

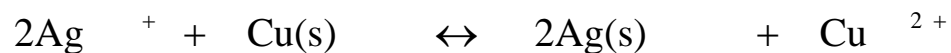
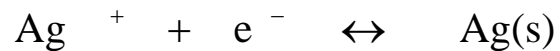
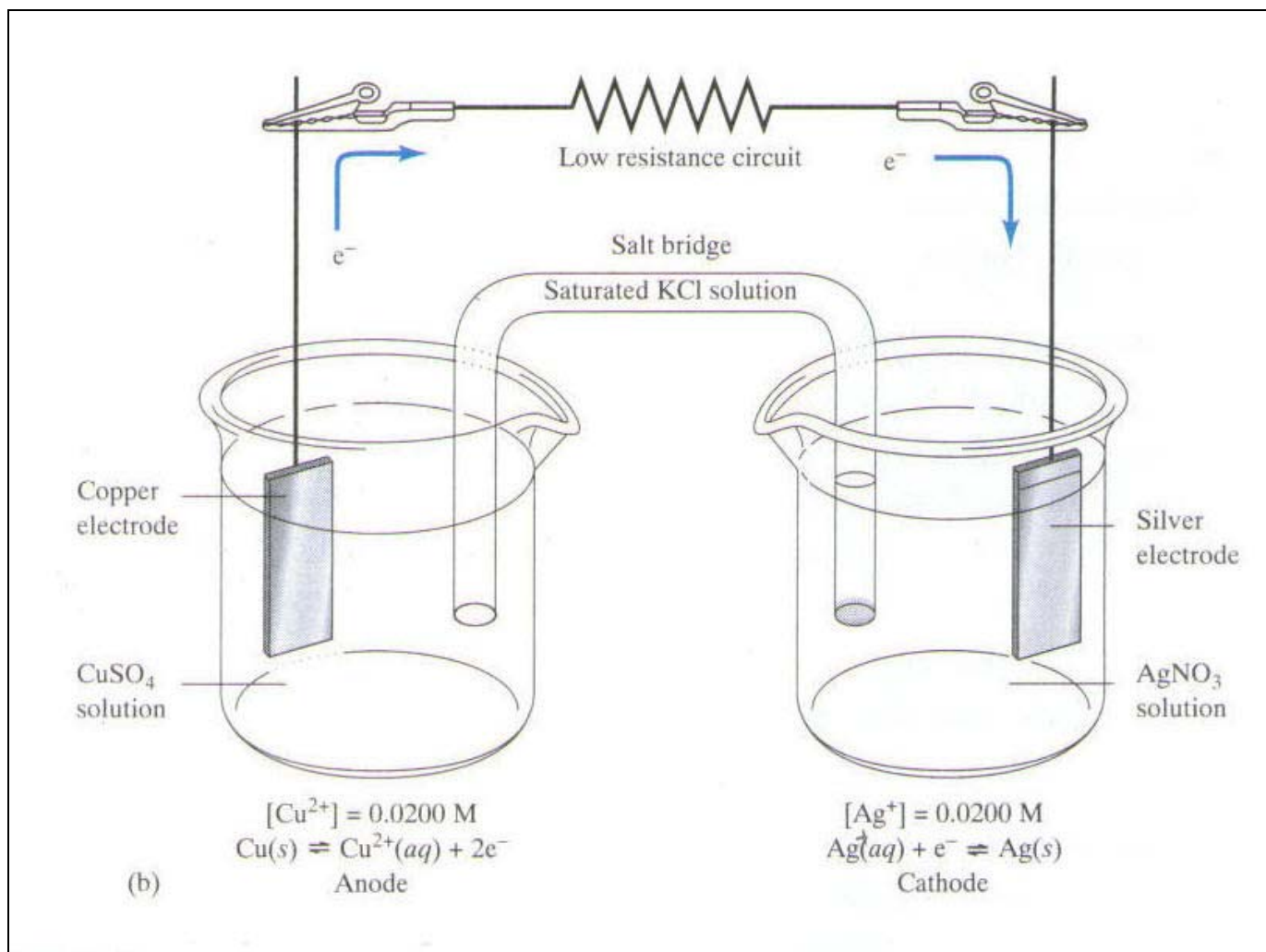
# Unit 2

## Electrochemical methods of Analysis

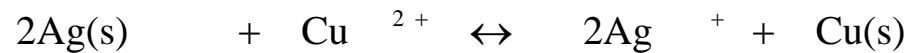
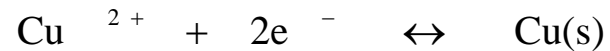
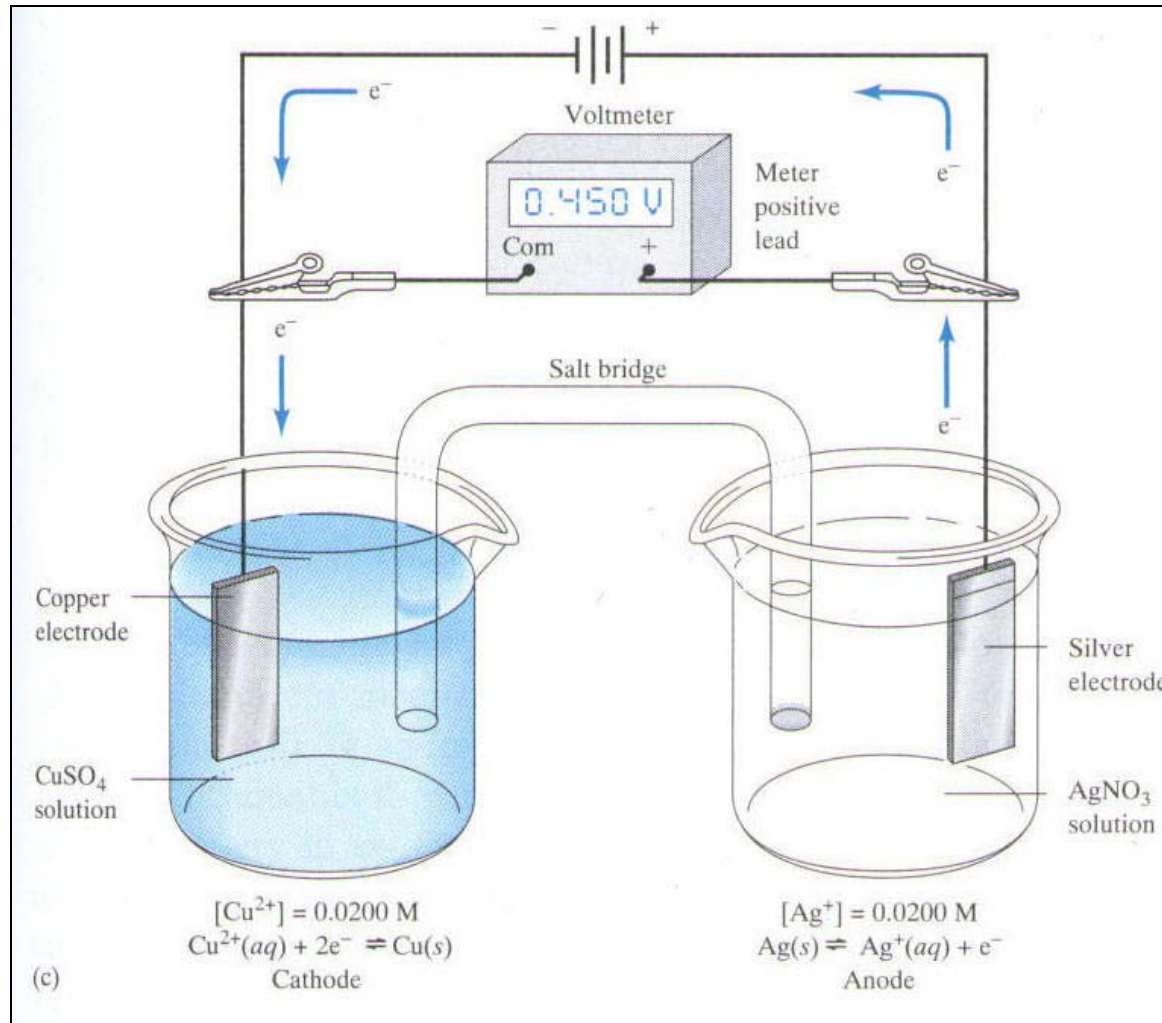
# Recall from Freshman Chemistry:

- **Oxidation:** Loss of electrons or increase in the oxidation number
- $\text{Fe}^{2+} + \text{e}^- \rightarrow \text{Fe}^{3+}$
- 
- **Reduction:** Gain of electrons or decreases in the oxidation state
- $\text{Cu}^{2+} + 2 \text{e}^- \rightarrow \text{Cu}$
- **Redox reaction**
- $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$
- **Oxidizing agent:** Species that is being reduced and causes an oxidation
- **Reducing agent:** Species that is being oxidized and cause a reduction

# Galvanic Cell = Battery



# Electrolytic Cells

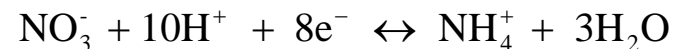
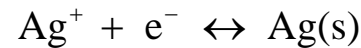


# Anodes and Cathodes

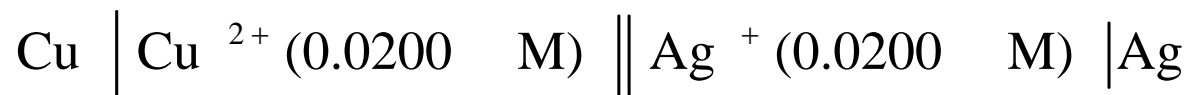
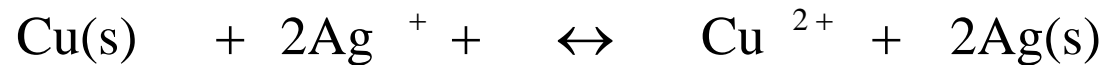
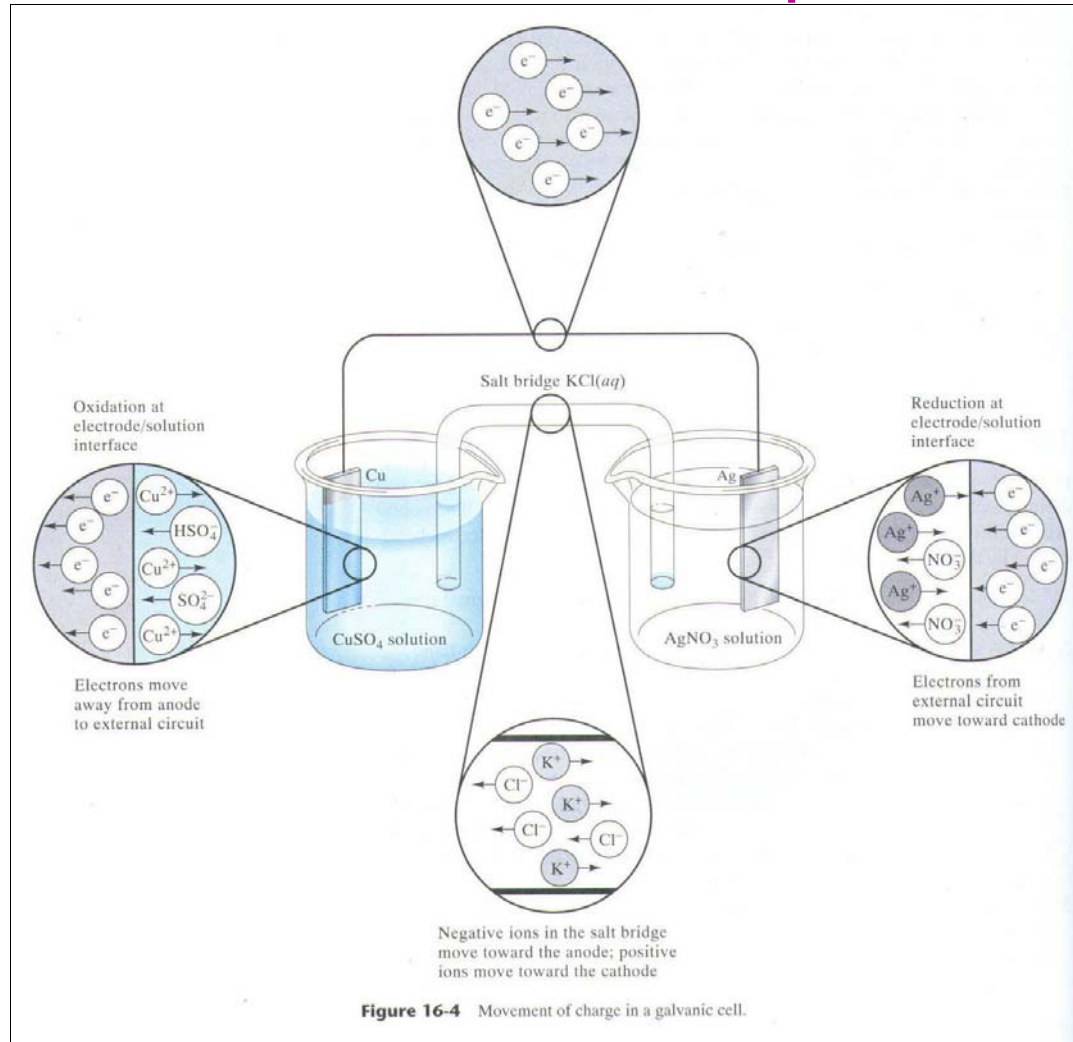
**Anode** - Oxidation takes place



**Cathode** - Reduction takes place



# Electrochemical Cell Representations



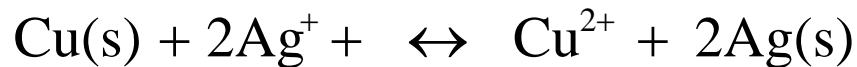
# Electrode Potentials

- **It is the driving force for either reduction or oxidation half reaction, when by convention, they are both written as reductions.**
- **$\text{Cu}^{2+} + 2\text{e}^- \leftrightarrow \text{Cu}$**
- **$\text{Ag}^+ + \text{e}^- \leftrightarrow \text{Ag}$**

# Cell Potential (Voltage)

**Cell potential or Cell voltage:** it is the driving force (or chemical pressure) that pushes electrons through the external circuit of an electrochemical cell.

It is also called electromotive force of the cell.



**$E_{\text{cell}}$  is also related to the free energy of the reaction**

$$\Delta G = -nFE_{\text{cell}}$$

where  $\Delta G$  = Free Energy

$n$  = number of electrons trans.

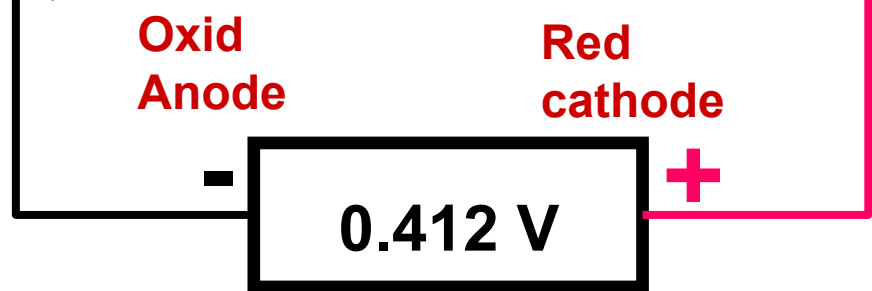
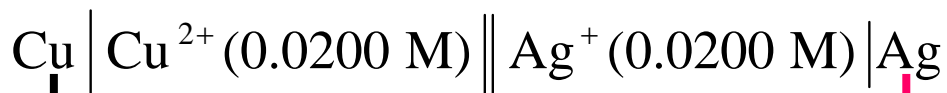
$F$  = Faraday constant

$E_{\text{cell}}$  = Cell Potential

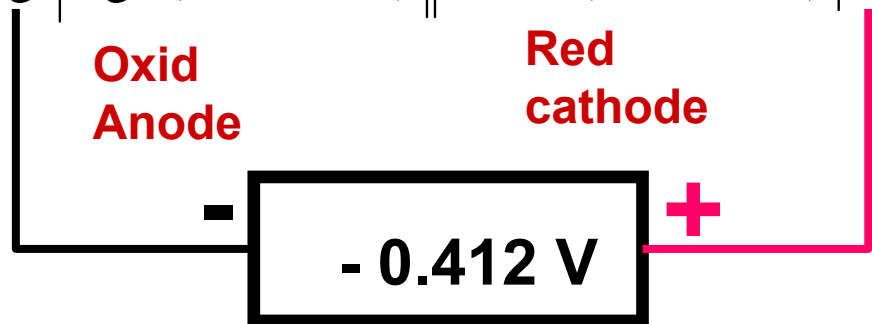
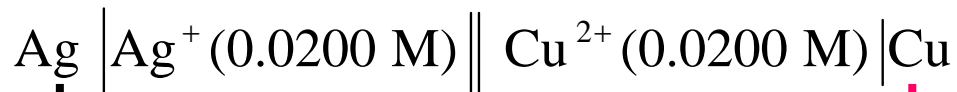
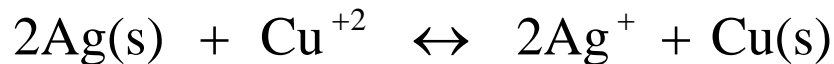
$$\Delta G^\circ = -nFE_{\text{cell}}^\circ = -RT \ln K_{\text{eq}}$$



# Sign Convention

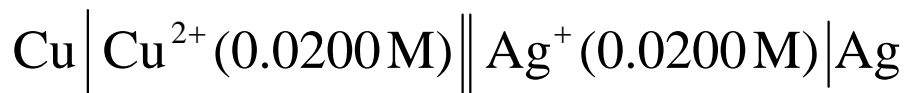
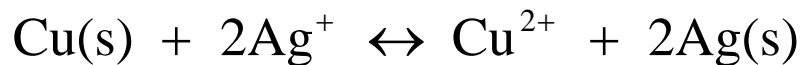


**Volt Meter**



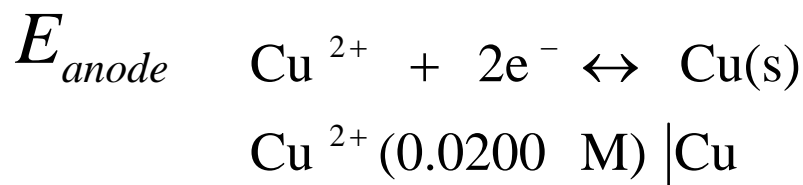
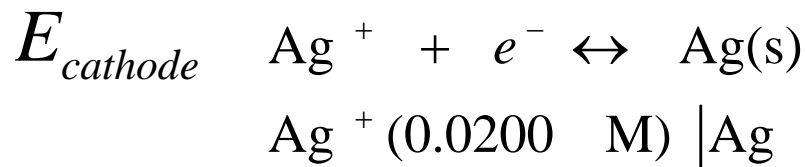
**Volt Meter**

# Half-Cells= Half-cell reaction



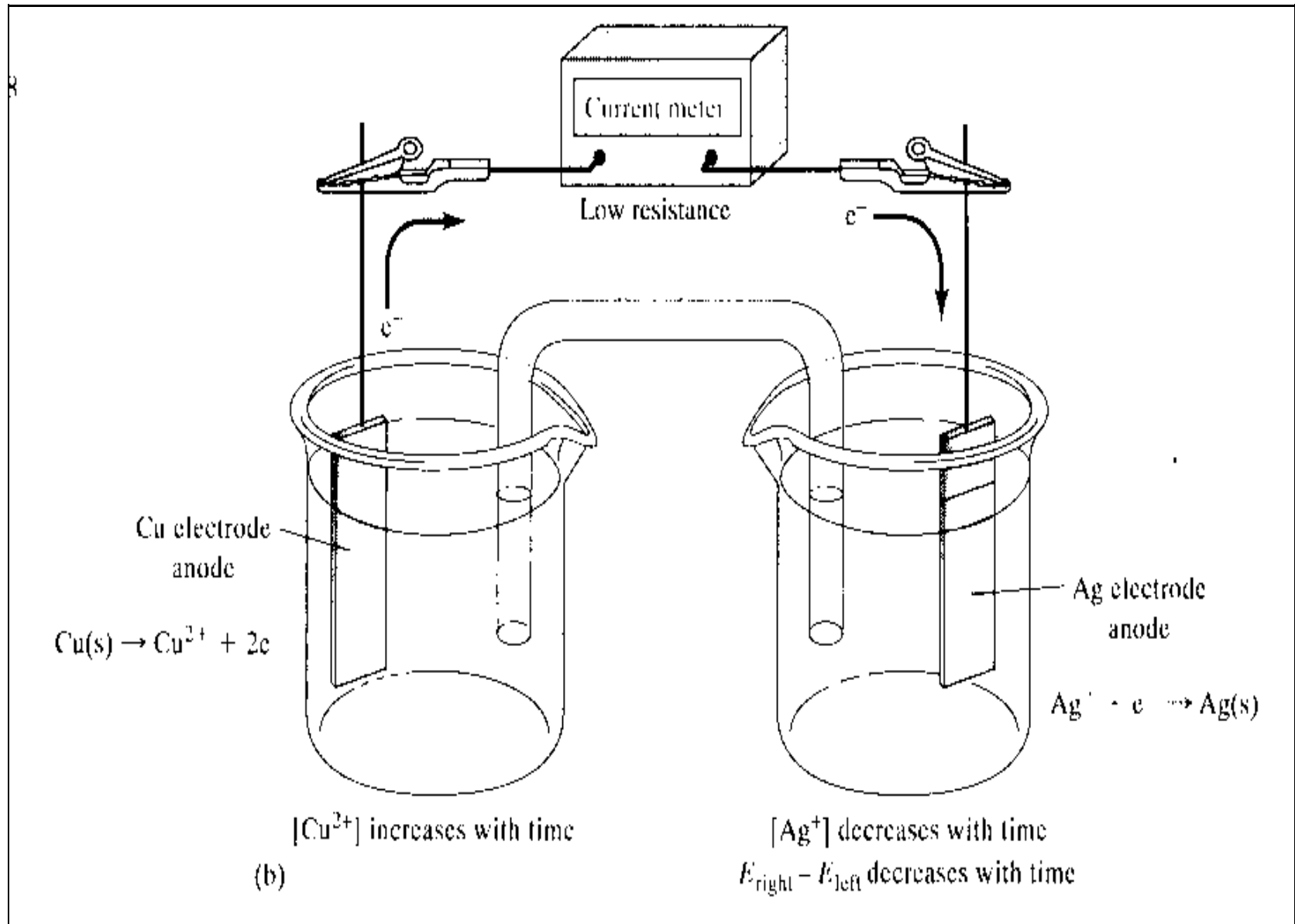
$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

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

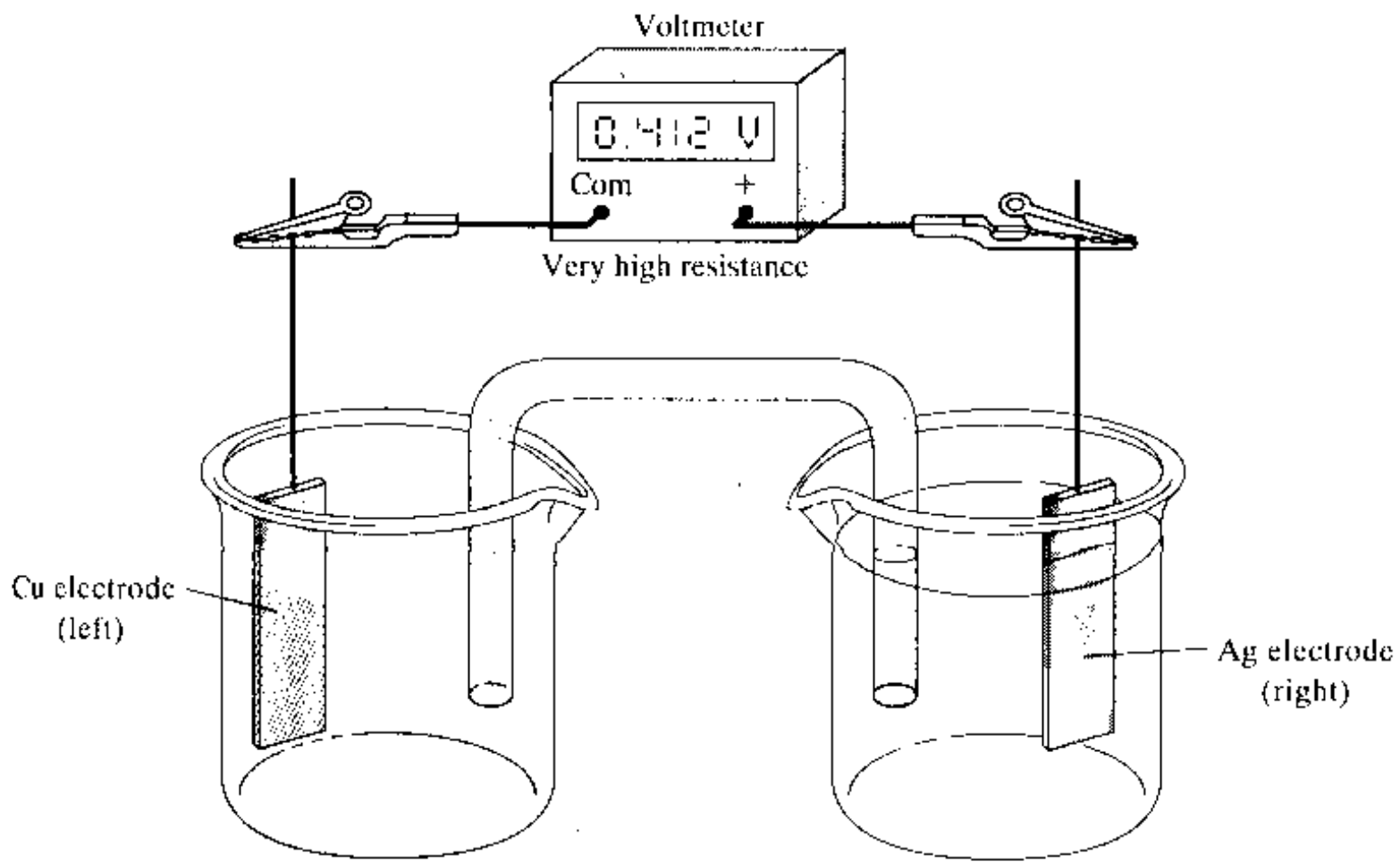


**By convention, all Half-Cell reactions are written as reduction half-reactions**

# Current Flows and Concentrations Change



# Initial Potential



$$[\text{Cu}^{2+}] = 0.0200 \text{ M}$$

$$E_{\text{left}} = 0.2867 \text{ V}$$

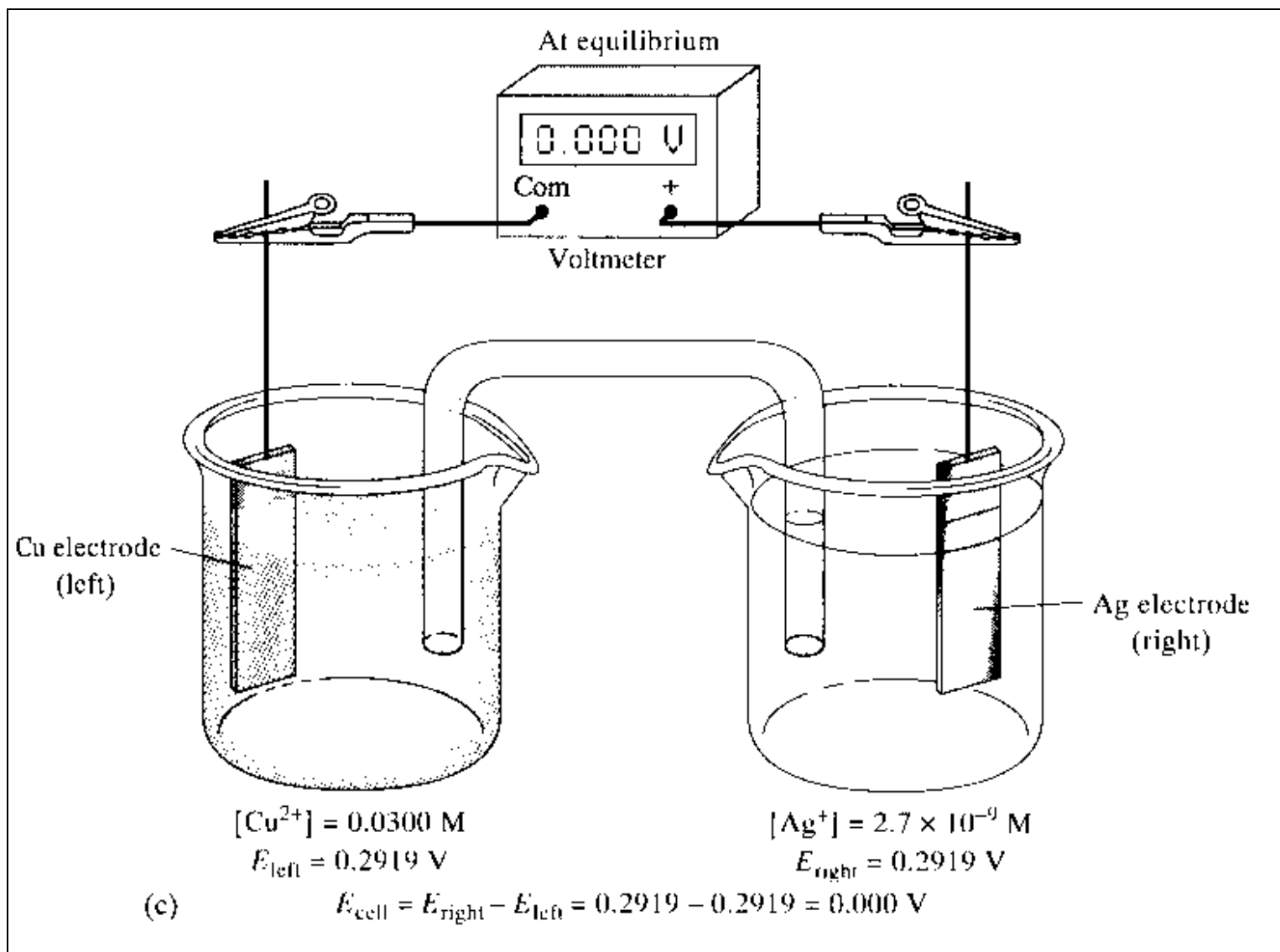
$$[\text{Ag}^+] = 0.0200 \text{ M}$$

$$E_{\text{right}} = 0.6984 \text{ V}$$

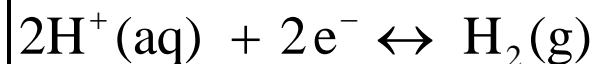
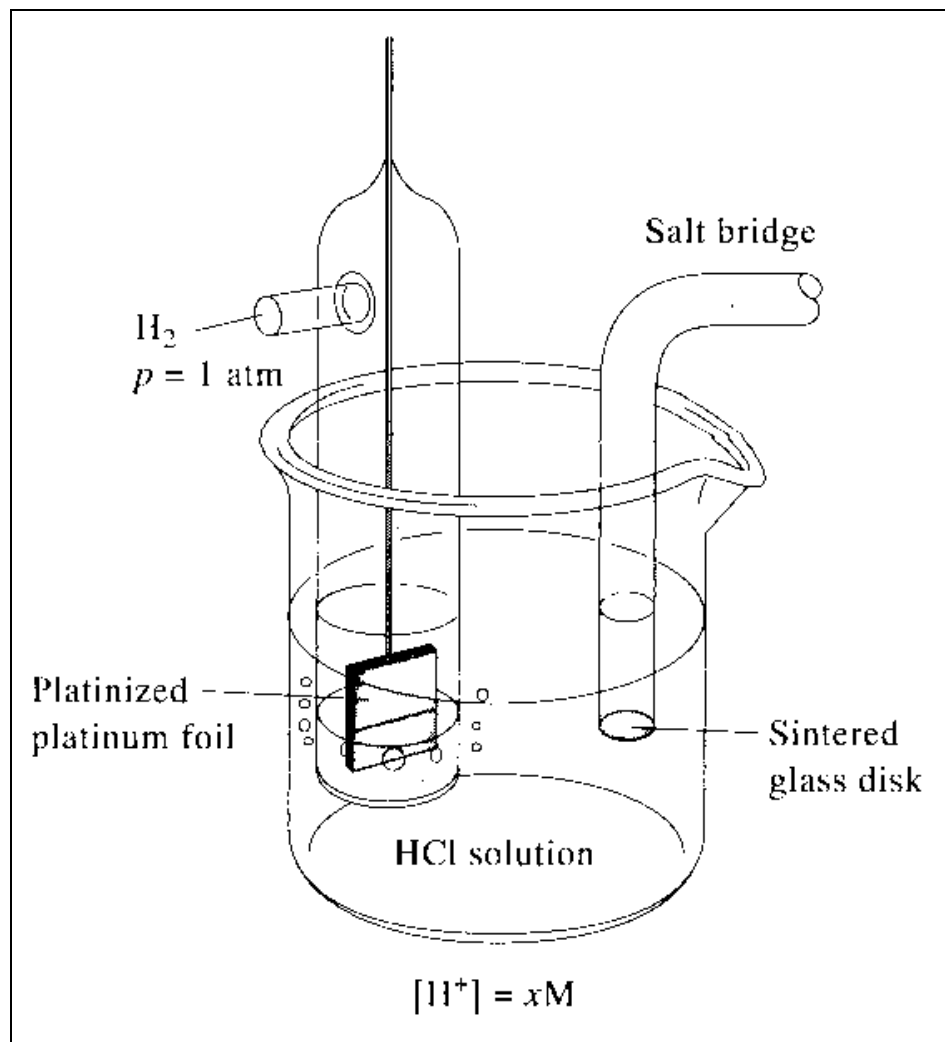
(a)

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.6984 - 0.2867 = 0.412 \text{ V}$$

# Concentrations Change Until Equilibrium is Obtained

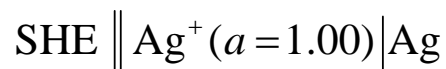
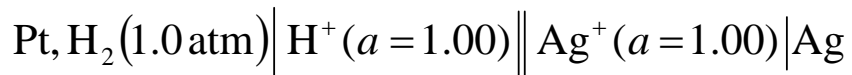
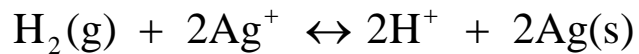
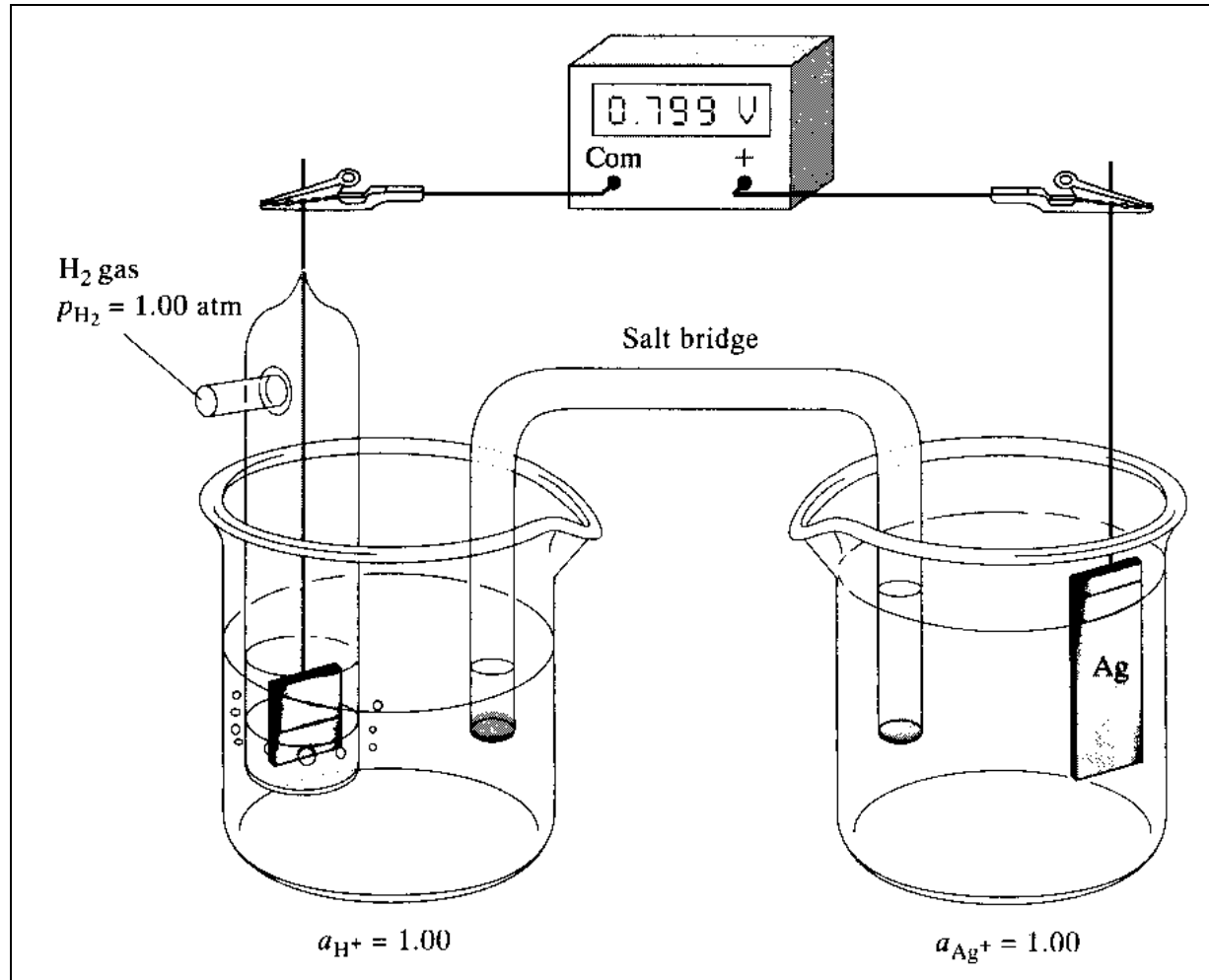


# Standard Hydrogen Electrode (SHE)



$$E_{SHE}^\circ = 0.00 \text{ volts}$$

# Standard Cell Potentials



$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = +0.799 \text{ V}$$

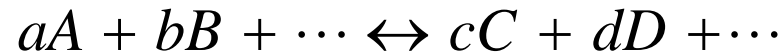
# Table of Standard electrode Potentials

## Standard Electrode Potentials

Reaction	$E^0$ at 25°C, V
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+ 1.359
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	+ 1.229
$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	+ 1.087
$\text{Br}_2(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-$	+ 1.065
$\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	+ 0.799
$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$	+ 0.771
$\text{I}_3^- + 2\text{e}^- \rightleftharpoons 3\text{I}^-$	+ 0.536
$\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+ 0.337
$\text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$	+ 0.334
$\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^-$	+ 0.268
$\text{AgCl}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-$	+ 0.222
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + 2\text{S}_2\text{O}_3^{2-}$	+ 0.017
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	<b>0.000</b>
$\text{AgI}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{I}^-$	- 0.151
$\text{PbSO}_4 + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}$	- 0.350
$\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}(\text{s})$	- 0.403
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	- 0.763



# Nernst Equation – Potentials as a function of Concentration



$$E = E^\circ - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$E = E^\circ - \frac{0.0592}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

**Remember -**

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

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

# Classification of Electrochemical methods of Analysis

- **Bulk Methods**: Based on phenomenon occurs in the bulk of solution. Measurement of properties of the whole solution.
  - Conductimetry is an example
- **Interfacial Methods**: Signal is a function of phenomena taking place at the electrode-solution interface. Possess wider usage.
  - pH measurement using a pH electrode

# Interfacial Electrochemical methods

- **Static Methods:**

No current passes in the electrochemical cell

e.g. Potentiometry

- **Dynamic Methods:**

Current flows in the electrochemical cell

- Constant Current Methods

- Fixed current allows complete oxidation or reduction of the analyte. Quantity of electricity (**Coulometry**) or material deposited on electrodes (**Electrogravimetry**) are determined

- Controlled-Potential Methods:

- Constant potential is applied during analysis while measurements of other variables are carried out. Sensitive and can be carried out for small volumes.
- For example: **Voltammetry**: Potential is systematically varied during analysis

# Controlling and measuring Current and Potential

- **Electrochemical Cell Consists of :**
  - Two or more electrodes, Electrolyte, Electronics for controlling and measuring the current and potential
  - Indicator (Working) Electrode: One whose potential is sensitive to the analyt's concentration
  - Counter (Reference) Electrode: It completes the electric circuit and provides a reference potential against which the working electrode potential is measured. Its potential remains constant
- **Electrochemical Cell Consists of three-electrode system**
  - Indicator electrode, Reference electrode & Auxiliary electrode

# Comments

- **Passage of a current changes the concentration of the analyte thus the potential of the counter electrode may change by time**
- **Counter electrode is replaced by : Reference electrode & Auxiliary electrode**
- **Reference electrode: No current flows through it and its potential stays constant**
- **Auxiliary electrode :It completes the electric circuit and allows for the current flow.**

# Experimental Design of the Electrochemical Cells

1. Potential measurement under static conditions of no current flow
2. Potential measurement while controlling the current
3. Current measurement while controlling the potential

- All above measurements are based on Ohm's law

$$E = iR$$

- **Instruments used for potential measurement:**

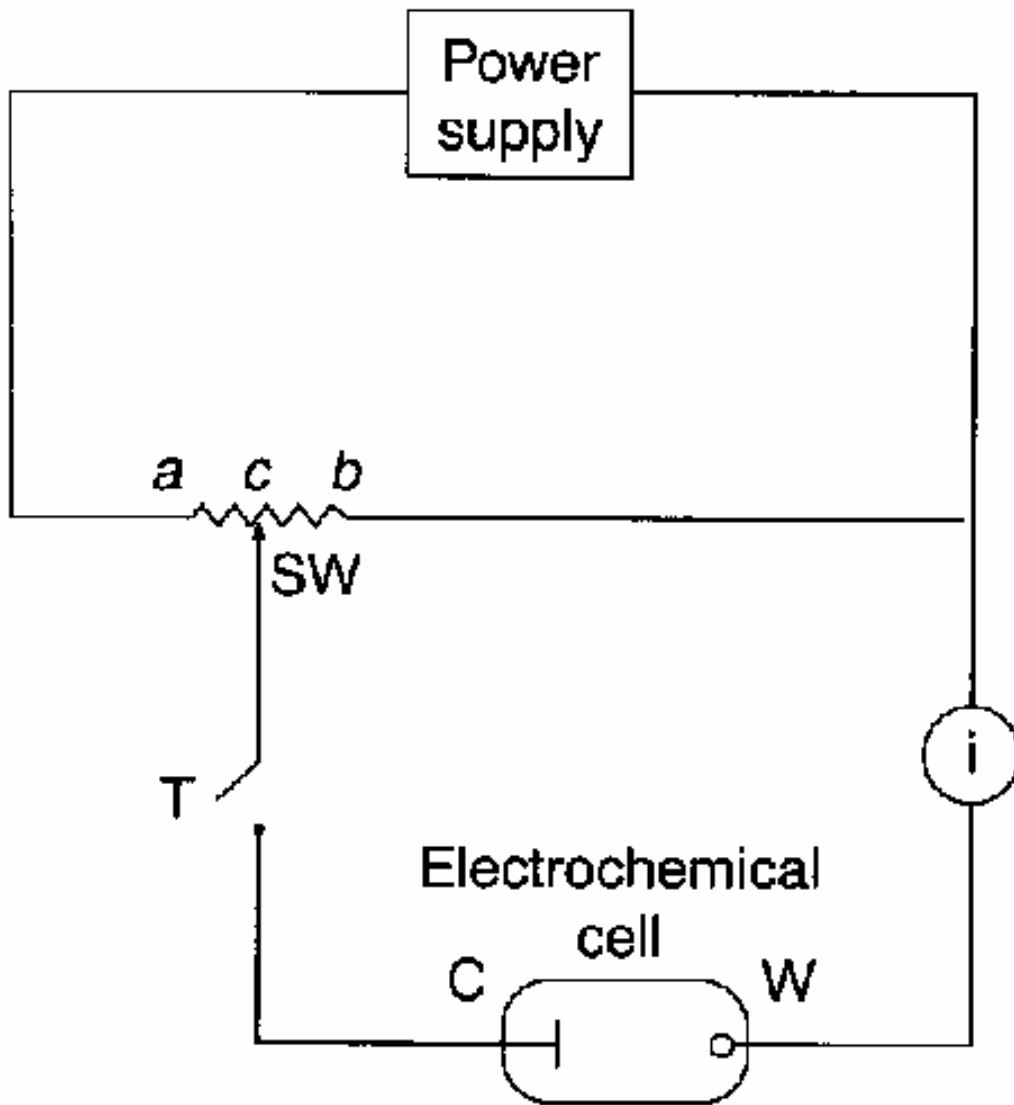
- Potentiometer: It measures the potential under conditions of zero current or changes in the cell composition would take place

- $i_{up} = E_{ps}/R_{ab}$ ;  $E_{ps} = \text{Power supply pot}$

- $i_{low} = E_{cell}/R_{cb}$ ;

- When  $i_{up} = i_{low} = 0$ ; no current flows

- $E_{cell} = R_{cb}/R_{ab} \times E_{ps}$



$$i_{up} = E_{ps}/R_{ab};$$

$E_{ps}$  = Power supply pot.

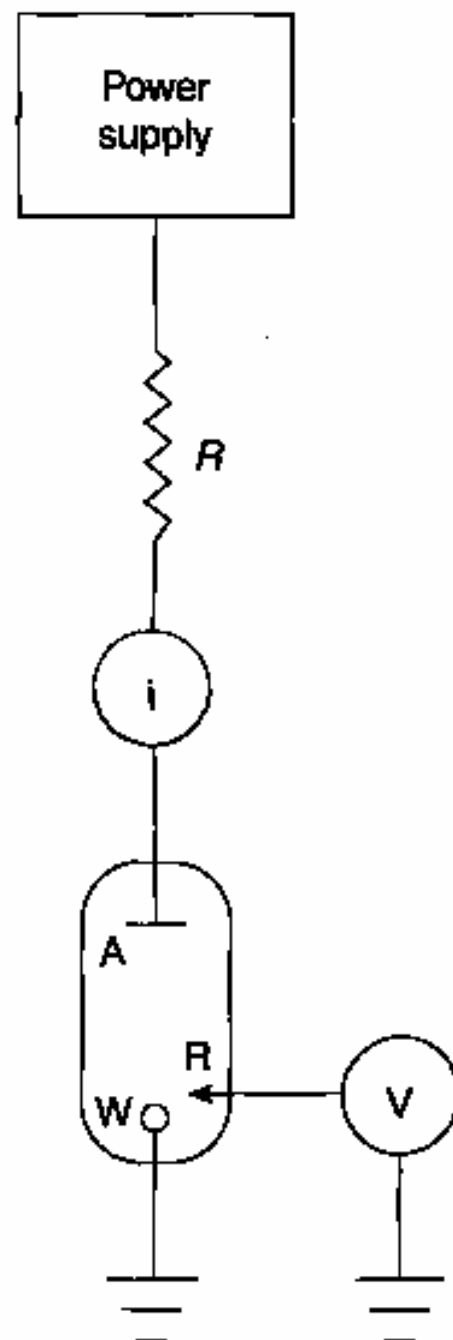
$$i_{low} = E_{cell}/R_{cb};$$

When  $i_{up} = i_{low} = 0$ ;  
no current flows

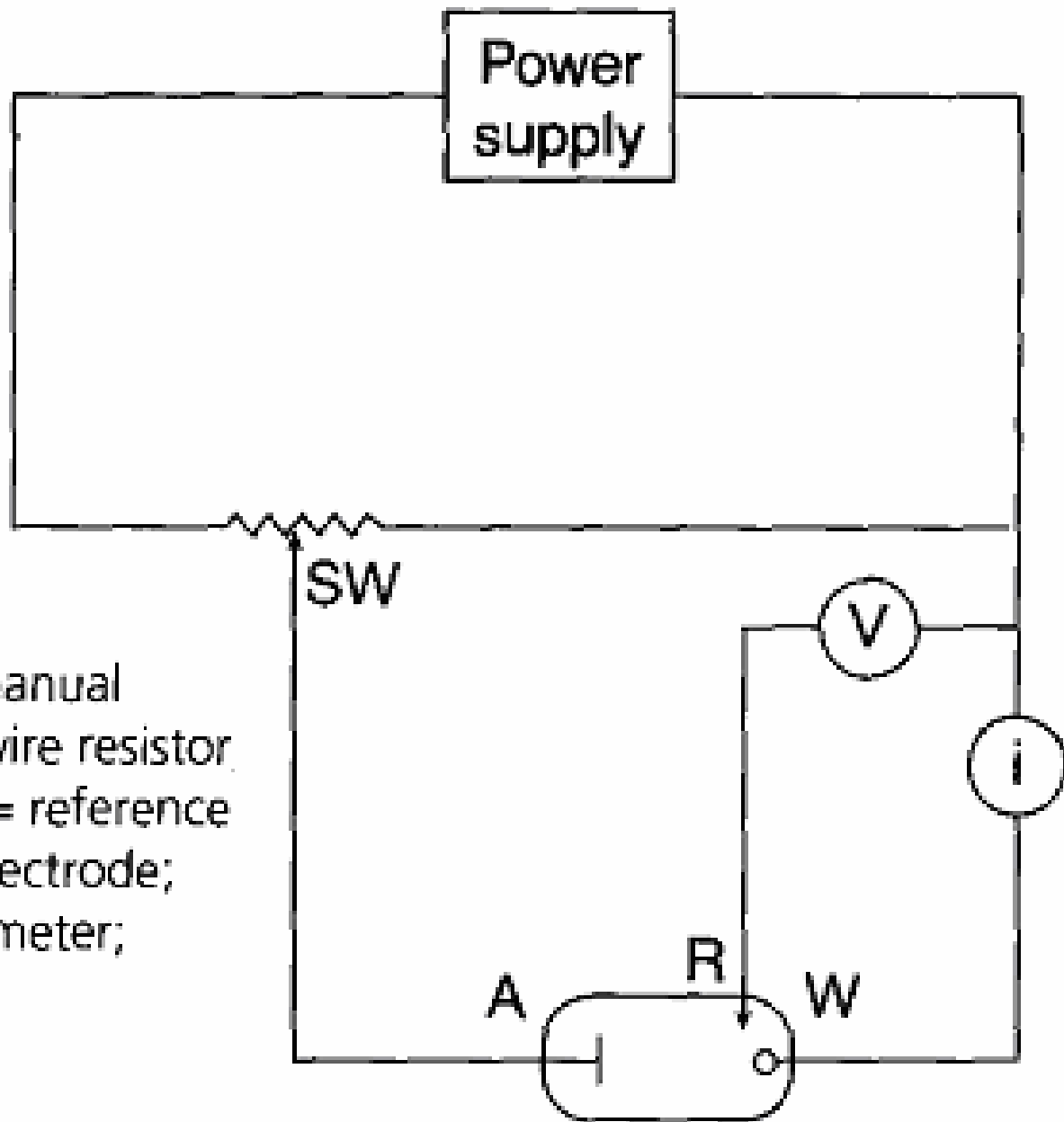
$$E_{cell} = R_{cb}/R_{ab} \times E_{ps}$$

Schematic diagram of a manual potentiostat: C = counter electrode; W = working electrode; SW = slide-wire resistor; T = tap key; i = galvanometer.

Schematic diagram of a galvanostat:  
 $R$  = resistor;  $i$  = galvanometer;  $A$  = auxiliary electrode;  
 $W$  = working electrode;  
 $R$  = reference electrode;  $V$  = voltmeter or potentiometer (optional).







Schematic diagram of a manual potentiostat: SW = slide-wire resistor; A = auxiliary electrode; R = reference electrode; W = working electrode; V = voltmeter or potentiometer; i = galvanometer.

# Galvanostat

- **Galvanostat: Device that is used to control the current in the dynamic methods**  
**When  $R \gg$  resistance of electrochemical cell**
- **$E_{ps} \gg E_{cell}$**
- **$i = E_{ps} / R$**
- **The potential of the working electrode is monitored by including a reference electrode and a potentiometer.**

# Potentiostats

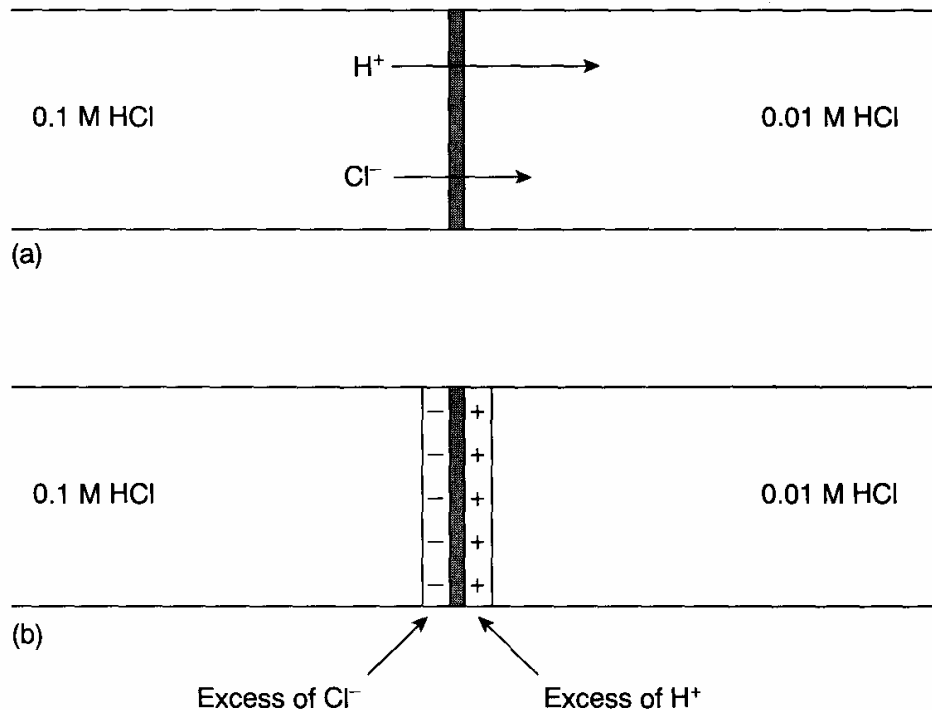
- **A device used to control the potential of the working electrode in the dynamic methods**
- **The potential of the working electrode is monitored by a reference electrode**
- **If the potential of the working electrode starts drifting from the desired value, the slide wire SW resistor is readjusted to get the potential back to its initial value**
- **The current flowing between Electrodes A and W is measured with a galvanostat**

# liquid junction potential

- It develops at the interface between any two ionic solutions that differ in composition because of a difference in mobilities of the ions.
- The interface between two ionic solutions containing different electrolytes or different concentrations of the same electrolyte is called a **liquid junction**.
  - These are designated by | in shorthand notation.
- A **junction potential** occurs at every liquid junction.
  - This puts a fundamental limitation on the accuracy of direct potentiometric measurements, because we usually don't know the contribution of the junction to the measured voltage.
- The junction potential is caused by unequal mobilities of the positive (+) and negative (-) ions.

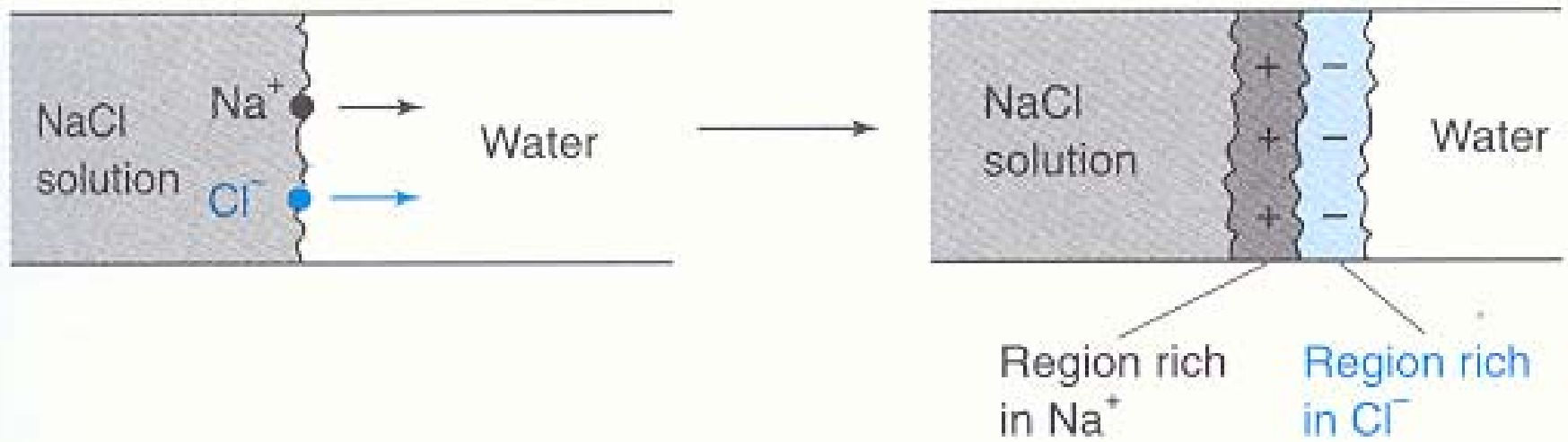
# Example

- Consider, solutions of 0.1 M HCl and 0.01 M separated by a porous membrane
- There is a net diffusion of  $\text{H}^+$  and  $\text{Cl}^-$  in the direction of the arrows.
- The mobility of  $\text{H}^+$  is greater than that for  $\text{Cl}^-$ , as shown by the difference in the lengths of their respective arrows.



- **As a result, the solution on the right side of the membrane develops an excess of  $H^+$  and has a positive charge.**
- **Simultaneously, the solution on the left side of the membrane develops a negative charge due to the greater concentration of  $Cl^-$ .**
- **The difference in potential across the membrane is called a liquid junction potential,  $E_{lj}$**
- **The magnitude of the liquid junction potential is determined by the ionic composition of the solutions on the two sides of the interface and may be as large as 30-40 mV.**
- **For example, a liquid junction potential of 33.09 mV has been measured at the interface between solutions of 0.1 M HCl and 0.1 M NaCl.**

- Consider a solution of NaCl in contact with distilled water.
- The chloride ions have a greater mobility when the sodium and chloride ions begin to diffuse from the NaCl solution.
  - Chloride is less attracted to the water molecules.
- This causes a two regions to form, one rich in Cl<sup>-</sup> and one rich in Na<sup>+</sup>.
- The result is a potential difference at the junction of the NaCl and H<sub>2</sub>O phase.



# Junction Potential Example

- A 0.1 M NaCl solution was placed in contact with a 0.1 M NaNO<sub>3</sub> solution. Which side of the junction will be positive and which will be negative?

## Solution:

- [Na<sup>+</sup>] is equal on both sides, so there is no net diffusion of Na<sup>+</sup> across the junction.
- Cl<sup>-</sup> will diffuse into the NaNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> will diffuse into the NaCl.
  - But the mobility of Cl<sup>-</sup> is greater than NO<sub>3</sub><sup>-</sup> (because it's smaller).
- The NaCl region will be depleted of Cl<sup>-</sup> faster than the NaNO<sub>3</sub> region will be depleted of NO<sub>3</sub><sup>-</sup>.
- The NaNO<sub>3</sub> side will become negative and the NaCl side will become positive.



# Minimization of Liquid Junction Potential

- The magnitude of a salt bridge's liquid junction potential is minimized by using a salt, such as KCl, for which the mobilities of the cation and anion are approximately equal.
- The magnitude of the liquid junction potential also is minimized by incorporating a high concentration of the salt in the salt bridge. For this reason salt bridges are frequently constructed using solutions that are saturated with KCl.
- Nevertheless, a small liquid junction potential, generally of unknown magnitude, is always present.
- When the potential of an electrochemical cell is measured, the contribution of the liquid junction potential must be included.
- Thus,

$$E_{\text{cell}} = E_{\text{c}} - E_{\text{a}} + E_{\text{li}}$$

# Reference Electrodes

- One of the half-cells provides a known reference potential, and the potential of the other half-cell indicates the analyte's concentration.
- By convention, the reference electrode is taken to be the anode; thus, the shorthand notation for a potentiometric electrochemical cell is

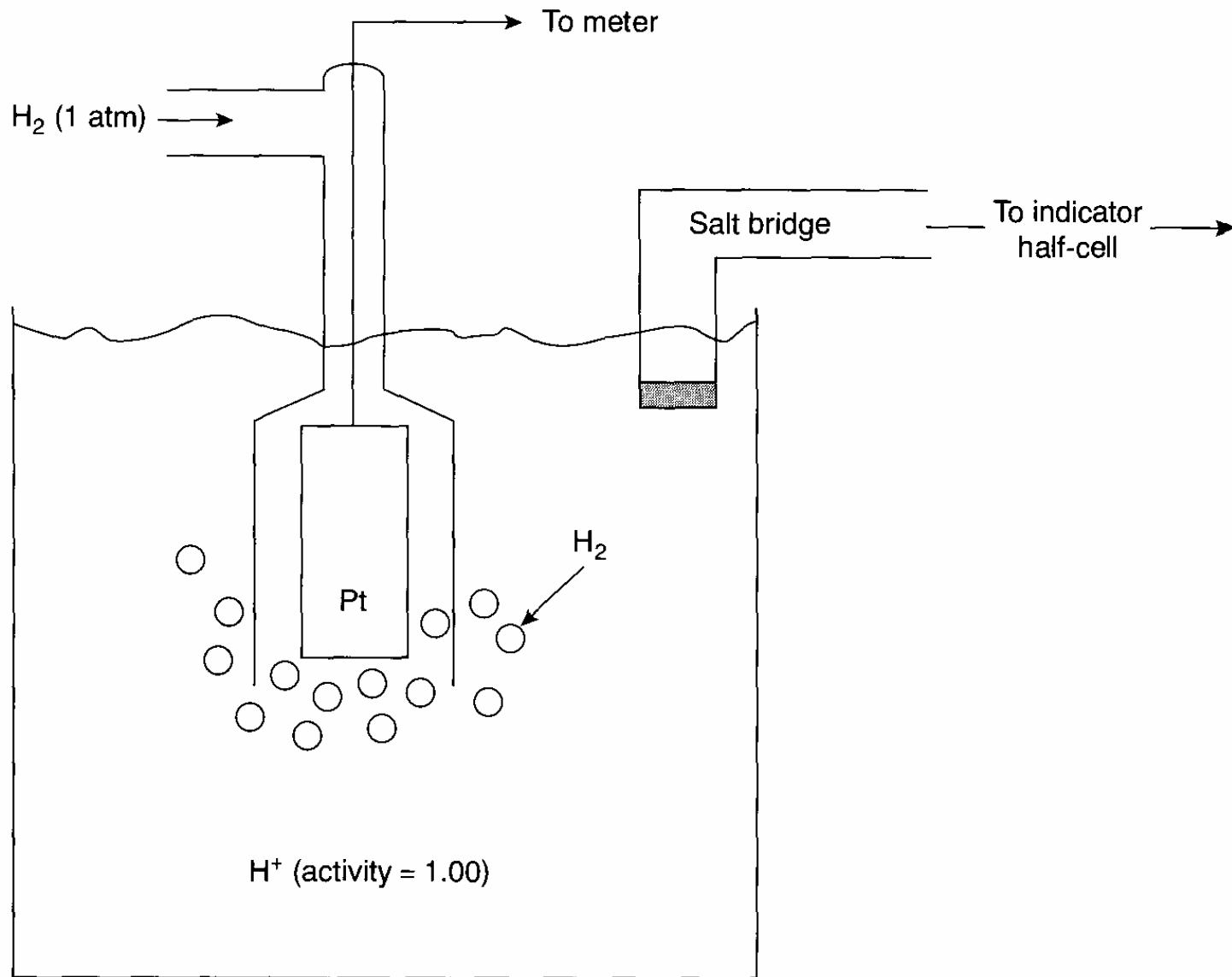
Reference                      Indicator

$$E_{cell} = E_{ind} - E_{ref} + E_{lj}$$

- The ideal reference electrode must provide a stable potential so that any change in  $E_{cell}$  is attributed to the indicator electrode, and, therefore, to a change in the analyte's concentration.

## Common reference electrodes

- **Standard Hydrogen Electrode (SHE)**
- It is rarely used for routine analytical work, but is important because it is the reference electrode used to establish standard-state potentials for other half-reactions.
- A conventional salt bridge connects the **SHE** to the indicator half-cell.
- The shorthand notation for the standard hydrogen electrode is
- **Pt(s), H<sub>2</sub> (g, 1 atm) | H<sup>+</sup> (aq, a = 1.00)**
- **2H<sup>+</sup>(aq) + 2e<sup>-</sup> → H<sub>2</sub>(g); E° = 0 V**



**Schematic diagram of the standard hydrogen electrode (SHE)**

# Calomel Electrodes

- $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{Hg}(\text{l}) + 2\text{Cl}^-(\text{aq})$
- The Nernst equation for the calomel electrode is

$$E = E^{\circ} \text{Hg}_2\text{Cl}_2/\text{Hg} - (0.05916/2) \log [\text{Cl}^-]^2$$

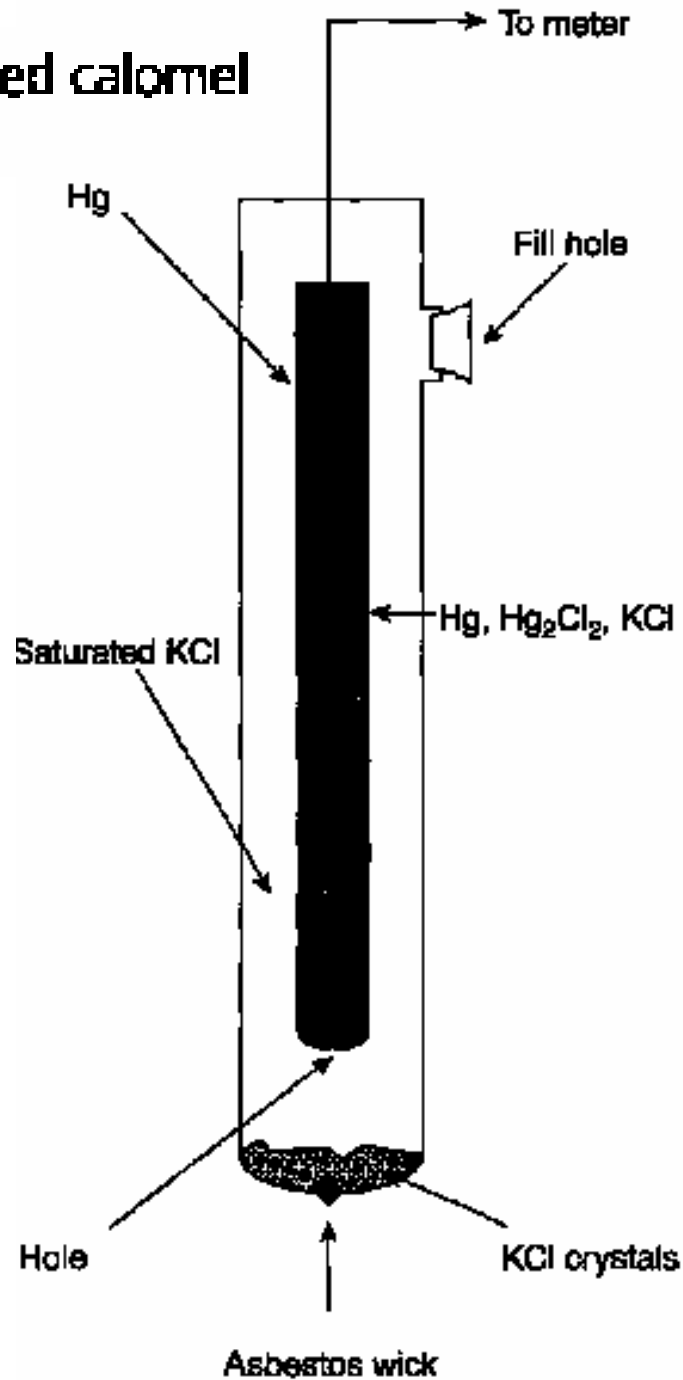
## saturated calomel electrode

- The saturated calomel electrode (SCE), which is constructed using an aqueous solution saturated with KCl, has a potential at 25 °C of +0.2444 V.

## Typical SCE

- A small hole connects the two tubes, and an asbestos fiber serves as a salt bridge to the solution in which the SCE is immersed. The stopper in the outer tube may be removed when additional saturated KCl is needed.

Schematic diagram of the saturated calomel electrode (SCE).



- The shorthand notation for the calomel electrode half-cell is
- **Hg(l) | Hg<sub>2</sub>Cl<sub>2</sub> (sat'd), KCl (aq, saturated) ||**
- The SCE has the advantage that the concentration of Cl<sup>-</sup>, and, therefore, the potential of the electrode, remains constant even if the KCl solution partially evaporates.
- A significant disadvantage of the SCE is that the solubility of KCl is sensitive to a change in temperature. At higher temperatures the concentration of Cl<sup>-</sup> increases, and the electrode's potential decreases.
- Electrodes containing unsaturated solutions of KCl have potentials that are less temperature-dependent, but experience a change in potential if the concentration of KCl increases due to evaporation.
- Another disadvantage to calomel electrodes is that they cannot be used at temperatures above 80 °C.

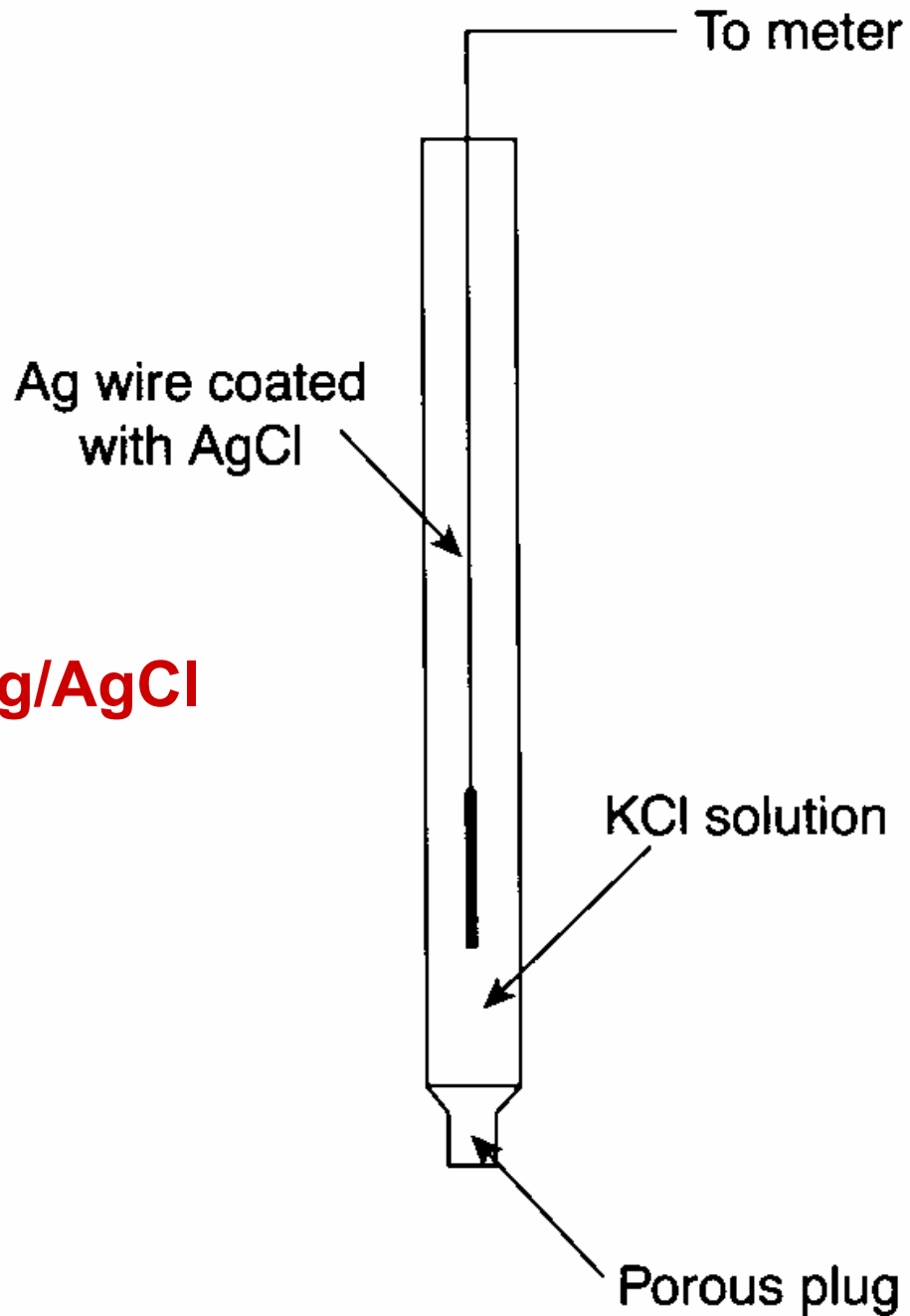
# Silver/Silver Chloride Electrodes

- $\text{Ag(s)} \mid \text{AgCl (sat'd, KCl (xM))} \parallel$
- $\text{AgCl(s)} + e^- \rightarrow \text{Ag(s)} + \text{Cl}^-(\text{aq})$
- The potential of the Ag/AgCl electrode is determined by the concentration of  $\text{Cl}^-$  used in its preparation.

$$E = E^{\circ} - 0.05916 \log[\text{Cl}^-]$$



**Schematic diagram of Ag/AgCl reference electrode**



- **The Ag/AgCl electrode prepared with saturated KCl is more temperature-sensitive than one prepared with an unsaturated solution of KCl.**
- **In comparison to the SCE the Ag/AgCl electrode has the advantage of being useful at higher temperatures.**
- **The Ag/AgCl electrode is more prone to reacting with solutions to form insoluble silver complexes that may plug the salt bridge between the electrode and the solution**

# Indicator Electrodes

- The potential of the indicator electrode in a potentiometric electrochemical cell is proportional to the concentration of analyte.
- Two classes of indicator electrodes are used in potentiometry: **metallic electrodes**, and **membrane ion-selective electrodes**.

# Metallic Electrodes

## Electrodes of the First Kind

- Metallic indicator electrodes in which a metal is in contact with a solution containing its ion are in general, for a metal M, in a solution of  $M^{n+}$ ,



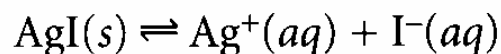
- $E_{cell} = K - (0.059/n) \log (1/[M^{2+}]) = K + (0.059/n) \log[M^{n+}]$
- Constant  $K$  includes the standard-state potential for the  $M^{n+}/M$  redox couple, the potential of the reference electrode, and the junction potential
- Electrodes of the first kind are limited to Ag, Bi, Cd, Cu, Hg, Pb, Sn, Tl, and Zn.
- Many of these electrodes, such as Zn, cannot be used in acidic solutions where they are easily oxidized.
- Their usage is limited due to slow kinetics, formation of oxides and interfering reactions

## Electrodes of the Second Kind

- A metal electrode can be made responsive to the concentration of anion if that anion forms a precipitate or a stable complex ion
- For example, silver forms an electrode of the second kind for halide and halide like anions.
- $\text{AgCl (s)} \rightleftharpoons \text{Ag (s)} + \text{Cl}^-$
- $\text{AgI (s)} \rightleftharpoons \text{Ag (s)} + \text{I}^-$
- The potential of such electrodes can be derived as follows:

$$E = E_{\text{Ag}^+/\text{Ag}}^\circ - 0.05916 \log \frac{1}{[\text{Ag}^+]} = +0.7996 - 0.05916 \log \frac{1}{[\text{Ag}^+]} \quad 11.4$$

If the solution is saturated with AgI, then the solubility reaction



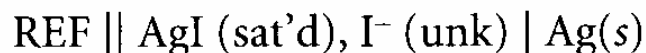
determines the concentration of  $\text{Ag}^+$ ; thus

$$[\text{Ag}^+] = \frac{K_{\text{sp, AgI}}}{[\text{I}^-]} \quad 11.5$$

where  $K_{\text{sp, AgI}}$  is the solubility product for AgI. Substituting equation 11.5 into 11.4

$$E = +0.7996 - 0.05916 \log \frac{[\text{I}^-]}{K_{\text{sp, AgI}}}$$

shows that the potential of the silver electrode is a function of the concentration of  $\text{I}^-$ . When this electrode is incorporated into a potentiometric electrochemical cell



the cell potential is

$$E_{\text{cell}} = K - 0.05916 \log [\text{I}^-]$$

where  $K$  is a constant that includes the standard-state potential for the  $\text{Ag}^+/\text{Ag}$  redox couple, the solubility product for AgI, the potential of the reference electrode, and the junction potential.

# Redox Electrodes

- An inert electrode, Pt, that serves as a means to supply electrons or as a sink for electrons involved in a redox half reaction
- $\text{Pt} \mid \text{Fe}^{3+}, \text{Fe}^{2+} \parallel$
- $\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$
- $E_{\text{cell}} = E^\circ - 0.059/n \log([\text{Fe}^{3+}]/[\text{Fe}^{2+}])$
- What is the role of **Pt** in this electrode?

# Membrane Ion-Selective Electrodes

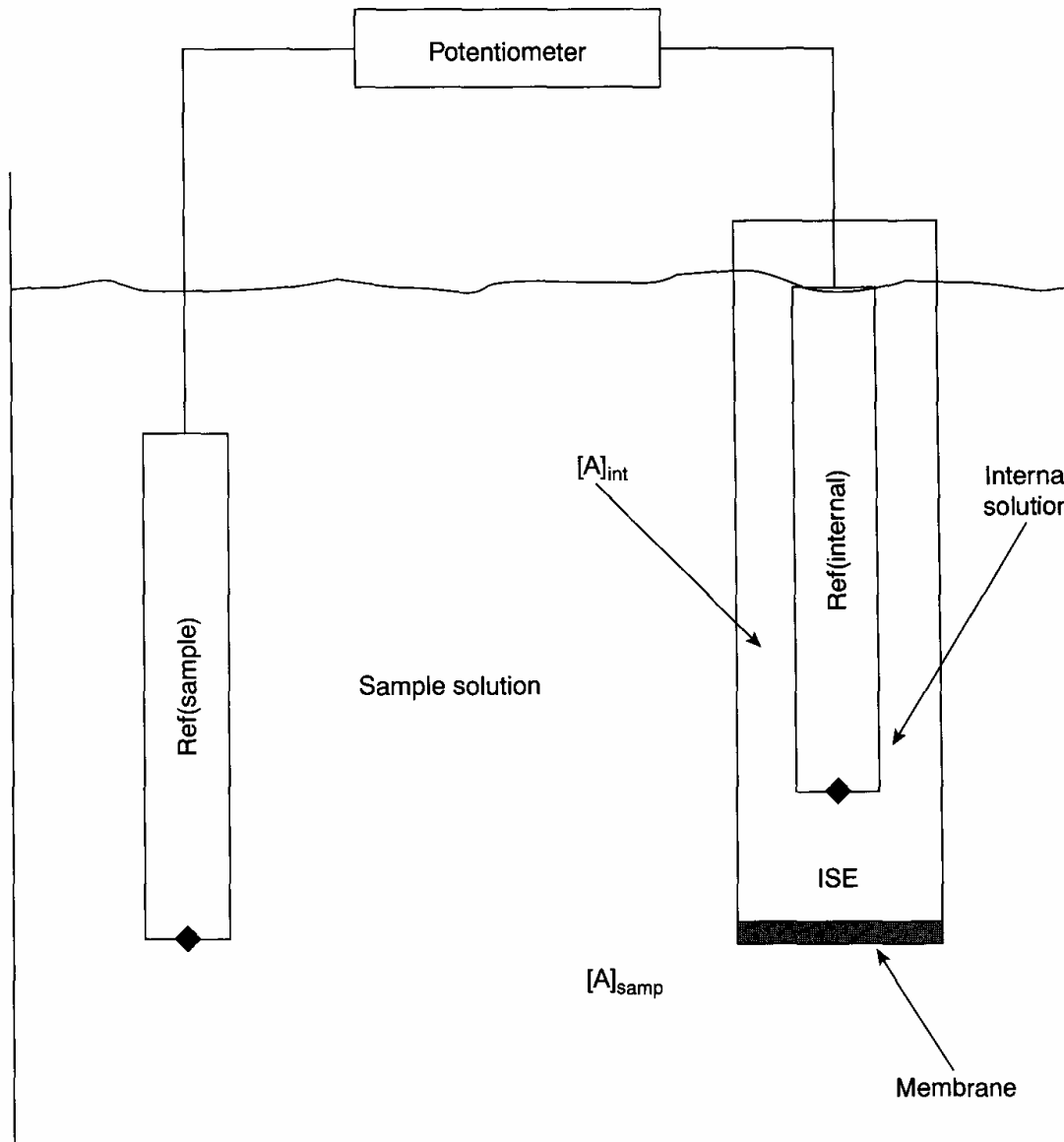
- **The discovery, that a thin glass membrane develops a potential, called a membrane potential, when opposite sides of this membrane are in contact with solutions of different pH led to the eventual development of a whole new class of indicator electrodes called ion-selective electrodes (ISEs).**



# Membrane Potentials

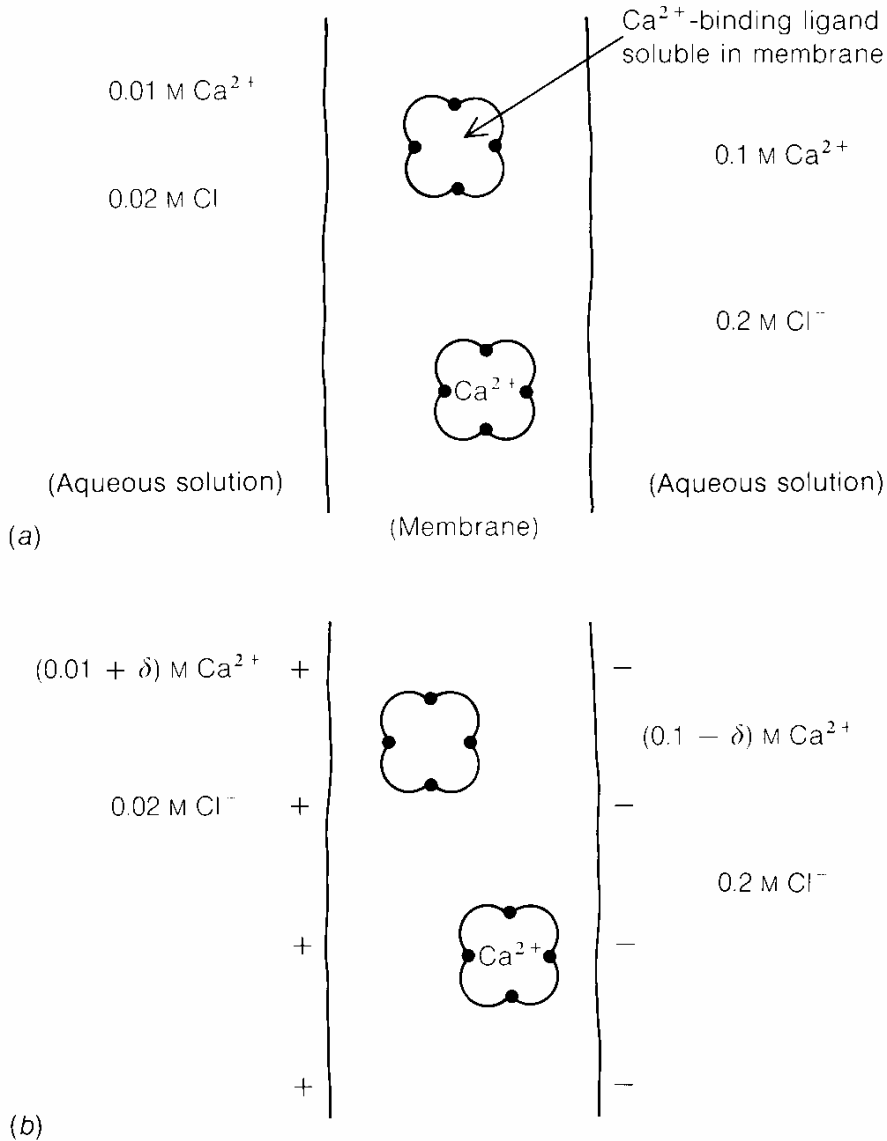
- ISE, such as the glass pH electrode, function by using a membrane that reacts selectively with a single ion.
- **Ref** <sub>(sample)</sub> || **[A]** <sub>sample</sub> | **Membrane** | **[A]** <sub>internal</sub> || **Ref** <sub>internal</sub>
- $E_{\text{cell}} = E_{\text{Ref (internal)}} - E_{\text{Ref (sample)}} + E_{\text{membrane}} + E_{\text{lj}} \dots\dots(a)$
- Liquid junction potential and reference electrode potentials are constant, thus any change in the cell's potential is attributed to the membrane potential.
- Current is carried through the membrane by the movement of either the analyte or an ion already present in the membrane's matrix.
-

- The membrane potential is given by:
- $E_{\text{mem}} = E_{\text{asym}} - (RT/zF) \ln ([A]_{\text{internal}} / [A]_{\text{sample}}) \dots (b)$
- $E_{\text{asym}}$  = Asymmetric potential : The membrane potential that develops when the concentrations on both sides are equal.
- Substituting eq. (b) into eq. (a) gives
- $E_{\text{cell}} = K + (0.059/z) \log [A]_{\text{sample}}$
- This equation applies to all types of ISE's.



**Electrochemical cell for potentiometry with an ion selective membrane electrode**

# Developing membrane potential at the surface of Ca-SE



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

# Mechanism of Ca-membrane selective electrode

- **As  $\text{Ca}^{2+}$  migrates from the region of high activity to the region of low activity, positive charge is built up on the low-activity side. Eventually the charge buildup prevents further migration of  $\text{Ca}^{2+}$  to the positively charged side.**
- **This is the same thing that happens at a liquid junction, and a constant potential difference across the junction or membrane is reached.**

## How does an ion-selective electrode work?

- imagine a membrane separating two solutions containing  $\text{CaCl}_2$ .
- The membrane contains a ligand that can bind and transport  $\text{Ca}^{2+}$ , but not  $\text{Cl}^-$ .
- Initially the potential difference across the membrane is zero, because both solutions are neutral.
- However, there will be a tendency for the ions on the side of high activity (concentration) to diffuse to the side with low activity (concentration).
- Chloride has no way to cross the membrane, but  $\text{Ca}^{2+}$  can bind to the ligand dissolved in the membrane and cross from one side to the other.

# Selectivity of Membranes

- The membrane potential is proportional to the concentration of all ions in the sample solution capable of interacting at the membrane's active sites

$$E_{\text{cell}} = K + \frac{0.05916}{z_A} (\log [A] + K_{A,I} [I]^{z_A/z_I} A^{1/z_I})$$

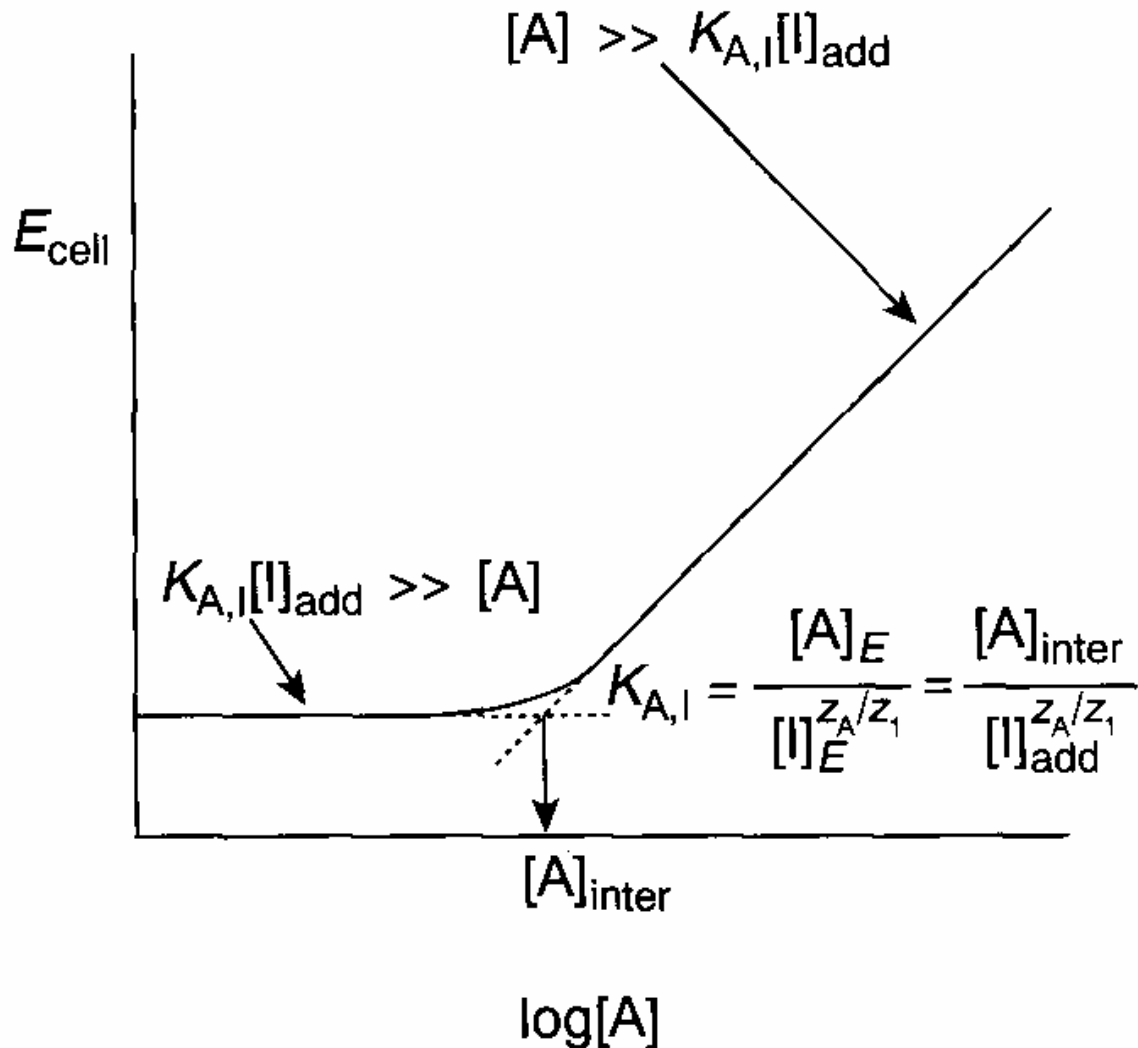
$K_{A,I}$  = Selectivity coefficient

$$K_{A,I} = \frac{[A]_E}{[I]_E^{z_A/z_I}}$$

$[A]_E$  and  $[I]_E$  are the concentrations of analyte interferent yielding identical cell potentials

When  $K_{A,I}$  is 1 the membrane responds equally to the analyte and interferent

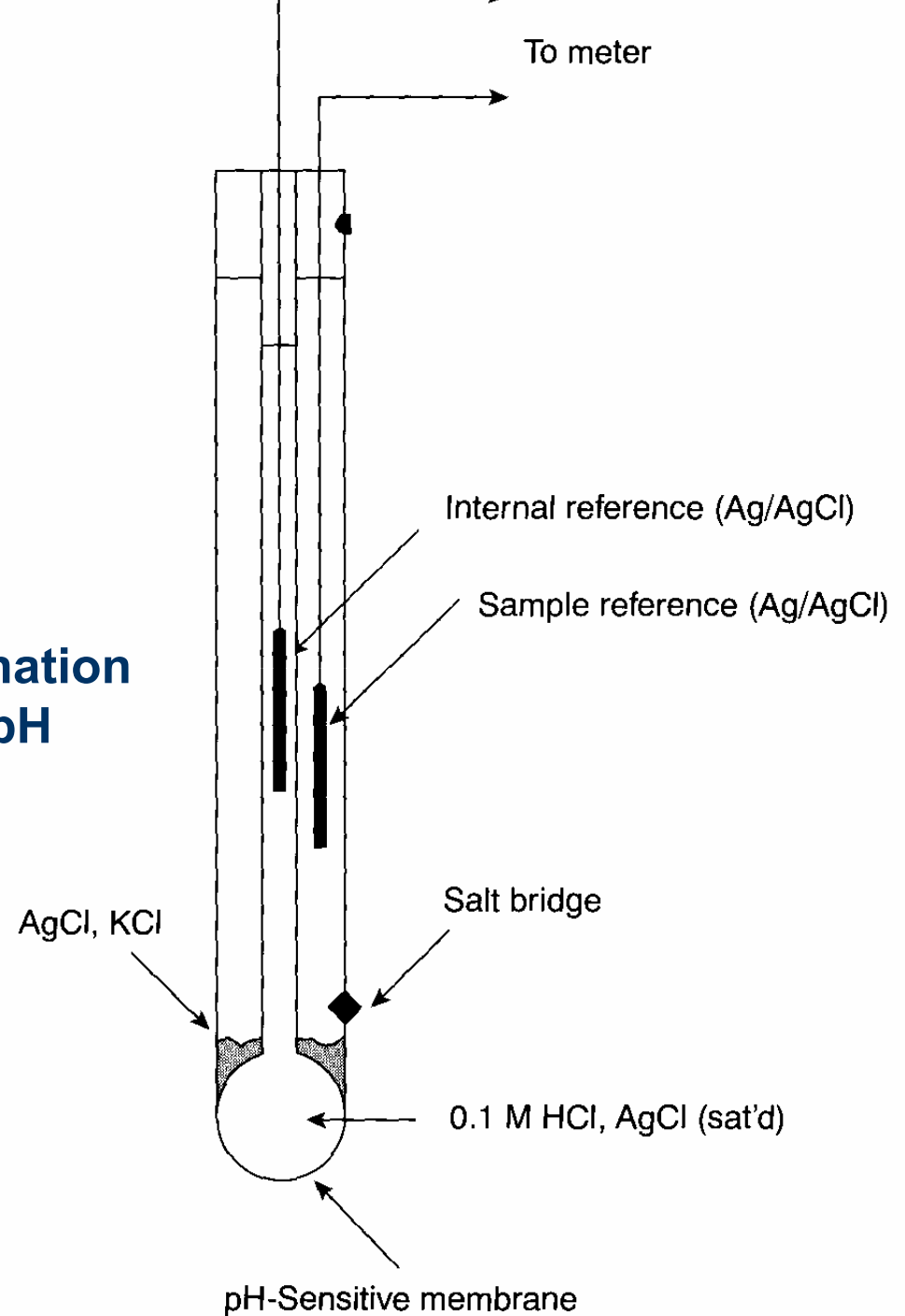
**Plot of cell potential versus the log of the analyt's concentration in the presence of a fixed concentration of interferent showing the determination of the selectivity coefficient**

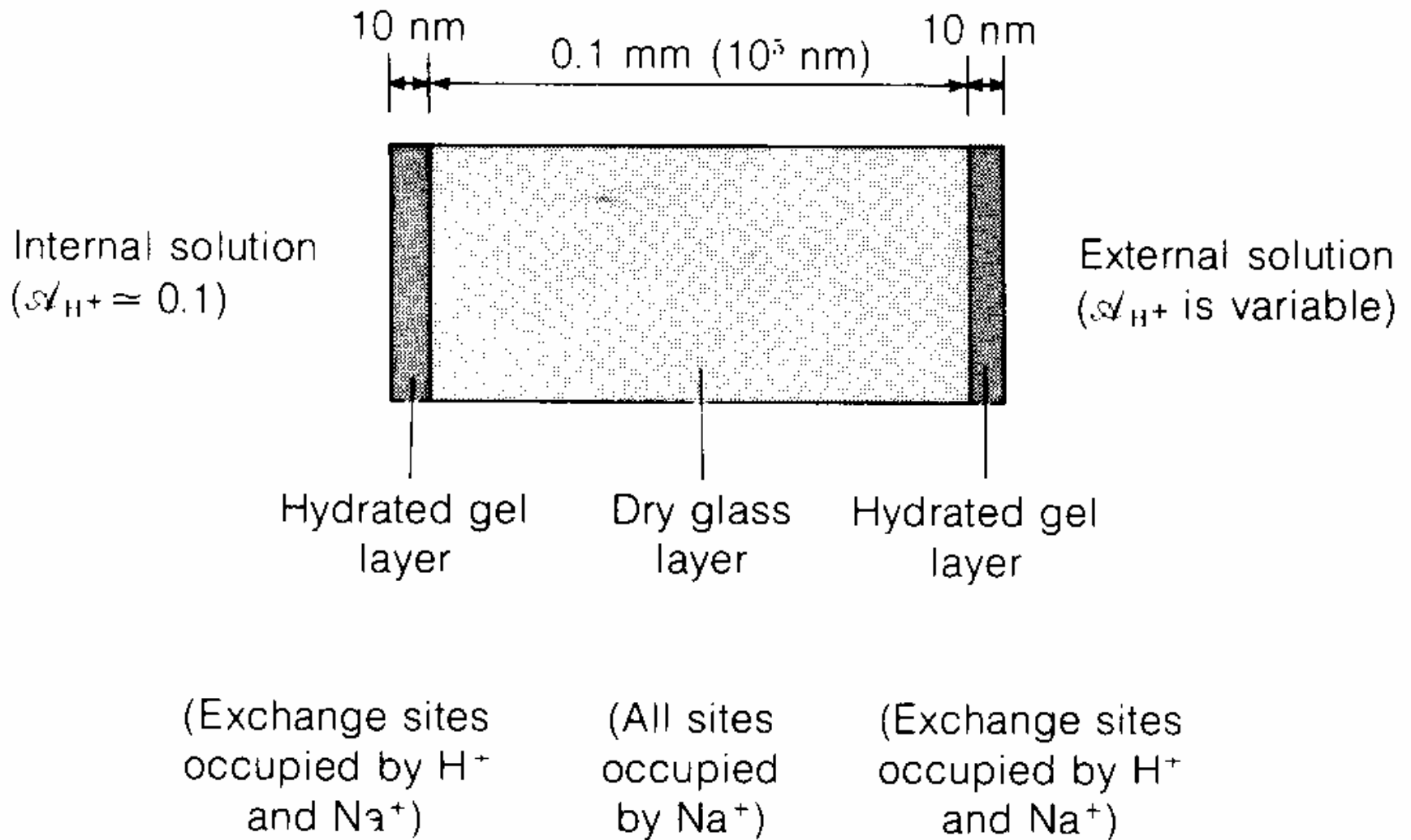




# Glass Electrode

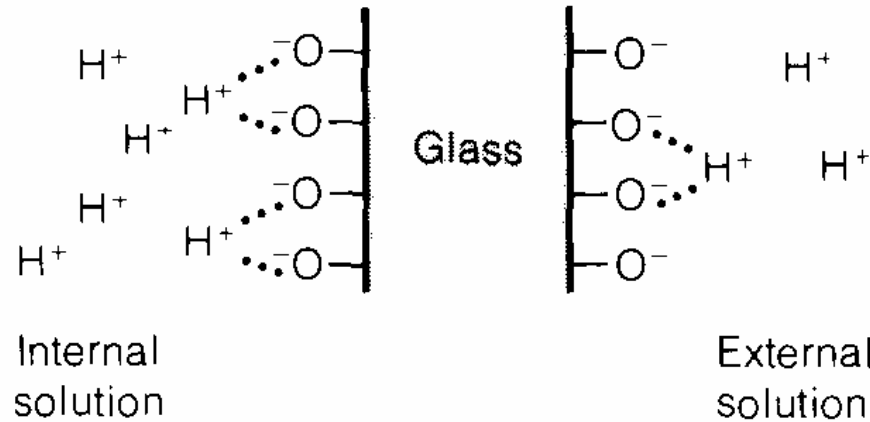
Schematic diagram of a combination glass electrode for measuring pH



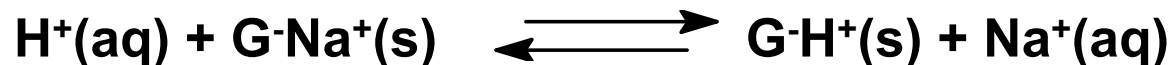


## pH Glass membrane

## Mechanism of membrane potential at the glass membrane surface



- Hydration of the glass membrane results in the formation of negatively charged sites,  $G^-$ , that are part of the glass membrane's silica framework.
- Sodium ions, which are able to move through the hydrated layer, serve as the counter ions.
- Hydrogen ions from solution diffuse into the membrane and, since they bind more strongly to the glass than does  $Na^+$ , displace the sodium ions

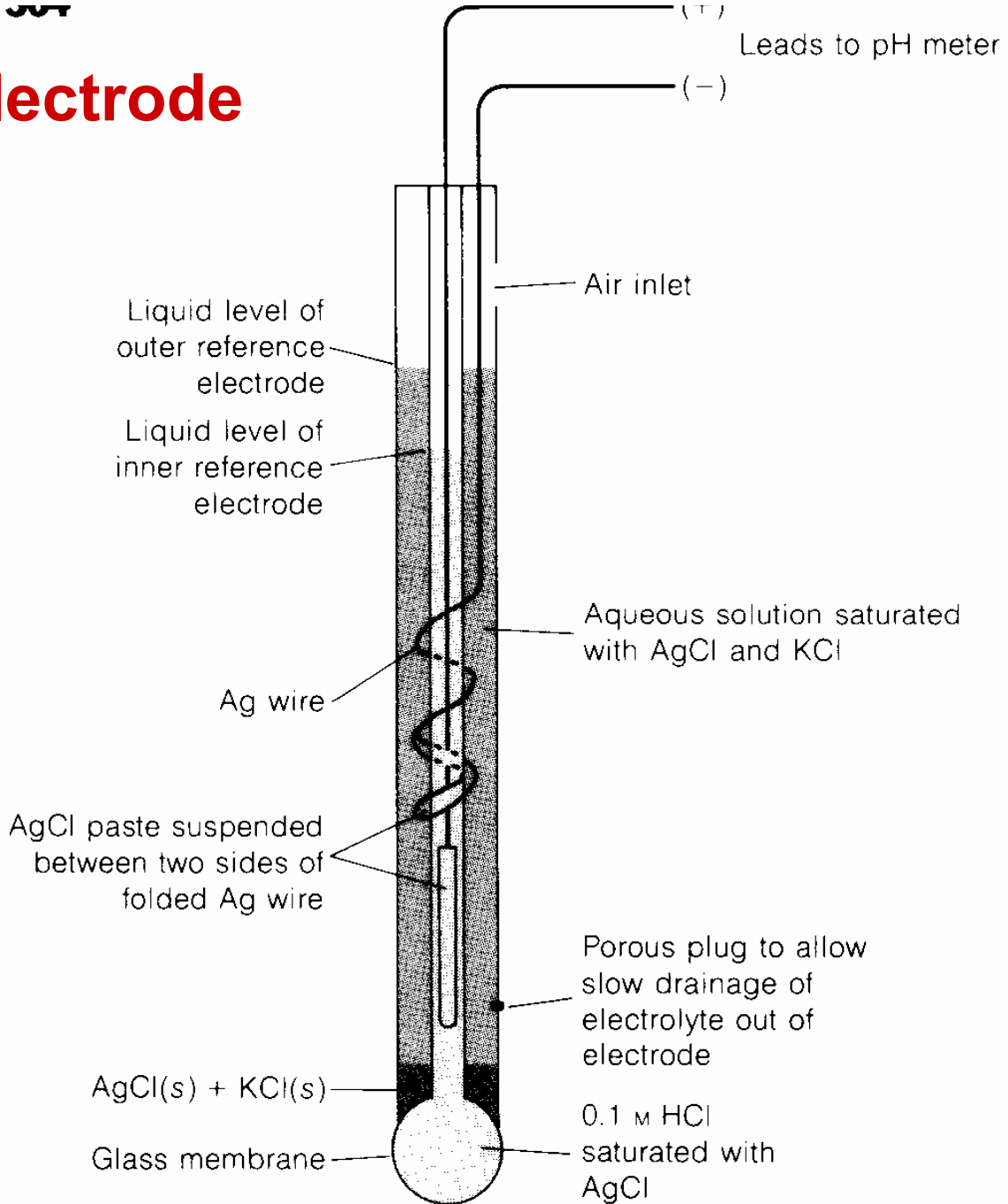


giving rise to the membrane's selectivity for  $H^+$ .

The transport of charge across the membrane is carried by the  $Na^+$  ions. The potential of glass electrodes

$$E_{\text{cell}} = K + 0.05916 \log [H^+]$$

# Combined Glass Electrode



## **Alkaline (Sodium) Error**

- When the concentration of  $H^+$  is very low and that of  $Na^+$  is high the electrode responds to  $Na^+$  as well as to  $H^+$ . This arises because  $Na^+$  can participate in ion exchange with the hydrated gel layer.
- To reduce the alkaline error, lithium has largely replaced sodium in glass electrodes.

## **Acid Error**

- In very acidic solutions, the measured pH is higher than the actual pH. The reason for this is not clear, but it may be related to the decreased activity of water in concentrated acid solution.

# Representative examples of glass membrane ISE

Analyte	Membrane Composition	Selectivity Coefficients <sup>a</sup>
Na <sup>+</sup>	11% Na <sub>2</sub> O, 18% Al <sub>2</sub> O <sub>3</sub> , 71% SiO <sub>2</sub>	$K_{\text{Na}^+/\text{H}^+} = 1000$ $K_{\text{Na}^+/\text{K}^+} = K_{\text{Na}^+/\text{Li}^+} = 10^{-3}$
Li <sup>+</sup>	15% Li <sub>2</sub> O, 25% Al <sub>2</sub> O <sub>3</sub> , 60% SiO <sub>2</sub>	$K_{\text{Li}^+/\text{Na}^+} = 0.3$ $K_{\text{Li}^+/\text{K}^+} = 10^{-3}$
K <sup>+</sup>	27% Na <sub>2</sub> O, 5% Al <sub>2</sub> O <sub>3</sub> , 68% SiO <sub>2</sub>	$K_{\text{K}^+/\text{Na}^+} = 0.05$

<sup>a</sup>Selectivity constants are approximate, and those found experimentally may vary substantially from the listed values.<sup>3</sup>

## **Crystalline solid –state ion-selective electrode**

- **Electrodes based on sparingly soluble inorganic crystalline material:  $\text{Ag}_2\text{S}$  or mixture of  $\text{Ag}_2\text{S}$  and either a second silver salt or another metal sulfide**
- **Representative examples of polycrystalline ISE are listed in the following table**

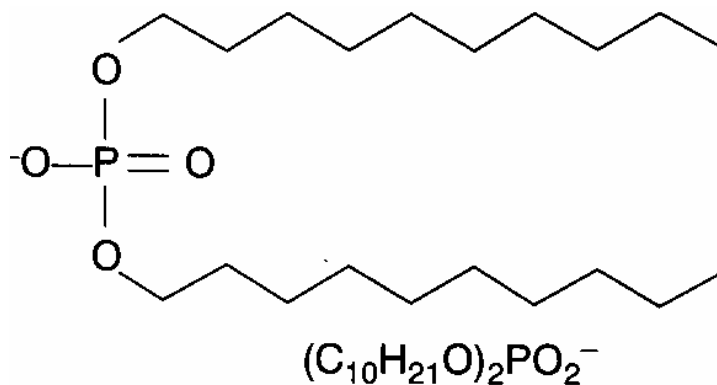
Analyte	Membrane Composition	Selectivity Coefficients <sup>a</sup>
Ag <sup>+</sup>	Ag <sub>2</sub> S	$K_{Ag^+/Cu^{2+}} = 10^{-6}$ $K_{Ag^+/Pb^{2+}} = 10^{-10}$ Hg <sup>2+</sup> interferes
Cd <sup>2+</sup>	CdS/Ag <sub>2</sub> S	$K_{Cd^{2+}/Fe^{2+}} = 200$ $K_{Cd^{2+}/Pb^{2+}} = 6$ Ag <sup>+</sup> , Hg <sup>2+</sup> , Cu <sup>2+</sup> must be absent
Cu <sup>2+</sup>	CuS/Ag <sub>2</sub> S	$K_{Cu^{2+}/Fe^{3+}} = 10$ $K_{Cu^{2+}/Cu^+} = 1$ Ag <sup>+</sup> , Hg <sup>2+</sup> must be absent
Pb <sup>2+</sup>	PbS/Ag <sub>2</sub> S	$K_{Pb^{2+}/Fe^{3+}} = 1$ $K_{Pb^{2+}/Cd^{2+}} = 1$ Ag <sup>+</sup> , Hg <sup>2+</sup> , Cu <sup>2+</sup> must be absent
Br <sup>-</sup>	AgBr/Ag <sub>2</sub> S	$K_{Br^-/I^-} = 5000$ $K_{Br^-/CN^-} = 100$ $K_{Br^-/Cl^-} = 5 \times 10^{-3}$ $K_{Br^-/OH^-} = 1 \times 10^{-5}$ S <sup>2-</sup> must be absent
Cl <sup>-</sup>	AgCl/Ag <sub>2</sub> S	$K_{Cl^-/I^-} = 1 \times 10^6$ $K_{Cl^-/CN^-} = 1 \times 10^4$ $K_{Cl^-/Br^-} = 100$ $K_{Cl^-/OH^-} = 0.01$ S <sup>2-</sup> must be absent
CN <sup>-</sup>	AgI/Ag <sub>2</sub> S	$K_{CN^-/I^-} = 100$ $K_{CN^-/Br^-} = 1 \times 10^{-4}$ $K_{CN^-/Cl^-} = 1 \times 10^{-6}$ $K_{CN^-/OH^-} = 1 \times 10^{-8}$ S <sup>2-</sup> must be absent
I <sup>-</sup>	AgI/Ag <sub>2</sub> S	$K_{I^-/S^{2-}} = 30$ $K_{I^-/CN^-} = 0.01$ $K_{I^-/Br^-} = 1 \times 10^{-4}$ $K_{I^-/Cl^-} = 1 \times 10^{-6}$ $K_{I^-/OH^-} = 1 \times 10^{-7}$
SCN <sup>-</sup>	AgSCN/Ag <sub>2</sub> S	$K_{SCN^-/I^-} = 1000$ $K_{SCN^-/Br^-} = 100$ $K_{SCN^-/CN^-} = 100$ $K_{SCN^-/Cl^-} = 0.1$ $K_{SCN^-/OH^-} = 0.01$ S <sup>2-</sup> must be absent
S <sup>2-</sup>	Ag <sub>2</sub> S	Hg <sup>2+</sup> interferes

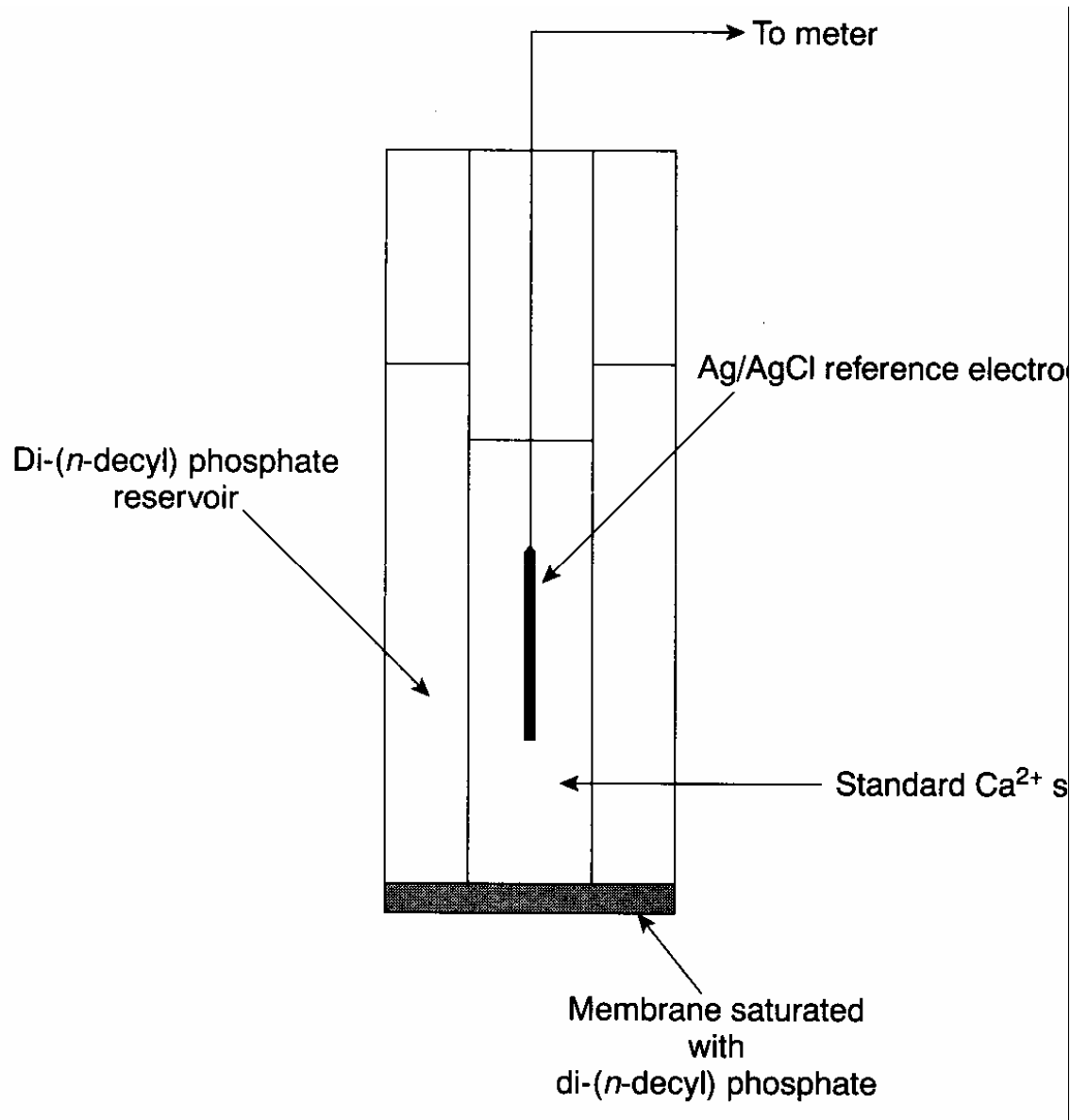
<sup>a</sup>Selectivity constants are approximate, and those found experimentally may vary substantially from the listed values.<sup>3</sup>



# Liquid-Based Ion-Selective Electrodes

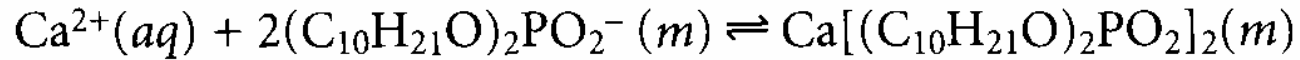
- Use a hydrophobic membrane containing a selective, liquid organic complexing agent.
- Three types of organic liquids have been used:
  - Cation exchangers, anion exchangers, and neutral ionophores.
- For Calcium selective electrode, porous plastic membrane saturated with di-(n-decyl) phosphate is used.





**Schematic diagram of a calcium liquid membrane ISE**

A membrane potential develops as the result of a difference in the equilibrium position of the complexation reaction



on the two sides of the membrane, where (*m*) indicates that the species is present in the membrane. The cell potential for the  $\text{Ca}^{2+}$  ion-selective electrode is

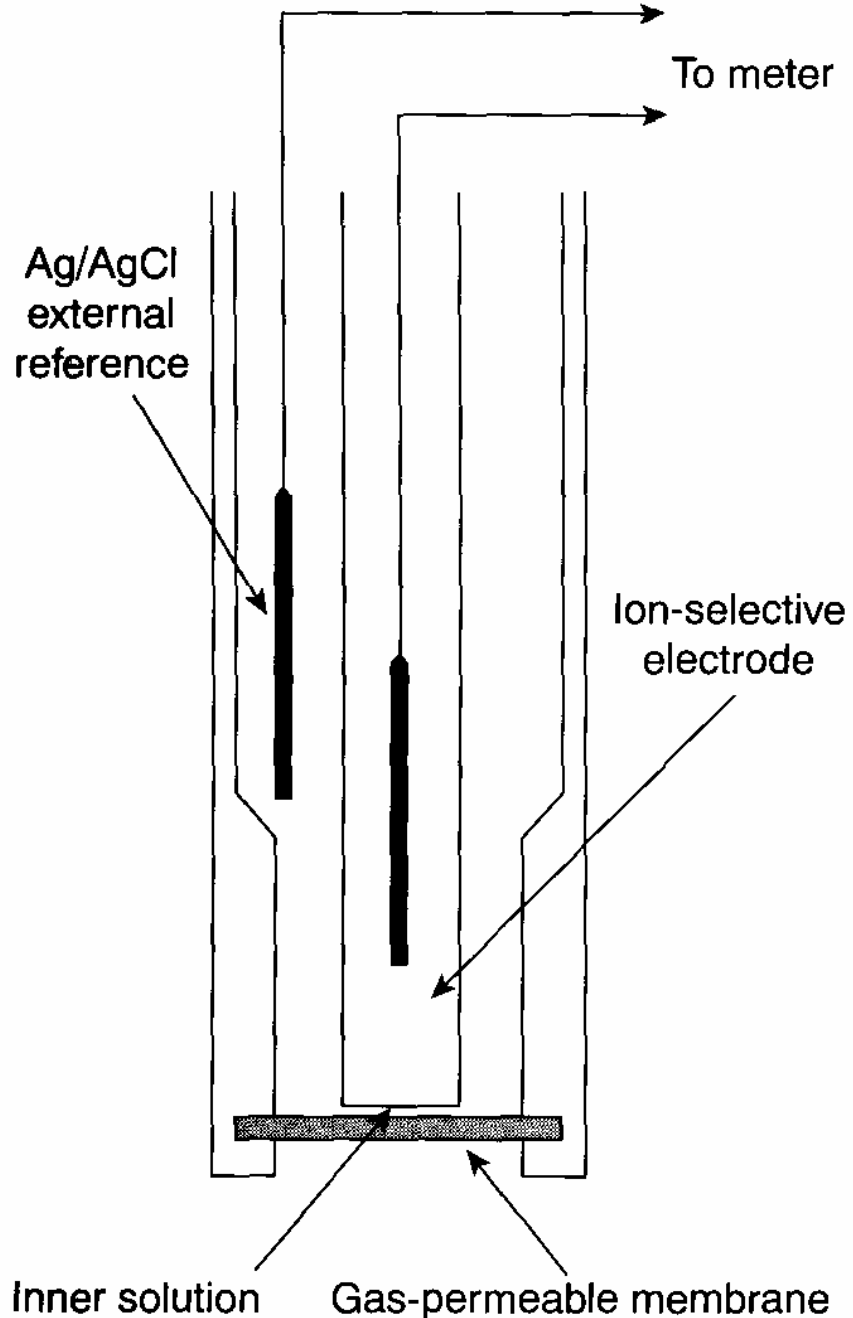
$$E_{\text{cell}} = K + \frac{0.05916}{2} \log [\text{Ca}^{2+}]$$

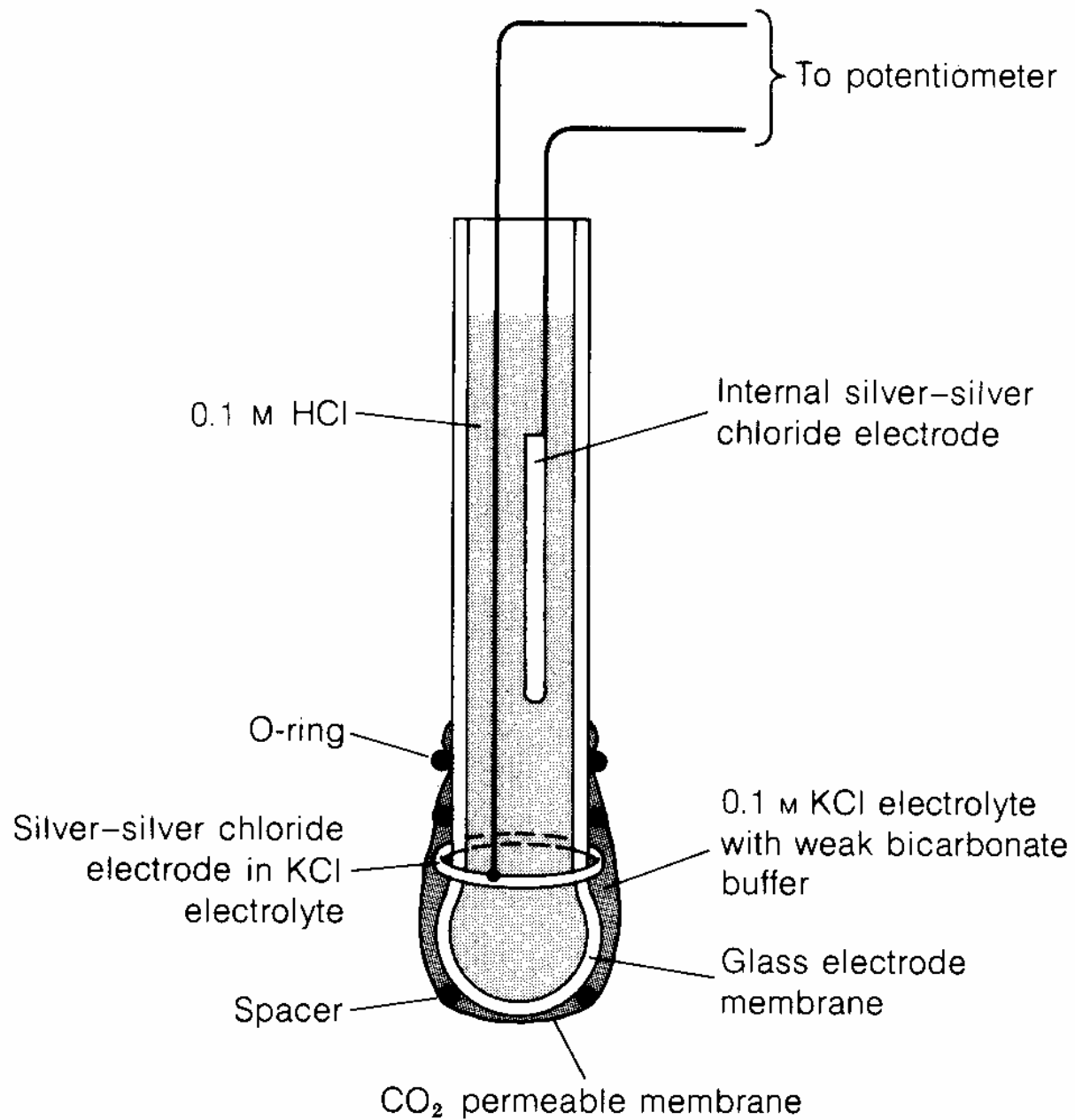
# Representative examples of liquid-based ISE

Analyte	Membrane Composition	Selectivity Coefficients <sup>a</sup>
Ca <sup>2+</sup>	di-( <i>n</i> -decyl) phosphate in PVC	$K_{Ca^{2+}/Zn^{2+}} = 1-5$ $K_{Ca^{2+}/Al^{3+}} = 0.90$ $K_{Ca^{2+}/Mn^{2+}} = 0.38$ $K_{Ca^{2+}/Cu^{2+}} = 0.070$ $K_{Ca^{2+}/Mg^{2+}} = 0.032$
K <sup>+</sup>	Valinomycin in PVC	$K_{K^+/Rb^+} = 1.9$ $K_{K^+/Cs^+} = 0.38$ $K_{K^+/Li^+} = 1 \times 10^{-4}$ $K_{K^+/Na^+} = 1 \times 10^{-5}$
Li <sup>+</sup>	ETH 149 in PVC	$K_{Li^+/H^+} = 1$ $K_{Li^+/Na^+} = 0.05$ $K_{Li^+/K^+} = 7 \times 10^{-3}$
NH <sub>4</sub> <sup>+</sup>	Nonactin and monactin in PVC	$K_{NH_4^+/K^+} = 0.12$ $K_{NH_4^+/H^+} = 0.016$ $K_{NH_4^+/Li^+} = 4.2 \times 10^{-3}$ $K_{NH_4^+/Na^+} = 2 \times 10^{-3}$
ClO <sub>4</sub> <sup>-</sup>	Fe( <i>o</i> -phen) <sub>3</sub> <sup>3+</sup> in <i>p</i> -nitrocymene with porous membrane	$K_{ClO_4^-/OH^-} = 1$ $K_{ClO_4^-/I^-} = 0.012$ $K_{ClO_4^-/NO_3^-} = 1.5 \times 10^{-3}$ $K_{ClO_4^-/Br^-} = 5.6 \times 10^{-4}$ $K_{ClO_4^-/Cl^-} = 2.2 \times 10^{-4}$
NO <sub>3</sub> <sup>-</sup>	tetradodecyl ammonium nitrate in PVC	$K_{NO_3^-/Cl^-} = 6 \times 10^{-3}$ $K_{NO_3^-/F^-} = 9 \times 10^{-4}$

<sup>a</sup>Selectivity constants are approximate, and those found experimentally may vary substantially from the listed values.<sup>3</sup>

# Schematic diagram of a gas – sensing membrane electrode





- $\text{CO}_2 (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{HCO}_3^- (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq})$
- $E_{\text{cell}} = K' + 0.0591 \log [\text{CO}_2]$

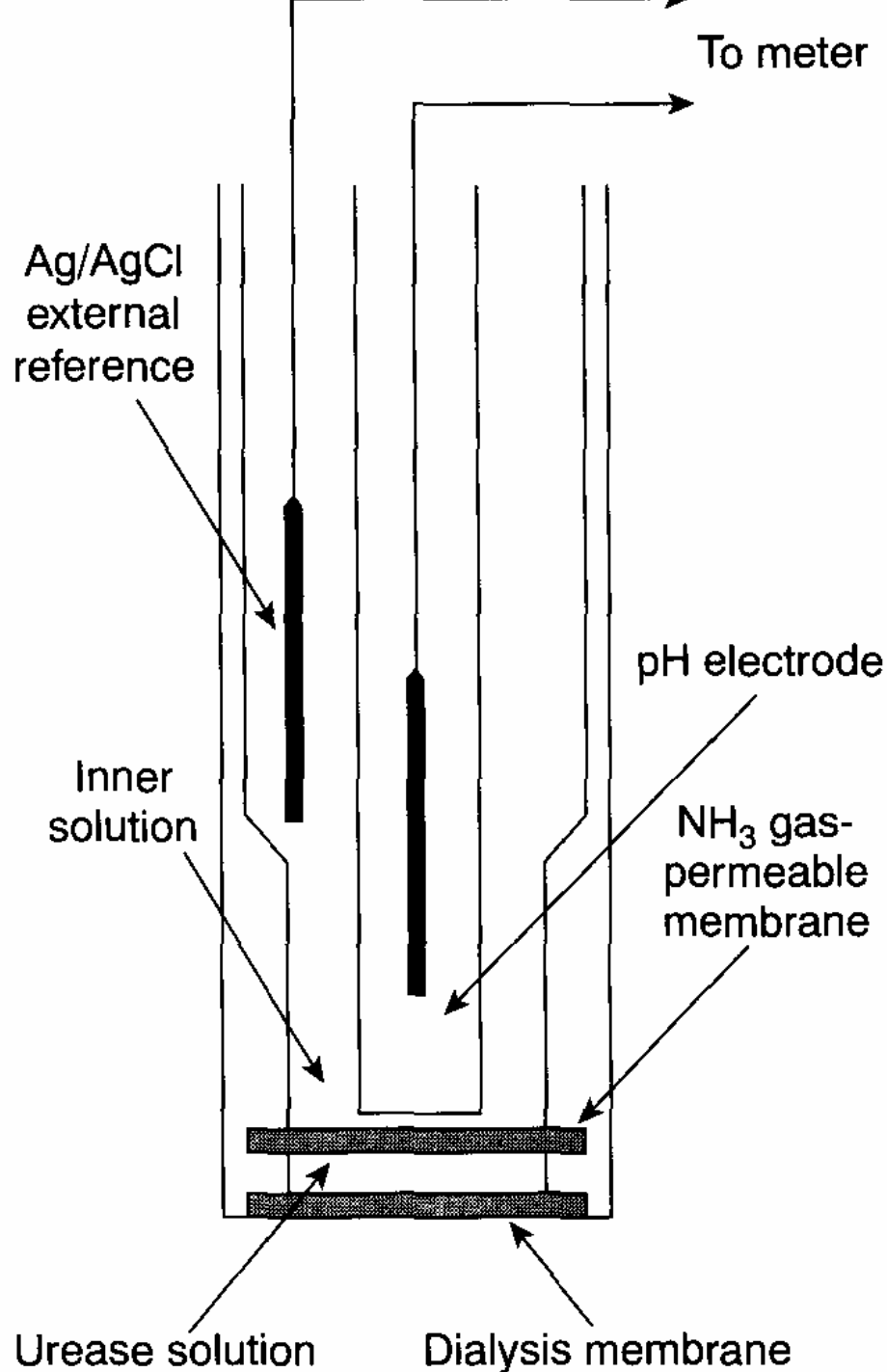
# Characteristics of gas-sensing membrane electrodes

Analyte	Reaction in Inner Solution	Inner Solution	Ion-Selective Electrode
CO <sub>2</sub>	$\text{CO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+$	0.01 M NaHCO <sub>3</sub> , 0.01 M NaCl	glass pH electrode
HCN	$\text{HCN} + \text{H}_2\text{O} \rightleftharpoons \text{CN}^- + \text{H}_3\text{O}^+$	0.01 M KAg(CN) <sub>2</sub>	Ag <sub>2</sub> S membrane electrode
HF	$\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{F}^- + \text{H}_3\text{O}^+$	1 M H <sub>3</sub> O <sup>+</sup>	F <sup>-</sup> electrode
H <sub>2</sub> S	$\text{H}_2\text{S} + \text{H}_2\text{O} \rightleftharpoons \text{HS}^- + \text{H}_3\text{O}^+$	pH 5 citrate buffer	Ag <sub>2</sub> S membrane electrode
NH <sub>3</sub>	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	0.01 M NH <sub>4</sub> Cl, 0.1 M KNO <sub>3</sub>	glass pH electrode
NO <sub>2</sub>	$2\text{NO}_2 + 3\text{H}_2\text{O} \rightleftharpoons \text{NO}_3^- + \text{NO}_2^- + 2\text{H}_3\text{O}^+$	0.02 M NaNO <sub>2</sub> , 0.1 M KNO <sub>3</sub>	glass pH electrode
SO <sub>2</sub>	$\text{SO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{H}_3\text{O}^+$	0.001 M NaHSO <sub>3</sub> , pH 5	glass pH electrode

Source: Data compiled from Cammann, K. *Working with Ion-Selective Electrodes*. Springer-Verlag: Berlin, 1977.

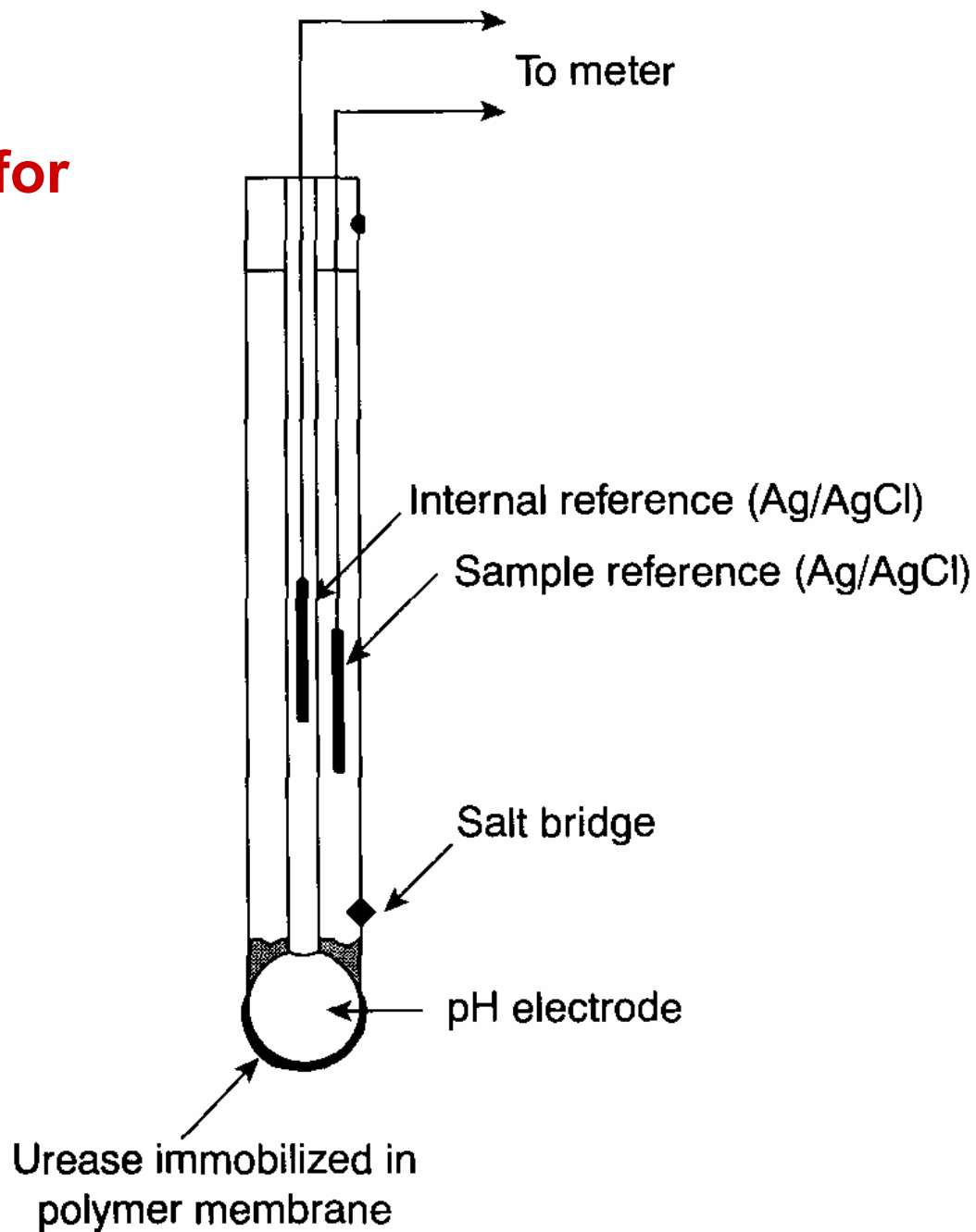


**Schematic diagram of an enzyme-based potentiometric biosensor for urea in which urease is trapped between two membranes**



- $\text{NH}_4^+ (\text{aq}) + \text{H}_2\text{O} (\text{l}) \rightleftharpoons \text{H}_3\text{O}^+ (\text{aq}) + \text{NH}_3 (\text{aq})$
- $E_{\text{cell}} = K - 0.05916 \log [\text{urea}]$

**Schematic diagram of a second enzyme-based potentiometric biosensor for urea in which urease is immobilized in a polymer matrix**



# Representative examples of potentiometric biosensors

Analyte	Biologically Active Phase <sup>a</sup>	Substance Determined
5'-adenosinemonophosphate (5'-AMP)	AMP-deaminase (E)	NH <sub>3</sub>
L-arginine	arginase + urease (E)	NH <sub>3</sub>
asparagine	asparaginase (E)	NH <sub>4</sub> <sup>+</sup>
L-cysteine	<i>Proteus morgani</i> (B)	H <sub>2</sub> S
L-glutamate	yellow squash (T)	CO <sub>2</sub>
L-glutamine	<i>Sarcina flava</i> (B)	NH <sub>3</sub>
oxalate	oxalate decarboxylase (E)	CO <sub>2</sub>
penicillin	penicillinase (E)	H <sub>3</sub> O <sup>+</sup>
L-phenylalanine	L-amino acid oxidase and horseradish peroxidase (E)	I <sup>-</sup>
sugars	bacteria from human dental plaque (B)	H <sub>3</sub> O <sup>+</sup>
urea	urease (E)	NH <sub>3</sub> or H <sub>3</sub> O <sup>+</sup>

Source: Compiled from Cammann, K. *Working with Ion-Selective Electrodes*. Springer-Verlag: Berlin, 1977; and Lunte, C. E.; Heineman, W. R. "Electrochemical Techniques in Bioanalysis." In Steckham, E., ed. *Topics in Current Chemistry*, Vol. 143, Springer-Verlag: Berlin, 1988, p. 8.<sup>3,6</sup>

<sup>a</sup>Abbreviations: E = enzyme; B = bacterial particle; T = tissue.

# Quantitative Applications Activity versus Concentration

potential of an electrochemical cell is a function of activity, not concentration. Thus, the Nernst equation for a metallic electrode of the first kind is more appropriately written as

$$E_{\text{cell}} = K - \frac{0.05916}{n} \log \frac{1}{a_{\text{M}^{n+}}} \quad 11.14$$

where  $a_{\text{M}^{n+}}$  is the activity of the metal ion. As described in Chapter 6, the activity of an ion is equal to the product of its concentration,  $[\text{M}^{n+}]$ , and a matrix-dependent activity coefficient,  $\gamma_{\text{M}^{n+}}$ .

$$a_{\text{M}^{n+}} = [\text{M}^{n+}] \gamma_{\text{M}^{n+}} \quad 11.15$$

Substituting equation 11.15 into equation 11.14 and rearranging gives

$$E_{\text{cell}} = K - \frac{0.05916}{n} \log \frac{1}{\gamma_{\text{M}^{n+}}} - \frac{0.05916}{n} \log \frac{1}{[\text{M}^{n+}]} \quad 11.16$$

Equation 11.16 can be solved for the metal ion's concentration if its activity coefficient is known. This presents a serious complication since the activity coefficient may be difficult to determine. If, however, the standards and samples have an identical matrix, then  $\gamma_{\text{M}^{n+}}$  remains constant, and equation 11.16 simplifies to

$$E_{\text{cell}} = K' - \frac{0.05916}{n} \log \frac{1}{[\text{M}^{n+}]}$$

where  $K'$  includes the activity coefficient.

# Quantitative Analysis using external standards

The concentration of  $\text{Ca}^{2+}$  in a water sample was determined by the method of external standards. The ionic strength of the samples and standards was maintained at a nearly constant level by making each solution 0.5 M in  $\text{KNO}_3$ . The measured cell potentials for the external standards are shown in the following table.

$[\text{Ca}^{2+}]$ (M)	$E_{\text{cell}}$ (V)
$1.00 \times 10^{-5}$	-0.125
$5.00 \times 10^{-5}$	-0.103
$1.00 \times 10^{-4}$	-0.093
$5.00 \times 10^{-4}$	-0.072
$1.00 \times 10^{-3}$	-0.065
$5.00 \times 10^{-3}$	-0.043
$1.00 \times 10^{-2}$	-0.033

What is the concentration of  $\text{Ca}^{2+}$  in a water sample if its cell potential is found to be  $-0.084$  V?

## **SOLUTION**

Linear regression gives the equation for the calibration curve as

$$E_{\text{cell}} = 0.027 + 0.0303 \log [\text{Ca}^{2+}]$$

Substituting the cell potential for the sample gives the concentration of  $\text{Ca}^{2+}$  as  $2.17 \times 10^{-4}$  M. Note that the slope of the calibration curve is slightly different from the ideal value of  $0.05916/2 = 0.02958$ .

# Quantitative analysis using the method of Standard Additions

- Because of the difficulty of maintaining a constant matrix for samples and standards, many quantitative potentiometric methods use the method of standard additions.
- A sample of volume,  $\underline{V}_x$ , and analyte concentration,  $\underline{C}_x$ , is transferred to a sample cell, and the potential,  $(\underline{E}_{cell})_x$ , measured.
- A standard addition is made by adding a small volume,  $\underline{V}_s$ , of a standard containing a known concentration of analyte,  $\underline{C}_s$ , to the sample, and the potential,  $(\underline{E}_{cell})_s$ , measured. Provided that  $\underline{V}_s$  is significantly smaller than  $\underline{V}_x$ , the change in sample matrix is ignored, and the analyte's activity coefficient remains constant.

## Example

- **The concentration of  $\text{Ca}^{2+}$  in a sample of sea water is determined using a Ca ion-selective electrode and a one-point standard addition. A 10.00-mL sample is transferred to a 100-mL volumetric flask and diluted to volume. A 50.00-mL aliquot of sample is placed in a beaker with the Ca ion-selective electrode and a reference electrode, and the potential is measured as -0.05290 V. A 1.00-mL aliquot of a  $5.00 \times 10^{-2}$  M standard solution of  $\text{Ca}^{2+}$  is added, and a potential of -0.04417 V is measured. What is the concentration of  $\text{Ca}^{2+}$  in the sample of sea water?**



To begin, we write Nernst equations for the two measured cell potentials. The cell potential for the sample is

$$(E_{\text{cell}})_X = K + \frac{0.05916}{2} \log C_X$$

and that following the standard addition is

$$(E_{\text{cell}})_S = K + \frac{0.05916}{2} \log \left( \frac{V_X}{V_T} C_X + \frac{V_S}{V_T} C_S \right)$$

where  $V_T$  is the total volume ( $V_S + V_X$ ) after the standard addition. Subtracting the first equation from the second equation gives

$$(E_{\text{cell}})_S - (E_{\text{cell}})_X = \frac{0.05916}{2} \log \left( \frac{V_X}{V_T} C_X + \frac{V_S}{V_T} C_S \right) - \frac{0.05916}{2} \log C_X$$

Replacing  $(E_{\text{cell}})_S - (E_{\text{cell}})_X$  with  $\Delta E$  and rearranging yields

$$\frac{2\Delta E}{0.05916} = \log \left[ \frac{(V_X/V_T)C_X + (V_S/V_T)C_S}{C_X} \right] = \log \left( \frac{V_X}{V_T} + \frac{V_S C_S}{V_T C_X} \right)$$

Substituting known values for  $\Delta E$ ,  $V_X$ ,  $V_S$ ,  $V_T$ , and  $C_S$ ,

$$\frac{2(0.00873)}{0.05916} = \log \left[ \frac{50.00 \text{ mL}}{51.00 \text{ mL}} + \frac{(1.00 \text{ mL})(5.00 \times 10^{-2} \text{ M})}{(51.00 \text{ mL})C_X} \right]$$

$$0.2951 = \log \left( 0.9804 + \frac{9.804 \times 10^{-4}}{C_X} \right)$$

# Numerical Example

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$$0.2951 = \log \left( 0.9804 + \frac{9.804 \times 10^{-4}}{C_X} \right)$$

## Numerical example

### EXAMPLE: Response of an Ion-Selective Electrode

When an  $F^-$  electrode was immersed in standard  $F^-$  solutions (maintained at a constant ionic strength of 0.1 M with  $NaNO_3$ ), the following potentials (versus S.C.E.) were observed:

$[F^-](M)$	$E$ (mV)	
$1.00 \times 10^{-5}$	100.0	} -58.5 mV
$1.00 \times 10^{-4}$	41.5	
$1.00 \times 10^{-3}$	-17.0	} -58.5 mV

Since the ionic strength was held constant, the response should depend upon the logarithm of the  $F^-$  concentration. What potential is expected if  $[F^-] = 5.00 \times 10^{-5} M$ ? What concentration of  $F^-$  will give a potential of 0.0 V?

We seek to fit the calibration data with an equation in the form of Equation 15-26:

$$E = m \log [F^-] + b$$

$y$                        $x$

Plotting  $E$  versus  $\log [F^-]$  gives a straight line with a slope of  $-58.5$  mV and a  $y$ -intercept of  $-192.5$  mV. Setting  $[F^-] = 5.00 \times 10^{-5} M$  gives

$$E = (-58.5) \log [5.00 \times 10^{-5}] - 192.5 = 59.1 \text{ mV}$$

If  $E = 0.0$  mV, we can solve for the concentration of  $[F^-]$ :

$$0.0 = (-58.5) \log [F^-] - 192.5 \Rightarrow [F^-] = 5.1 \times 10^{-4} M$$