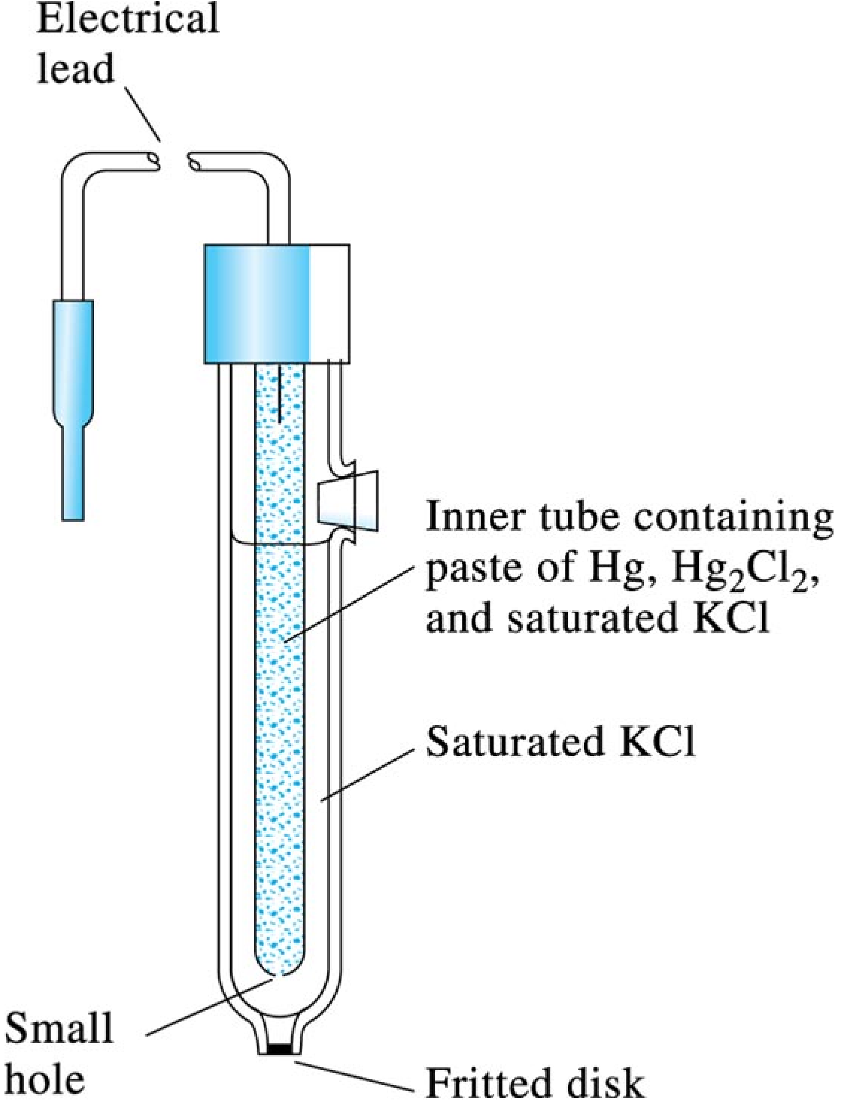
$$\mathrm{Hg} \,|\, \mathrm{Hg_2Cl_2(sat'd),\ KCl}(x\ \mathrm{M}) \,\|$$

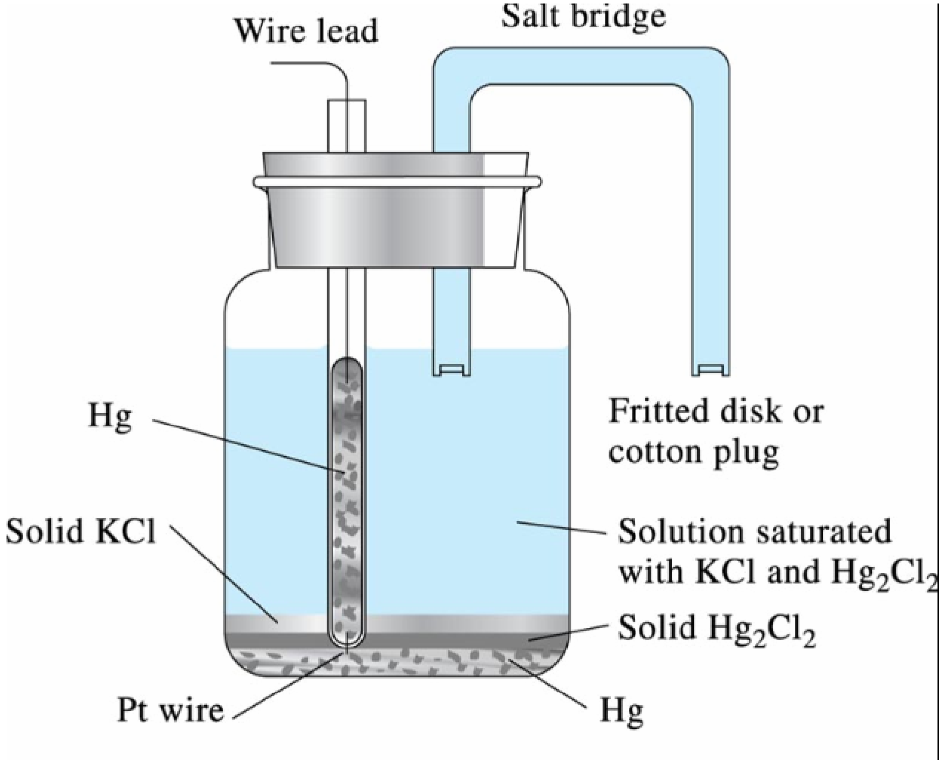
  - where *x* represents the molar concentration of potassium chloride in the solution.
  - Concentrations of potassium chloride that are commonly used in calomel reference electrodes are 0.1 M, 1 M, and saturated (about 4.6 M).
  - The saturated calomel electrode (SCE) is the most widely used because it is easily prepared. The potential is 0.2444 V at 25°C.
- The electrode reaction in calomel half-cell:

$$\mathrm{Hg_2Cl_2}(s) + 2e^- \rightleftharpoons 2\mathrm{Hg}(l) + 2\mathrm{Cl}^-(aq)$$

Typical Commercial Saturated Calomel Electrode

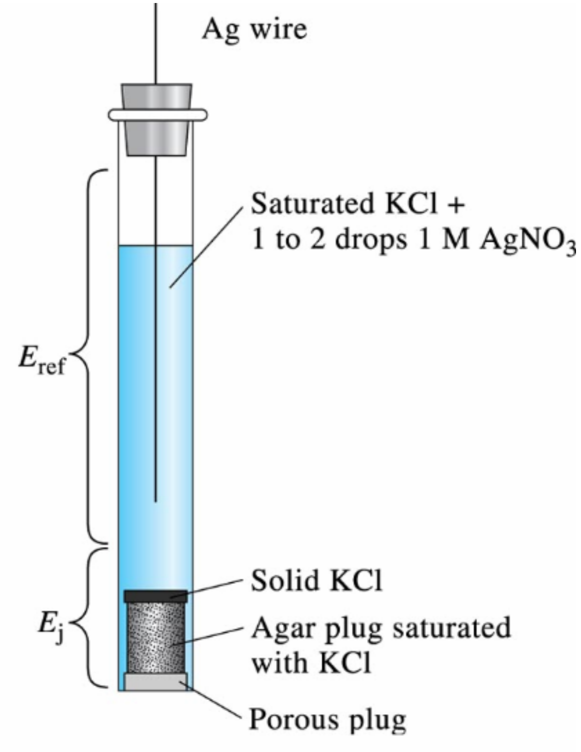
Typical Saturated Calomel Electrode available in Lab





Silver/Silver Chloride Reference Electrode

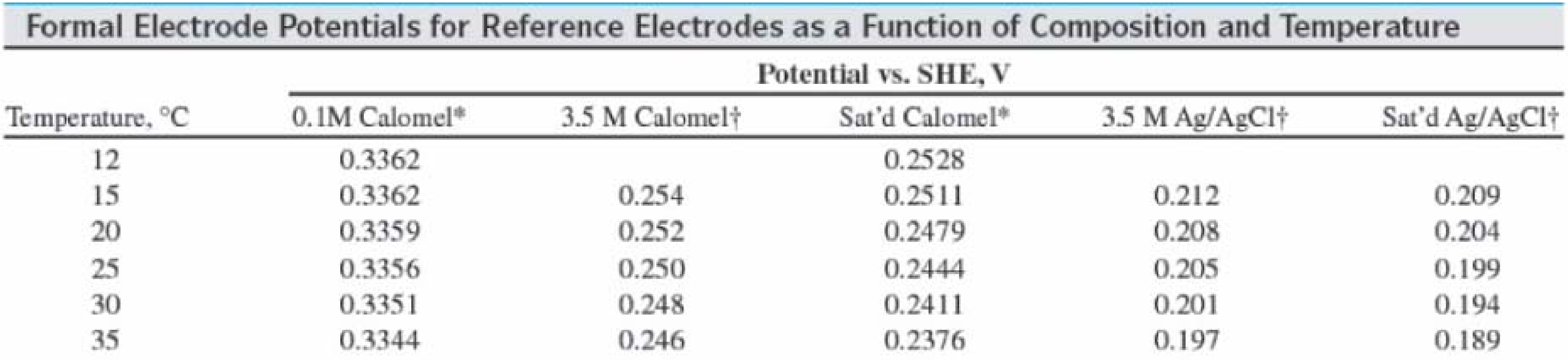
- Electrode: $\mathrm{Ag}|\mathrm{AgCl(sat'd),\ KCl(sat'd)}\|$
- The half-reaction is $\boxed{\mathrm{AgCl}(s) + \mathrm{e}^- \rightleftharpoons \mathrm{Ag}(s) + \mathrm{Cl}^-}$
- The potential of this electrode is 0.199 V at 25°C



the reference electrode potential E_{ref} and the junction potential E_{j}.

Reference Electrodes

- Formal potentials

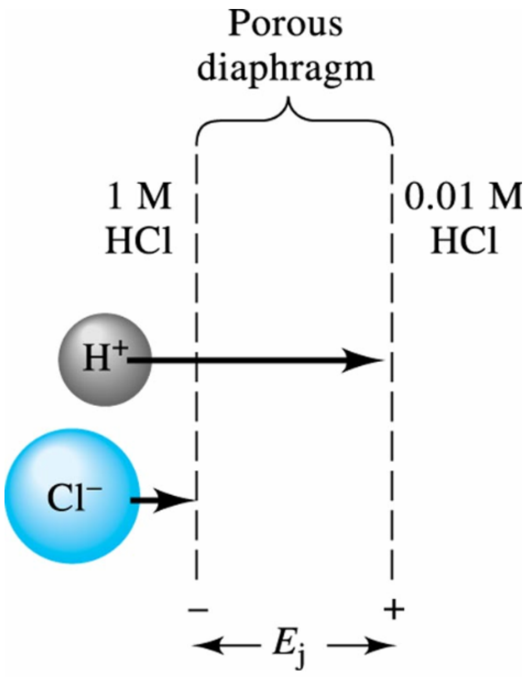


Formal Electrode Potentials for Reference Electrodes as a Function of Composition and Temperature

	Potential vs. SHE, V				
Temperature, °C	0.1M Calomel*	3.5 M Calomel†	Sat'd Calomel*	3.5 M Ag/AgCl†	Sat'd Ag/AgCl†
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

Liquid-Junction Potentials

- Ex:
  - A liquid junction consisting of a 1 M HCl solution that is in contact with a solution that is 0.01 M HCl
  - Both H^+ and Cl^- ions tend to diffuse across the inert porous barrier
  - H^+ ions diffuse more rapidly than Cl^- ions, and a separation of charge results
  - The potential difference resulting from this charge separation is the junction potential
- The magnitude of the liquid-junction potential can be minimized by placing a salt bridge between the two solutions:
  - The mobilities of the negative and positive ions are nearly equal
  - A saturated solution of potassium chloride is good from both standpoints. The net junction potential with such a bridge is typically a few millivolts



Indicator Electrodes

- Ideal indicator electrode:
  - responds rapidly and reproducibly to changes in the concentration of an analyte ion (or groups of analyte ions).
- Three types:
  - Metallic
    - electrodes of the first kind
    - electrodes of the second kind
    - inert redox electrodes
  - Membrane
  - Ion-sensitive field effect transistor

Electrodes of the First Kind

- A pure metal electrode that is in direct equilibrium with its cation in the solution:

$$X^{n+}(aq) + ne^- \rightleftharpoons X(s)$$

- For which

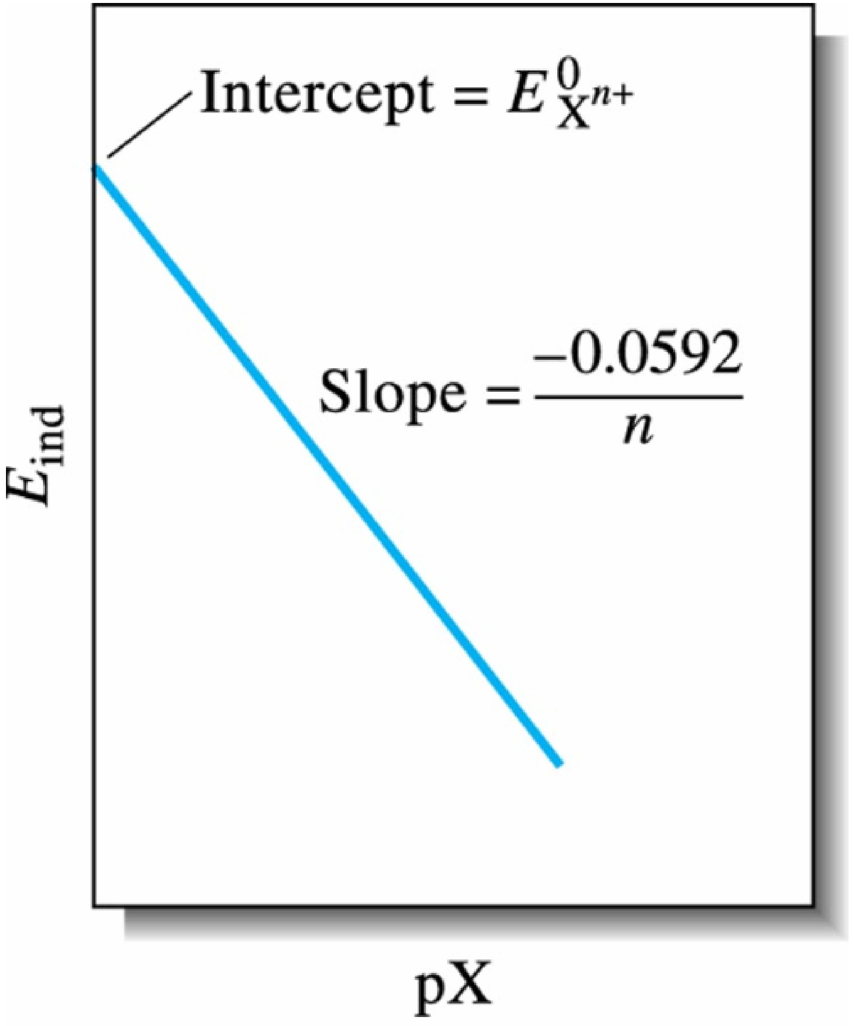
$$E_{\text{ind}} = E^{0}_{X^{n+}/X} - \frac{0.0592}{n}\log\frac{1}{a_{X^{n+}}} = E^{0}_{X^{n+}/X} + \frac{0.0592}{n}\log a_{X^{n+}}$$

  - where E_{ind} is the electrode potential of the metal electrode and a_{xn+} is the activity of the ion (or, in dilute solution, approximately its molar concentration, $[X^{n+}]$).

- Or

$$E_{\text{ind}} = E^{0}_{X^{n+}/X} + \frac{0.0592}{n}\log a_{X^{n+}} = E^{0}_{X^{n+}/X} - \frac{0.0592}{n}\,\text{pX}$$

$$E_{\mathrm{ind}} = E^0_{\mathrm{X}^{n+}/\mathrm{X}} + \frac{0.0592}{n}\log a_{\mathrm{X}^{n+}} = E^0_{\mathrm{X}^{n+}/\mathrm{X}} - \frac{0.0592}{n}\,\mathrm{pX}$$



Electrodes of the First Kind

- 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 metals do not provide reproducible potentials
- Limited electrodes are:
  - Ag/Ag$^+$ and Hg/Hg^{2+} in neutral solutions and Cu/Cu^{2+}, Zn/Zn^{2+}, Cd/Cd^{2+}, Bi/Bi^{3+}, Tl/Tl$^+$, and Pb/Pb^{2+} in deaerated solutions.

Electrodes of the Second Kind

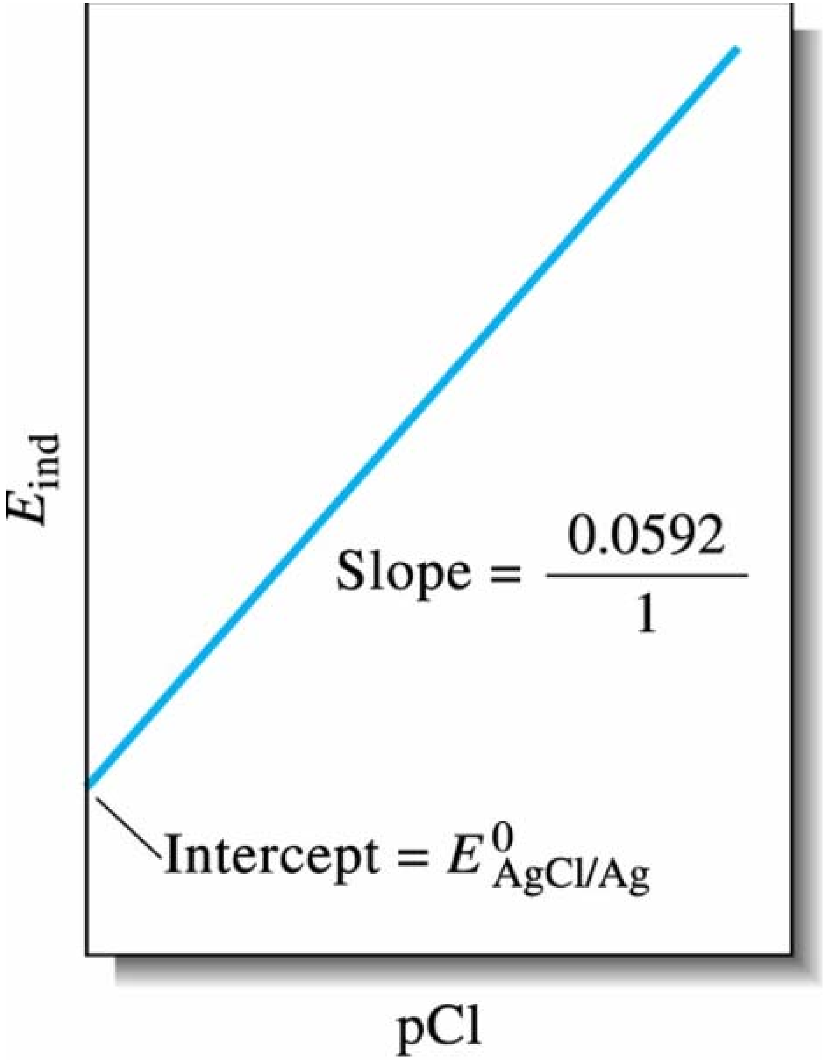
- Metal electrode respond to the activities of anions that form sparingly soluble precipitates or stable complexes with such cations.
- Ex:

$$\mathrm{AgCl}(s) + e^- \rightleftharpoons \mathrm{Ag}(s) + \mathrm{Cl}^-(aq) \qquad E^0_{\mathrm{AgCl/Ag}} = 0.222\ \mathrm{V}$$

- the Nernst expression for this process at 25°C is

$$E_{\mathrm{ind}} = E^0_{\mathrm{AgCl/Ag}} - 0.0592 \log a_{\mathrm{Cl^-}} = E^0_{\mathrm{AgCl/Ag}} + 0.0592\ \mathrm{pCl}$$

$$\boxed{E_{\mathrm{ind}} = E^{0}_{\mathrm{AgCl/Ag}} - 0.0592 \log a_{\mathrm{Cl^-}} = E^{0}_{\mathrm{AgCl/Ag}} + 0.0592\ \mathrm{pCl}}$$



Electrodes of the Second Kind

- Mercury serves as an indicator electrode of the second kind for the EDTA anion Y^{4-}:

$$\mathrm{HgY^{2-}} + 2e^- \rightleftharpoons \mathrm{Hg}(l) + \mathrm{Y^{4-}} \qquad E^0 = 0.21\ \mathrm{V}$$

- For which:

$$E_{\mathrm{ind}} = 0.21 - \frac{0.0592}{2}\log\frac{a_{\mathrm{Y^{4-}}}}{a_{\mathrm{HgY^{2-}}}}$$

- the Nernst expression for this process:

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

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

Inert Metallic Electrodes for Redox Systems

- Several inert conductors can be used to monitor redox systems. Such as
  - platinum, gold, palladium, and carbon
- Ex:
  - Platinum electrode immersed in a solution containing cerium (III) and cerium (IV):

$$E_{\text{ind}} = E^{0}_{\text{Ce}^{4+}/\text{Ce}^{3+}} - 0.0592 \log \frac{a_{\text{Ce}^{3+}}}{a_{\text{Ce}^{4+}}}$$

  - a convenient indicator electrode for titrations involving standard cerium(IV) solutions

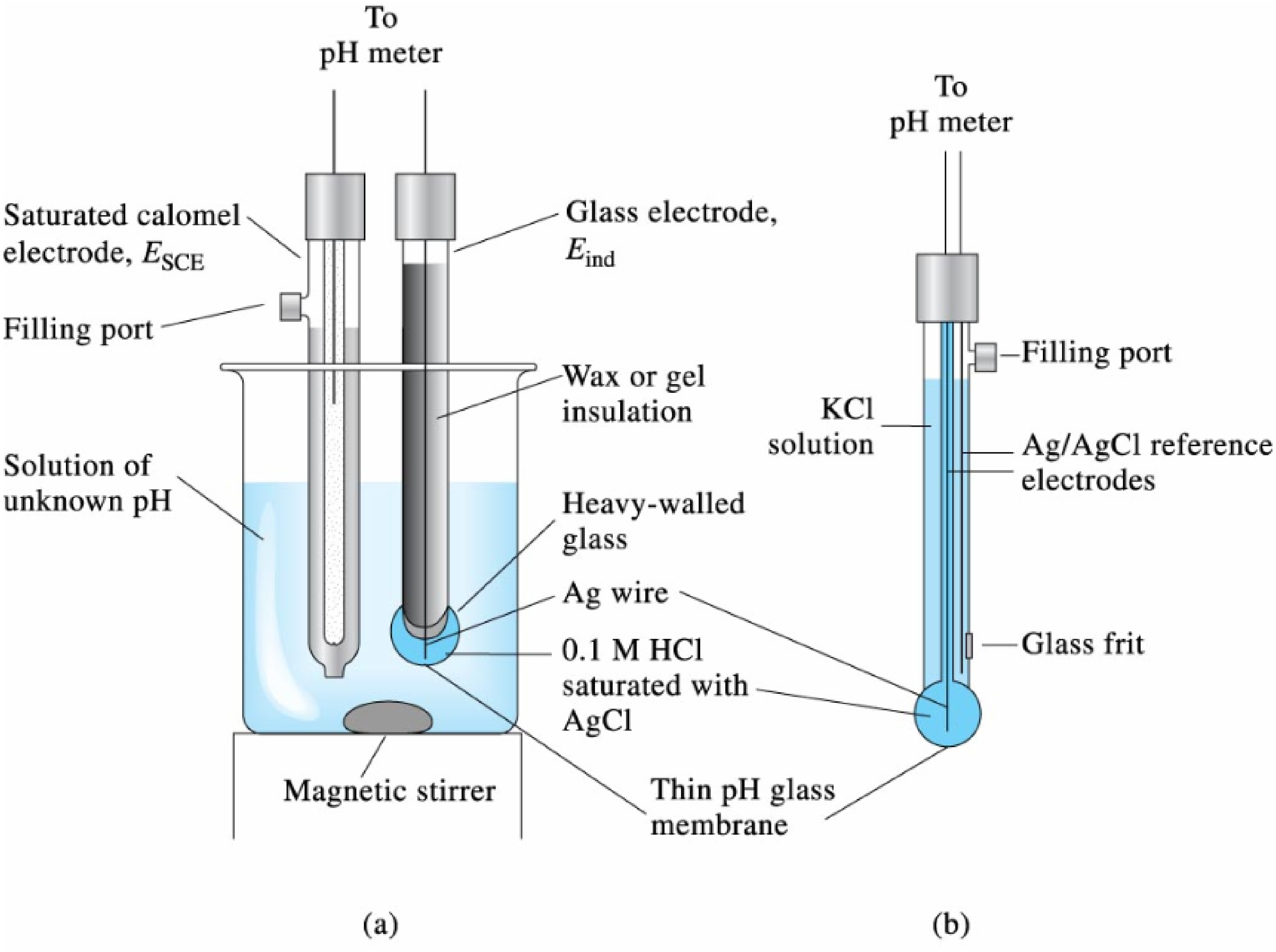
Indicator Electrode - Membrane Electrodes

- Fundamentally different from metal electrodes both in design and in principle.
- Sometimes called **p-ion electrodes** because the data obtained from them are usually presented as p-functions, such as pH, pCa, or pNO_3.
- Ex: pH meter
  - A thin glass membrane that separates two solutions with different hydrogen ion concentrations.
  - the sensitivity and selectivity of glass membranes toward hydrogen ions are reasonably well understood.

pH-sensitive Glass Membrane Electrode

- A glass electrode system contains two reference electrodes: the external calomel electrode (Immersed in a solution of unknown pH) and the internal silver/silver chloride electrode.
  - The internal electrode consists of
    - a thin, pH-sensitive glass membrane sealed onto one end of a heavy-walled glass or plastic tube
    - a small volume of dilute hydrochloric acid saturated with silver chloride is contained in the tube. A silver wire in this solution forms a silver/silver chloride reference electrode.
    - It is the thin glass membrane bulb at the tip of the electrode that responds to pH.

Typical electrode system for measuring pH

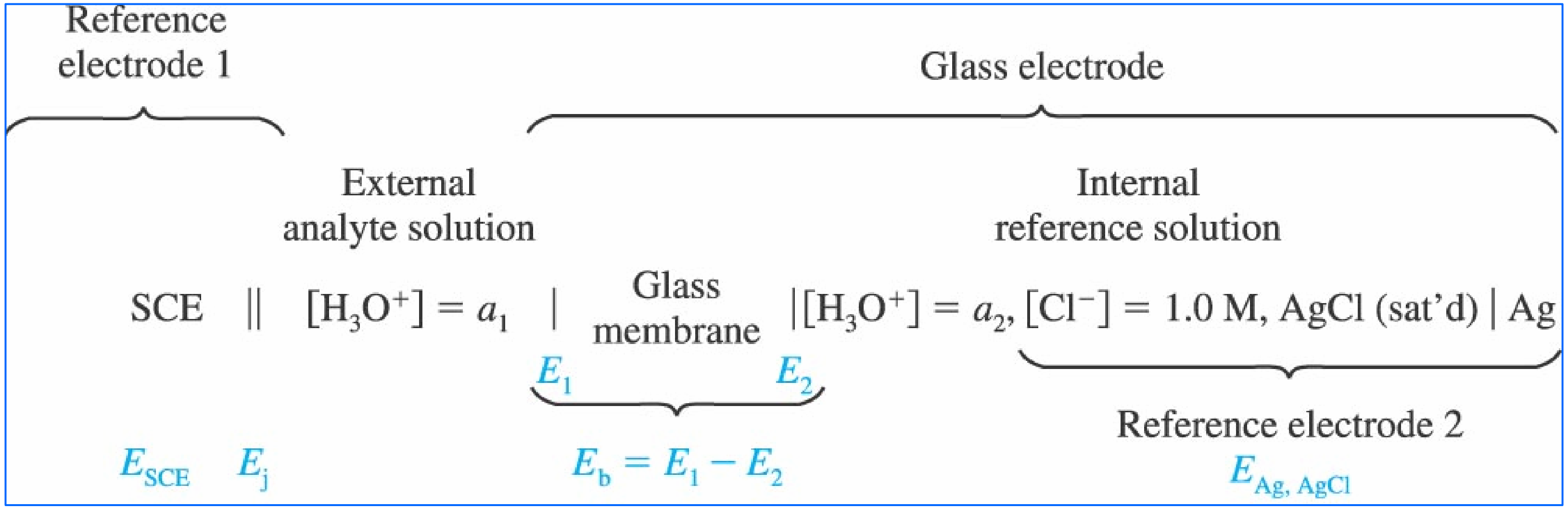


pH Meter

- 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.

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



Reference electrode 1

Glass electrode

External analyte solution

Internal reference solution

SCE || $[H_3O^+] = a_1$ | Glass membrane | $[H_3O^+] = a_2$, $[Cl^-] = 1.0$ M, AgCl (sat'd) | Ag

E_1 E_2

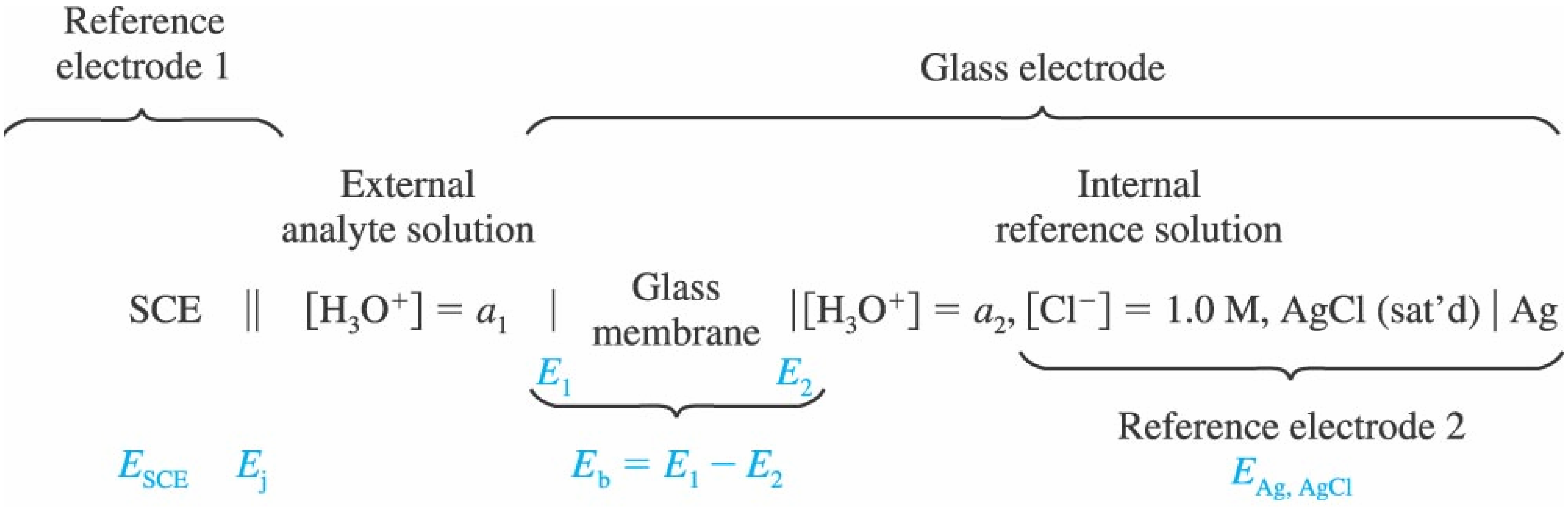
Reference electrode 2

E_{SCE} E_j

$E_b = E_1 - E_2$

$E_{Ag,\,AgCl}$

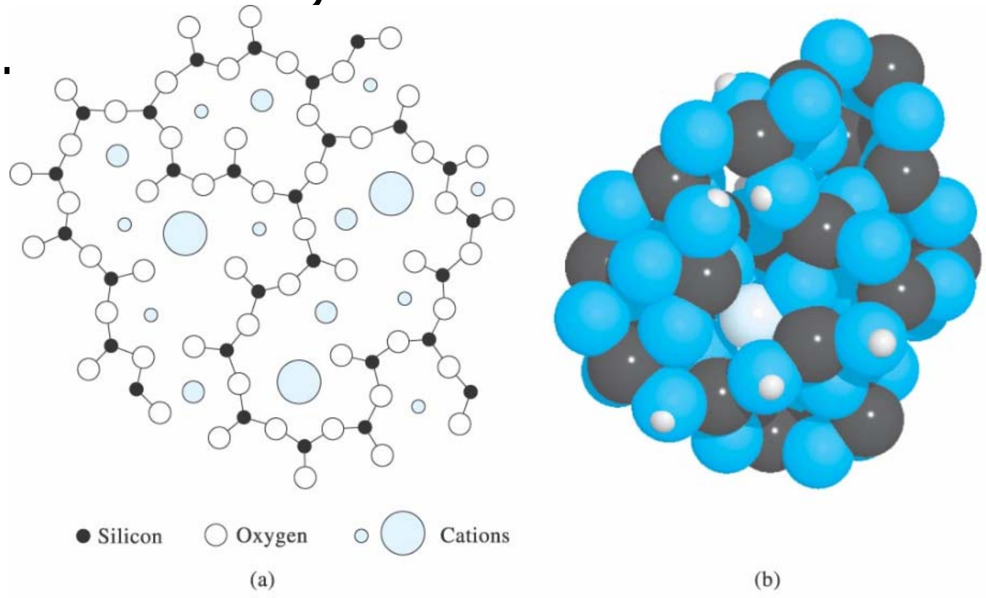
Cell Potentials



- 4 potentials:
  - $E_{Ag,AgCl}$ 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*.

The Composition and Structure of Glass Membranes

- Glass composition affects the sensitivity of membranes to protons and other cations.

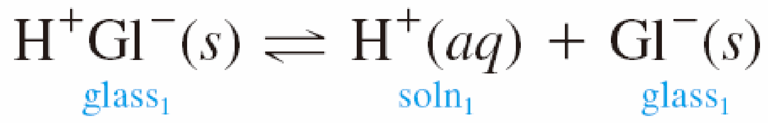


Cross-sectional view of a silicate glass structure

- 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: $\underset{\text{soln}}{H^+} + \underset{\text{glass}}{Na^+Gl^-} \rightleftharpoons \underset{\text{soln}}{Na^+} + \underset{\text{glass}}{H^+Gl^-}$

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:



$$\underset{\text{glass}_1}{H^+Gl^-(s)} \rightleftharpoons \underset{\text{soln}_1}{H^+(aq)} + \underset{\text{glass}_1}{Gl^-(s)}$$

$$\underset{\text{glass}_2}{H^+Gl^-(s)} \rightleftharpoons \underset{\text{soln}_2}{H^+(aq)} + \underset{\text{glass}_2}{Gl^-(s)}$$

  - 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:

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

  - 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:

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

  - with

$$\boxed{L' = -0.0592 \log a_2}$$

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 (所以需校正)

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

$$\Downarrow$$

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

where *L* is a combination of the three constant terms

Describing Selectivity

- The effect of an alkali metal ion on the potential across a membrane can be accounted for by inserting an additional term:

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

  - where $k_{H,B}$ is the **selectivity coefficient** for the electrode.
  - Selectivity coefficients range from zero (no interference) to values greater than unity.
  - If an electrode for ion A responds 20 times more strongly to ion B than to ion A, $k_{H,B} = 20$.

Glass Electrodes for Other Cations

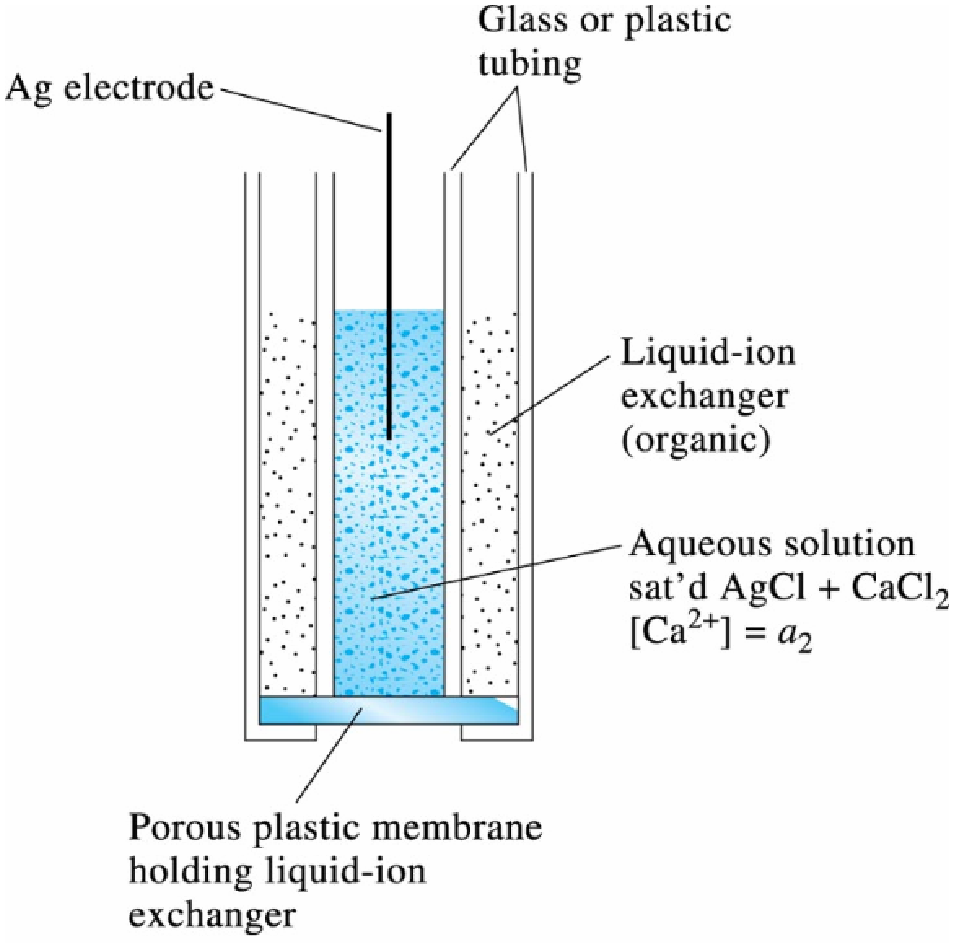
- Glass compositions that permit the determination of cations other than hydrogen:
  - Incorporation of Al_2O_3 or B_2O_3 into the glass has the desired effect.
  - Glass electrodes that permit the direct potentiometric measurement of such singly charged species as Na^+, K^+, NH_4^+, Rb^+, Cs^+, Li^+, and Ag^+ have been developed.
  - Glass electrodes for Na^+, K^+, NH_4^+ and total concentration of univalent cations are available.

Liquid-membrane Electrode

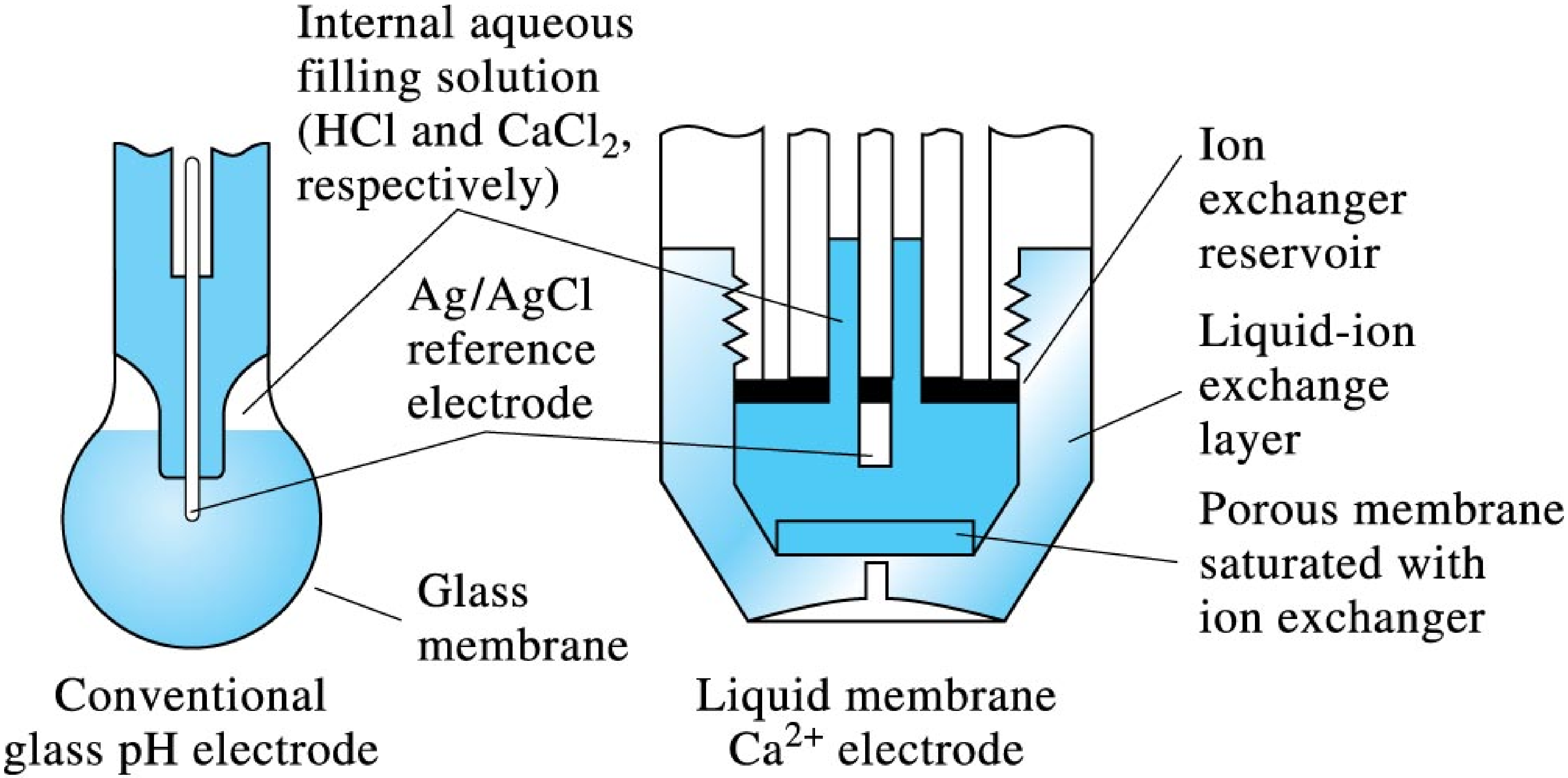
- The potential of liquid-membrane electrodes develops across the interface between the solution containing the analyte and a liquid-ion exchanger that selectively bonds with the analyte ion.
  - Liquid-membrane electrodes have been developed for the direct potentiometric measurement of numerous polyvalent cations as well as certain anions.

Liquid-membrane Electrode for Calcium

- The membrane electrode consists of
  - A conducting membrane that selectively binds calcium ion
  - An internal solutions containing a fixed concentration of calcium chloride
  - A silver electrode that is coated with silver chloride to form an internal reference electrode

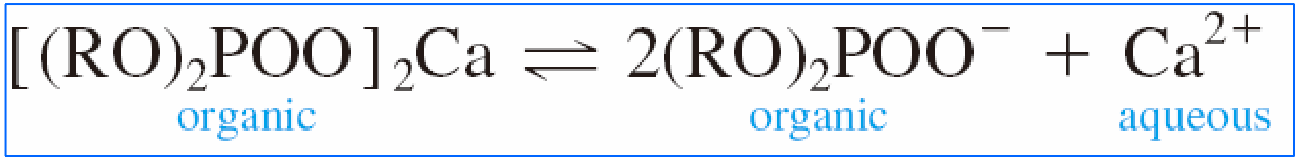


Comparison of a liquid-membrane calcium ion electrode with a glass pH electrode



Liquid-membrane Electrode

- Internal solution/analyte solution separation membrane:
  - the ion exchanger is dissolved in an immiscible organic liquid that is forced by gravity into the pores of a hydrophobic porous disk. This disk serves as the membrane.
  - the Ion exchanger is immobilized in a tough PVC gel cemented to the end of a tube that holds the internal solution and reference electrode.
- The dissociation equilibrium develops at each membrane interface:



$$\underset{\text{organic}}{[(RO)_2POO]_2Ca} \rightleftharpoons \underset{\text{organic}}{2(RO)_2POO^-} + \underset{\text{aqueous}}{Ca^{2+}}$$

Membrane Potential

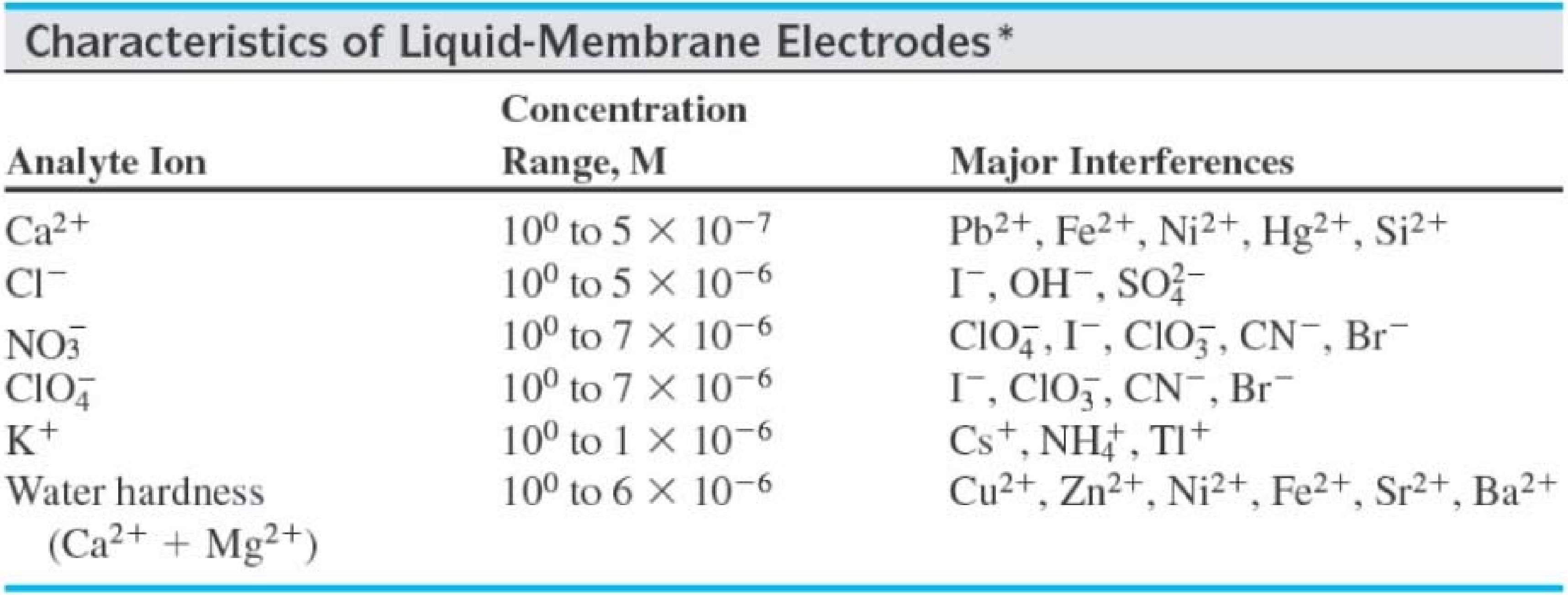
- A potential develops across the membrane when the extent of the ion exchanger dissociation at one surface differs from that at the other surface.
- The relation between the membrane potential and the calcium ion activities:

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

  - where a_1 and a_2 are the activities of calcium ion in the external analyte and internal standard solutions, respectively
- Since a_2 is a constant:

$$\boxed{E_b = N + \frac{0.0592}{2} \log a_1 = N - \frac{0.0592}{2} \text{pCa}}$$

Commercially Available Liquid-membrane Electrodes



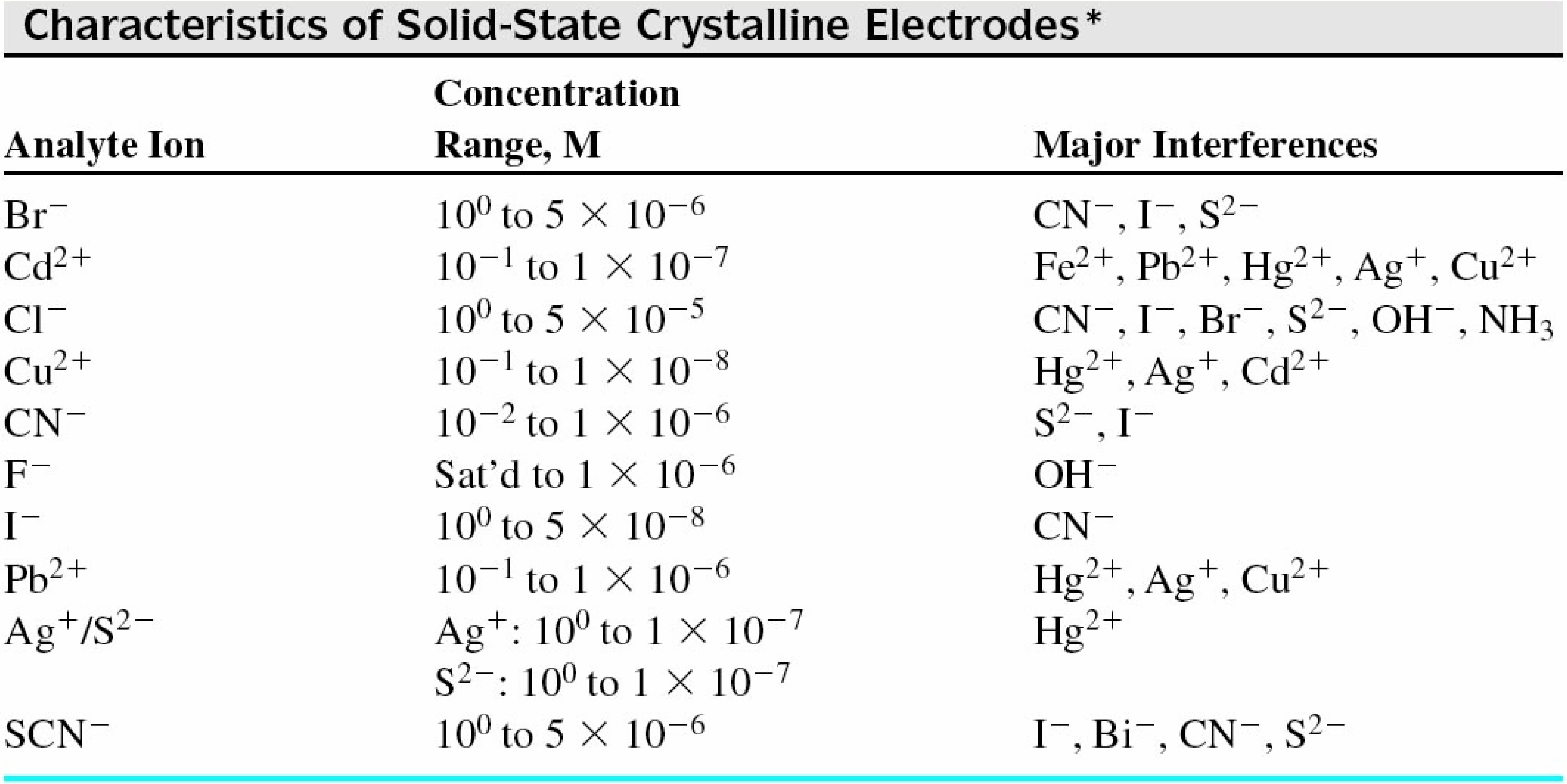
Characteristics of Liquid-Membrane Electrodes*

Analyte Ion	Concentration Range, M	Major Interferences
Ca^{2+}	10^0 to 5×10^{-7}	Pb^{2+}, Fe^{2+}, Ni^{2+}, Hg^{2+}, Si^{2+}
Cl^-	10^0 to 5×10^{-6}	I^-, OH^-, SO_4^{2-}
NO_3^-	10^0 to 7×10^{-6}	ClO_4^-, I^-, ClO_3^-, CN^-, Br^-
ClO_4^-	10^0 to 7×10^{-6}	I^-, ClO_3^-, CN^-, Br^-
K^+	10^0 to 1×10^{-6}	Cs^+, NH_4^+, Tl^+
Water hardness ($Ca^{2+} + Mg^{2+}$)	10^0 to 6×10^{-6}	Cu^{2+}, Zn^{2+}, Ni^{2+}, Fe^{2+}, Sr^{2+}, Ba^{2+}

Crystalline-membrane Electrodes

- Some solid membranes that are selective toward anions in the same way that some glasses respond to cations:
  - Membranes prepared from cast pellets of silver halides are for the selective determination of chloride, bromide, and iodide ions.
  - An electrode based on a polycrystalline Ag_2S membrane is for the determination of sulfide ion.
  - In both types, silver ions are sufficiently mobile to conduct electricity through the solid medium.

Commercially Available Solid-stage Crystalline Electrodes

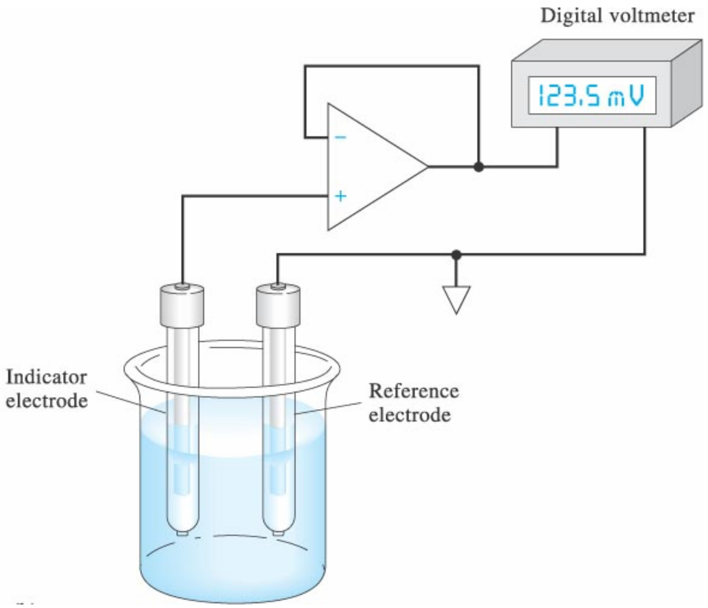


Characteristics of Solid-State Crystalline Electrodes*

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^-, Bi^-, CN^-, S^{2-}

Instruments for Measuring Cell Potential

- The voltmeter should have an electrical resistance that is several orders of magnitude greater than the resistance of the cell being measured:
  - Numerous high-resistance, direct reading digital voltmeters with internal resistances of > 10^{11} ohms are available.
  - These meters are commonly called pH meters, pIon meters or ion meters.



Direct Potentiometry

- Direct potentiometric measurements provide a rapid and convenient method to determine the activity of a variety of cations and anions:
  - 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.

Direct Potentiometry

- The potential of the cell:

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

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

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

$$\text{pX} = -\log a_{\text{X}} = \frac{E_{\text{cell}} - (E_{\text{j}} - E_{\text{ref}} + L)}{0.0592/n}$$

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

For an anion A^{n-}

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

The Standard-Addition Method

- The standard-addition method involves determining the potential of the electrode system before and after a measured volume of a standard has been added to a known volume of the analyte solution.

- 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.

- Assume that the activity of Pb^{2+} is approximately equal to $[Pb^{2+}]$:

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

  - where E'_{cell} is the initial measured potential (−0.4706 V).
- After the standard solution is added:

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

OR

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

  - where the potential E''_{cell} becomes (−0.4490 V)
- From the two equations:

$$-\log\frac{[\mathrm{Pb}^{2+}]}{0.09091\,[\mathrm{Pb}^{2+}] + 1.818 \times 10^{-3}} = \frac{2(E''_{\mathrm{cell}} - E'_{\mathrm{cell}})}{0.0592}$$

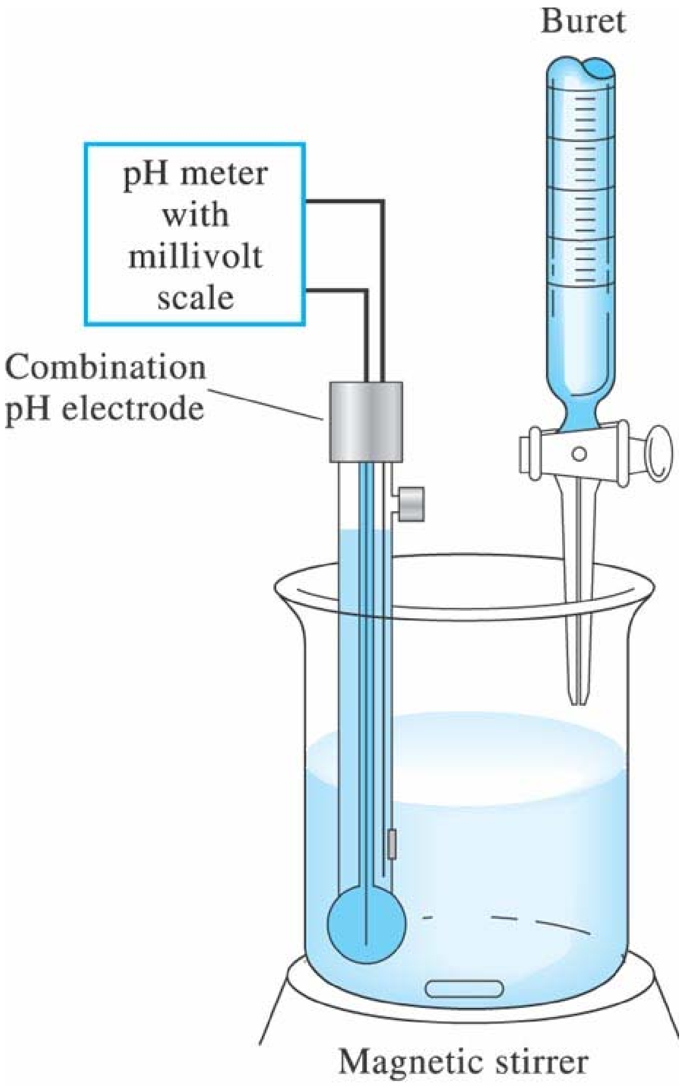
⇨ $$\boxed{[\mathrm{Pb}^{2+}] = 4.08 \times 10^{-4}\,\mathrm{M}}$$

Potentiometric Titrations

- A potentiometric titration involves measurement of the potential of a suitable indicator electrode as a function of titrant volume.
- The measurement is base on the titrant volume that causes a rapid change in potential near the equivalence point.
- Potentiometric titrations provide data that are more reliable than data from titrations that use chemical indicators.
  - They are particularly useful with colored or turbid solutions and for detecting the presence of unsuspected species.

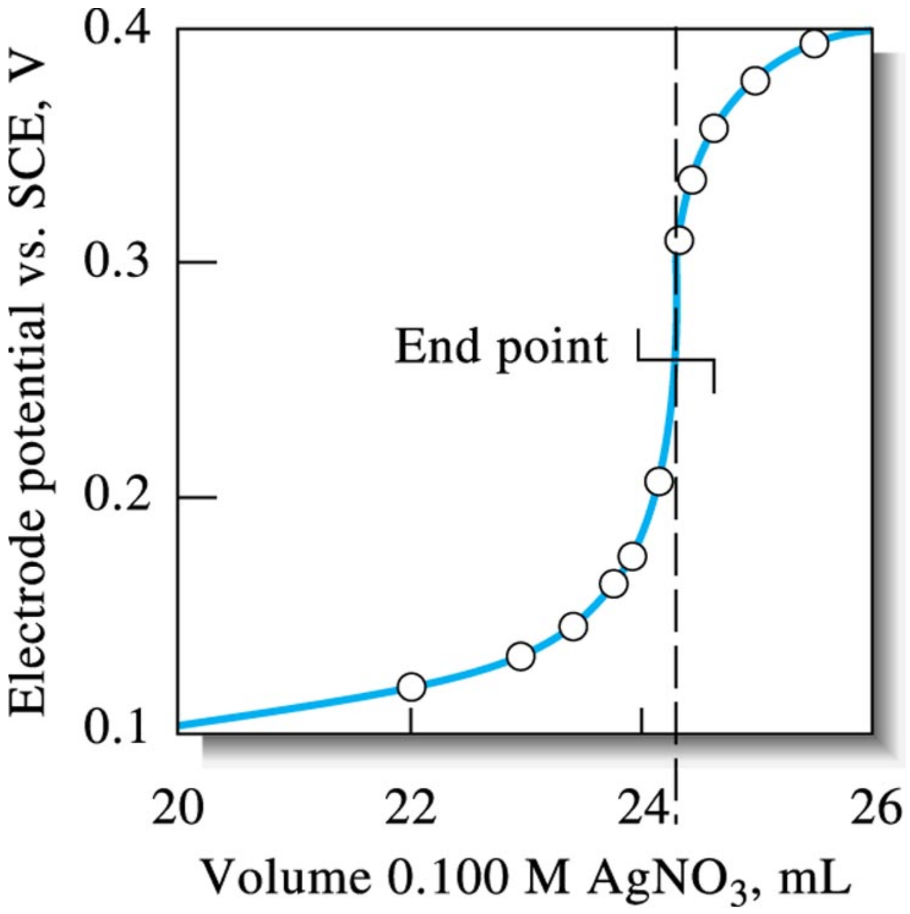
Potentiometric Titrations

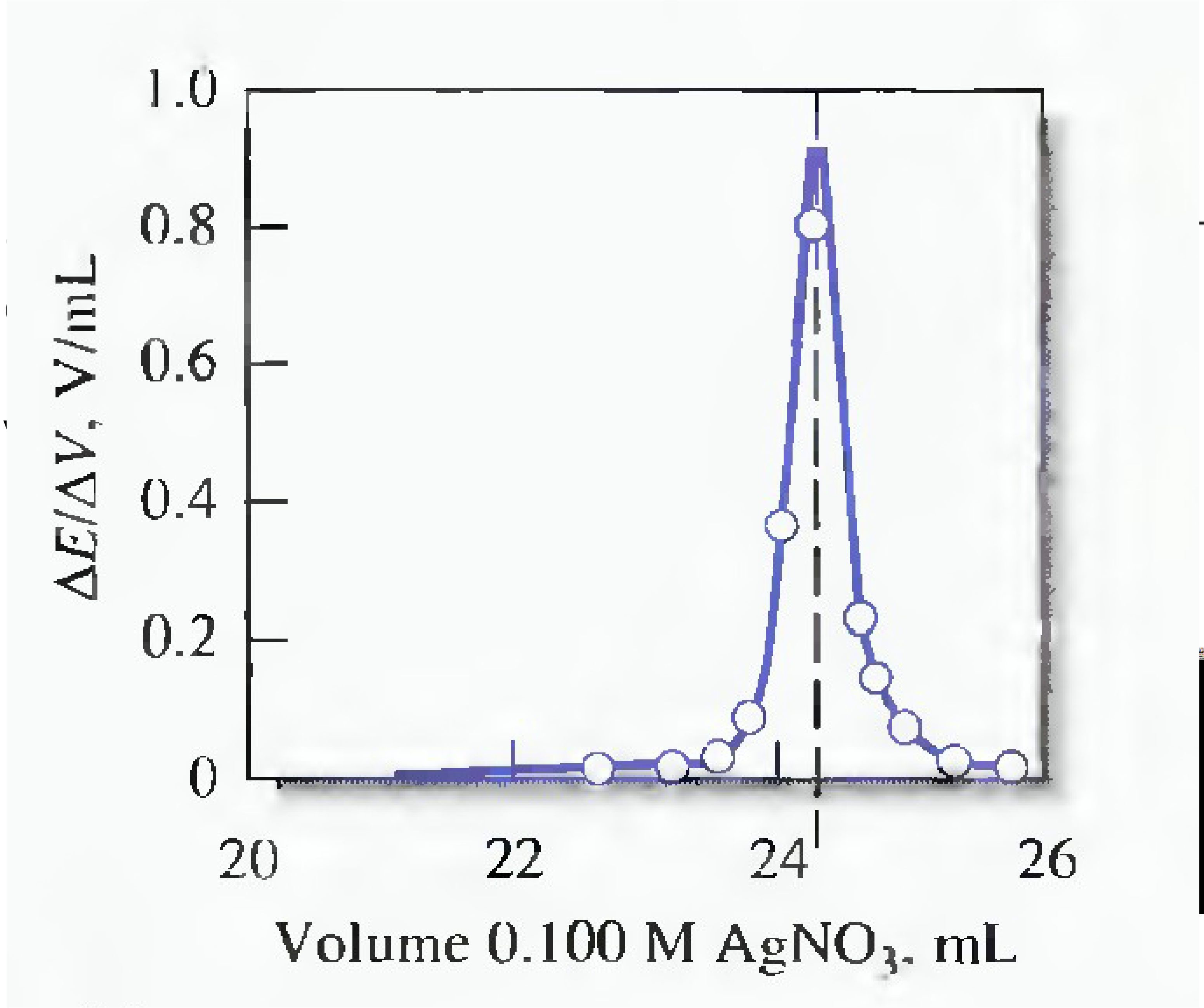
- Potentiometric titrations are not dependent on measuring absolute values of E_{cell}.
- Potentiometric titration results depend most heavily on <u>having a titrant of accurately known concentration</u>.



Detecting the End Point

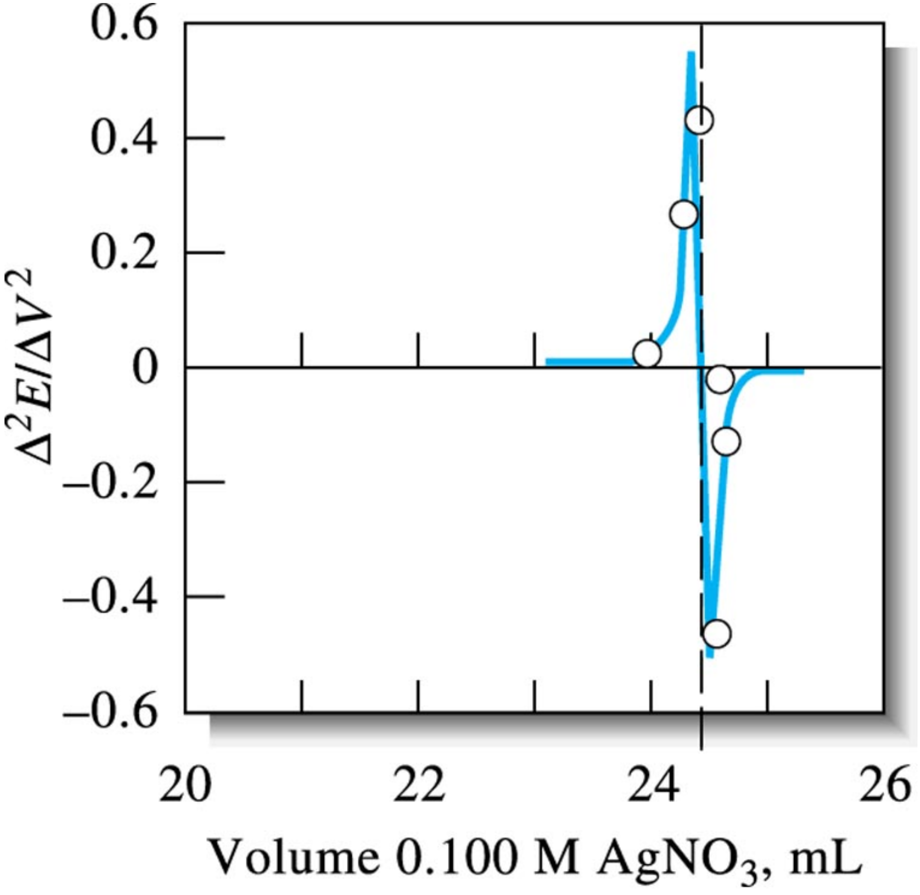
- A direct plot of potential as a function of reagent volume
  - the inflection point in the steeply rising portion of the curve, and take it as the end point.




1.0
0.8
0.6
0.4
0.2
0
$\Delta E/\Delta V$, V/mL
20
22
24
26
Volume 0.100 M $AgNO_3$, mL

Detecting the End Point

- 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: $\boxed{[\mathrm{HA}] \approx [\mathrm{A}^-]}$
- Therefore:

$$K_a = \frac{[\mathrm{H_3O^+}]\cancel{[\mathrm{A}^-]}}{\cancel{[\mathrm{HA}]}} = [\mathrm{H_3O^+}]$$

$$\mathrm{p}K_a = \mathrm{pH}$$

  - It is important to note that the use of concentrations instead of activities may cause the value of Ka differ from its published value by a factor of 2 or more.
- A more correct form:

$$K_a = \frac{a_{\mathrm{H_3O^+}}a_{\mathrm{A^-}}}{a_{\mathrm{HA}}} = \frac{a_{\mathrm{H_3O^+}}\gamma_{\mathrm{A^-}}\cancel{[\mathrm{A}^-]}}{\gamma_{\mathrm{HA}}\cancel{[\mathrm{HA}]}} = \frac{a_{\mathrm{H_3O^+}}\gamma_{\mathrm{A^-}}}{\gamma_{\mathrm{HA}}}$$

-

EXAMPLE 21-2

- 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.

- Since $$K_a(\text{exptl}) = a_{H_3O^+} = K\left(\frac{\gamma_{HA}}{\gamma_{A^-}}\right)$$ and
  - the activity coefficient for H_3PO_4 is *ca.* 1
  - the activity coefficient for $H_2PO_4^-$ is *ca.* 0.78
  - the activity coefficient for HPO_4^{2-} is *ca.* 0.36
- Therefore:

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

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

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

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

Potentiometric Determination of Equilibrium Constants

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

EXAMPLE 21-3

- Calculate the formation constant K_f for $Ag(CN)_2^-$:

$$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$$

if the cell $\text{SCE} \,\|\, Ag(CN)_2^-(7.50 \times 10^{-3}\text{ M}), CN^-(0.0250\text{ M}) \,|\, Ag$

develops a potential of −0.625 V.

- If $Ag^+ + e^- \rightleftharpoons Ag(s) \qquad E^0 = +0.799\text{ V}$

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

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

- Apply the Nernst equation for the silver electrode:

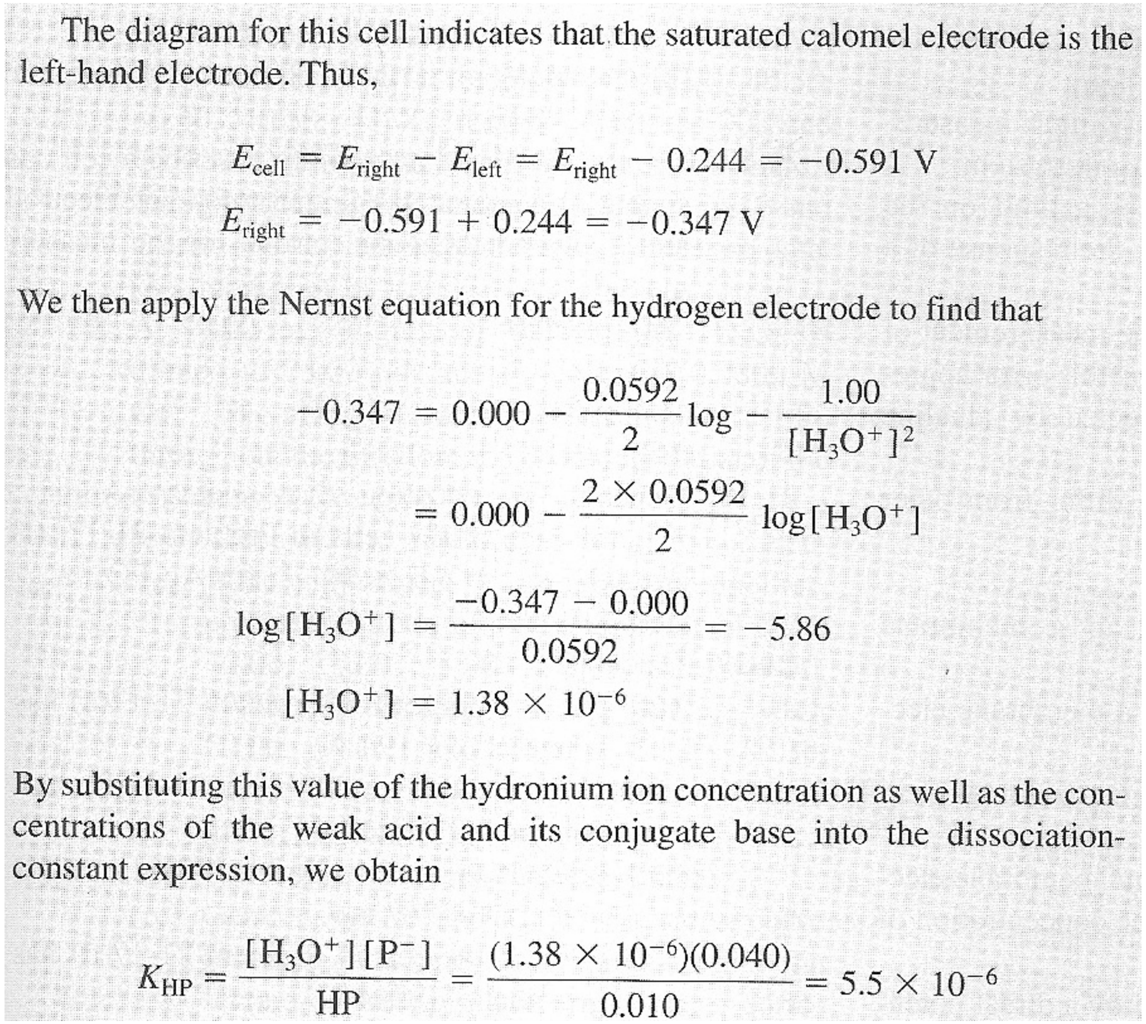
$$-0.381 = 0.799 - \frac{0.0592}{1}\log\frac{1}{[Ag^+]}$$ ⇨ $$[Ag^+] = 1.2 \times 10^{-20}$$

⇨ $$K_f = \frac{[Ag(CN)_2^-]}{[Ag^+][CN^-]^2} = \frac{7.50 \times 10^{-3}}{(1.2 \times 10^{-20})(2.5 \times 10^{-2})^2}$$

$$= 1.0 \times 10^{21} \approx 1 \times 10^{21}$$

EXAMPLE 21-4

- Calculate the dissociation constant K_{HP} for the weak acid HP if the cell: $\text{SCE}\,\|\,\text{HP}(0.010\text{ M}),\ \text{NaP}(0.040\text{ M})\,|\,\text{Pt},\ H_2\ (1.00\text{ atm})$ develops 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

$$-0.347 = 0.000 - \frac{0.0592}{2}\log - \frac{1.00}{[H_3O^+]^2}$$

$$= 0.000 - \frac{2 \times 0.0592}{2}\log[H_3O^+]$$

$$\log[H_3O^+] = \frac{-0.347 - 0.000}{0.0592} = -5.86$$

$$[H_3O^+] = 1.38 \times 10^{-6}$$

By substituting this value of the hydronium ion concentration as well as the concentrations of the weak acid and its conjugate base into the dissociation-constant expression, we obtain

$$K_{HP} = \frac{[H_3O^+][P^-]}{HP} = \frac{(1.38 \times 10^{-6})(0.040)}{0.010} = 5.5 \times 10^{-6}$$