POTENTIOMETRY

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pH is a Potentiometric Measurement

- The Measuring System consists of a pH Measuring Electrode (indicating electrode) and Reference Electrode

- The **Potential Difference** Between the Two Electrodes is a Function of the pH Value of the Measured Solution.

- **The Analyte Solution** Must Be Conductive and is Part of the Electrical Circuit.

Potentiometric Analysis

- Based on potential measurement of electrochemical cells without any appreciable current
- The use of electrodes to measure voltages from chemical reactions

DEFINITION

Potentiometry:

"Measuring the potential or Emf of a solution by using the set of Indicator electrode and reference electrode".

Nernest equation

The potential(E)of a metal elctrode at25°C,immersed into a solution of its own ions is given by

$$E=E0 + \frac{0.0592}{n} \times \log c$$

Where, E0 = standard potential of the electrode
n = valency of ions
c = concentration of ions

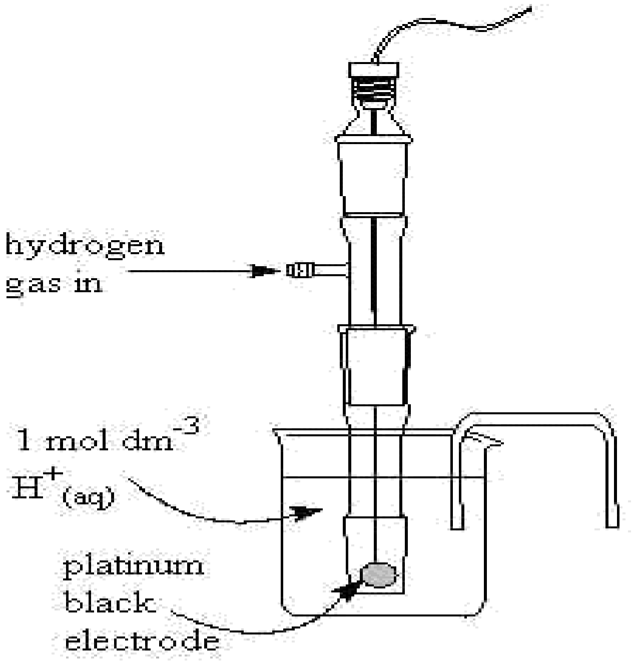
Components of a Potentiometric Cell

1. Reference electrode
2. Salt bridge
3. Analyte
4. Indicator electrode

$$\begin{array}{l} \text{RE} \;\big|\; \text{SB} \;\big|\; \text{A} \;\big|\; \text{IE} \\ -\,E_{ref} \;+\, E_{j} \qquad +\, E_{ind} \end{array}$$

Reference electrode

- Half-cell with known potential (E_{ref})
- Left hand electrode (by convention)
- Easily assembled
- Rugged
- Insensitive to analyte concentration
  - Reversible and obeys Nernst equation
  - Constant potential
  - Returns to original potential



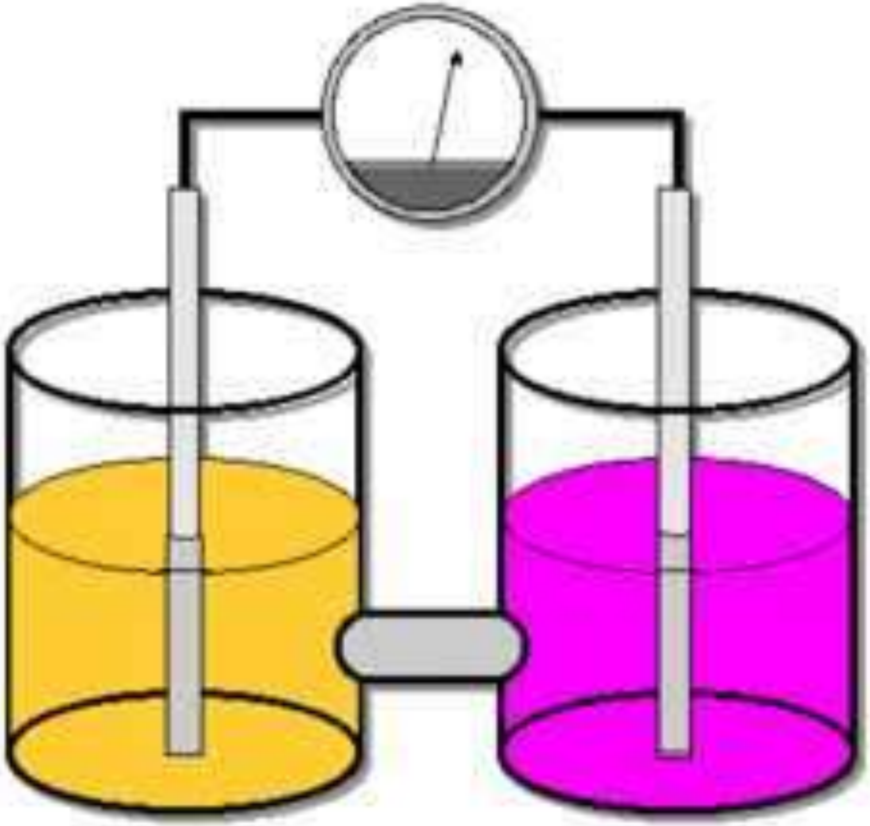
Indicator electrode

- Generates a potential (E_{ind}) that depends on analyte concentration
- Selective
- Rapid and reproducible response

Salt bridge

- Prevents mixing up of analyte components
- Generates potential (E_j) = negligible

Potentiometric methods



Reference electrode

The part of the cell that is held constant

Indicating electrode

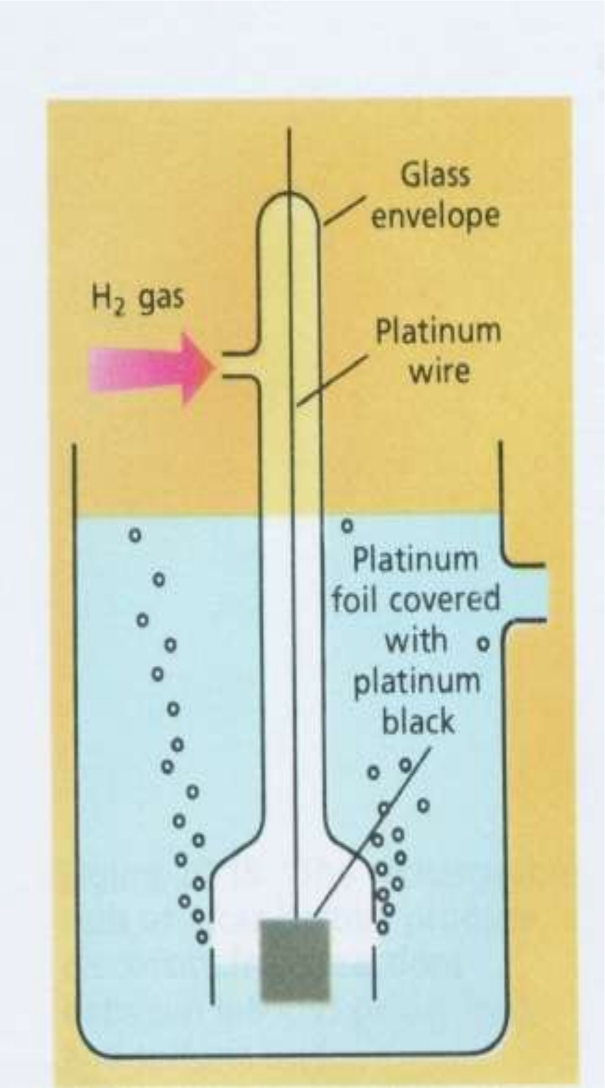
The part of the cell that contains the solution we are interested in measuring

Reference Electrodes

1. Standard Hydrogen Electrode
2. Saturated Calomel Reference Electrode
3. Silver/Silver Chloride -Reference Electrode

HYDROGEN ELECTRODE

- It can be used as Indicator as well as Reference eletrode.
- It can be consist of platinum foil coated with platinum balck and has a wire contacts through a mercury.
- This assembly is enclosed in a glass covering.
- Hydrogen gas is passed at 1atmospheric pressure continuously.
- **(Pt (H_2 (1 atm), H^+ (1M)**



- Then eletrode is dipped into the standard acid /unknown solution.
- All the times surface of the electrode and the solution should be saturated with the gas.
- potential ,

  - $E=E0H+0.0592\log[H+]$
    $=E0H-0.0592pH(pH=-\log [H+]$
  - $E=-0.0592\ pH$.
  - $E0$=std Eof H_2 electrode ,taken as 0

❖Advantages and Disadvantages of H2Electrode:

❖ **Advantages**:

- It can be used over the entire pH.
- Itcan be used as a reference electrode when dipped with standard acid solution and as a indicator electrode when dipped into a sample solution.
- It is the primary reference standard against which the potentials of other electrodes are measured.

❖ Disadvantages

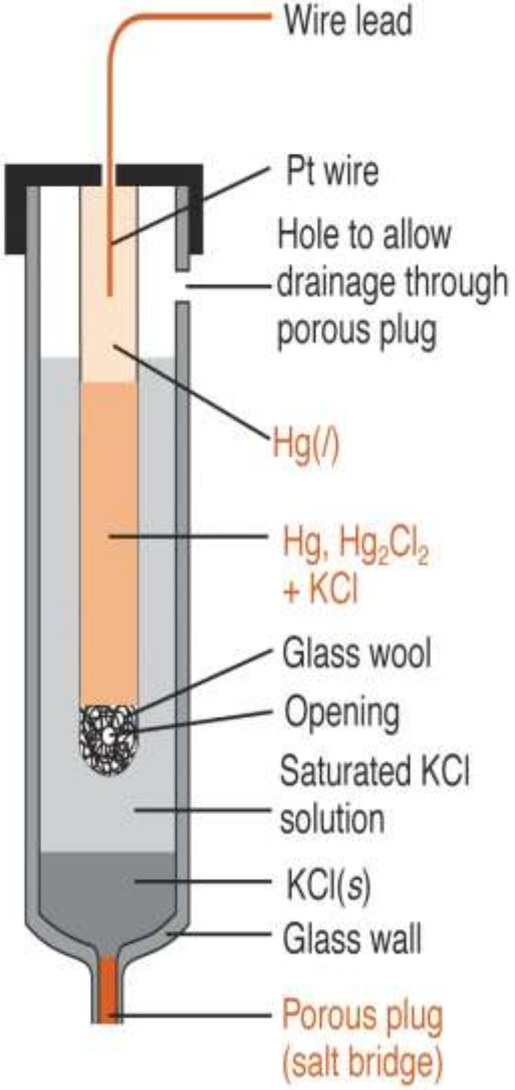
❖ It is effected by the presence of oxidizing agent and reducing agent.

❖ It is rather difficult to regulate the pressure of H2 gas to be exactly 1 atm throughout the experiment.

❖ Platinum foil gets easily poisoned by the impurities present in the H2 gas and Hcl solution.

Saturated calomel elctrode

- It consist of inner jacket and outer sleeve
- Inner tube has a wire contact with mercury(Hg) and plugged with a mixture of calomel(Hg2cl2)and KCL.
- This is surrounded by an outer sleeve
- Tip is filled with Crystals of KCL and porous plug of asbestos.
- The space between inner jacket and outer sleeve is filled with saturated KCL/1N KCL/0.1 N KCL.
- Potential of the electrode depends on the Concentration of the KCL Solution and Temperature.



- **0.2444 V at 25°C**

Equation: $Hg_2Cl_2(s)+2e^- \Leftrightarrow 2Hg(l)+2Cl^-(aq)$

- Merits:

  Easy of construction

  Stability of Potential.

- Demerits:

  Dependent on temp

  Toxic

- Applications:

  Used in pH Measurement

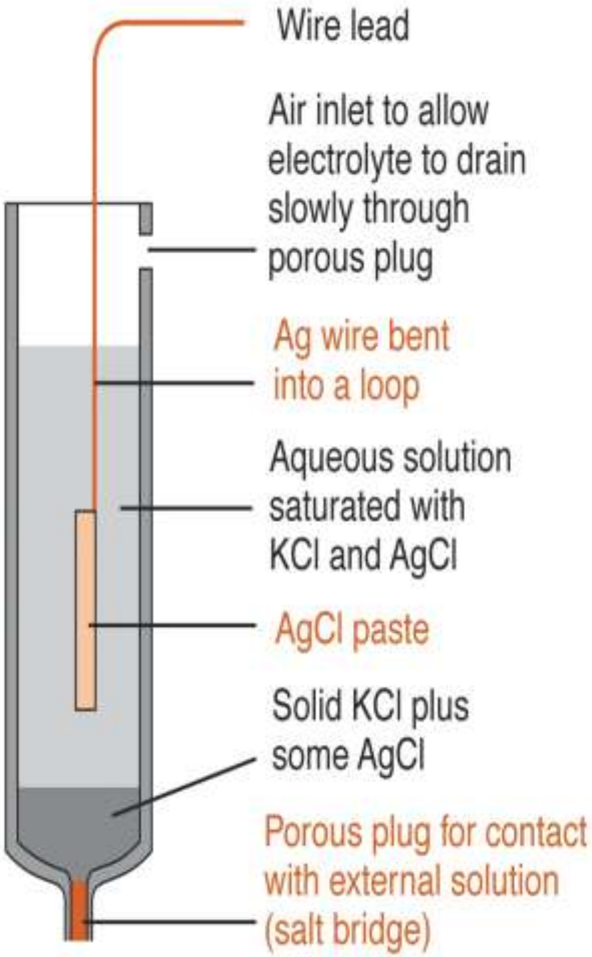
Silver –Silver Chloride electrode

- It is also widely used reference electrode,

Because,It is simple
In expensive
Very stable
Non –toxic.

- It is mainly used with Saturated KCL Electrode (kcl electrolyte) but can be used with low concentration such as 1MKCL and even directly in sea water.

“Ag-wire coated electrolytically with AgCl2 and dipped into KCL



Potential depends on the concentration of the KCL and temperature.

$$\mathrm{Ag}\,|\,\mathrm{AgCl}\ (\text{satd}),\mathrm{KCl}\ (\text{satd})\,\|$$

$$\mathrm{AgCl(s)} + e^{-} \Leftrightarrow \mathrm{Ag(s)} + \mathrm{Cl^{-}(aq)}$$

$$E^\circ = 0.199\ \mathrm{V}$$

- Advantage:
  - Easy to use
- Dis advantage:
  - Difficult to prepare.

Liquid Junction Potential

- Liquid junction - interface between two solutions containing different electrolytes or different concentrations of the same electrolyte
- A junction potential occurs at every liquid junction.
  - Caused by unequal mobilities of the + and - ions.

Indicator Electrodes

I. Metallic IE
   A. Electrodes of the First Kind
   B. Electrodes of the Second Kind
   C. Inert Metallic Electrodes (for Redox Systems)

II. Membrane IE/Ion –Selective Electrodes.
   A. Glass pH IE
   B. Glass IE for other cations
   C. Liquid Membrane IE
   D. Crystalline-Membrane IE

III. Gas Sensing Probes/Gas Sensing Electrode.

METALLIC INDICATOR ELECTRODES

Electrodes of the First Kind

- Pure metal electrode in direct equilibrium with its cation
- Metal is in contact with a solution containing its cation.

$$M^{+n}(aq) + ne^{-} \Leftrightarrow M(s)$$

indicating electrode

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

Disadvantages of First Kind Electrodes

- Not very selective
  - Ag^+ interferes with Cu^{+2}
- May be pH dependent
  - Zn and Cd dissolve in acidic solutions
- Easily oxidized (deaeration required)
- Non-reproducible response

Electrodes of the Second Kind

- Respond to anions by forming precipitates or stable complex

- Examples:
  1. Ag electrode for Cl^- determination

$$AgCl(s) + e^- \leftrightarrow Ag(s) + Cl^- \quad E^0 = +0.222\ V$$

$$E_{ind} = +0.222 - \frac{0.0592}{n} \log a_{Cl^-}$$

$$= +0.222 + 0.0592pCl$$

  2. Hg electrode for EDTA determination

Inert Metallic (Redox) Electrodes

- Inert conductors that respond to redox systems
- Electron source or sink
- An inert metal in contact with a solution containing the soluble oxidized and reduced forms of the redox half-reaction.
- May not be reversible

- Examples:
  - Pt, Au, Pd, C

Ion selective electrodes

- Other synonym:Membrane electrodes
- **Definition**:

  " ISE are known as specific ion electrode, it is a membrane that Converts the activity of a specific ion dissolved in a solution into an electrode

Potential".

- The voltage is theoritically dependent on the negative logerithem of the ionic activity, according to the Nernest equation.

- **Uses:**

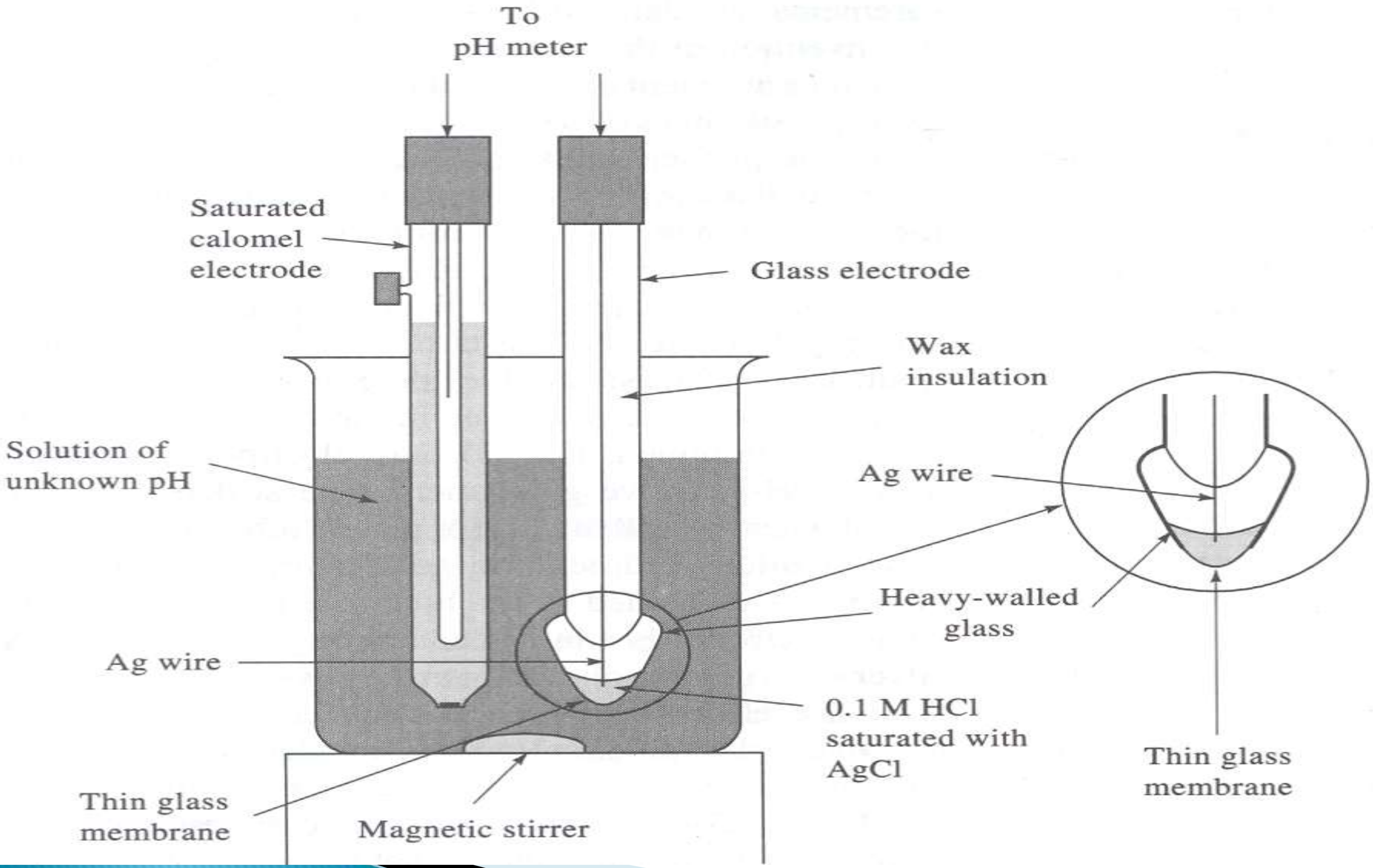
ISE are used in analytical chrmistry,bio-chemical/ biophysical research.

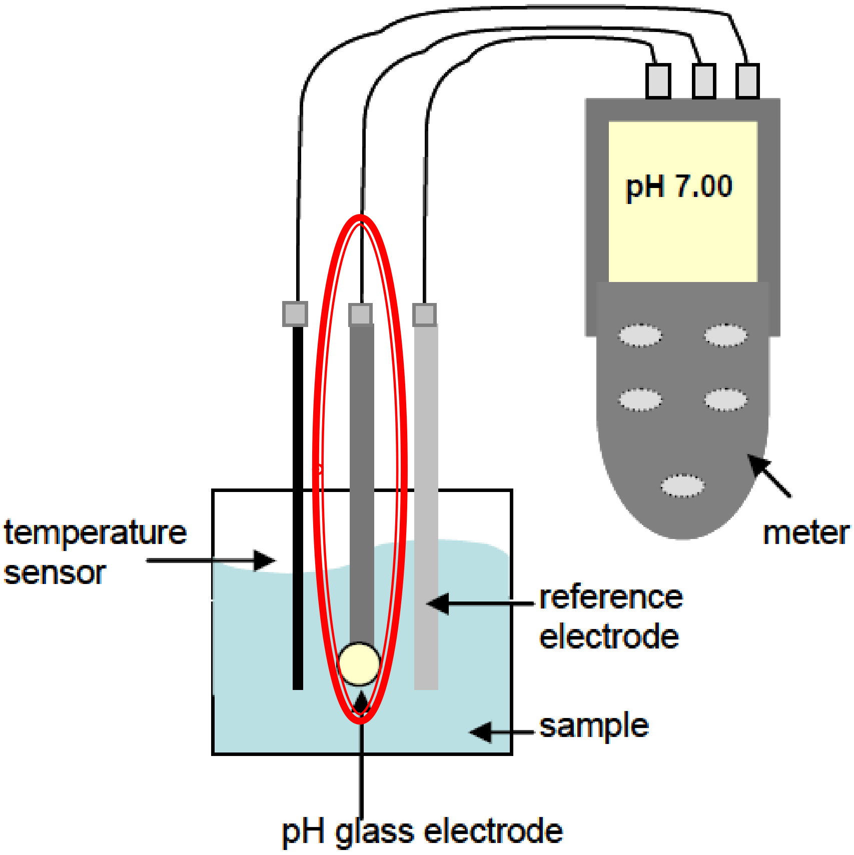
whwre, measurements of ionic concentration in aqueous solutions are required.

- **TYPES OF ISE:**

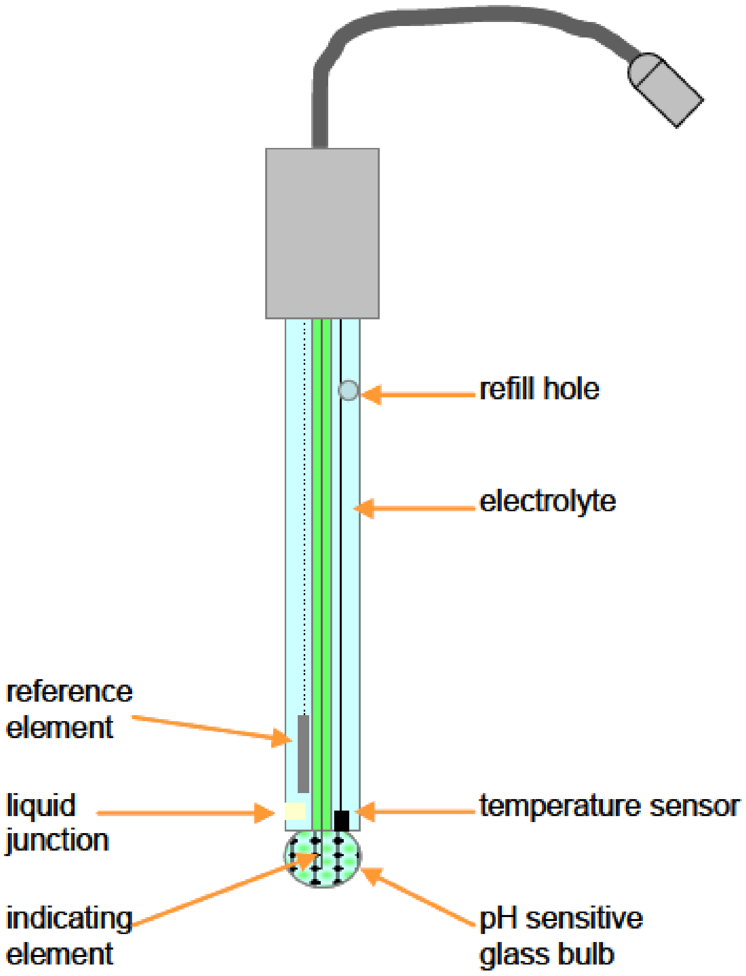
1.Glass Membrane electrode
2.Liquid-Liquid electrode/Liquid membrane electrode.
3.Crystal Membrane electrode.
4.Gas sensing electrode.

1.Glass pH Electrode



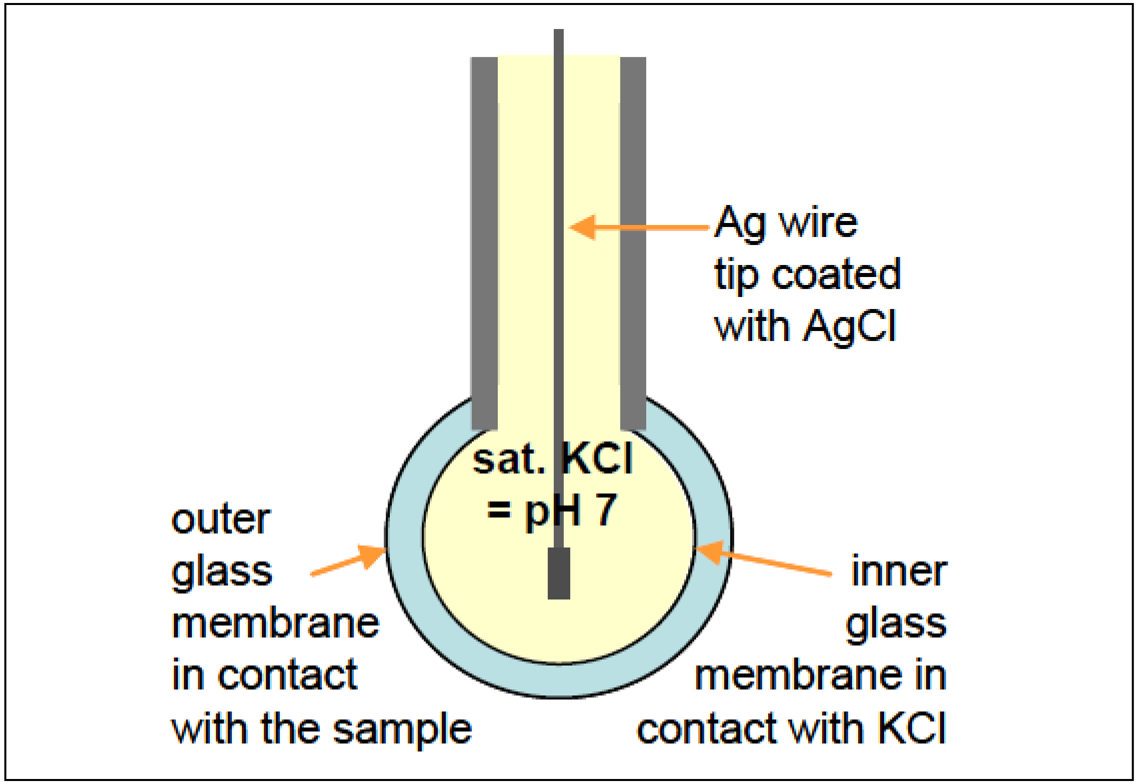


pH measurement system



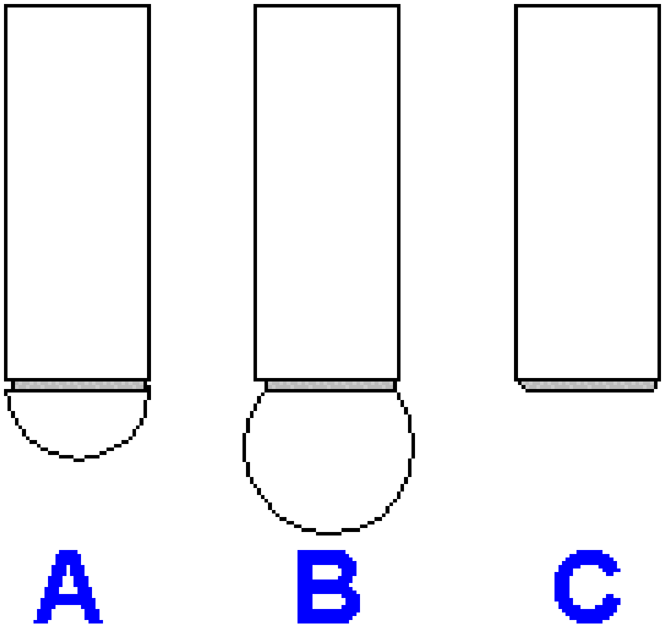
Combined PH glass electrode

Principle of pH meter



Working principle of pH glass membrane electrode

Style of glass electrode



- The glass membrane itself is not limited to any configuration or shape; its only requirement is contact with solution.

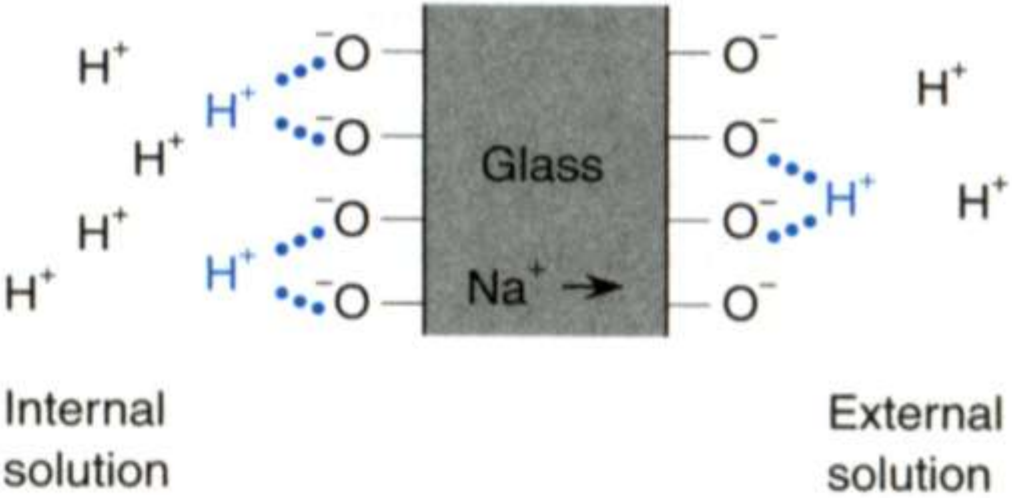
- Therefore, different styles of glass electrodes have evolved to maximize pH sensing ability and extend longevity in some of the more difficult applications.

Properties of Glass pH electrode

- Potential not affected by the presence of oxidizing or reducing agents
- Operates over a wide pH range
- Fast response
- Functions well in physiological systems
- Very selective
- Long lifespan

Theory of the glass membrane potential

- For the electrode to become operative, it must be soaked in water.
- During this process, the outer surface of the membrane becomes hydrated.
- When it is so, the sodium ions are exchanged for protons in the solution:
- change with other ions.

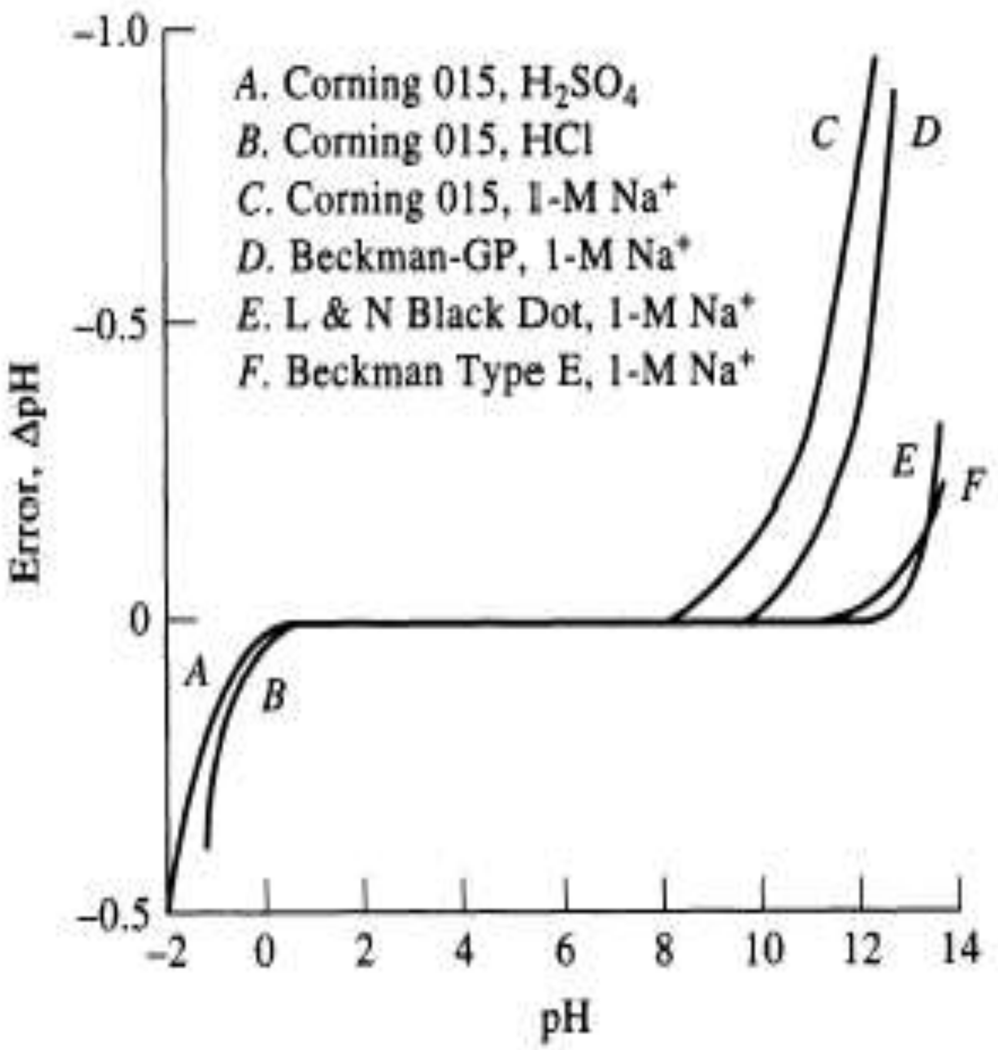


Charge is slowly carried by migration of Na+ across glass membrane

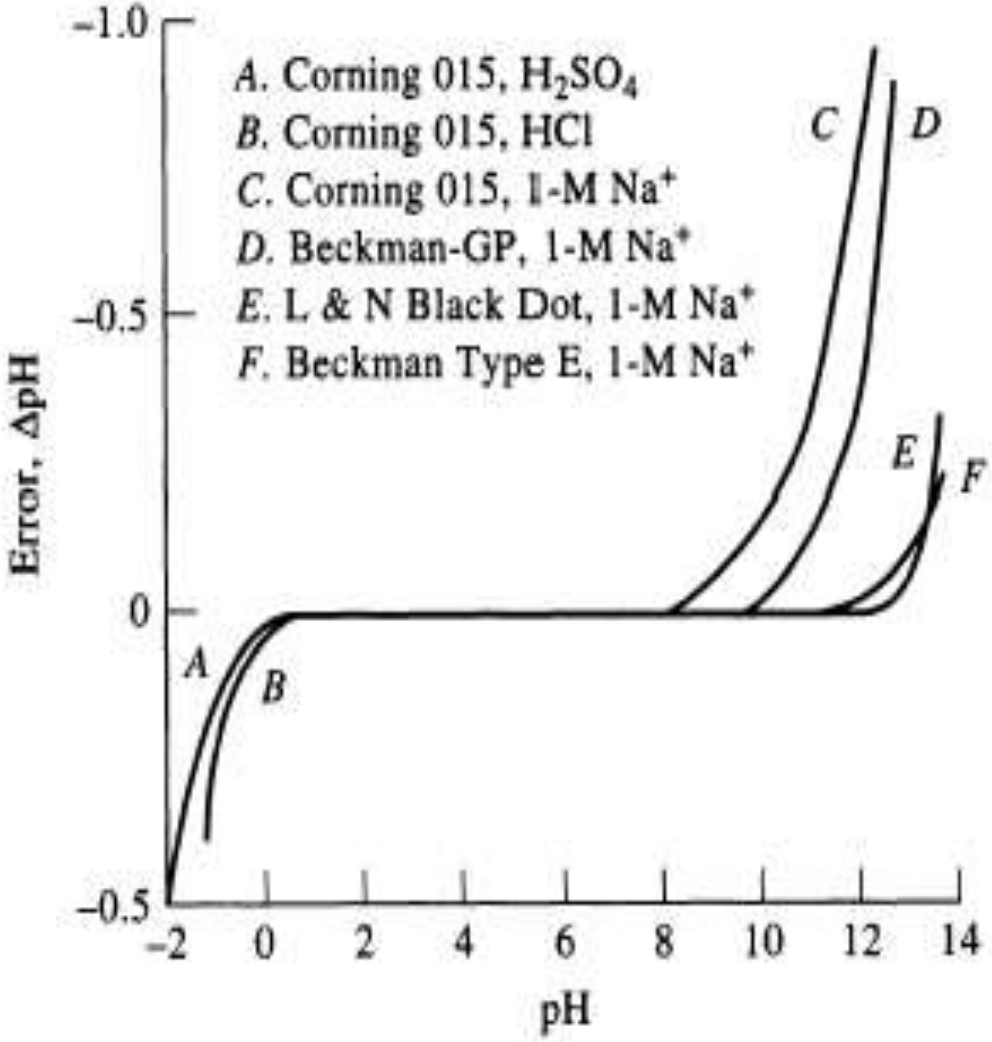
Potential is determined by external [H^+]

Alkaline error

- Exhibited at pH > 9
- Electrodes respond to H^+ and alkali cations
- C,D,E and F: measured value is < true value
    - Electrode also responds to other cations
- Higher pH at lower $[Na^+]$



Acid error



- Exhibited at pH < 0.5
- pH readings are higher (curves A and B)
  - Saturation effect with respect to H^+

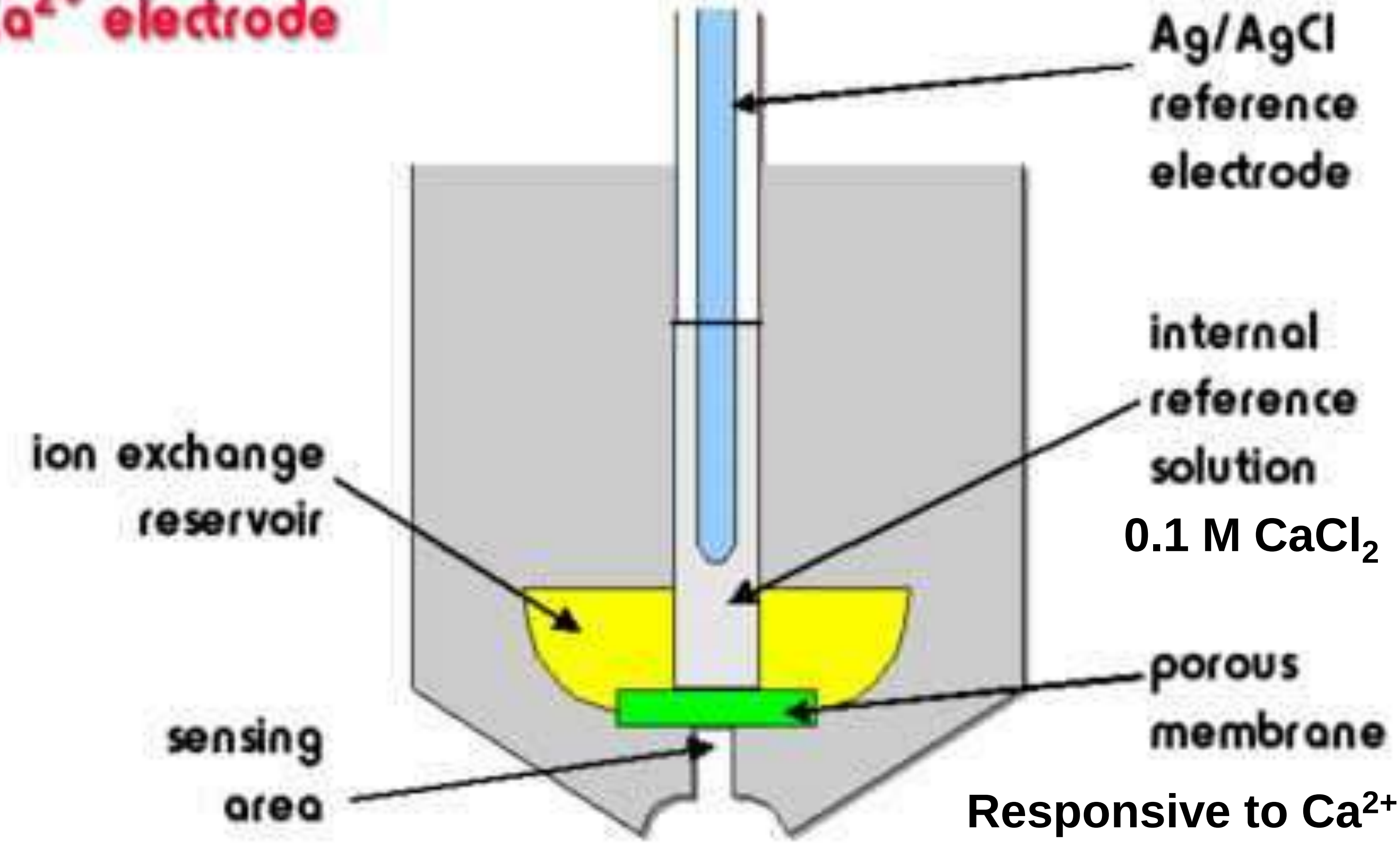
2.Liquid Membrane Electrodes

- Potential develops across the interface between the analyte solution and a liquid ion exchanger (that bonds with analyte)
- Similar to a pH electrode except that the membrane is an organic polymer saturated with a liquid ion exchanger
- Used for polyvalent ions as well as some anions

- Example:
- Calcium dialkyl phosphate insoluble in water, but binds Ca^{2+} strongly

Liquid membrane electrodes

Ca^{2+} electrode



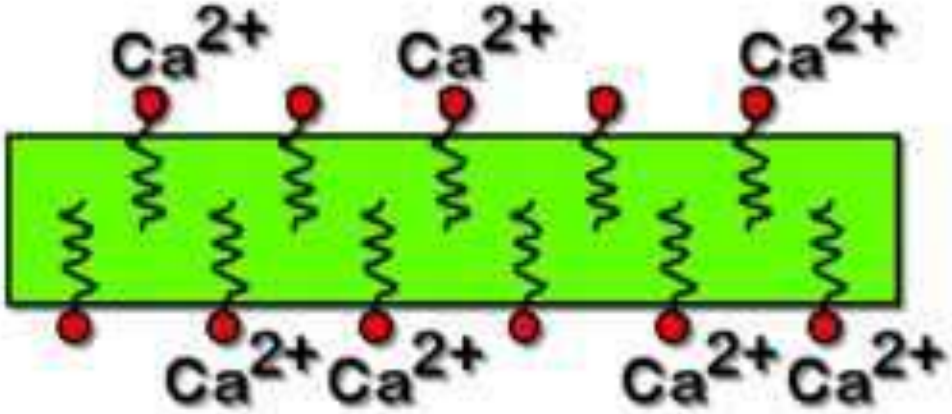
0.1 M $CaCl_2$

Responsive to Ca^{2+}

Liquid membrane electrodes

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

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

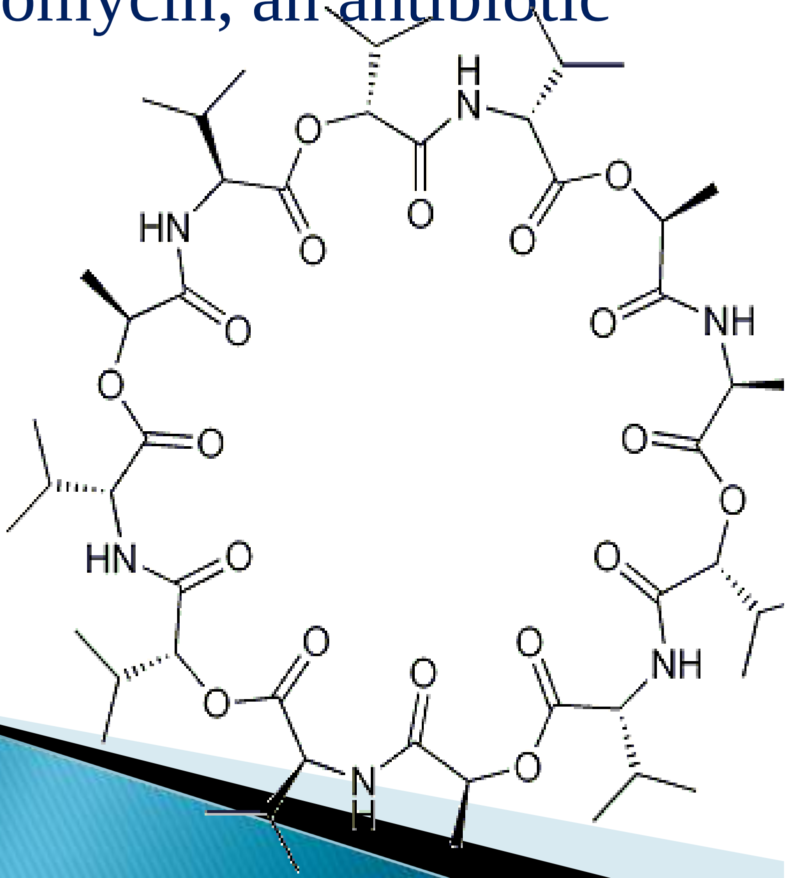


Characteristics of Ca^{+2} ISE

- Relatively high sensitivity
- Low LOD
- Working pH range: 5.5 – 11
- Relevant in studying physiological processes

A K$^+$-selective electrode

- Sensitive membrane consists of valinomycin, an antibiotic



3.Crystalline-Membrane Electrodes

- Solid state electrodes
- Usually ionic compound
- Crushed powder, melted and formed
- Sometimes doped to increase conductivity
- Operation similar to glass membrane

❖Crystalline-Membrane Electrodes:

- AgX membrane: Determination of X^-
- Ag_2S membrane: Determination of S^{-2}
- LaF_3 membrane: Determination of F^-

$$\underbrace{LaF_2^+}_{\text{solid}} + \underbrace{F^-}_{\text{analyte}} \leftrightarrow \underbrace{LaF_3}_{\text{solid}}$$

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

EX:F$^-$ Selective Electrode

- A LaF_3 is doped with EuF_2.
- Eu^{2+} has less charge than the La^{3+}, so an anion vacancy occurs for every Eu^{2+}.
- A neighboring F^- can jump into the vacancy, thereby moving the vacancy to another site.
- Repetition of this process moves F^- through the lattice.

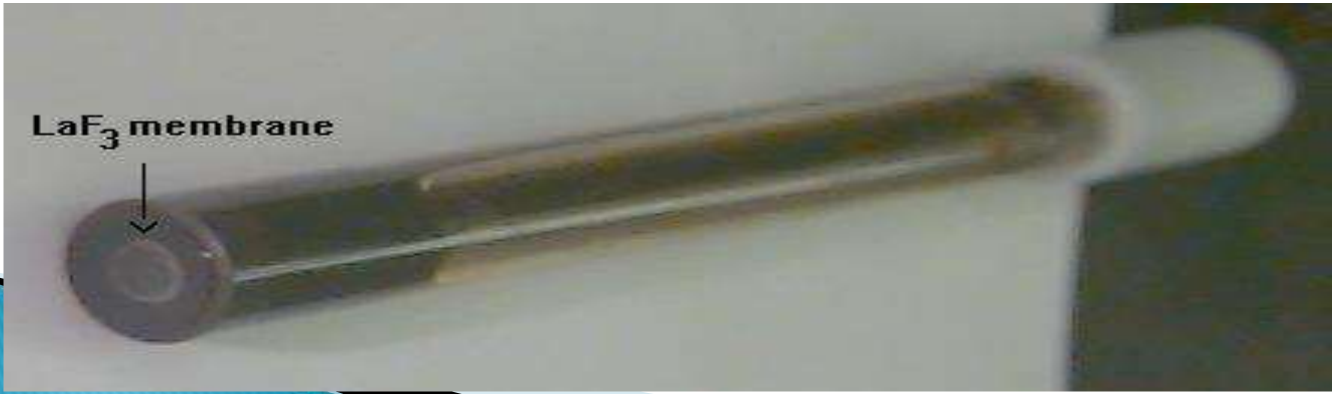
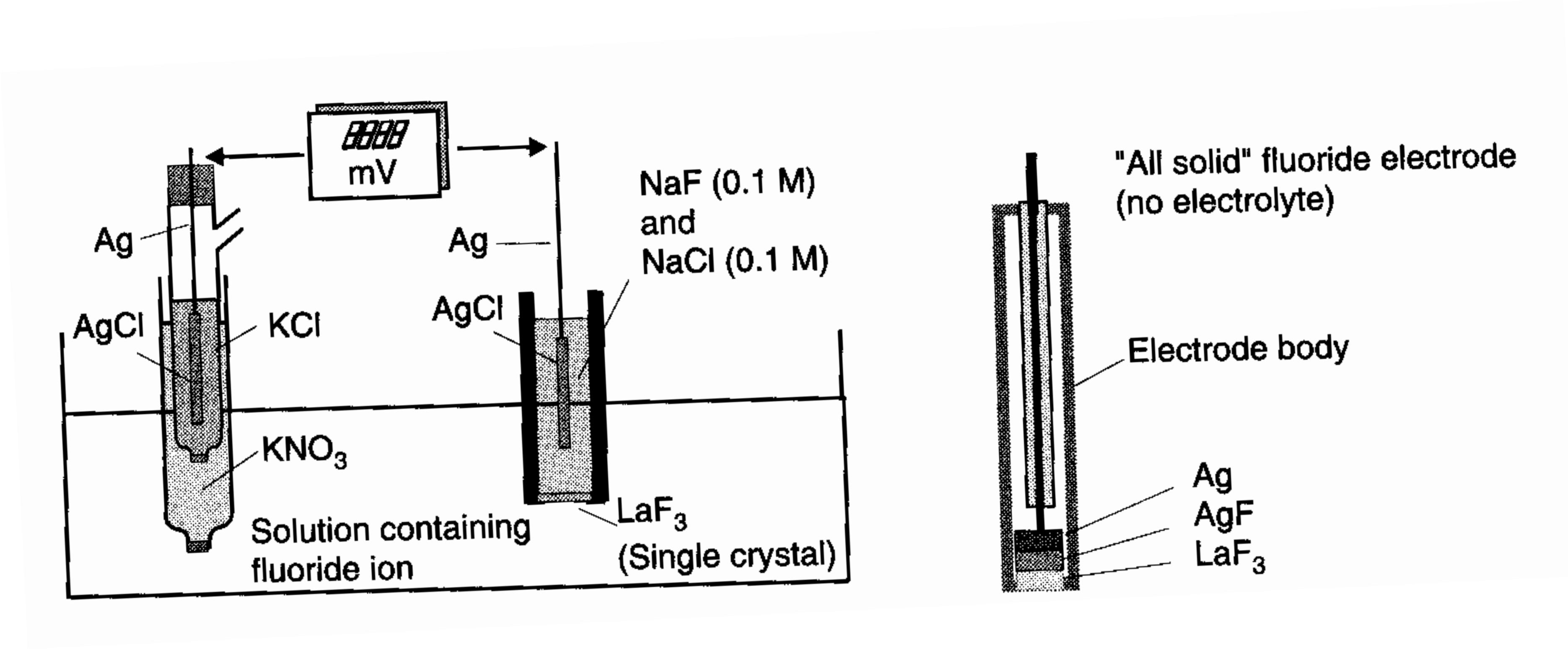


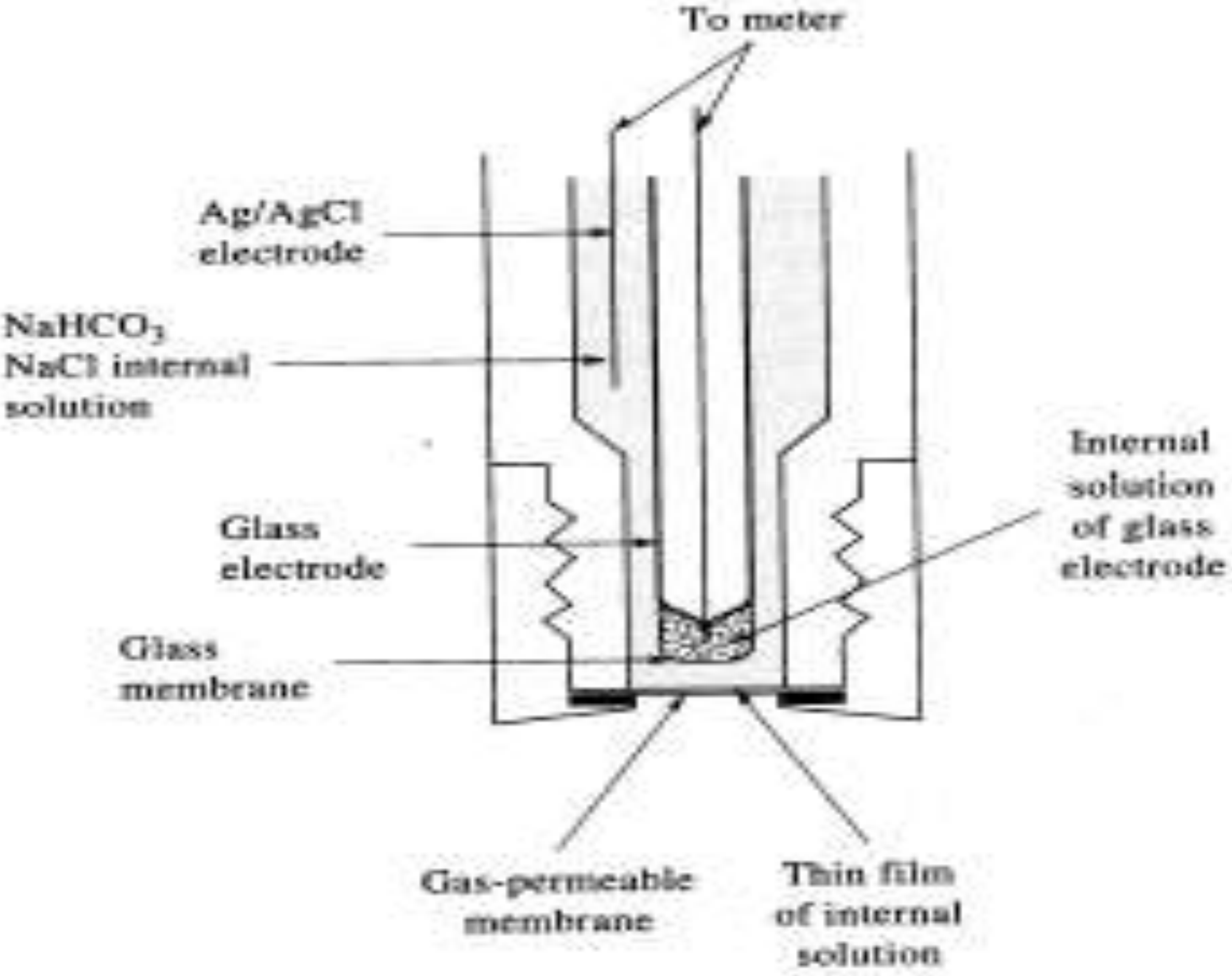
Fig:Fluoride Electrode



4.Gas Sensing Electrode

- A galvanic cell whose potential is related to the concentration of a gas in solution
- Consist of RE, ISE and electrolyte solution
- A thin gas-permeable membrane (PTFE) serves as a barrier between internal and analyte solutions
- Allows small gas molecules to pass and dissolve into internal solution
- O_2, NH_3/NH_4^+, and $CO_2/HCO_3^-/CO_3^{2-}$

Fig: Gas Sensing Electrode



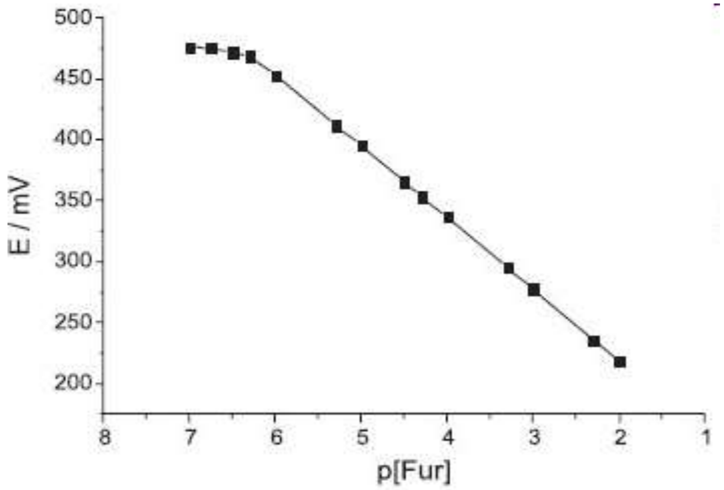
❖DIRECT POTENTIOMETRY

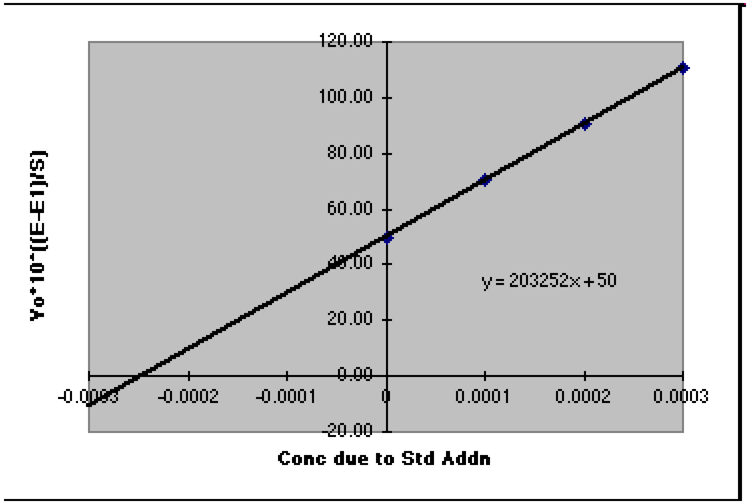
- A rapid and convenient method of determining the activity of cations/anions

Potentiometric Measurement

1. Calibration Method

2. Standard Addition Method

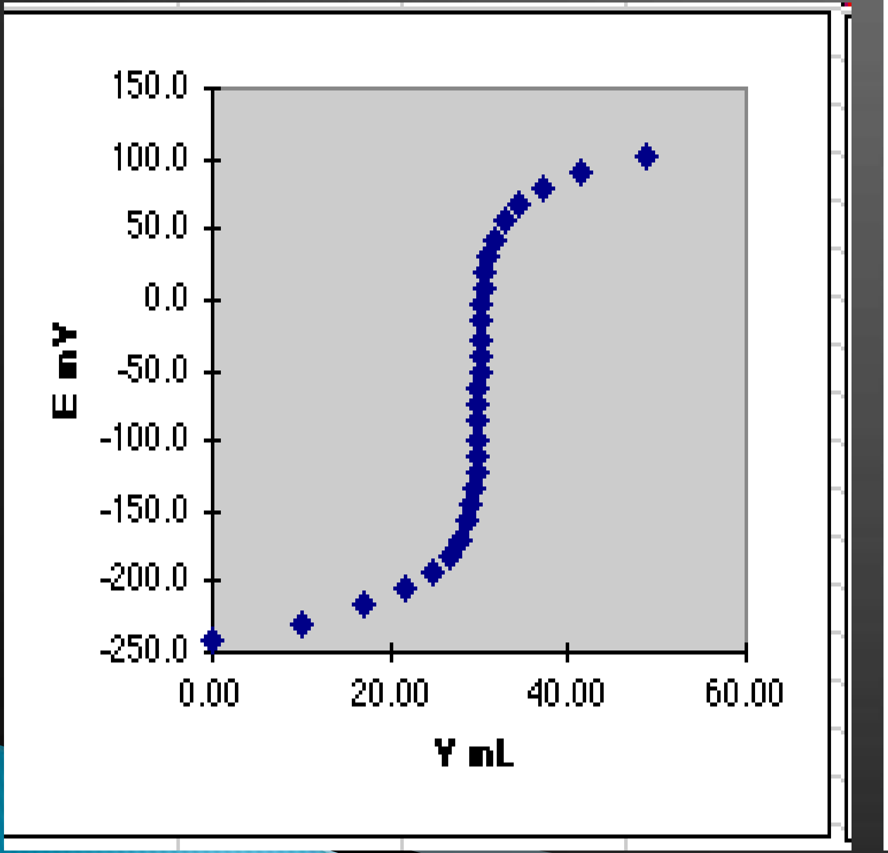


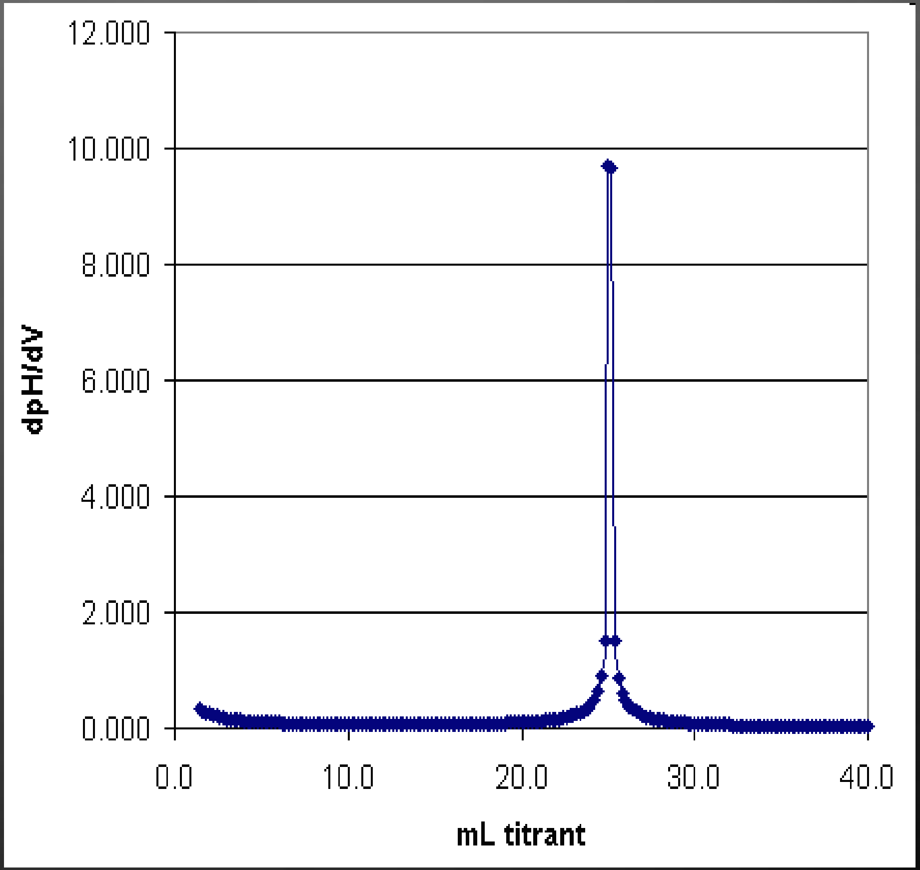


Potentiometric Titration

- Involves measurement of the potential of a suitable indicator electrode as a function of titrant volume
- Provides MORE RELIABLE data than the usual titration method
- Useful with colored/turbid solutions
- May be automated
- More time consuming

Potentiometric Titration Curves





potentiometric titrations

- Is a technique similar to direct titration of a redox reaction.

- No indicator is used, (instead the potential across the analyte) typically an electrolyte solution is measured.

- To do this, two electrodes are used, an indicator electrode and a reference electrode.

- The indicator electrode forms an electrochemical half cell with the interested ions in the test solution.

- The reference electrode forms the other half cell, holding a consistent electrical potential.

When potentiometric titrations is used?

- **It is used when the endpoints are very difficult to determine either when:**

1- very diluted solution.

2-coloured and turbid solution.

3-absence of a suitable indicator.

instruments

- PH meter
  - ✓ Reference electrode.
  - ✓ Indicator electrode.
  - ✓ Voltmeter which measures the potential difference.

- Magnetic stirrer.
  - ✓ hot plate (use the stirrer and make sure heat is off).
  - ✓ magnet capsule .

- Glass (burrete and beaker)

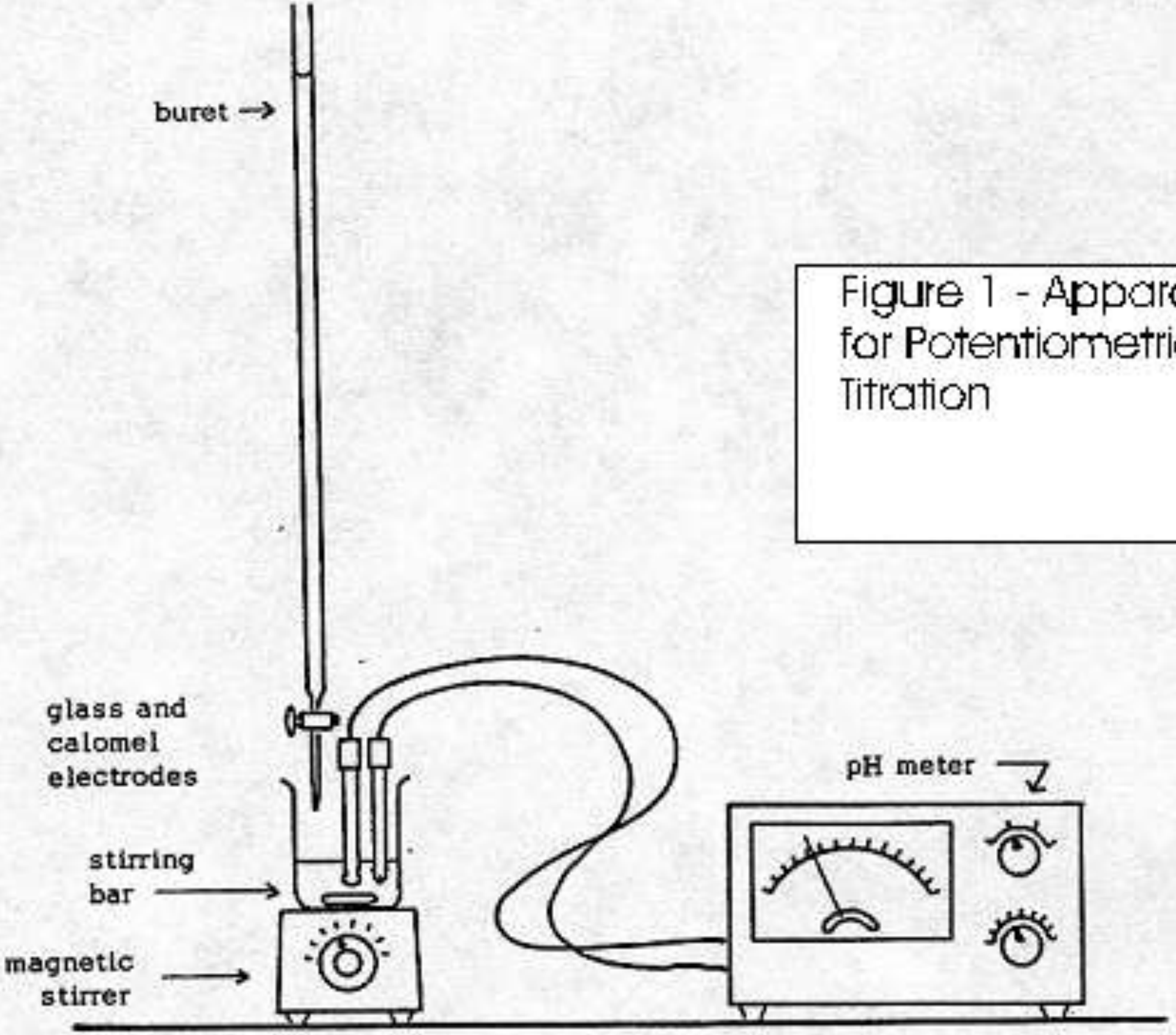
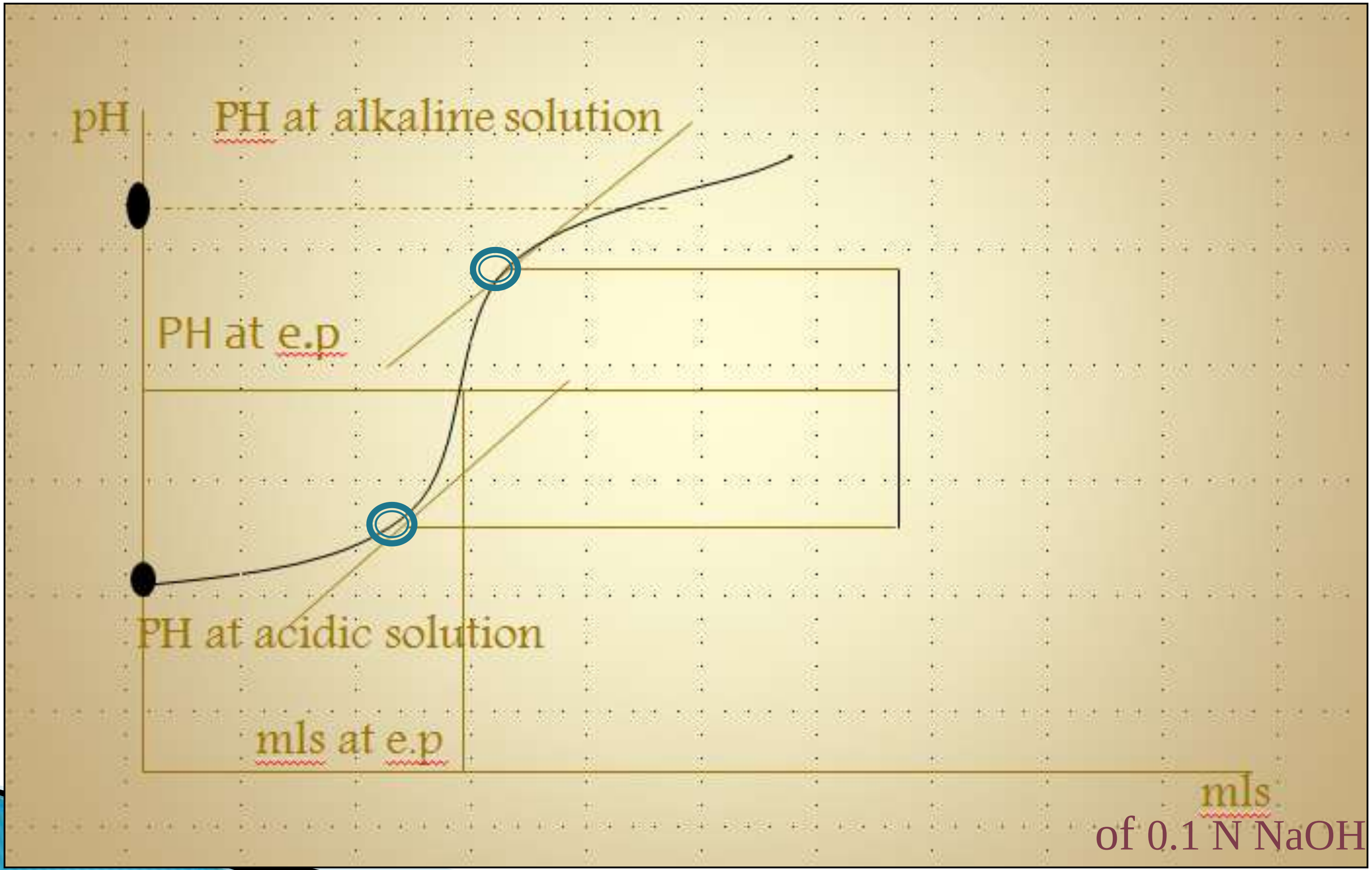


Figure 1 - Apparatus for Potentiometric Titration

Potentiometric titration curve of (0.1 N) NaOH against (?? N) acetic acid :



IMORTANT TO KNOW

- Do not place the electrodes anywhere except attached to the electrode holder.

- At the end of the experiment rinse the electrodes and place each one in its housing as required.

- Never touch the glass part of the electrode with anything except soft tissue paper. While in use, the bulb of the glass electrode should be immersed in solution.

- For short-term storage the combined glass electrode should be immersed in solution of 2 M KCl.

- Buffer solutions of known pH are used for the pH calibration.

- For high accuracy, calibration and measurements are to be performed at the same temperature.

1-the **outside surface** of the glass membrane is in contact with the sample being measured.

2-and the **inside surface** contact the inner filling solution .

3-A complex mechanism at each glass liquid interface defines the potential of the pH glass electrode.

4-While the pH inner glass /filling solution potential is **constant** , the outside potential varies based on the hydrogen ion concentration in the sample.

Applications of Potentiometry:

1. Direct potentiometry:

- ✓ A rapid and convinient method of detecting the activity of cations and anions.
- ✓ The technique used in this method is a comparison of the potential developed by the indicator electrode when it is immersed in the solution with that when it is immersed in standard solution of the analyte.

2. The calibration curve method:

- ✓ It is applied for determination of substance by direct potentiometry.
- ✓ In which we plot potential of the cell Vs a series of standard solution of extragrade of the substance to be determined.

✓ Then measure the potential prodused when using the unknown solution and from the calibration curve we can obtain its concentrations.

3. Environmental chemistry:

✓ **Pollution monitoring:** CN,F,S,Li,Na, etc…..in effluents and natural water

4. Agriculture :

NO3,Cl,I,K,Ca,CN, in Soil, plant material, Fertilizers, Feedstuffs.

Applications of Potentiometric Analysis

Special Applications: Potentiometric pH Measurement using Glass electrode

- One drop of solution
- Tooth cavity
- Sweat on skin
- pH inside a living cell
- Flowing liquid stream
- Acidity of stomach

5 . **Food processing:**

No3,No2 in Meat, and preservatives.

6. **Florin in drinking water and other drinkers.**
7. **Salt content of Meat,Fish,Dairy products,Fruits,Juices,Brewing Solutions.**
8. **Potentiometric titrations:**

- **Acid-Basetitrations (aqueous and non aqueous)**
- **Redox titrations**
- **Diazotisation titrations**
- **Precipitation titrations**
- **Complexometric titrations**
- **Dead stop end point technique.**

1.Acid –base titrations:

✓Titrations can be done in aqueous and non-aqueous medium.

✓E+k-0.0592pH.

❖Ex:-Aqueous medium:any strength-0.01N,0.1N,1N.

○ Acid-base combinations:

✓Weak acid - Weak base (CH3COOH Vs NH4OH)

Weak acid-Strong base (CH3COOH-NAOH)

✓Strong acid-Strong base (HCL-NAOH)

Strong acid-Weak base (HCL-NH4OH)

○Mixture of acids Vs bases: (CH3COOH+HCL)Vs NAOH

○Mixture of bases Vs acids: (NH4OH+NAOH) Vs HCL.

○Poly basis acids Vs bases: Citric acid Vs NAOH
Tartaric acid Vs NAOH.

- Non aqueous medium:
- ✓ Weak acidVs pottasium(KOME)/Lithium methoxide(Liome)
- ✓ Ex:-Barbituric acid Vs LiOMe
- ✓ Weak bases Vs perchloric acid
- ✓ Ex:-Ephedrine Hydrochloride /Q.sulphate/Metronidazole/Chloroquine phosphate Vs 0.1NHCLO4.
- ❖ Indicator electrode:Glass electrode
- ❖ Reference electrode:SCE

2. Redox-titrations:

- Reaction:Ce4+ + Fe2+ Ce3+ + Fe3+
- Ce4+ is an oxydising agent which oxidises Fe2+ (ferrous) to Fe3+(ferric ion), in this process Ce4+(cerric) gets redused to Ce3+ (cerrous ions).
- E =E0 + 0.0592/n.log(ox)/(Red).
- Where,E0= std potential.
- n= no.of electrons involved in the reaction,
- (ox)= conc. Of oxidant
- (Red)= conc of reductant.

- Reference electrode:SCE,Ag-Agcl2 electrode.
- Indicator electrode:platinum wire or foil.

mv scale is used for end point detection.

Ex:-Ferrous ammonium sulphate in dilute H2SO4VsKMNO4/K2Cr2O7.

3. Diazotisation titrations:

- ✓ Drugs or substances containing aromatic amino group can be titrated against sodium nitrate in acidic medium.
- ✓ Result in the formation of diazonium salt this type of titration is called as Diazotisation titration.

- ✓ End point detecting:by
- ✓ a)Starch iodide paper(externalindicator method)
- ✓ Potentiometric method of detecting end point.
- ✓ Reference electrode:SCE
- ✓ Indicator electrode:Glass electrode.
- ✓ Ex: Alkaloids,Amines,Sulpha drugs which contain primary aromatic amino group can be titrated against0.1N sodium Nitrate in HCl .

4) Precipitation titrations:

✓ For quantitative determination of several ions or elements precipitating agents are used as titrants,

✓ End point is determined by potentiometric method.

✓ $E=E0+0.0592/n.\log[Mn+]$

where, $[Mn+]$=conc of ions

n= electronic state.

❖ Reference electrode:SCE,H_2,Ag-$AgCl_2$ electrode

❖ Indicator electrode:Silver wire electrode.

- Ex: Determination of Hg,Ag,Pb,Cu, and other ions using precipitants to form insoluble salts.

5) Complexometric titrations:

- ✓ Metalic ions (divalent)can be titrated against disodium edetate solutions by potentiometric method
- ✓ Measurements are made inmv scale.

- Reference electrode:SCE/ any other.
- Indicator electrode:Ag / Hg electrode.
- Ex:-Di and Trivalent ions.

  (mix of Bi3+,Cd2+,Ca2+ by using EDTA).

Applications of Potentiometer as (I.Pmethods)

S.NO	DRUGS	TITRANT	INDICATOR ELECTRODE	REFERENCE ELECTRODE
1	Amoxicillin sodium	Mercuric nitrate	Pt/Hg	Hg-mercurous sulphate
2	Acebutalol HCl	NaOH	Glass	SCE/Ag-AgCl
3	Dextromorphan HCl	NaOH	Glass	SCE/Ag-AgCl
4	DiphenoxylateHCl	Ethanolic NaOH	Glass	SCE/Ag-AgCl
5	Disulfiram	Ag_2NO_3	Silver	SCE
6	Hydralazine HCl	Potassium iodate	platinum	SCE
7	Lomustine	silvernitrate	silver	Calomel
8	Metoclopromide HCl	NaOH	Glass	SCE
9	Naldixic acid	Ethanolic sodium of hydroxide	Glass	Ag-AgCl
10	Phenobarbitone sodium	NaOH	Glass	SCE
11	Promithazine HCl	NaOH	Glass	SCE
12	propranalolHCl	NaOH	Glass	SCE
13	Sodium stibogluconate injection	Ferric ammonium sulphate	pt	Ag-AgCl

THANKYOU