

Chapter 2

Electroanalytical Methods- Potentiometry

Potentiometry

Potential is measured under the conditions of no current flow

The measured potential is proportional to the concentration of some component of the analyte

The potential that develops in the *electrochemical cell* is the result of the *free energy change* that would occur if the chemical phenomena were to proceed until the *equilibrium condition* has been satisfied.

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

Basic Principles of Potentiometry

- Combining two half-cells (two half-redox reactions) and measuring the potential difference between them that gives E_{cell}
- If the potential of one half-cell (one-half reaction) is held constant then the potential of the other half (half cell or half reaction) will be known and consequently the concentration of the species on this side can be measured.

Electrode Potentials:

Standard potential for cell, E^0_{cell} , follows Nernst Equation:

$$E^0_{\text{cell}} = (RT/nF) \ln K$$

R is gas law constant, T is temperature, K is equilibrium constant, F is the Faraday, and n is number of equivalents of electricity

Electrode potential is sum of two half-reactions.

Cannot determine potential of a single electrode, measure differences in potential.

Potentiometric Methods:

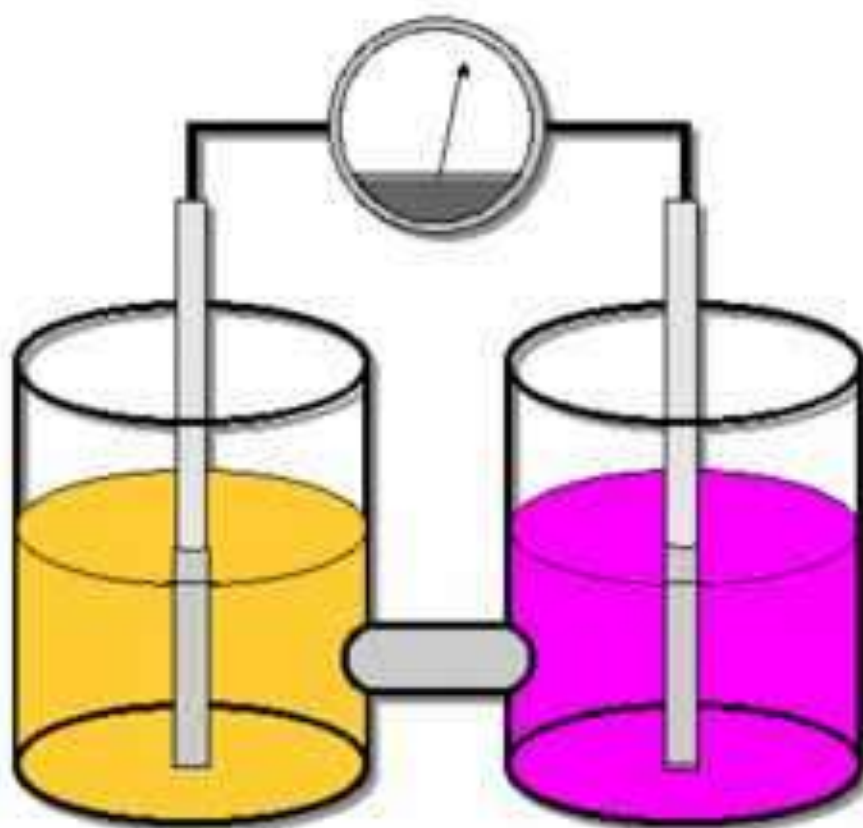
To perform potentiometry, the following is needed:

- Reference Electrode**
- Indicator Electrode**
- Potential Measuring Device**

Potentiometric methods

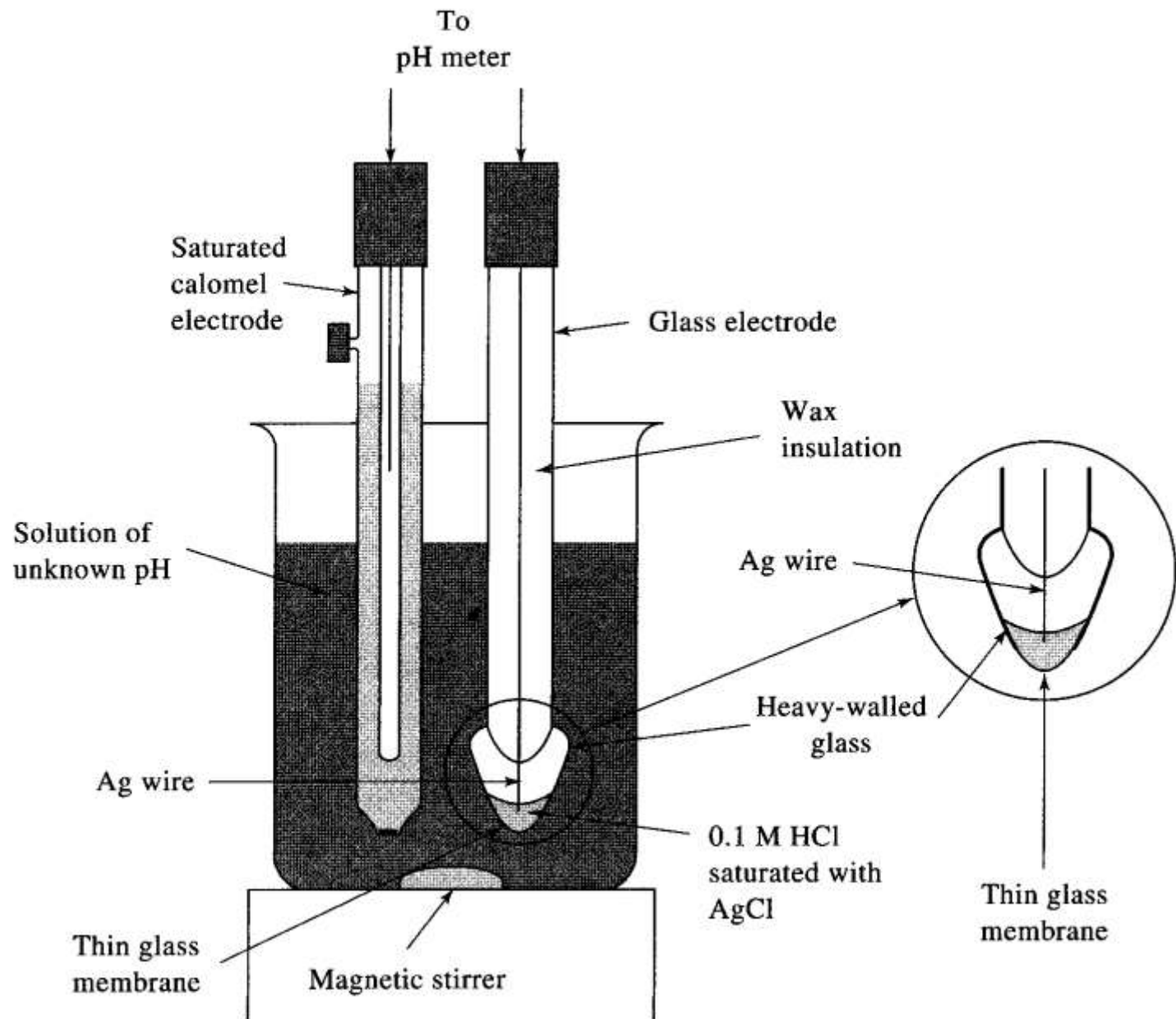
Reference electrode

The part of the cell that is held constant



Indicating electrode

The part of the cell that contains the solution we are interested in measuring



Schematic Representation of cells

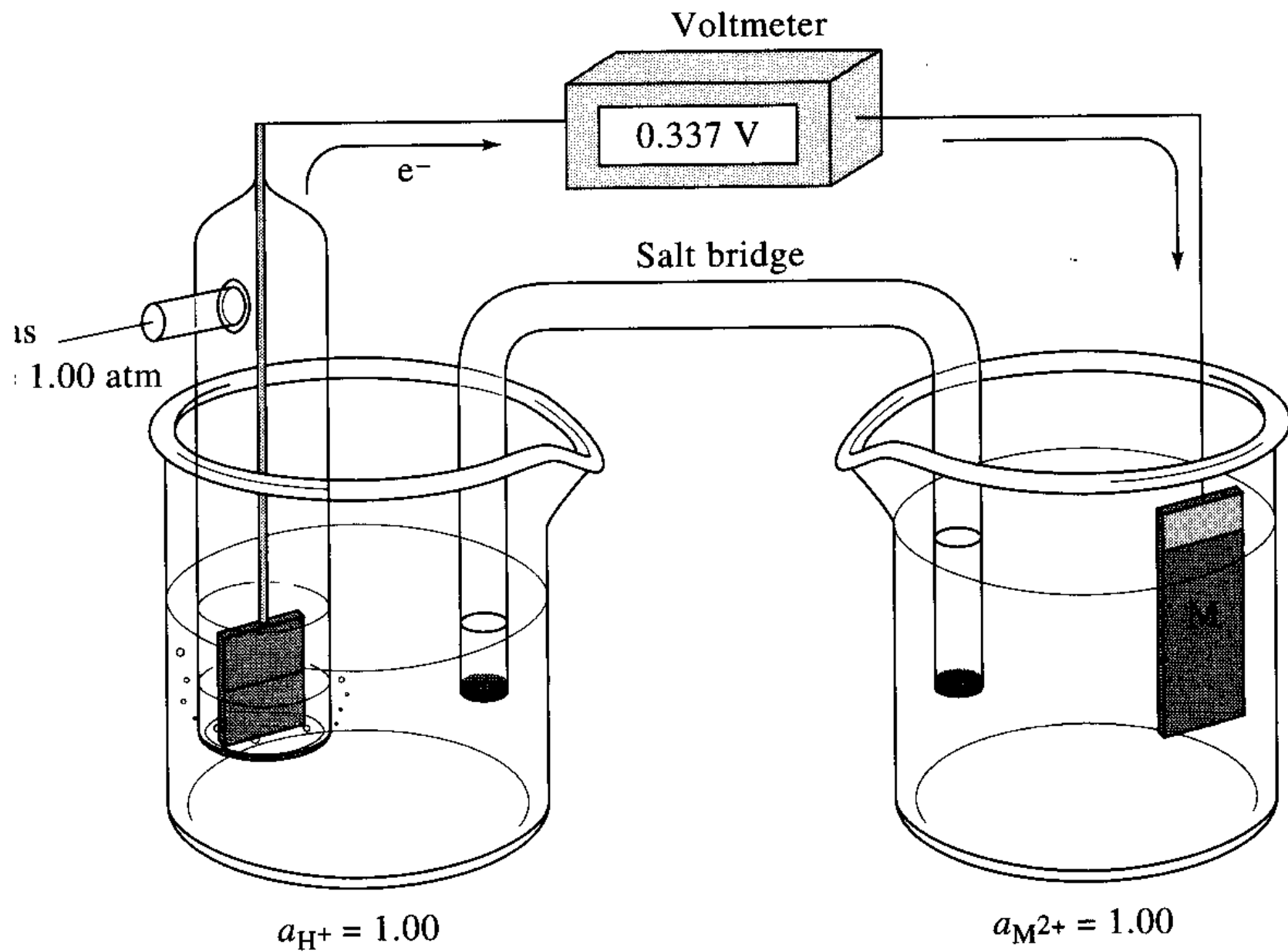
- $\text{Cd} | \text{Cd}^{2+} ([\text{Cd}^{2+}] = 0.010 \text{ M}) || \text{AgNO}_3 (0.50 \text{ M}) | \text{Ag}$
- $\text{Cd} | \text{Cd}^{2+} ([\text{Cd}^{2+}] = 0.010 \text{ M}) || (\text{AgCl}_{\text{satd}}) | \text{Ag}$
- $\text{Cd} | \text{Cd}^{2+} ([\text{Cd}^{2+}] = 0.010 \text{ M}) || \text{H}^+, \text{H}_2 (\text{g}) | \text{Pt}$
- $\text{Cd} | \text{Cd}^{2+} ([\text{Cd}^{2+}] = 0.010 \text{ M}) || \text{Fe}^{3+}, \text{Fe}^{2+} | \text{Pt}$

Electrode Potentials

- The electrode potentials represent a measure of the driving force for the two half-reactions of the electrochemical cell.
 - By convention, all reactions are written as reductions.
 - The potential of an electrochemical cell is the difference between the potential of the cathode and that of the anode.
 - No method exists for determining the absolute value of the potential of a single electrode, since all voltage-measuring devices determine only the difference in potential as defined in this manner.
 - BUT... a relative half-cell potential can be measured against a common **reference electrode**.

The Standard Hydrogen Electrode (SHE)

- Hydrogen gas electrodes were widely used in early electrochemistry studies and by convention **the potential of this electrode is assigned the value of exactly zero** volt at all temperatures.
- It can act as an anode or a cathode, depending upon the half-cell with which it is coupled.
 - Hydrogen is oxidized to hydrogen ions when the electrode is anode.
 - Hydrogen ions are reduced to hydrogen gas when the electrode is the cathode.



- **Electrode potentials are defined as cell potentials for a cell consisting of the electrode in question acting as a cathode and the SHE acting as an anode.**
- **In this case, the standard electrode potential for $M^{2+}(aq) + 2e^- = M(s)$ is 0.337 V given by the symbol E^0 .**

NOTE: the standard electrode potential for a half reaction is the electrode potential when the reactants and products are all at unit activity.

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
$\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^-$	+0.268
$\text{AgCl}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-$	+0.222
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + 2\text{S}_2\text{O}_3^{2-}$	+0.010
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.000
$\text{AgI}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{I}^-$	-0.151
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}$	-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

- The magnitudes of these standard electrode potentials show the relative strengths of the ionic species as electron acceptors (oxidizing agents).
 - The larger the value, the larger the oxidizing power.
- What if the value is negative?
 - The agent is a poor oxidizer, but **product** is a good reducing agent.

Nernst Equation

- The standard electrode potential for a half reaction is the electrode potential when the reactants and products are all at unit activity.
 - What if the activity is not unity?
 - Use the **Nernst Equation** which accounts for the effect of activity on the electrode potential.

Nernst Equation



the potential is given by the generalized form of the Nernst equation

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}}} = E^0 - \frac{RT}{nF} \ln \frac{(\text{Red})}{(\text{Ox})} = E^0 - \frac{2.303RT}{nF} \log \frac{(\text{Red})}{(\text{Ox})} \quad (2.5)$$

where E^0 = standard electrode potential in volts

R = molar gas constant (8.314 J/K-mole)

T = absolute temperature in kelvins

(Red) or a_{Red} = activity of the reduced form

(Ox) or a_{Ox} = activity of the oxidized form

If numerical values are inserted for the constants and the temperature is 25°C, the Nernst equation becomes

$$E = E^0 - \frac{0.05916}{n} \log \frac{a_{\text{Red}}}{a_{\text{Ox}}} \quad (2.6)$$

The departure of activity from concentration for charged species is a function of the ionic strength, I , of the solution: assumption that ions do not interact in solution (a reasonable approximation for $I < 0.01$), and a solvent of water at 25°C, the Debye-Hückel limiting law can be used to estimate f_i :

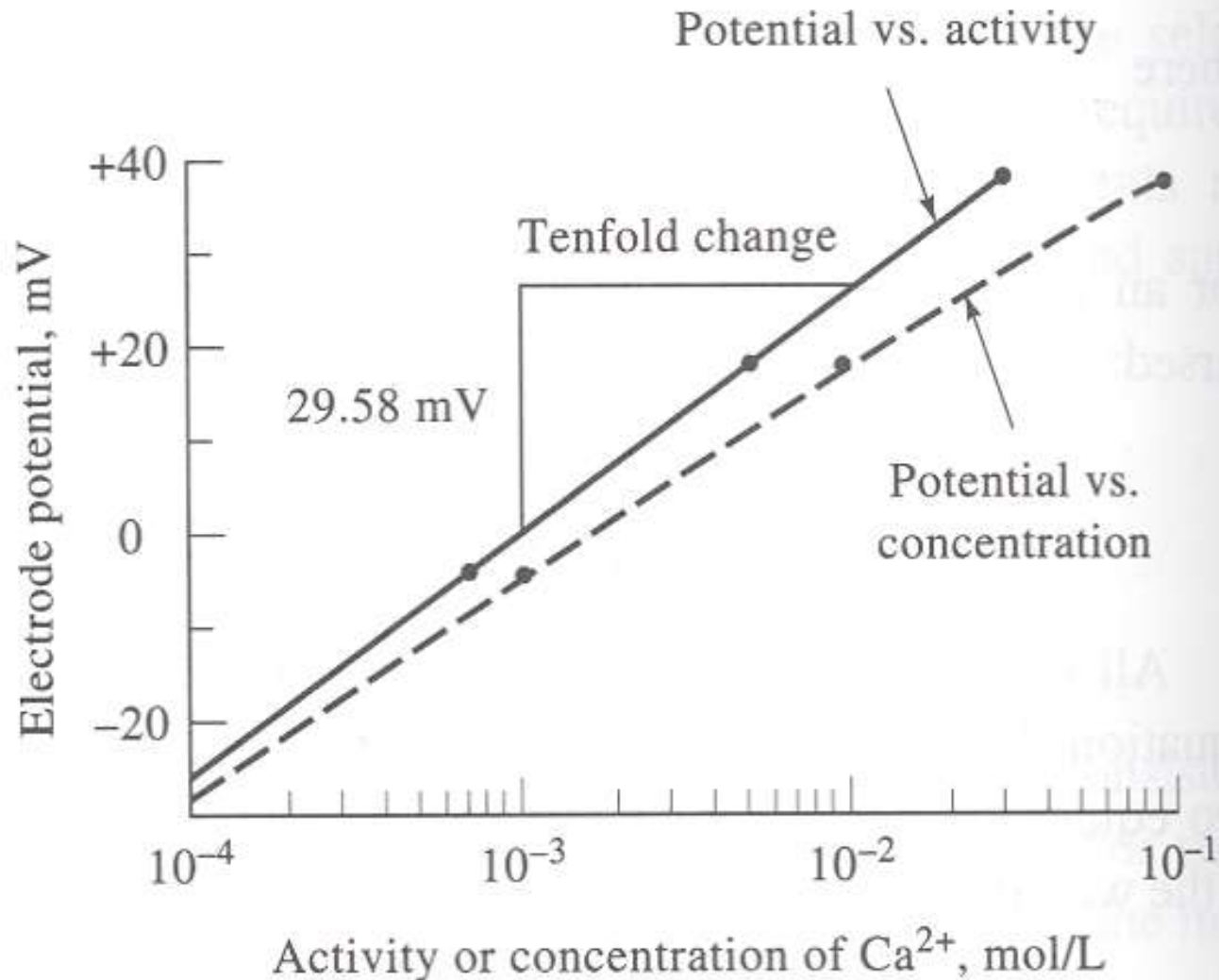
$$-\log f_i = 0.5z_i^2 I^{1/2} \quad (2.10)$$

For solutions of higher ionic strength, the form

$$-\log f_i = \frac{0.5z_i^2 I^{1/2}}{1 + I^{1/2}} \quad (2.11)$$

$$I = \frac{1}{2} \sum c_i z_i^2$$

Example of Activity vs. Concentration Discrepancy:



Examples of Nernst Equation

What is the electrode potential for a half-cell consisting of a cadmium electrode immersed in a solution that is 0.0150 M in Cd^{2+} ?

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
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$\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{Hg}(\text{l}) + 2\text{Cl}^-$	+0.268
$\text{AgCl}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-$	+0.222
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + 2\text{S}_2\text{O}_3^{2-}$	+0.010
$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.000
$\text{AgI}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{I}^-$	-0.151
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}$	-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

Simple metal electrodes

A bare metal in contact with a solution of its cation.



indicating
electrode

$$E_{ind} = E^{\circ} - \frac{0.0592}{n} \log \frac{1}{[M^{n+}]}$$

Simple metal electrodes

Example: Silver sensing electrode.

$$\begin{aligned} E_{\text{ind}} &= 0.800 \text{ V} - 0.0592 \log \frac{1}{[\text{Ag}^+]} \\ &= 0.800 \text{ V} - 0.0592 \text{ pAg} \end{aligned}$$

If we use a SCE then

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{SCE}}$$

$$\text{pAg} = (0.800\text{V} - 0.244\text{V} - E_{\text{cell}}) / 0.0592$$

Example

A silver wire is dipped into a silver nitrate solution. A potential of 0.450 V was measured vs. SCE.

What is $[Ag^+]$ for the unknown solution?

$$pAg = (0.800V - 0.244V - E_{cell}) / 0.0592$$

Example

$$pAg = (0.800V - 0.244V - E_{\text{cell}}) / 0.0592$$

$$E_{\text{cell}} = 0.450 \text{ V}$$

$$\begin{aligned} pAg &= (0.800V - 0.244V - 0.450V) / 0.0592 \\ &= 1.791 \end{aligned}$$

$$[Ag^+] = 1.618 \times 10^{-2} \text{ M}$$

Simple metal electrodes

Metal electrodes are also sensitive to anions that form low solubility precipitates with metal cations.

Example: Cl^- with a silver electrode.



end up with



Simple metal electrodes

Example: Cl^- with a silver electrode.

$$E^\circ_{\text{AgCl}} = E^\circ_{\text{Ag}} - 0.0592 \log \frac{[\text{Cl}^-]}{K_{\text{SPAgCl}}}$$

This is obtained by substituting $\frac{[\text{Cl}^-]}{K_{\text{SPAgCl}}}$

for $[\text{Ag}^+]$ because $K_{\text{SP}} = [\text{Ag}^+][\text{Cl}^-]$

Simple metal electrodes

Example: Cl with a silver electrode.

We can express the E_{cell} as

$$E^{\circ}_{\text{AgCl}} = E^{\circ}_{\text{Ag}} + 0.0592 \log K_{\text{sp}} + 0.0592 \text{ pCl}$$

$$\begin{aligned} E_{\text{ind}} &= E^{\circ}_{\text{AgCl}} - 0.0592 [\text{Cl}] \\ &= 0.222 + \text{pCl} \end{aligned}$$

We're really measuring a decrease in $[\text{Ag}^+]$. pCl goes down as pAg goes up.

Simple metal electrodes

For some metals, a good electrode can't be made or no metal is involved - just ions.

An inert indicating electrode like Pt can be used. This type of electrode only measures the ratios of the ions.

No quantitation but suitable for titrations.

Examples of Nernst Equation

Calculate the platinum electrode potential for a immersed in a solution prepared by saturating a 0.0150 M solution of KBr with Br₂.



Calculate the potential for a platinum electrode immersed in the same solution with the unsaturated concentration of Br₂ = 1.00 x 10⁻³M.

Reaction	E ⁰ at 25°C, V
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	+1.359
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$2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.000
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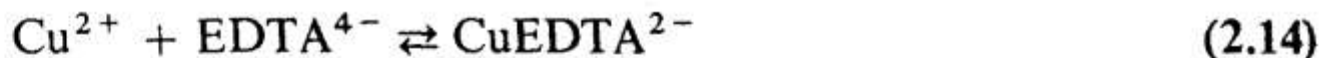
Examples of Nernst Equation

Calculate the potential of a silver electrode in a solution that is saturated with silver iodide and has an iodide ion activity of exactly 1.00.

(K_{sp} for AgI = 8.3×10^{-17})

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
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Effect of Complexation on Electrode potential



(where EDTA^{4-} is the basic form of the tetra-acid), for which the formation constant is written as

$$K_f = \frac{(\text{CuEDTA}^{2-})}{(\text{Cu}^{2+})(\text{EDTA}^{4-})} = 6.17 \times 10^{18} \quad (2.15)$$

For the half-reaction involving copper ions and copper (Equation 2.2), the Nernst equation is expressed by

$$\text{Cu}^{2+} + 2e \longrightarrow \text{Cu}$$
$$E = E_{\text{Cu}^{2+}, \text{Cu}}^0 - \frac{RT}{nF} \ln \frac{1}{(\text{Cu}^{2+})} \quad (2.16)$$

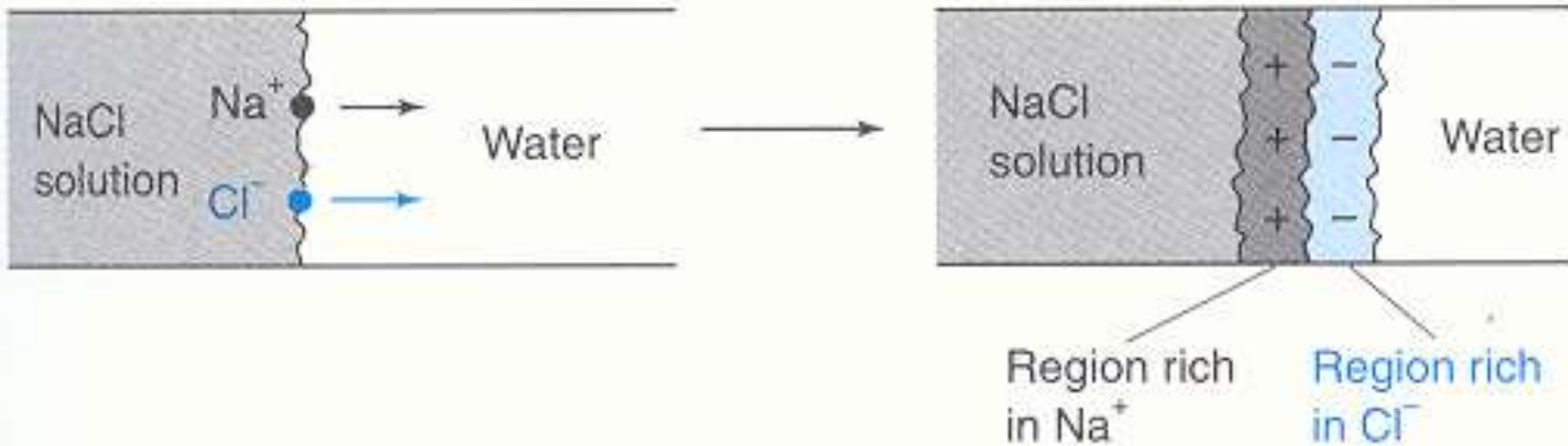
Combining Equation 2.15 with 2.16 yields the potential of a copper electrode in aqueous EDTA^{4-} systems:

$$E_{\text{Cu}} = E_{\text{Cu}^{2+}, \text{Cu}}^0 + \frac{RT}{nF} \ln \frac{1}{K_f(\text{EDTA}^{4-})} + \frac{RT}{nF} \ln (\text{CuEDTA}^{2-}) \quad (2.17)$$

Liquid Junction Potential

- The interface between two 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 + and - ions.

Liquid Junction Potential



- 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^- and one rich in Na^+ .
- The result is a potential difference at the junction of the NaCl and H_2O phase.

Liquid Junction Potential Example

- A 0.1 M NaCl solution was placed in contact with a 0.1 M NaNO₃ solution. Which side of the junction will be positive and which will be negative?

Solution:

- [Na⁺] is equal on both sides, so there is no net diffusion of Na⁺ across the junction.
- Cl⁻ will diffuse into the NaNO₃ and NO₃⁻ will diffuse into the NaCl.
 - But the mobility of Cl⁻ is greater than NO₃⁻ (because it's smaller).
- The NaCl region will be depleted of Cl⁻ faster than the NaNO₃ region will be depleted of NO₃⁻.
- The NaNO₃ side will become negative and the NaCl side will become positive.

Calculation of Cell Potentials

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

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

- What is the cell potential of



- The activities are unity so the standard potentials are also the electrode potentials.
- What happens when the above is run in reverse?

Calculation of Cell Potentials

- Calculate the cell potential for
 $\text{Zn}|\text{ZnSO}_4(c_{\text{ZnSO}_4}=5.00 \times 10^{-4} \text{ M}), \text{PbSO}_4(\text{sat}, \text{d})|\text{Pb}$
 - E^0 and the cell voltage do NOT depend on how you write the cell reaction.
 - Will this cell be galvanic or electrolytic?

Calculation of Cell Potentials

Calculate the cell potential for



Potentiometric Methods:

To perform potentiometry, the following is needed:

- Reference Electrode**
- Indicator Electrode**
- Potential Measuring Device**

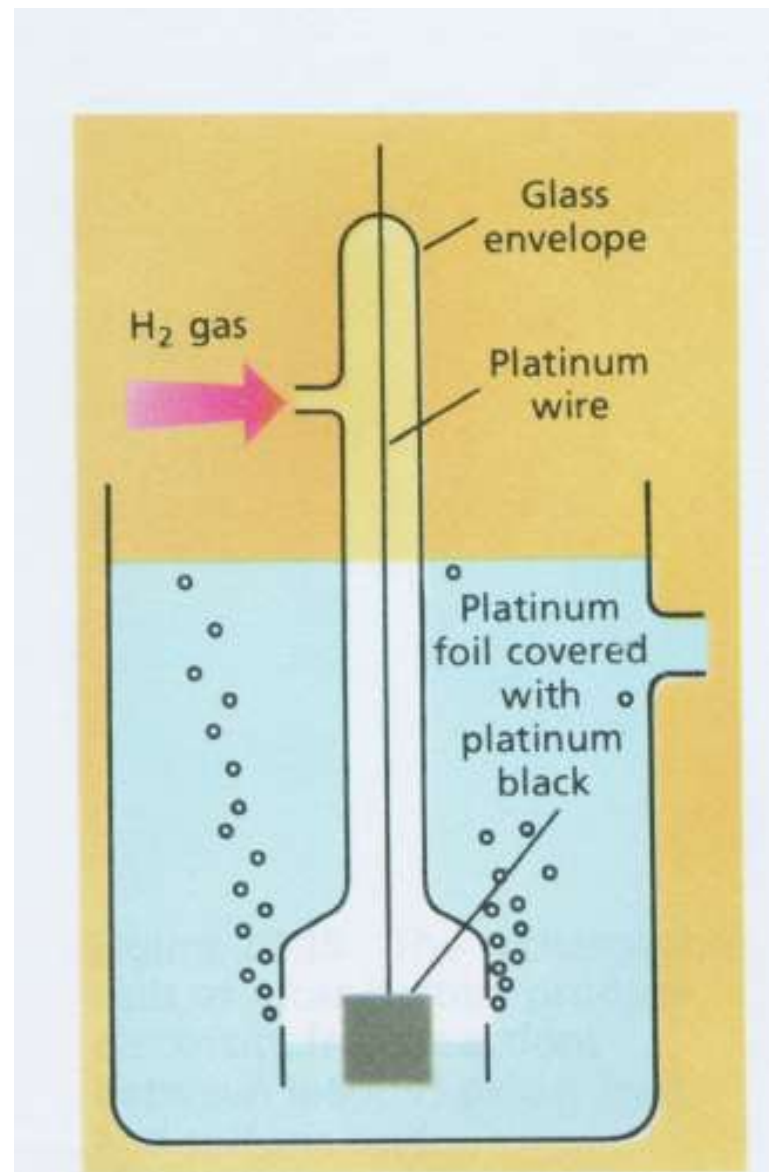
Reference Electrodes

Characteristics of Ideal Reference Electrode:

- 1) Reversible and follow Nernst equation**
- 2) Potential should be constant with time**
- 3) Should return to original potential after being subjected to small currents**
- 4) Little hysteresis with temperature cycling**
- 5) Should behave as ideal nonpolarized electrode**

Reference Electrodes

- Hydrogen Gas Electrode
- $\text{Pt} (\text{H}_2 (1 \text{ atm}), \text{H}^+ (1\text{M}))$



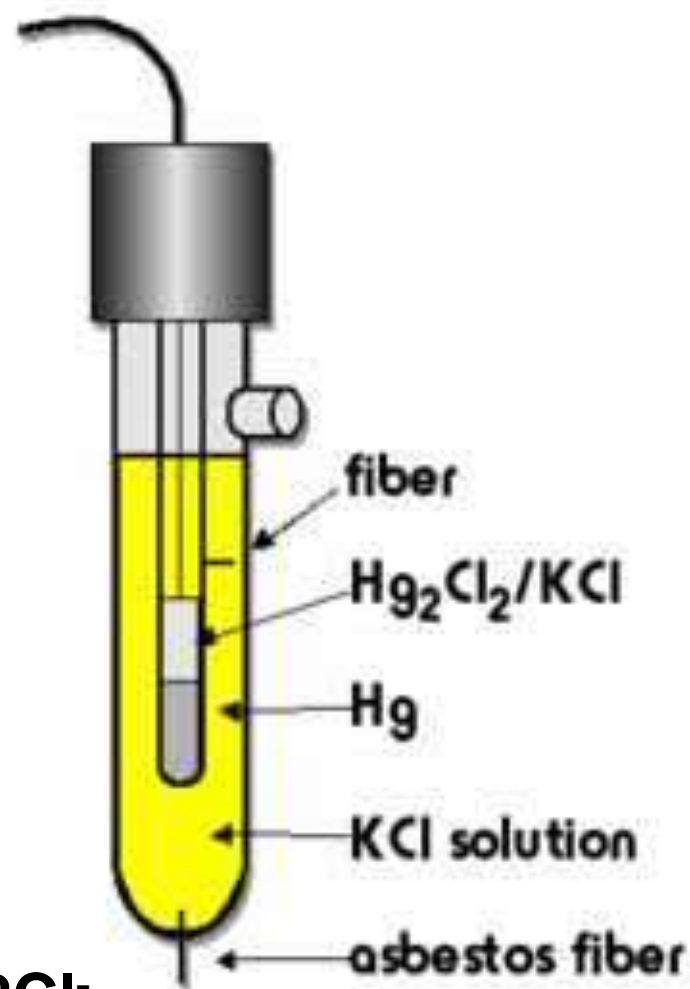
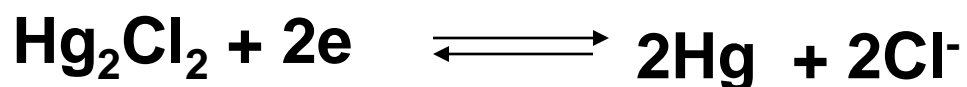
Reference electrodes

Calomel electrode (SCE)

A much more common reference electrode.



Chloride is used to maintain constant ionic strength.



Reference electrodes

Calomel electrode

Different KCl concentrations can be used.

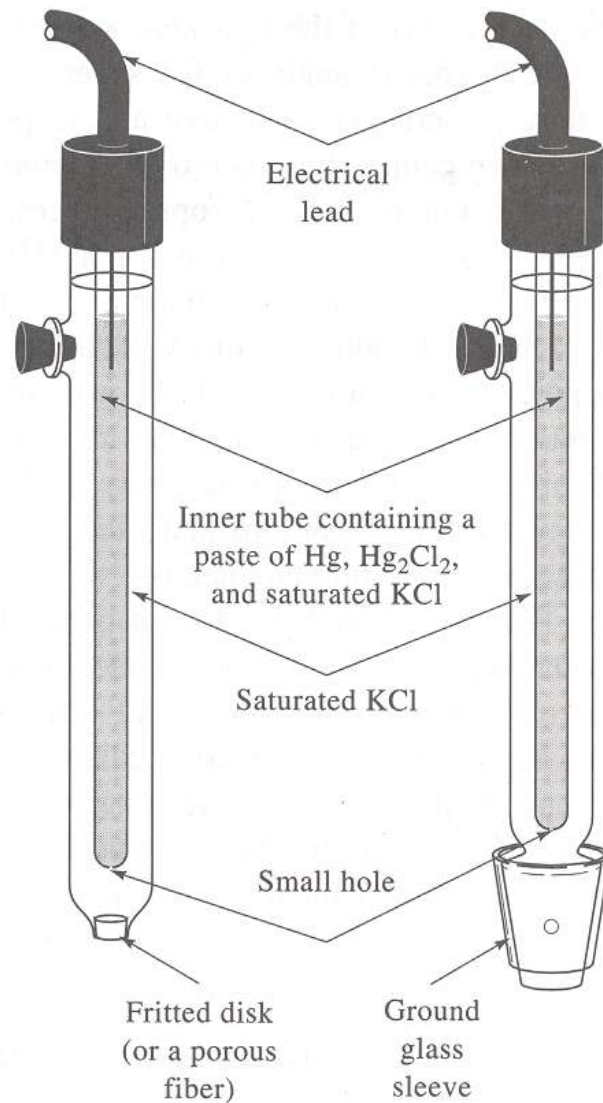
0.1 M - least temperature sensitive

Saturated - easier to make and maintain.

$$E = 0.2444V \quad 25^{\circ}\text{C}$$

The electrode may be separate or built into the sensing electrode - **combination electrode**.

Example of typical calomel reference electrodes

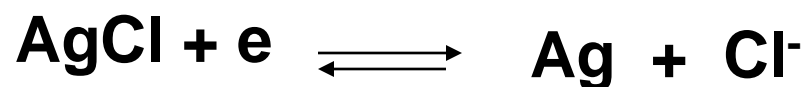


Reference electrodes

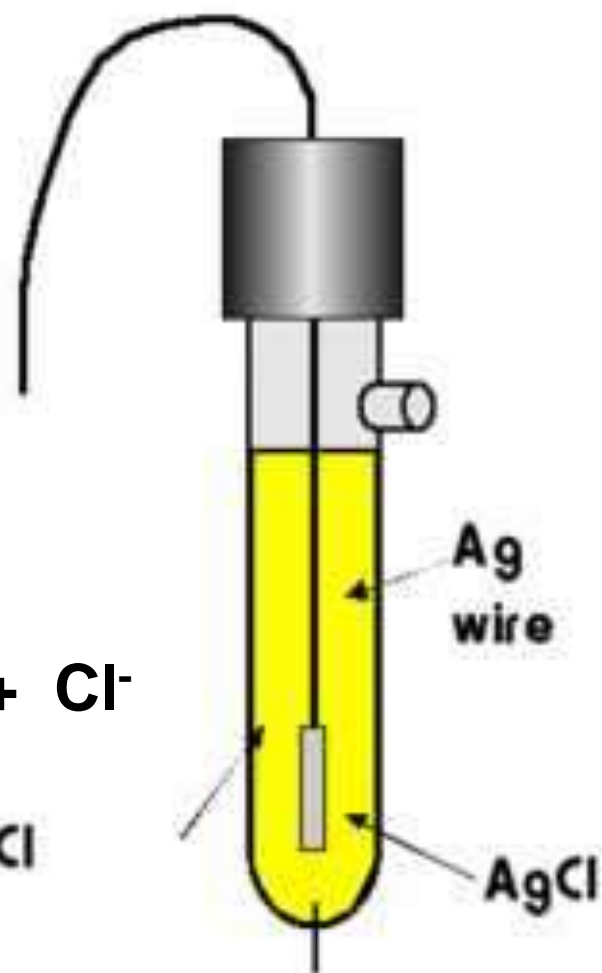
Ag/AgCl

Another common reference electrode.

Easier to produce a combination electrode.



saturated AgCl/KCl

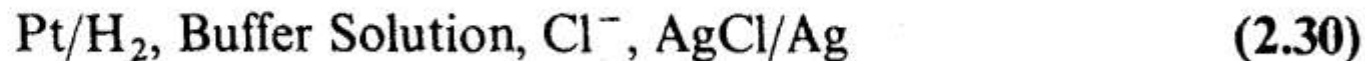


Operational definition of pH

$$\text{pH} = \text{pH}_s + \frac{(E - E_s)F}{RT \ln 10} \quad (2.29)$$

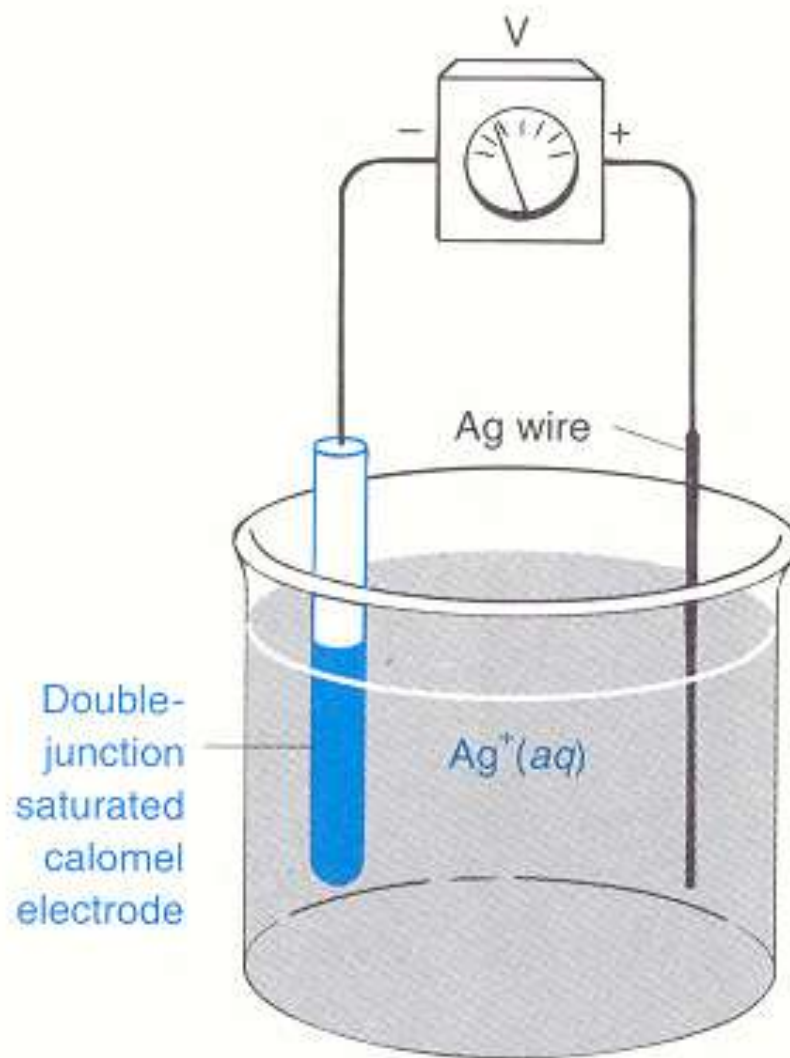
where E = electromotive force of a cell containing the unknown solution
 E_s = electromotive force of a cell containing a standard reference buffer solution of known or defined pH, that is, pH_s

In actual practice, the NBS pH standards were assigned pH_s values from measurements of a hydrogen gas–silver/silver chloride cell without liquid junction,



Indicator Electrodes used in Potentiometry

Metallic Indicator electrodes



Uses of metallic electrodes

- Using a silver and calomel electrode allows for the direct determination of $[\text{Ag}^+]$.
- Can also be used for indirect determination of halide concentrations through the solubility product constant.
 - Consider the titration of 100 mL of 0.100 M NaCl solution w/ 0.100 M AgNO_3 .

Ion-Selective Membrane Electrodes

- An ion-selective electrode consists of a thin membrane across which only the intended ion can migrate.
 - Ideally, other ions cannot cross the membrane.
- Just like a junction potential, an electric potential develops across the membrane due to the difference in concentration (actually activity) of the ion on the two sides of the membrane.
- The electric potential difference is Nernstian:

$$E = \text{Constant} + \frac{0.0592}{n} \log (M^n)$$

- For every factor-of-10 difference in activity of a +1 charged ion, a difference of 0.0592 V builds up across a membrane

Electrode Potential and Interference Effect

$$E_{\text{cell}} = E_{\text{constant}} + E_{\text{ISE}} = E'_{\text{constant}} + 0.0591 \log a_i$$

$$E_{\text{cell}} = E'_{\text{constant}} + 0.0591 \log (a_i + k_{ij} a_j^{n/z})$$

a_i = activity of the interferent ion of charge z

k_{ij} = selectivity coefficient

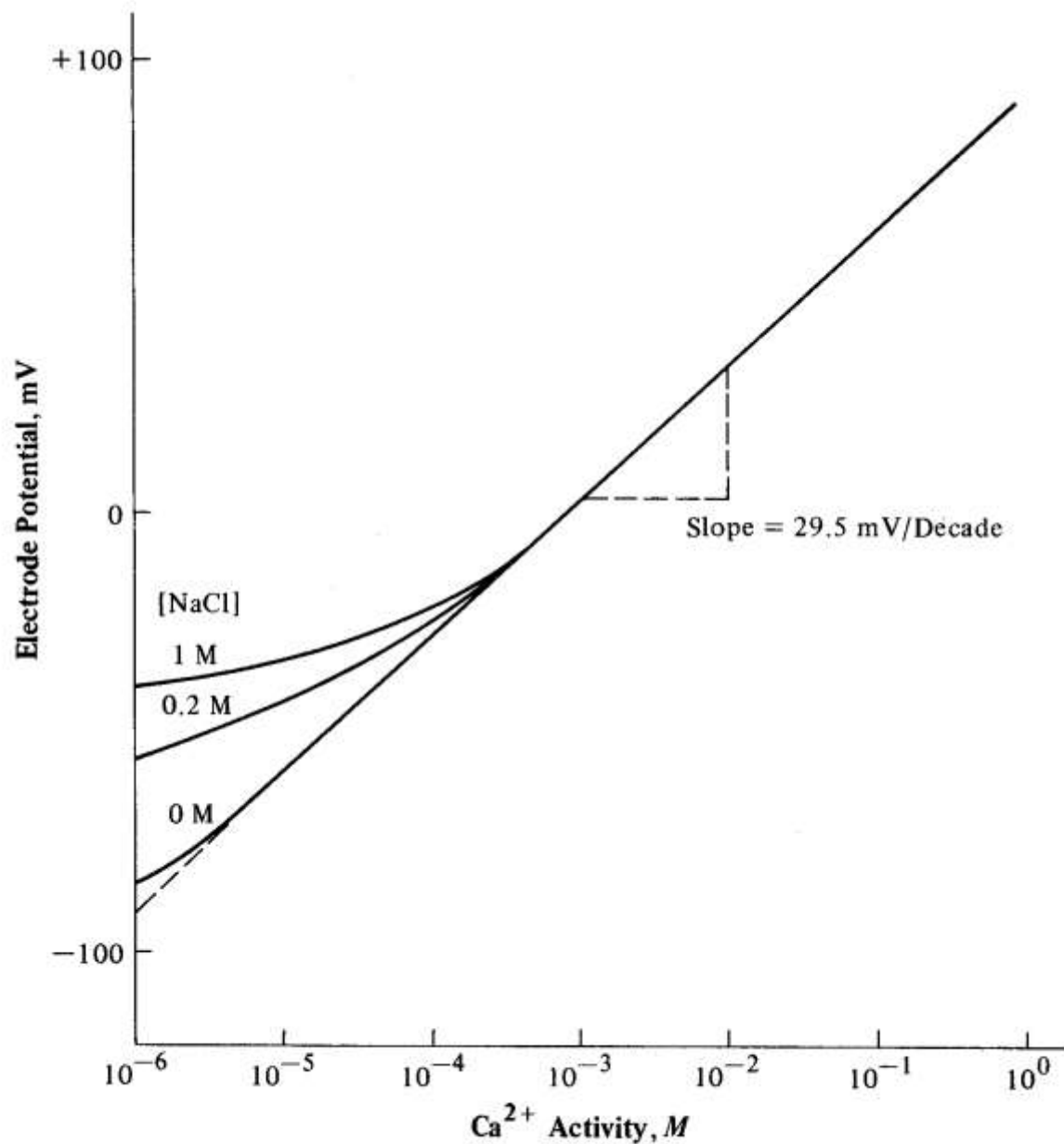


FIGURE 2.5. Response of a calcium ion-selective electrode to pure CaCl_2 solutions, and to CaCl_2 solutions with 0.2 or 1 M NaCl also present. Redrawn

Membrane Electrodes:

Two types:

- 1) Responsive to ionic species**
- 2) Applied to determination of molecular analytes**
 - a) gas-sensing probes**
 - b) enzymatic electrodes**

Properties of Ion-Selective Electrodes:

Minimal solubility of ion-selective medium in analyte solution

Electrical conductivity

Selective reactivity with analyte, usually ion-exchange, crystallization, or complexation.

Types of Ion-selective Electrodes

There is four classes of ion-selective electrodes:

1. Glass membranes

- These are selective to H^+ and certain monovalent cations.**

2. Solid-state electrodes

- These are made of inorganic salt crystals.**
- The inorganic salt is made such to have vacancies in its lattice structure.**
- The vacancies allow the ion (needed to fill the vacancy) to migrate through the salt.**

3. Liquid-based electrodes

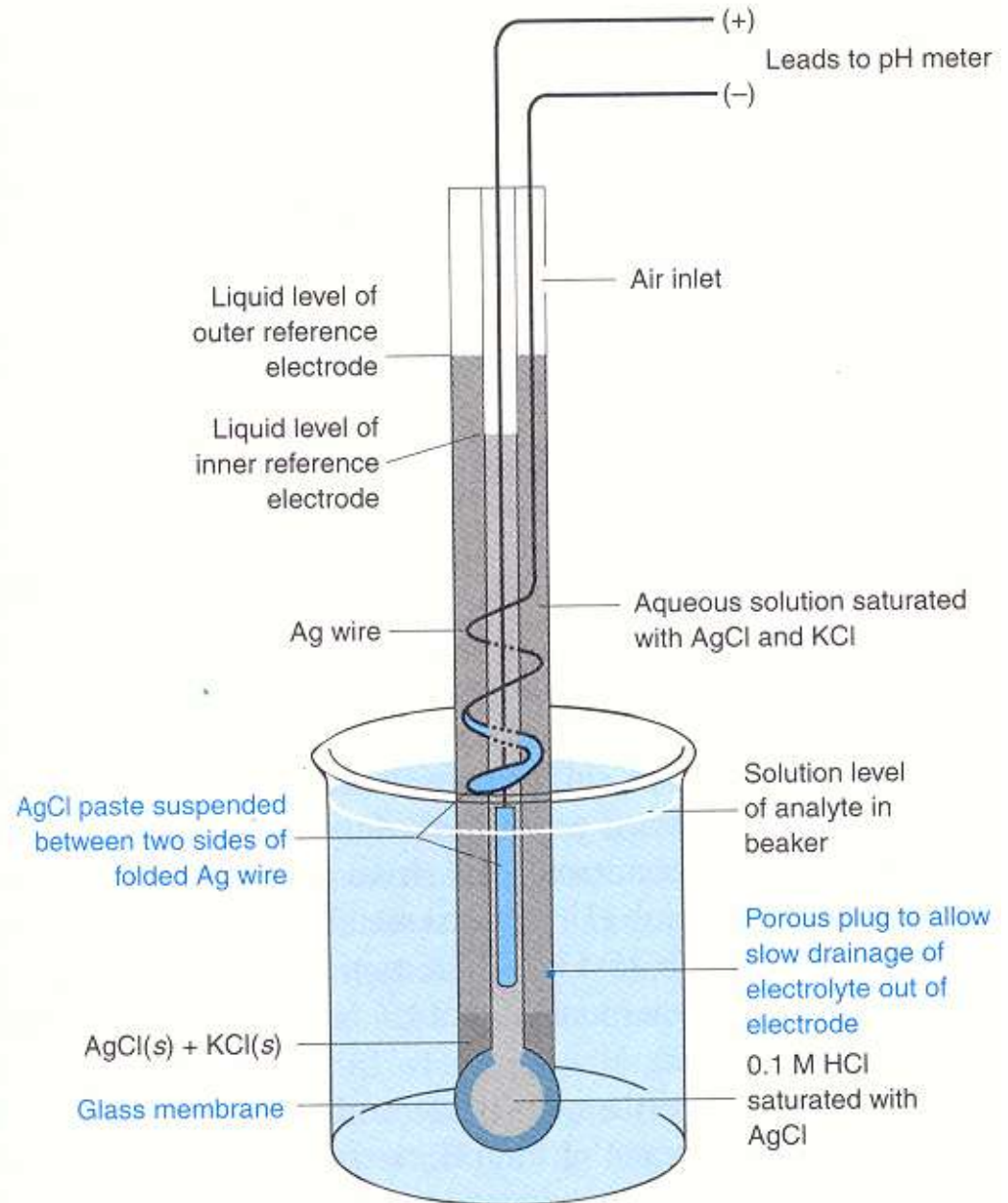
- A mobile carrier transports the selected ion across a membrane impregnated with a liquid solution of the carrier.**

4. Molecular (Compound) Electrodes

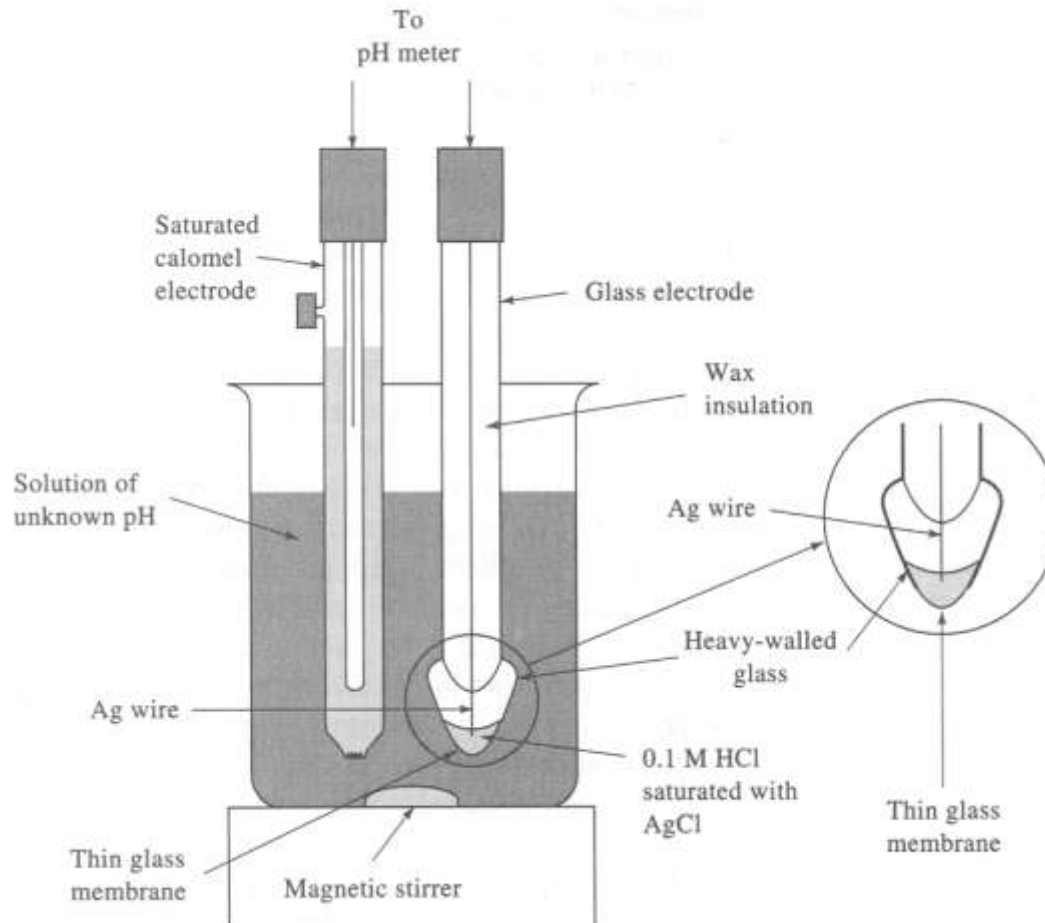
- 1. These contain a conventional electrode surrounded by a membrane that isolates (or generates) the analyte to which the electrode responds.**
- 2. For example, a CO₂ electrode responds the change in pH due to the presence of the CO₂.**

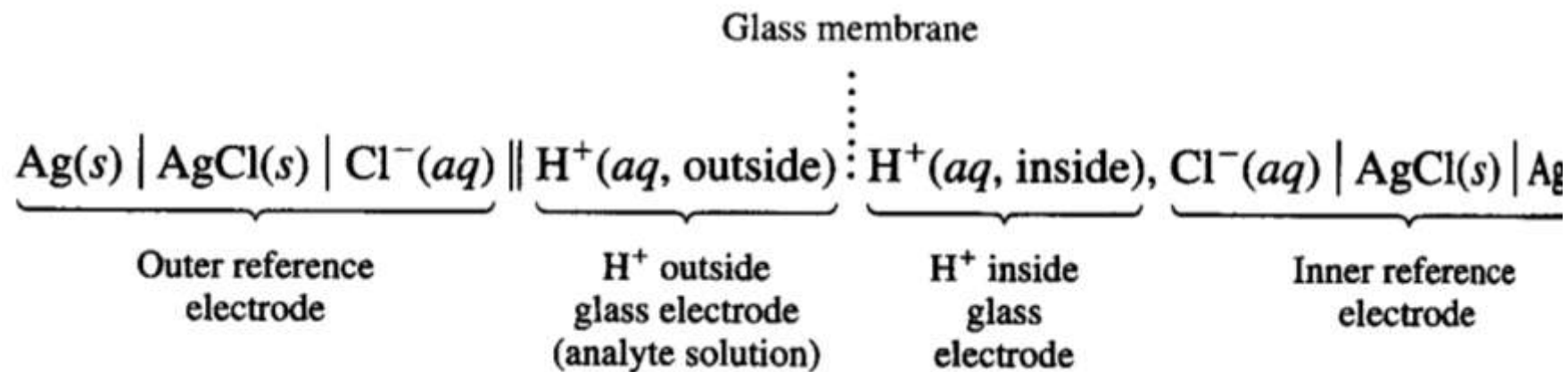
Glass Electrodes for measuring pH

- These consists of a thin glass bulb at the bottom that is selective to H^+ .
- Two reference electrodes (usually Ag/AgCl) measure the potential difference across the membrane.



Typical pH Electrode





Calibrating Glass Electrodes

- **Glass electrodes must always be calibrated because the concentration of H^+ inside the glass is always changing.**
- **Must also account for junction potentials.**
- **Calibration is done using standard buffer solutions.**

Errors in pH measurement

- **Standards:** The pH measurement cannot be any more accurate than the standards (typically ± 0.01 pH unit).
- **Junction potential:** Changing the ionic composition of the analyte (compared to standard), changes the junction potential that exists at the porous plug. Gives an uncertainty of at least 0.01 pH unit.
- **Junction potential drift:** The presence of a reducing agent in the analyte can cause Ag(s) to be precipitated inside the plug, changing the junction potential.

- **Alkaline error:** the electrode also responds to alkaline ions (Li^+ , Na^+). Having high concentrations of these causes the apparent pH to be lower than the true pH.
- **Acid error:** The measured pH is always higher than the actual pH in strong acid solutions because the glass surface becomes saturated with H^+ and cannot be protonated at anymore sites.
- **Equilibration time:** Electrode must equilibrate with the solution.
- **Hydration of glass:** A dry electrode don't work.
- **Temperature:** this affects ion mobility and consequently the pH measurement.

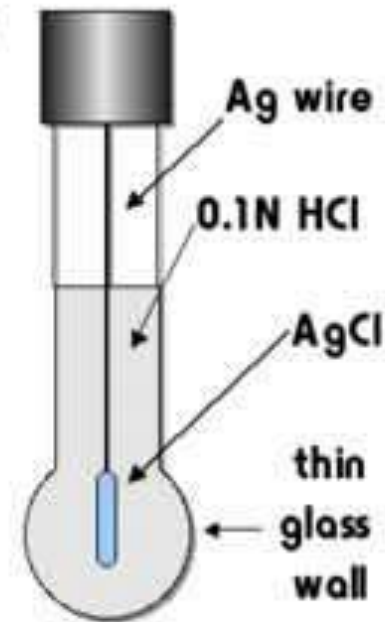
Membrane electrodes Potential

A potential difference is created across a membrane that can be measured.

There is no change in the solution or actual contact.

pH electrode

- first discovered
- still the most significant
- relies on a glass membrane.



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

$$E_{\text{cell}} = K + 0.0591/n \log a_i \quad \text{at } 25^\circ \text{C}$$

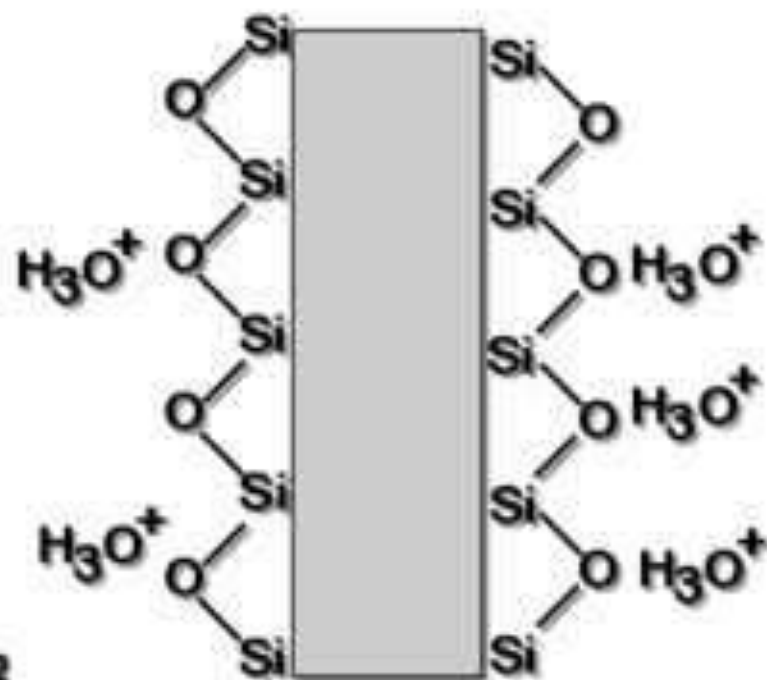
Membrane electrodes

H_3O^+ partially populates both the inner and outer SiO_2 surfaces.

The concentration difference results in a potential across the glass membrane.

A special glass is used:

22% Na_2O , 6% CaO , 72% SiO_2



Membrane electrodes

pH electrodes

In order to work, the glass must be hydrated - already have partial silicate production

This explains why electrodes are always kept moist or in a solution.

While the electrode is reasonable selective of H_3O^+ , other ions can cause a response.

Selectivity Coefficient

No electrode responds exclusively to one kind of ion. •

The glass pH electrode is among the most selective, but it –
also responds to high concentration of Na⁺.

When an electrode used to measure ion A, also •
responds to ion X, the **selectivity coefficient** gives the
relative response of the electrode to the two different
species.

$$k_{A,X} = \frac{\text{response to X}}{\text{response to A}}$$

The smaller the selectivity coefficient, the less interference –
by X.

Solid state electrodes

A very popular type of ion specific electrode.
As easy to maintain as a pH electrode.

F electrode

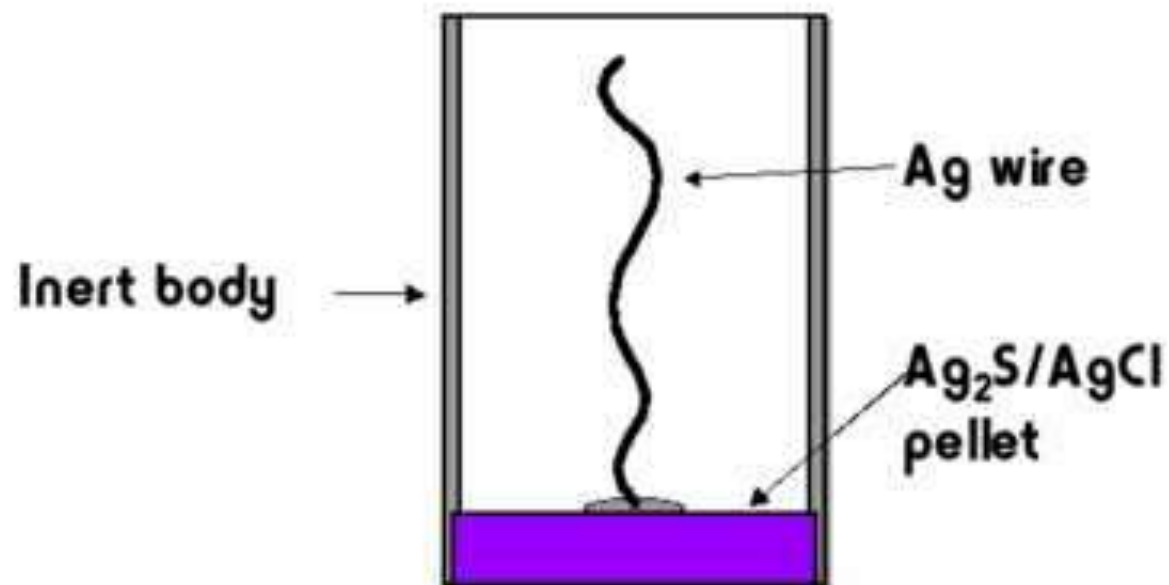
The original solid state

Works by creating defects in a LaF_3 crystal.

Other solid state electrodes work based on the presence of a primary absorbed ion.

Solid state electrodes

Cl^- electrode



Solid state electrodes

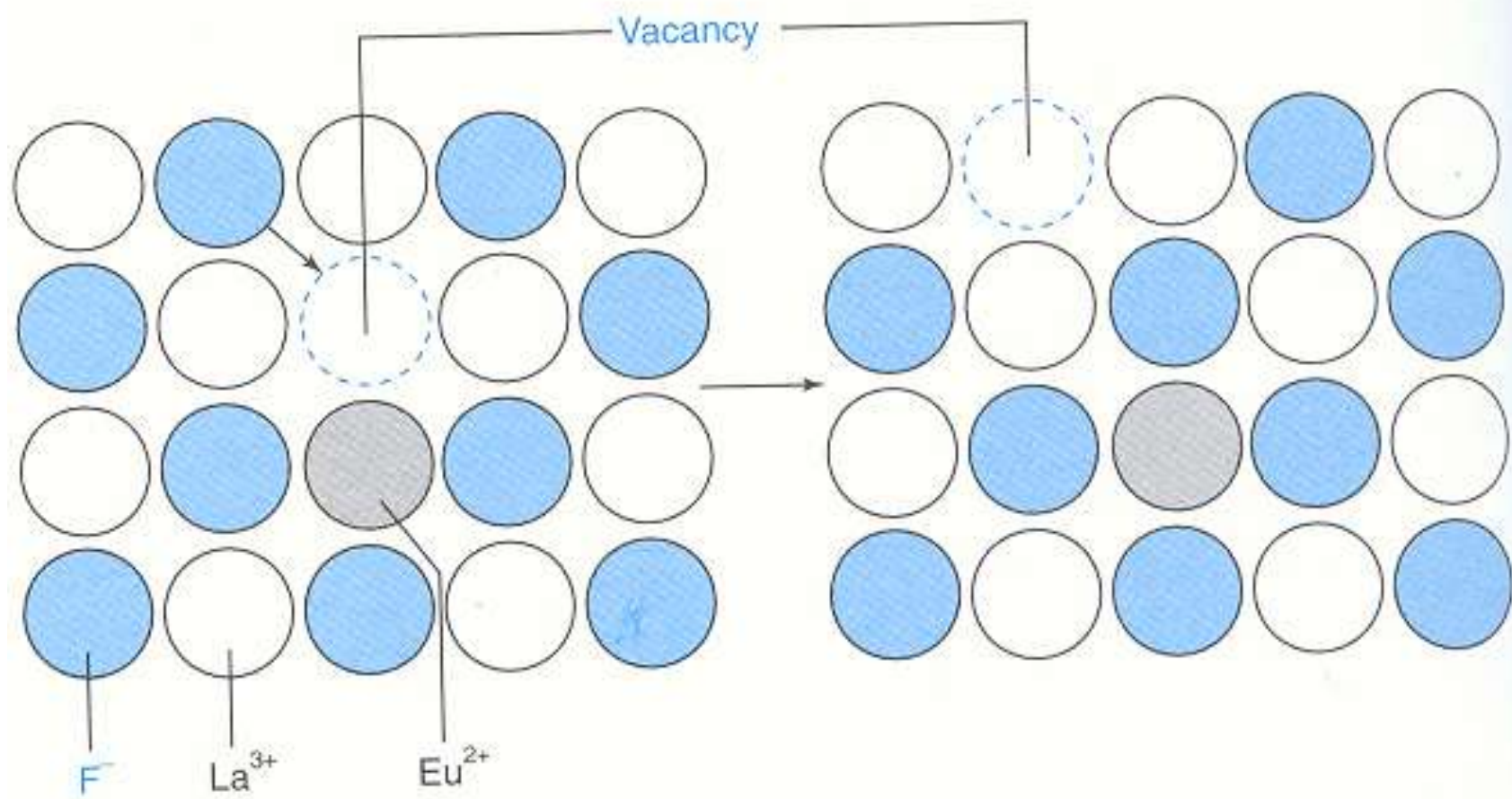
The Cl⁻ electrode will produce a concentration dependent response for both Cl⁻ and Ag⁺
Both can be primary absorbed ions.

Interferences are observed for S²⁻, Br⁻, I⁻, CN⁻ and ammonia.

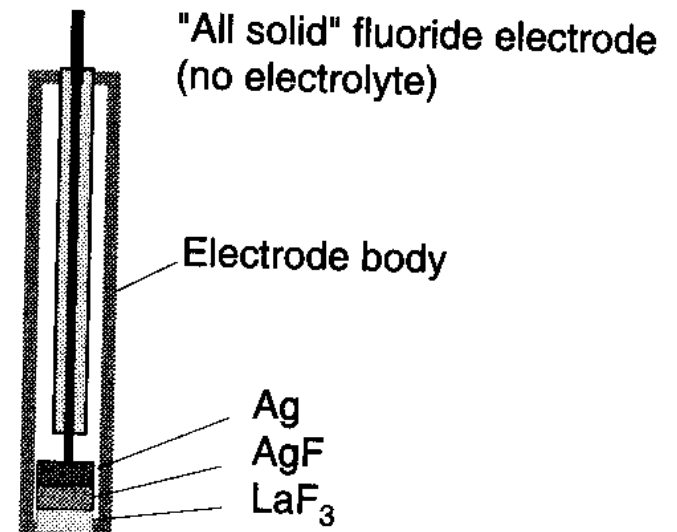
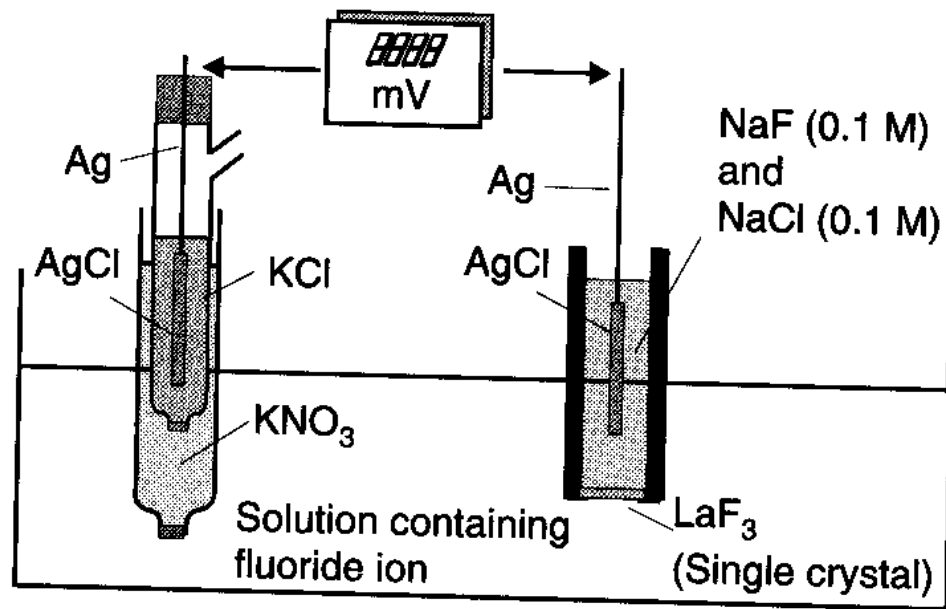
Why?

Solid-State Electrodes (F⁻ selective electrode)

- **A LaF₃ is doped with EuF₂.**
- **Eu²⁺ has less charge than the La³⁺, so an anion vacancy occurs for every Eu²⁺.**
- **A neighboring F⁻ can jump into the vacancy, thereby moving the vacancy to another site.**
- **Repetition of this process moves F⁻ through the lattice.**



Fluoride Electrode



Solid-state Electrodes

- Another common inorganic crystal electrode uses Ag_2S as the membrane.
- The crystal lattice is made to have vacancies which allow Ag^+ and S^{2-} to migrate through.
- The silver sulfide membrane can be doped with copper sulfide, cadmium sulfide, or lead sulfide making the electrode sensitive to Cu^{2+} , Cd^{2+} , or Pb^{2+} respectively.

Typical Properties of Some Commercial Ion-Selective Electrodes

<i>Electrode</i>	<i>Concentration Range, M</i>	<i>Principal Interferences^a</i>
Liquid-Liquid Ion Exchange Electrodes		
Ca ²⁺	10 ⁰ –10 ⁻⁵	Zn ²⁺ (3); Fe ²⁺ (0.8); Pb ²⁺ (0.6); Mg ²⁺ (0.1); Na ⁺ (0.003)
Cl ⁻	10 ⁻¹ –10 ⁻⁵	I ⁻ (17); NO ₃ ⁻ (4); Br ⁻ (2); HCO ₃ ⁻ (0.2); SO ₄ ²⁻ , F ⁻ (0.1)
Divalent Cation	10 ⁰ –10 ⁻⁸	Fe ²⁺ , Zn ²⁺ (3.5); Cu ²⁺ (3.1); Ni ²⁺ (1.3); Ca ²⁺ , Mg ²⁺ (1); Ba ²⁺ (0.94); Sr ²⁺ (0.54); Na ⁺ (0.015)
BF ₄ ⁻	10 ⁻¹ –10 ⁻⁵	NO ₃ ⁻ (0.1); Br ⁻ (0.04); OAc ⁻ , HCO ₃ ⁻ (0.004); Cl ⁻ (0.001)
NO ₃ ⁻	10 ⁻¹ –10 ⁻⁵	ClO ₄ ⁻ (1000); I ⁻ (20); Br ⁻ (0.1); NO ₂ ⁻ (0.04); Cl ⁻ (0.004); CO ₃ ²⁻ (0.0002); F ⁻ (0.00006); SO ₄ ²⁻ (0.00003)
ClO ₄ ⁻	10 ⁻¹ –10 ⁻⁵	I ⁻ (0.01); NO ₃ ⁻ ; OH ⁻ (0.0015); Br ⁻ (0.0006); F ⁻ , Cl ⁻ (0.0002)
K ⁺	10 ⁰ –10 ⁻⁵	Cs ⁺ (1); NH ₄ ⁺ (0.03); H ⁺ (0.01); Na ⁺ (0.002); Ag ⁺ , Li ⁺ (0.001)
Solid-State Electrodes ^b		
F ⁻	10 ⁰ –10 ⁻⁶	Maximum level: OH ⁻ < 0.1 F ⁻
Ag ⁺ or S ²⁻	10 ⁰ –10 ⁻⁷	Hg ²⁺ < 10 ⁻⁷ M

^aNumber in parentheses is the relative selectivity for the interfering ion over the test ion (see "The Selectivity Ratio" below).

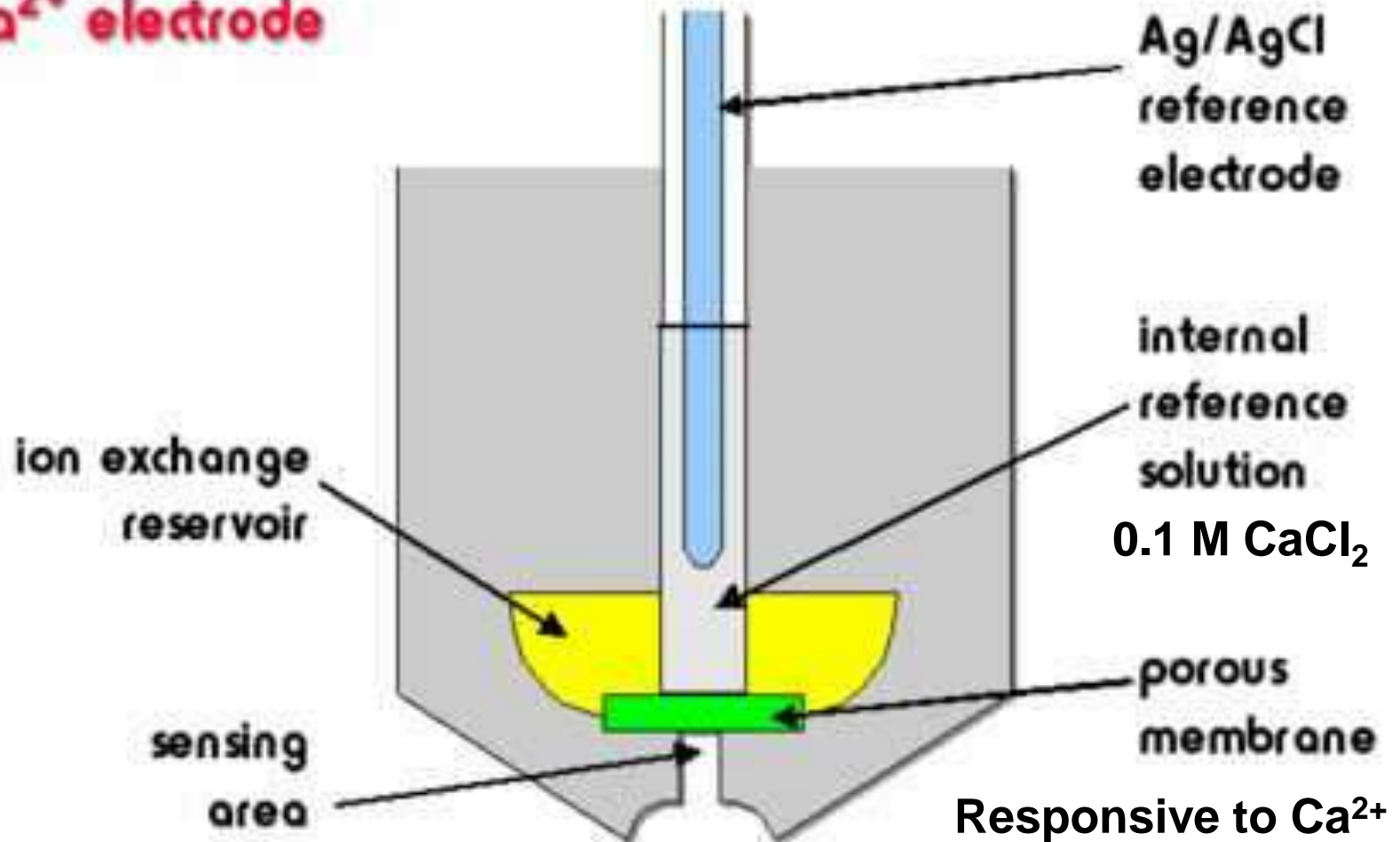
^bInterference concentrations given represent maximum tolerable concentrations.

Liquid membrane electrodes

- Similar to a pH electrode except the membrane is an organic polymer saturated with a liquid ion exchanger.
- Interaction of this exchanger with target ions results in a potential across the membrane that can be measured.
- The Ca^{2+} electrode is one of the best examples.

Liquid membrane electrodes

Ca^{2+} electrode

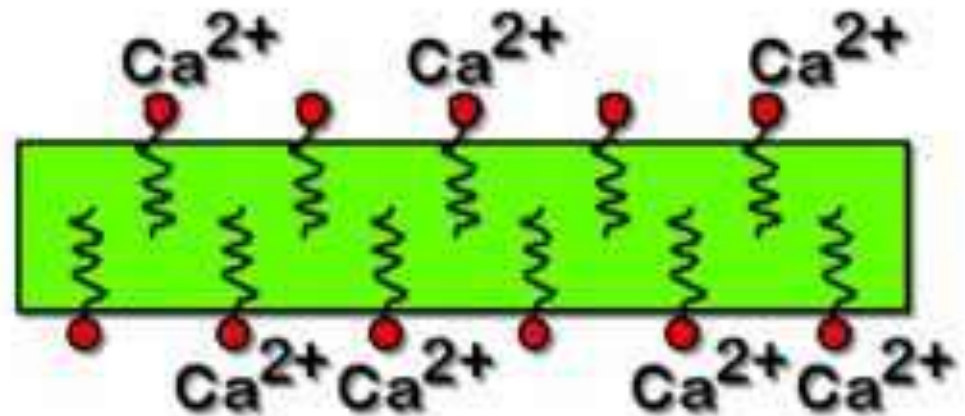


Liquid membrane electrodes

The reservoir forces exchanger into the membrane.
The exchanger forms complexes with the species of interest.

This

The results in a
concentration
difference and a
resulting ΔV that
we can measure.



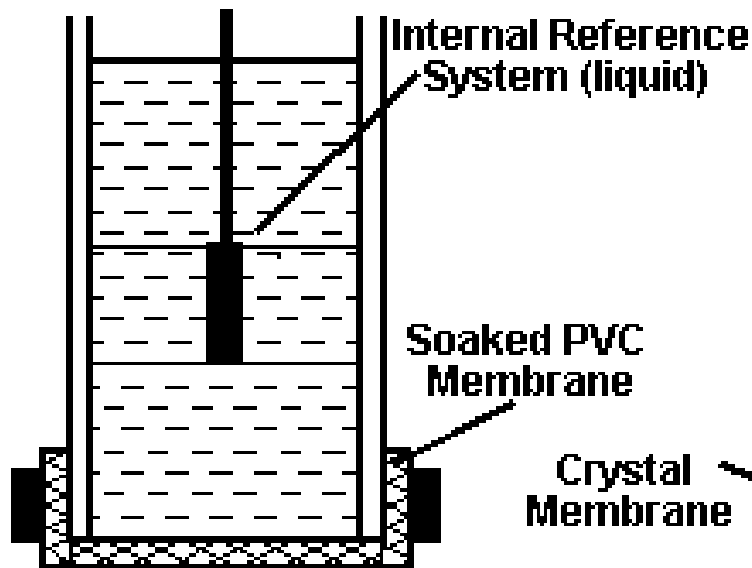
Liquid membrane electrodes

Ion	Concentration Range, M	Major Interferences
Ca^{2+}	$10^0 - 5 \times 10^{-7}$	Pb^{2+} , Fe^{2+} , Ni^{2+} , Hg^{2+} , Sr^{2+}
Cl^-	$10^0 - 5 \times 10^{-6}$	I^- , OH^- , SO_4^{2-}
NO_3^-	$10^0 - 7 \times 10^{-6}$	I^- , ClO_4^- , ClO_3^- , Br^- , CN^-
ClO_4^-	$10^0 - 7 \times 10^{-6}$	I^- , ClO_3^- , Br^- , CN^-
K^+	$10^0 - 1 \times 10^{-7}$	Cs^+ , NH_4^+ , Ti^+

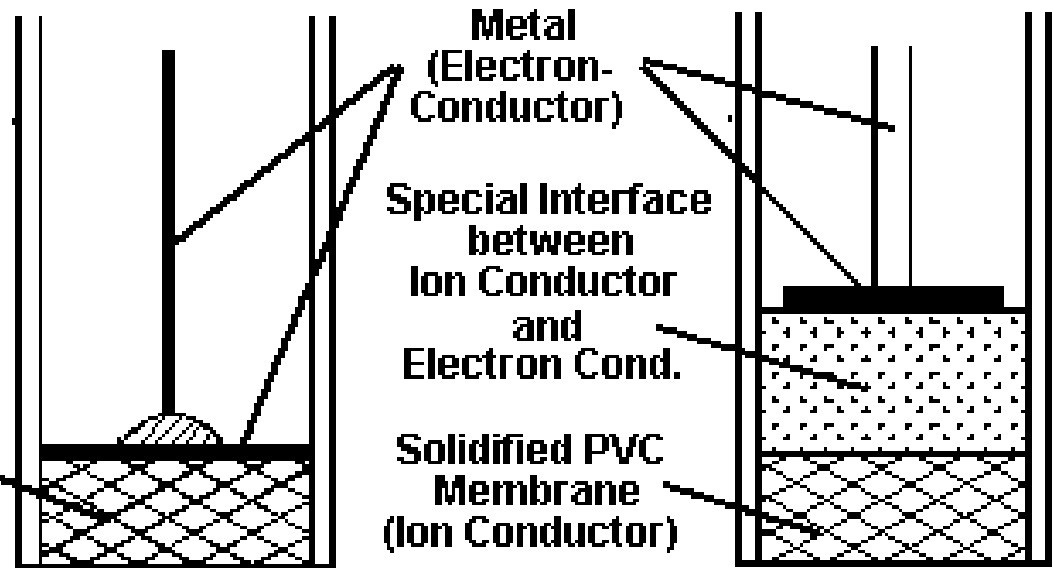
Ion-Selective Electrode Technology

Conventional ISE Technology

Advanced ELIT ISE Technology



Conventional PVC Membrane Type



ELIT Crystal Membrane Type

ELIT All Solid State PVC Electrode

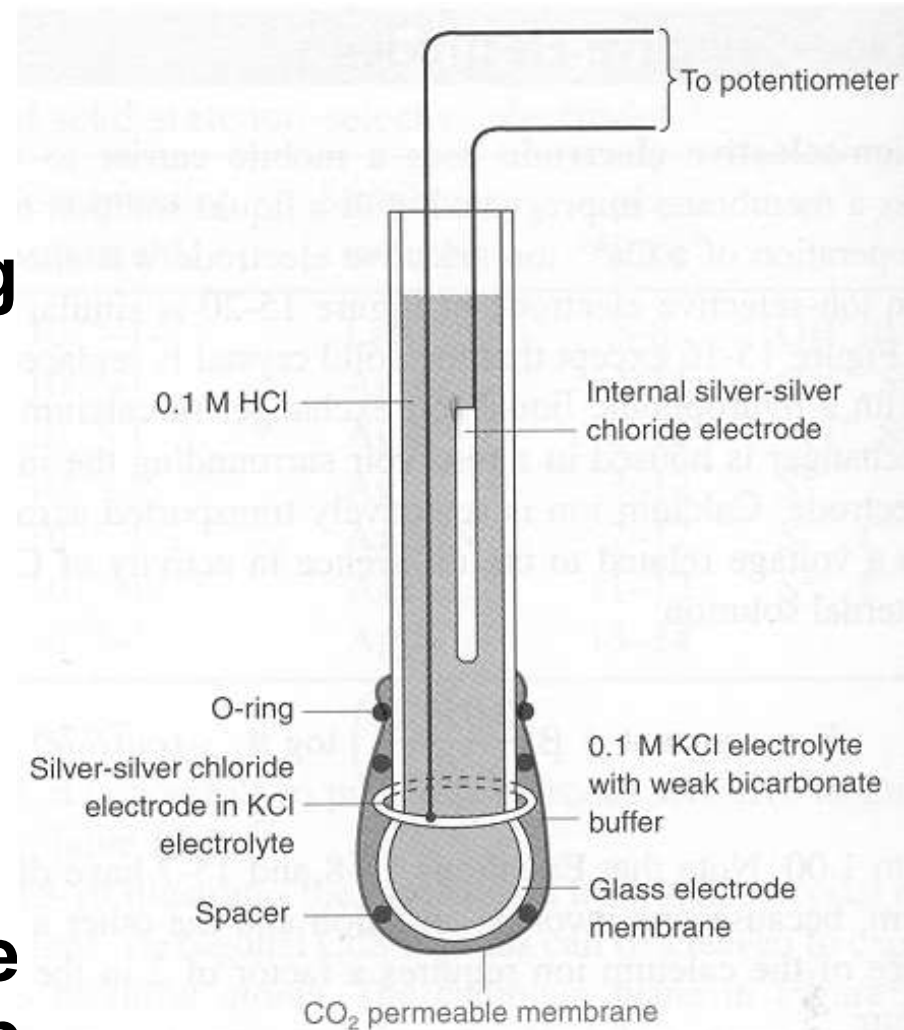
Molecular-Selective Electrodes:

Gas-Sensing Probes: Examples, hydrophobic membranes for CO_2 and NH_3

Enzyme Substrate Electrodes: Example, urease membrane for blood urea

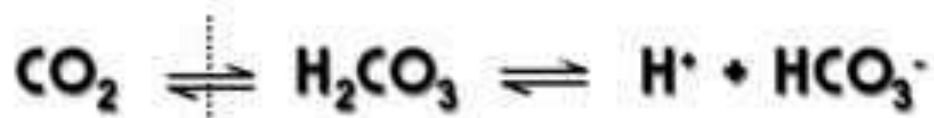
The CO₂ gas-sensing electrode

- When CO₂ diffuses through the semi-permeable membrane, the pH is lowered in the electrolyte compartment.
- This compartment is in contact with the glass pH electrode.
- Other acidic or basic gases (NH₃, SO₂, H₂S, NO_x) can be detected in a similar manner.



Gas sensing electrodes

Examples



pH electrode is used for indicating.



Silver electrode is used for indicating.

TABLE 23-5 Commercial Gas-Sensing Probes

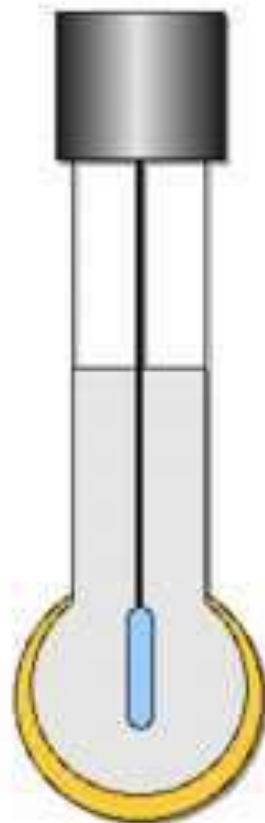
Gas	Equilibrium in Internal Solution	Sensing Electrode
NH ₃	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	Glass, pH
CO ₂	$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	Glass, pH
HCN	$\text{HCN} \rightleftharpoons \text{H}^+ + \text{CN}^-$	Ag ₂ S, pCN
HF	$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$	LaF ₃ , pF
H ₂ S	$\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$	Ag ₂ S, pS
SO ₂	$\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_3^- + \text{H}^+$	Glass, pH
NO ₂	$2\text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2^- + \text{NO}_3^- + 2\text{H}^+$	Immobilized ion exchange, pNO ₃

Enzyme electrodes

In this example, a normal pH electrode is coated with a urease impregnated gel.

Urea will permeate the gel where the enzyme will attack it, resulting in the formation of ammonium.

The resulting change in pH can be measured.



Enzyme electrodes

Advantages

The potential exists for developing electrodes for any permeable species where a pH dependent reaction results.

Disadvantages

Gels must be replaced regularly

Each measurement results in a cumulative response.

The response is time dependent.



Using Ion-Selective Electrodes

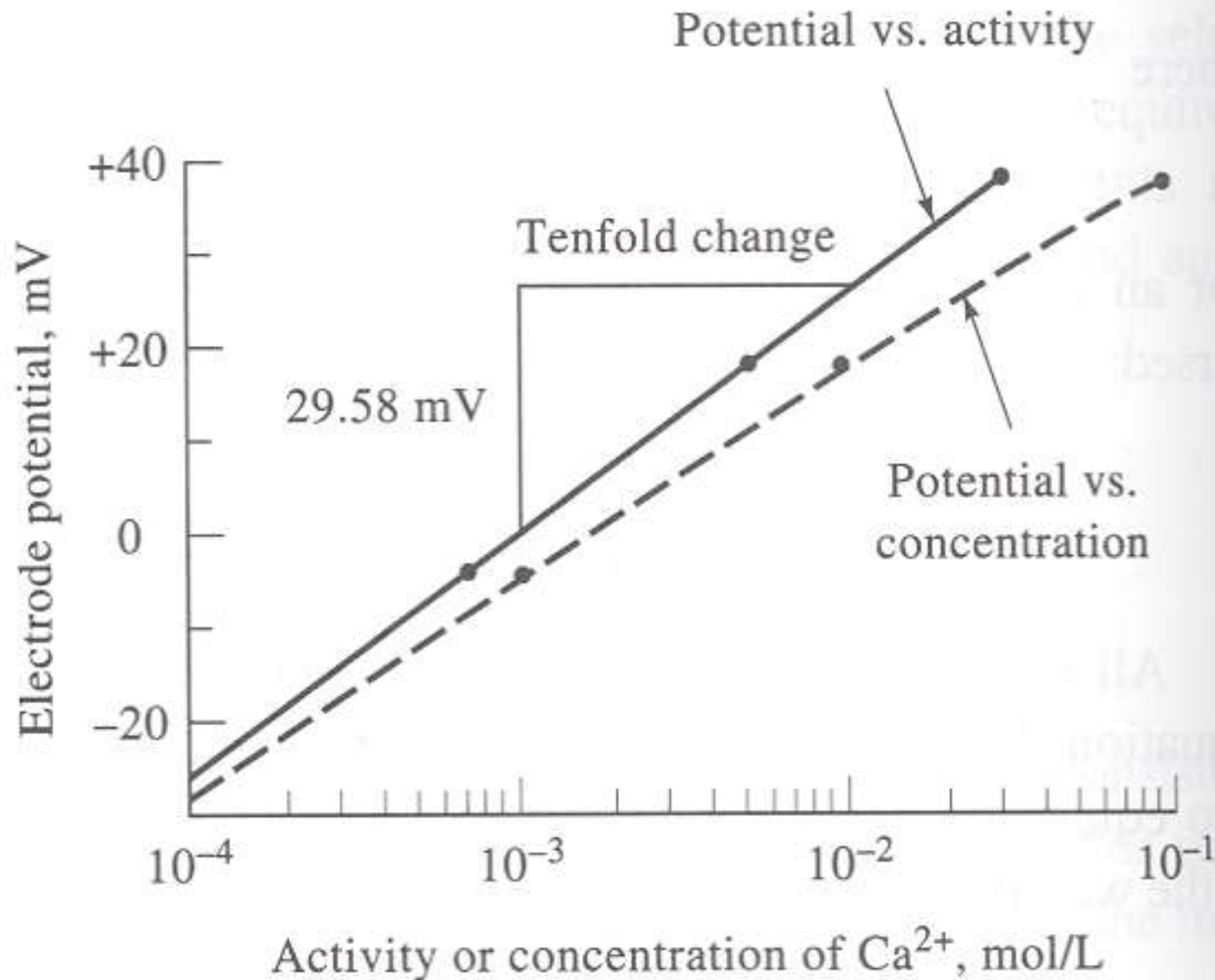
Advantages of ion-selective electrodes

- Linear response to $\log A$ over a wide range.**
- Don't consume unknown.**
- Don't contaminate unknown.**
- Have short response time.**
- Color and turbidity do not hinder the electrode.**

Disadvantages

- **Respond to the activity (not concentration).**
- **Only responds to uncomplexed analyte ions.**
- **Precision is rarely better than 1%.**
- **Certain ions interfere with or poison particular electrodes which leads to sluggish, drifting response.**
- **Some are fragile and have limited shelf life.**

Example of Activity vs. Concentration Discrepancy:



Potential measuring device

- The indicator electrode produces a voltage that is proportional to the concentration of the M^{\pm} concentration, and the measurement is made by a pH meter
- The indicator electrode is attached to control electronics which convert the voltage to a pH (in case of a pH electrode) reading and displays it on a meter



Analytical uses

Four general classes

Direct application of Nernst equation

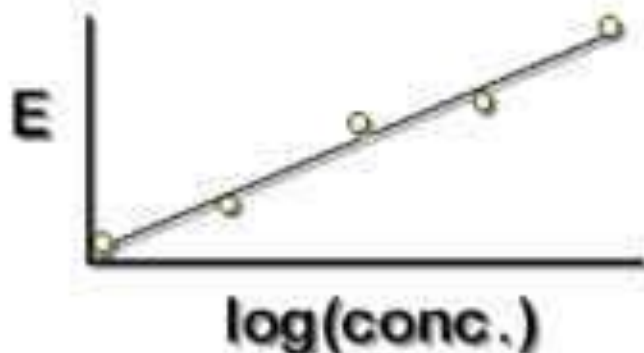
- simply calculate [] based on E_{cell} .
- not very good - must have ideal behavior and know all properties of the electrode.
- seldom done.

Analytical uses

Standard-Curve method

Measure a range of standards and produce a calibration curve.

Since the response is log based, you should use standards that vary by a factor of 10 (Example: 1, 10, 100, 1000 ppm)



Analytical uses

Standard addition

Significant problems can occur with using an ISE at low concentrations.

Long time to reach equilibrium

Large relative error.

Standard addition offers a way around these problems.

Analytical uses

Standard addition

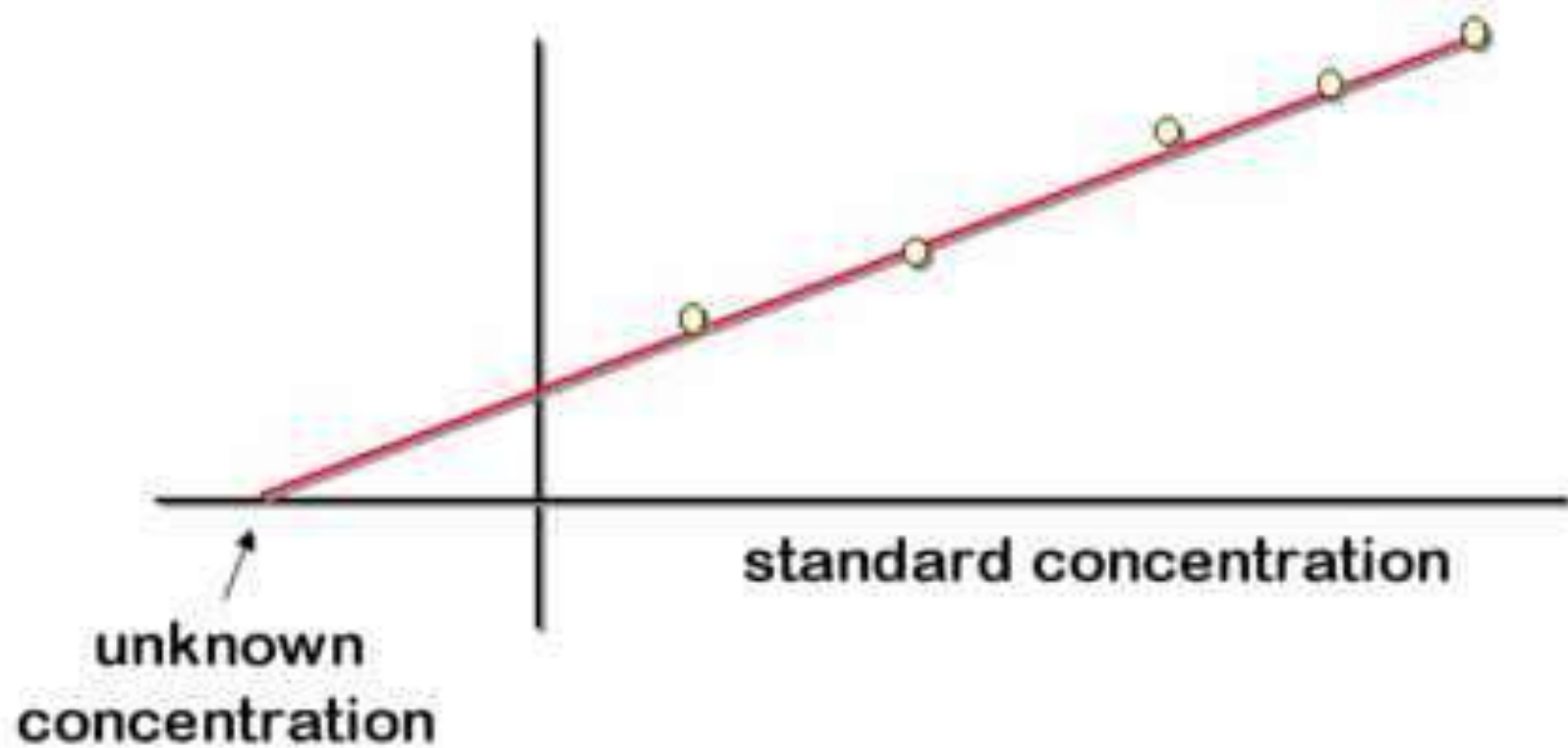
With this approach, an increasing amount of standard is added to your unknown.

A standard addition plot is then produced.

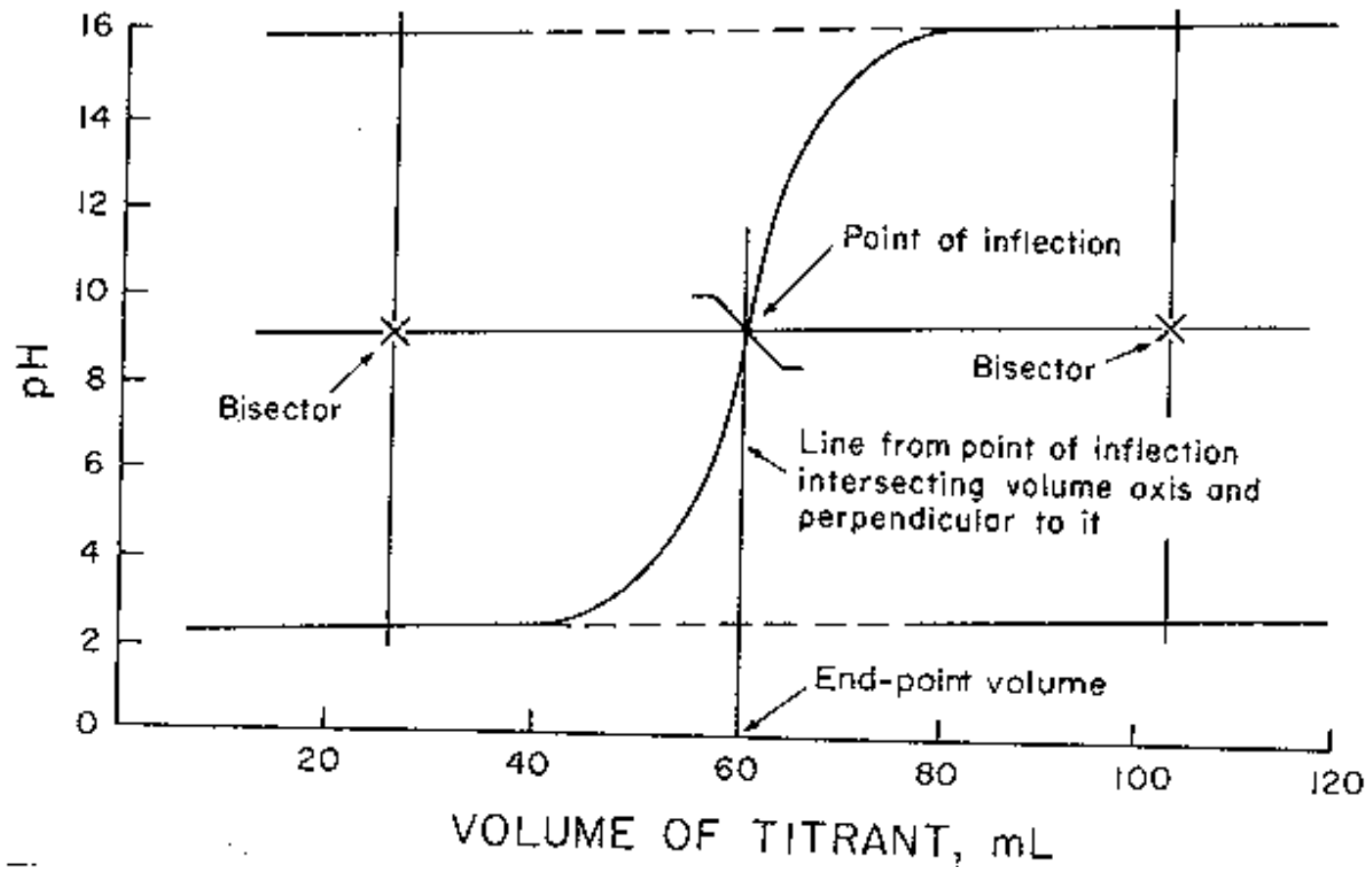
The $|X \text{ intercept}|$ represents your unknown concentration.

Analytical uses

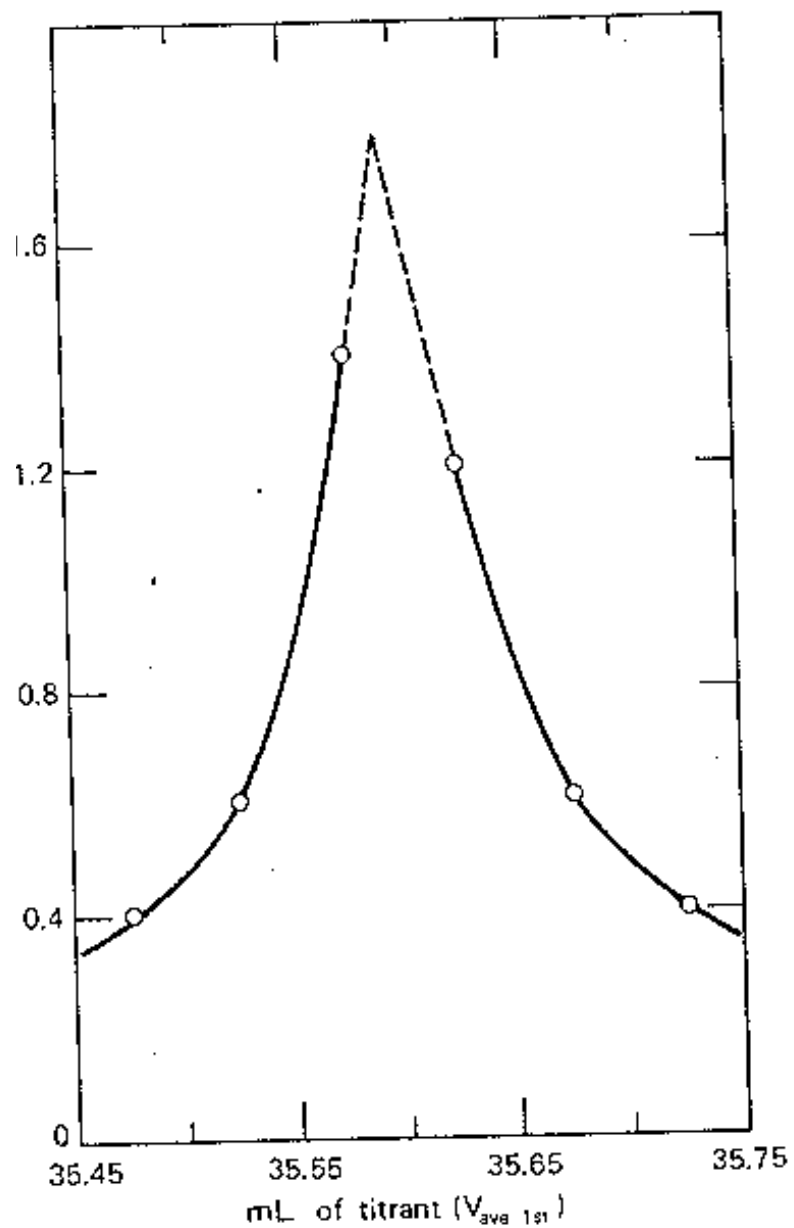
Standard addition



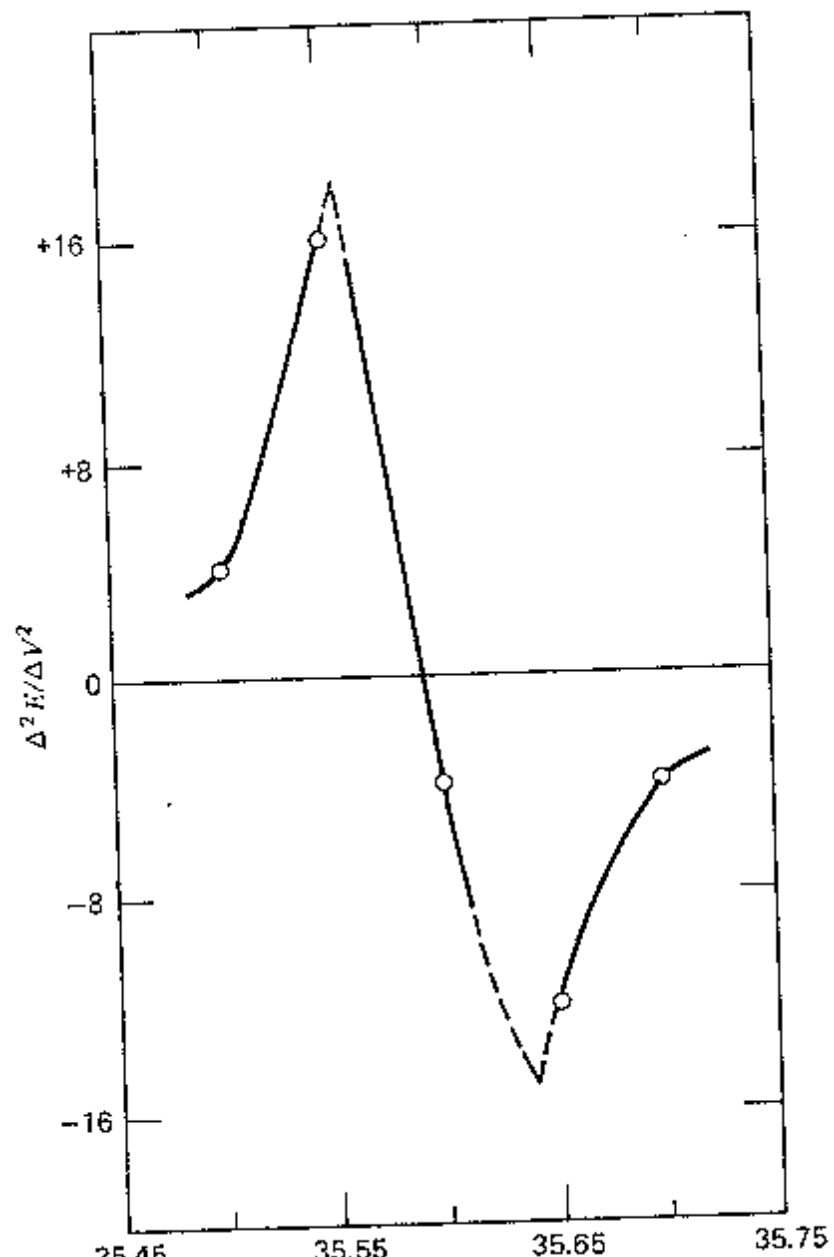
Potentiometric Titration



First derivative plot of a potentiometric titration curve



Second derivative plot of potentiometric titration curve



Practical Applications of Potentiometry with Ion-Selective Electrodes

- **ISE are unique in determining:**
 - 1. Free ions (good for toxicity)**
 - 2. Determination of anions.**
 - 3. Monitoring toxic gases e.g., SO₂, H₂S, NH₃, CN⁻.**
 - 4. Accessible to automated continues .**

Scope of Applications

1. Water analysis:

Surface, Sea, ground, potable, and waste water.

2. Atomospheric analysis:

Gases are absorbed in solutions aerosol is deposited on filters.

3. Sedimented dust and soil are tedious to prepare.

4. Analysis of foodstuffs.

5. Clinical analysis.

Requirements for Measurements with ISE's

- Constant temperature.
- Constant and relatively high ionic strength.
- A pH value lying within the optional of the electrode and the analyte.
- A suitable composition of the test solution considering the selectivity, precision, accuracy and sensitivity.

Determination of N-Compounds

- NH_3 – gas probe has been used for determination of ammoniacal nitrogen in various types of water
- NH_4/NH_3
Ammonia gas sensor
 $5 \times 10^{-6} \rightarrow 2 \text{ M } \text{NH}_3$
- NO_x
 $1 \mu\text{gm-3} \rightarrow 100 \mu\text{gm-3}$
 NO_2 gas probe.
- NO_x content in combustion products of oil and gases
 NO_3^- - ISE
- NO_3^- in water
 NO_3^- – ISE
- *Total nitrogen $\rightarrow \text{NH}_3 \rightarrow$ How?

Determination of Sulfur and others

- S^{2-} & H_2S

S^{2-} - ISE(Ag_2S – ISE) can be used

- SO_2 & SO_3

SO_2 gas sensor may be used

- SO_3^{2-} added to the foodstuff as conserving agent.

SO_2 probe may be used

- SO_4^{2-}
Ba – electrode; Pb – electrode
- Total sulfur
SO₂ probe or others
- Residual chlorine in waters.
Cl₂, HOCl, OCl⁻
(ability to oxidize I⁻ is measured using
I⁻ ISE)
- Determination of HF & F⁻
using F⁻ - ISE

Determination of Heavy Metals

- **Cu^{2+} : Good for trace analysis**
- **Pb^{2+} , Cd^{2+} : Poor reproducibility, good for potentiometric titrations**
- **Ag^+ : Not good for traces, since they are reduced and metal**
- **They cannot compete with voltammetry or spectroscopy**
- **They are used for studying the distribution of metals among**
- **various chemical forms in solution (Fe^{2+} , Fe^{3+})**

Applications

Pollution Monitoring: CN, F, S, Cl, NO₃ etc., in effluents, and natural waters.

Agriculture: NO₃, Cl, NH₄, K, Ca, I, CN in soils, plant material, fertilisers and feedstuffs.

Food Processing: NO₃, NO₂ in meat preservatives.

Salt content of meat, fish, dairy products, fruit juices, brewing solutions.

F in drinking water and other drinks.

Ca in dairy products

K in fruit juices

Corrosive effect of NO₃ in canned foods.

Detergent Manufacture: Ca, Ba, F for studying effects on water quality.

Paper Manufacture: S and Cl in pulping

Explosives: F, Cl, NO₃ in explosive materials and combustion products.

Electroplating: F and Cl in etching baths; S in anodising baths.

Biomedical Laboratories: Ca, K, Cl in body fluids (blood, plasma, serum, sweat).

F in skeletal and dental studies.

Education and Research: Wide range of applications.

Advantages of Ion-selective electrodes

- 1) When compared to many other analytical techniques, Ion-Selective Electrodes are relatively inexpensive and simple to use and have an extremely wide range of applications and wide concentration range.**
- 2) The most recent plastic-bodied all-solid-state or gel filled models are very robust and durable and ideal for use in either field or laboratory environments.**
- 3) Under the most favorable conditions, when measuring ions in relatively dilute aqueous solutions and where interfering ions are not a problem, they can be used very rapidly and easily (e.g. simply dipping in lakes or rivers, dangling from a bridge or dragging behind a boat).**
- 4) They are particularly useful in applications where only an order of magnitude concentration is required, or it is only necessary to know that a particular ion is below a certain concentration level.**

- 5) They are invaluable for the continuous monitoring of changes in concentration: e.g. in potentiometric titrations or monitoring the uptake of nutrients, or the consumption of reagents.**
- 6) They are particularly useful in biological and medical applications because they measure the activity of the ion directly, rather than the concentration.**
- 7) In applications where interfering ions, pH levels, or high concentrations are a problem, then many manufacturers can supply a library of specialized experimental methods and special reagents to overcome many of these difficulties.**
- 8) With careful use, frequent calibration, and an awareness of the limitations, they can achieve accuracy and precision levels of 2 or 3% for some elements and thus compare favorably with analytical techniques which require far more complex and expensive instrumentation.**
- 9) ISEs are one of the few techniques which can measure both positive and negative ions.**
- 10) ISEs can be used in aqueous solutions over a wide temperature range. Crystal membranes can operate in the range 0°C to 80°C and plastic membranes from 0°C to 50°C.**

Ammonium



Barium



Bromide



Cadmium



Calcium



Carbonate



Chloride



Copper



Cyanide



Fluoride



Iodide



Lead



Mercury



Nitrate



Nitrite



Perchlorate



Potassium



Silver



Sodium



Sulphide

Sulfide



Thiocyanate



(Sulphate)



Using Ba
electrode

ORDER NUMBER	direct ^{ION} ELECTRODE	CONCENTRATION RANGE (Mol/L)	LIMITS (ppm)	pH RANGE	TEMP RANGE (°C)	MAIN INTERFERENCES	ISAB
3051	Ammonium (NH ₄ ⁺)	5 x 10 ⁻¹ - 5 x 10 ⁻⁵	9000 - 0.09	1 - 8.6	0 - 50	K ⁺ , Na ⁺	CH ₃ COOH
3061	Barium (Ba ²⁺)	10 ⁻¹ - 10 ⁻⁵	1.4 - 13,700	3 - 10	0 - 50	Sr ²⁺ , K ⁺ , Na ⁺	CuSO ₄
3271	Bromide (Br ⁻)	10 ⁰ - 5 x 10 ⁻⁵	0.4 - 80,000	1 - 12	0 - 50	I ⁻ , CN ⁻ , S ²⁻	5M KNO ₃
3241	Cadmium (Cd ²⁺)	10 ⁻¹ - 1 x 10 ⁻⁵	0.1 - 11,200	3 - 7	0 - 50	Hg ²⁺ , Ag ⁺ , Cu ²⁺ Pb ²⁺ , Fe ³⁺	5M KNO ₃
3041	Calcium (Ca ²⁺)	10 ⁻¹ - 5 x 10 ⁻⁷	4,010 - 0.02	3.5 - 11	0 - 50	Ba ²⁺ , Al ³⁺ , Sr ²⁺	KCl
3091	Carbonate (CO ₃ ²⁻)	10 ⁻³ - 10 ⁻⁷	0.008 - 80	6.6 - 9.6	0 - 50	SCN ⁻ , I ⁻ , NO ₃ ⁻ NO ₂ ⁻ , CH ₃ COO ⁻	NaHCO ₂
3261	Chloride (Cl ⁻)	10 ⁰ - 3 x 10 ⁻⁶	35,500 - 1	1 - 12	0 - 50	I ⁻ , Br ⁻ , CN ⁻ , S ²⁻	5M KNO ₃
3227	Cupric (Cu ²⁺)	10 ⁰ - 1 x 10 ⁻⁷	0.008 - 84,000	2 - 7	0 - 50	Hg ²⁺ , Ag ⁺ , S ²⁻ Cl ⁻ , Br ⁻	5M KNO ₃
3291	Cyanide (CN ⁻)	10 ⁻² - 1 x 10 ⁻⁵	0.03 - 260	11 - 13	0 - 50	I ⁻ , S ²⁻	10M NaOH
3221	Fluoride (F ⁻)	10 ⁻¹ - 1 x 10 ⁻⁸	1,900 - 0.02	4 - 8	0 - 50	OH ⁻	TISAB
3281	Iodide (I ⁻)	10 ⁰ - 5 x 10 ⁻⁷	0.06 - 127,000	2 - 12	0 - 50	CN ⁻ , S ²⁻	5M KNO ₃
3231	Lead (Pb ²⁺)	10 ⁻¹ - 1 x 10 ⁻⁵	0.2 - 20,800	3 - 7	0 - 50	S ²⁻ , Hg ²⁺ , Ag ⁺ Cu ²⁺ , Fe ³⁺ , Cd ²⁺	5M NaClO ₄
3261	Mercury (Hg ²⁺)	10 ⁰ - 1 x 10 ⁻⁶	0.2 - 201,000	0 - 2	0 - 50	Ag ⁺ , S ²⁻	5M NaClO ₄
3021	Nitrate (NO ₃ ⁻)	10 ⁰ - 7 x 10 ⁻⁶	62,000 - 0.4	2 - 11	0 - 50	Cl ⁻ , NO ₂ ⁻	4M (NH ₄) ₂ SO ₄
3061	Perchlorate (ClO ₄ ⁻)	10 ⁰ - 2 x 10 ⁻¹	0.2 - 99,500	0 - 11	0 - 50	I ⁻ , SCN ⁻ , NO ₃ ⁻	CH ₃ COONa
3401	pH	-	-	2 - 12	5 - 45	C ₂ H ₃ O ₄ , ClO ₄ ⁻	-
3031	Potassium (K ⁺)	10 ⁰ - 10 ⁻⁵	0.04 - 39,000	1 - 9	0 - 50	Cs ⁺ , NH ₄ ⁺	4M KCl
3211	Silver (Ag ⁺)	10 ⁰ - 1 x 10 ⁻⁷	0.01 - 107,900	1 - 9	0 - 50	S ²⁻ , Hg ²⁺	5M KNO ₃
3315	Sodium (Na ⁺)	Sat - 10 ⁻⁶	1 ppb	9 - 12	0 - 50	Ag ⁺ , NH ₄ ⁺ , Li ⁺ , K ⁺	SISAB
3226	Sulphide (S ²⁻)	10 ⁰ - 1 x 10 ⁻⁷	0.003 - 32,000	13 - 14	0 - 50	Ag ⁺ , Hg ²⁺	10M NaOH
3229	Thiocyanate (SCN ⁻)	10 ⁻¹ - 2 x 10 ⁻⁶	1 - 5,800	2 - 12	0 - 50	I ⁻ , Cl ⁻ , S ²⁻	5M KNO ₃
3100	Water Hardness	2 x 10 ⁻¹ - 5 x 10 ⁻⁵	-	4.5 - 10	0 - 50	Ba ²⁺ , Sr ²⁺ , Cd ²⁺ Cu ²⁺ , Na ⁺ , K ⁺ , NH ₄ ⁺	LiAC

- Ammonia (NH_3) Copper (Cu^{+2}) Nitrogen Oxide (NO_x)
- Ammonium (NH_4^+) Cyanide (CN^-) Perchlorate (ClO_4^-)
- Bromide (Br^-) Flouride (F^-) Potassium (K^+)
- Cadmium (Cd^{+2}) Fluoroborate (BF_4^-) Silver/Sulfide ($\text{Ag}^+/\text{S}^{2-}$)
- Calcium (Ca^{+2}) Iodide (I^-) Sodium (Na^+)
- Carbon Dioxide (CO_2) Lead (Pb^{+2}))Surfactant (X^+, X^-)
- Chloride (Cl^-) Nitrate (NO_3^-)
- Water Hardness ($\text{Ca}^{+2}/\text{Mg}^{+2}$)