

Chapter-six

Potentiometry

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Potentiometric Measurements

- Based on measuring the potential of electrochemical cells without drawing appreciable current.
- The use of electrodes to measure voltages from chemical reactions
- Including:
 - a reference(counter) electrode, an indicator(working) electrode, and a potential measuring device(Salt bridge(SB), Analyte, A)
- Often, these two electrodes are housed together in one probe.
- Such a probe is called a **combination electrode**.
- Used to
 - locate end points in titrations.
 - Determine ion concentrations with ion-selective membrane electrodes
 - Measure the pH
 - determine thermodynamic equilibrium constants such as K_a , K_b , and K_{sp} .

Potentiometric measurements:

- are made using a potentiometer to determine the difference in potential between a working (an indicator) electrode and a counter (a reference) electrode.
- Cathode is the working /indicator electrode. (right half-cell)
- Anode is the counter /reference electrode. (left half-cell)

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

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

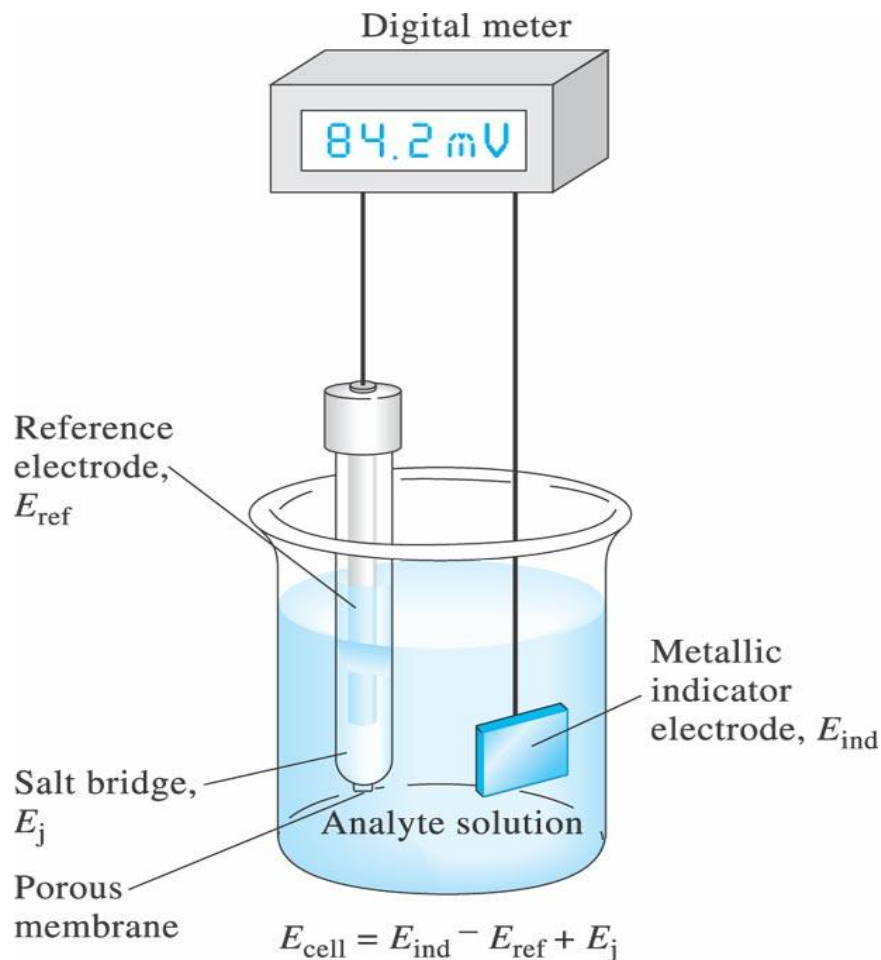
Where : E_{c} is the reduction potential at the cathode.

: E_{a} is the reduction potential at the anode.

- For most electroanalytical methods, the junction potential(E_{j}) is small enough to be neglected.

RE	SB	A	IE
$-E_{\text{ref}}$	$+E_{\text{j}}$		$+E_{\text{ind}}$

A typical cell for potentiometric analysis:



reference electrode | salt bridge | analyte solution | indicator electrode

E_{ref} E_j E_{ind}

6.1 Reference Electrodes, RE

- A half-cell with an accurately known electrode potential, E_{ref} ,
- is independent of the concentration of the analyte or any other ions in the solution
- Always treated as the left-hand electrode

Types of RE;

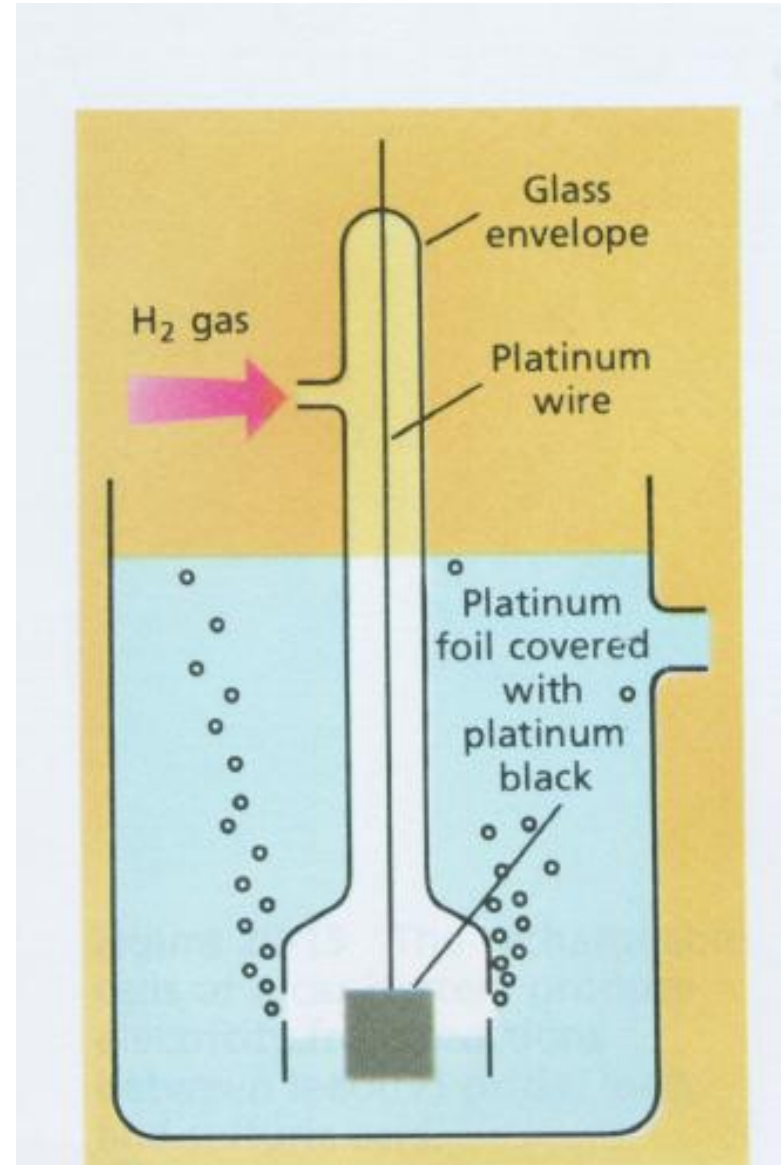
1. Standard Hydrogen Electrode, SHE
2. Calomel Reference Electrode, CRE
3. Silver/Silver Chloride Reference Electrode, Ag–AgCl electrode

1. Standard hydrogen electrode (SHE)

- Its potential is considered to be **zero**.
- H_2 is constantly bubbled into so/n.
 - $1 \text{ M } \text{H}^+_{(\text{aq})} + 2\text{e}^- = \text{H}_{2(\text{g})} (1 \text{ atm})$
 - $\text{pt}/ \text{H}_2, \text{H}^+ (1\text{N}) \parallel$
 - $E^0 \equiv 0 \text{ V}$ for this electrode
 - where ⁰ stands for **standard state**:
 - 1 M all solutes
 - 1 atm all gases
 - 25°C (298 K)

d-Limitation

1. It is **difficult** to be used and to keep H_2 - gas at **one atmosphere** during all determinations.
2. It needs periodical **replating** of Pt. Sheet with Pt. Black



2. Saturated Calomel Reference Electrode, SCE

- The SCE is an example of a **constant-potential** electrode.
- Its standard reduction potential at 25°C is +0.241V.
- It **consists** of **two** concentric **glasses** or tubes
- The **outer tube has a porous fiber tip**, which acts as the salt bridge to the analyte solution and the other half-cell.
- **Calomel** is made by thoroughly **mixing mercury metal (Hg) with mercurous chloride (Hg₂Cl₂), a white solid.**
- X= 1M or 0.1M



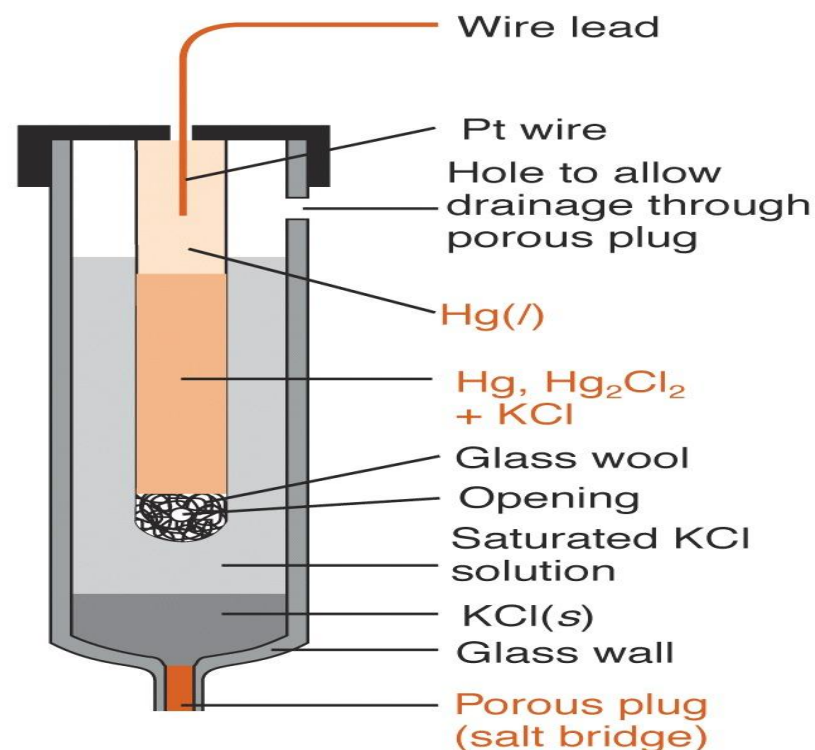
- ✓ When in use, the **half-cell** rxn occurs:



- ✓ The **Nernst** equation for this rxn is

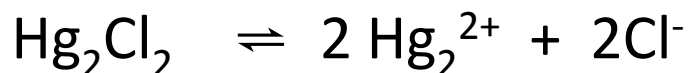
$$E = E^\circ - (0.05916/2) \log[\text{Cl}^-]^2 = \mathbf{0.244 \text{ V}}$$

- the potential of the indicator electrode vs. that of the SCE is measured.



Potential of the electrode depends on the chloride ion


$$E_{25} = E_{\text{Hg/Hg}^+}^0 - \frac{0.059}{2} \log \frac{1}{[\text{Hg}^{2+}]^2}$$



$$\text{Sp}_{\text{Hg}_2\text{Cl}_2} = [\text{Hg}_2^{2+}]^2 [\text{Cl}^-]^2$$

$$[\text{Hg}_2^{2+}]^2 = \frac{\text{Sp}_{\text{Hg}_2\text{Cl}_2}}{[\text{Cl}^-]^2}$$

$$K_{\text{sp}} = 1.8 \times 10^{-18}$$

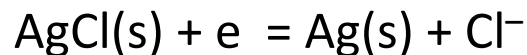
$$E_{\text{Hg/Hg}_2\text{Cl}_2}^{25} = E_0 - \frac{0.059}{2} \log \frac{[\text{Cl}^-]^2}{\text{Sp}_{\text{Hg}_2\text{Cl}_2}}$$


$$E = E^0 - (0.0591/2) \log [\text{Cl}^-]^2 = 0.244 \text{ V}$$

3. The Silver–Silver Chloride Electrode

- The commercial Ag-AgCl electrode is similar to the SCE in that it is enclosed in glass,
- Has nearly the same size and shape, and has a porous fiber tip for contact with the external solution.
- Internally, however, it is different.
- There is only one glass tube (unless it is a double-junction design) and a solution saturated in AgCl and KCl is inside.
- Ag wire coated at the end with a AgCl paste extends into this so/n from the external lead. See Figure 6.2.

Electrode: Ag(s) | AgCl (sat'd), KCl (xM) ||



The Nernst equation for this is

$$E = E^\circ - \frac{0.0592}{1} \log[\text{Cl}^-]$$

Cont...

- The standard reduction potential for this half-rxn is +0.22233 V.
- The potential is dependent only on the $[\text{Cl}^-]$, as was the potential of the SCE, & once again $[\text{Cl}^-]$ is constant because the so/n is saturated.
- Thus this electrode is also appropriate for use as a reference electrode.

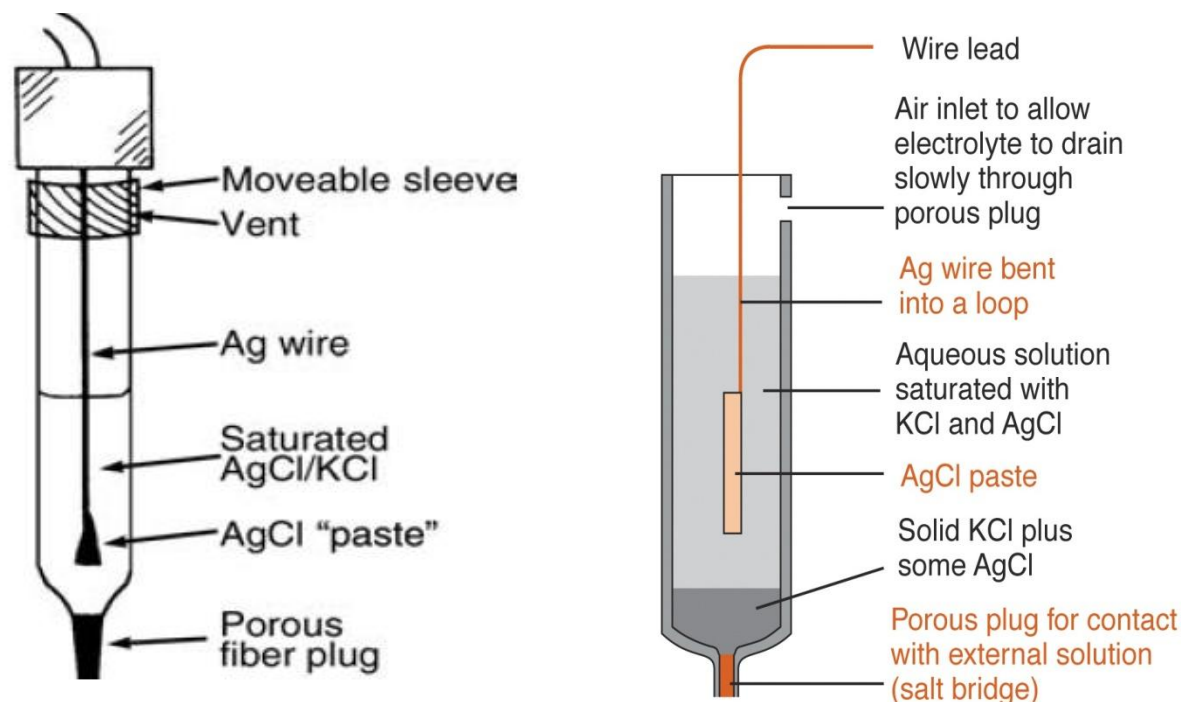


Fig. 6.2. A drawing of a commercial Ag–AgCl reference electrode. 10

Disadvantage of silver-silver chloride electrode

- It is more difficult to prepare than SCE.
- AgCl in the electrode has large solubility in saturated KCl

Advantage of Ag/AgCl electrodes over SCE.

- It has better **thermal** stability.
- Less **toxicity** and environmental problems with consequent cleanup and disposal difficulties.

6.2. Indicator electrode

- ❖ The **reference** electrode represents **half** of the complete
- ❖ The **other half** is the **indicator** or **working electrode**, whose response (potential) depends upon the analyte conc. develops.
- ❖ There are a number of **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**

- A. Glass pH IE
- B. Glass IE for other cations
- C. Liquid Membrane IE
- D. Crystalline-Membrane IE

III. **Gas Sensing Probes**

Electrode of the First Kind:

- Pure metal electrode in direct equilibrium with its cation
- Metal in contact with Cation: M/M^{n+}
- $M^{+n}(aq) + ne^- \rightleftharpoons M(s)$

$$E_{ind} = E^0 - \frac{0.0592}{n} \log \frac{1}{[M^{n+}]}$$

- Example: Ag/Ag^+



- Nernst Equation:

$$E = E^0_{Ag^+/Ag} - 2.303RT/nF(\log 1/a_{Ag^+})$$

- Where a_{Ag^+} = activity of silver ion
- $E_{measured} = E_{cell} = E_{ind \text{ vs NHE}} = E_{ind} - E_{NHE}$
- $E_{cell} = E_{ind}$

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

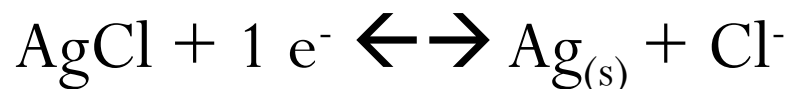
Electrode of the Second Kind:

- Respond to **anions** by forming precipitates or stable complex

Examples:

1. Ag electrode for Cl^- determination

- General Form: $\text{M} \mid \text{MX} \mid \text{X}^{n-}$
- Example: $\text{Ag} \mid \text{AgCl}_{(s)} \mid \text{Cl}^-$



- Nernst Equation:

$$E = E^\circ_{\text{AgCl/Ag}} - 2.303RT/nF(\log a_{\text{Cl}^-})$$

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

1. The pH Electrode

- The pH electrode consists of a closed-end glass tube that has a very thin fragile glass membrane at the tip.
- Inside the tube is a saturated solution of AgCl that has a particular pH.
- It is typically a 1 M solution of HCl.

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- While this is almost the same design as that of the Ag–AgCl reference electrode,
- the presence of HCl and the fact that the tip is fragile glass and does not have a porous fiber plug point out the difference.

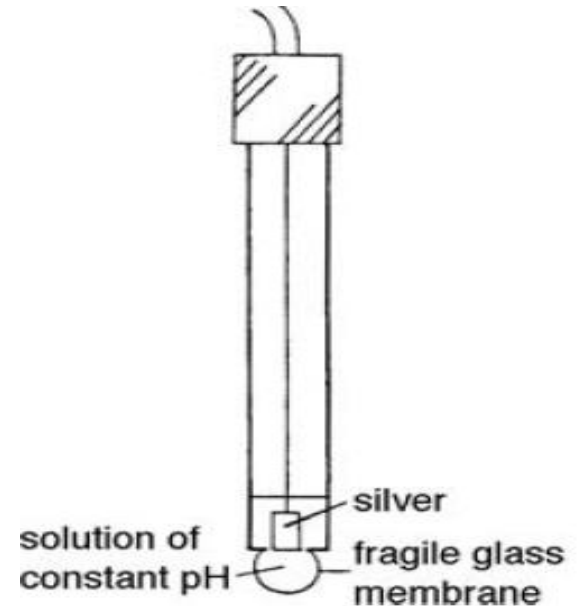


Fig. 6.3. A drawing of a pH electrode.

- ❖ The purpose of the Ag–AgCl combination is to prevent the potential that develops from changing due to possible changes in the interior of the electrode.
- ❖ The potential that develops is a **membrane potential**.

Cont...

➤ Specifically, it is the difference in the conc of the H-ions on opposite sides of the membrane that causes the potential (the membrane potential) to develop.

➤ There is **no half-cell rxn** involved.

The **Nernst** equation is

$$E = E^{\circ} - 0.0592 \log \frac{[\text{H}^+](\text{internal})}{[\text{H}^+](\text{external})}$$

since the **internal** $[\text{H}^+]$ is a **constant**, it can be combined with E° , which is also a constant, giving a **modified** E° , E^* , and eliminating $[\text{H}^+](\text{internal})$:

$$E = E^* + 0.0592 \log [\text{H}^+](\text{external})$$

In addition, we can recognize that **pH = $-\log [\text{H}^+]$** and substitute this into the above equation:

$$E = E^* - 0.0592 \text{ pH}$$

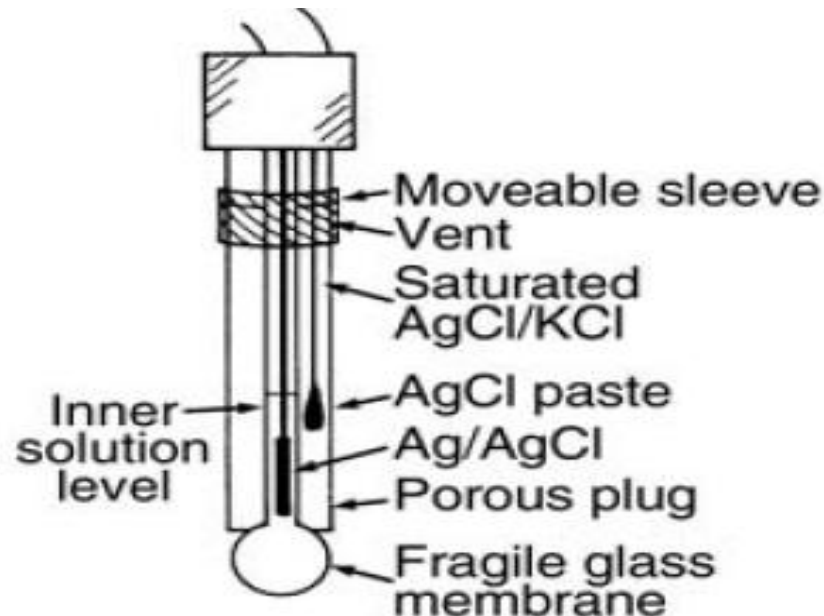
➤ The electrode is that the measured potential (measured against a reference electrode) is thus directly proportional to the pH of the so/ n .

Cont...

- ❑ A pH meter displays the **pH** directly, rather than the value of E.
- ❑ The pH meter is **standardized** (calibrated) with the use of buffer so/ns.
- ❑ For example, if the pH of a sample to be measured is expected to be 9.0, buffers of $\text{pH} = 7.0$ and $\text{pH} = 10.0$ should be used.
- ❑ Alternatively, of course, **homemade** buffer solutions may be used.

2.The Combination pH Electrode

- two half-cells (probes) are needed the pH electrode itself and a reference electrode, either the SCE or the silver–silver chloride electrode .
- two connections are made to the pH meter.
- This electrode incorporates both the reference probe and pH probe into a single probe.
- the most popular electrode today for measuring pH.



3. Ion-Selective Electrodes

❑ The concept of the pH electrode has been extended to include other ions as well.

❑ Considerable research has gone into the development of these **ion-selective electrodes** over the years, especially in studying the composition of the membrane that separates the internal solution from the analyte solution.

❑ The internal solution must contain a constant concentration of the analyte ion, as with the pH electrode.

❖ Today we utilize electrodes with: 1) glass membranes of varying compositions, 2) crystalline membranes, 3) liquid membranes, and 4) gas-permeable membranes.

❑ In each case, the interior of the electrode has a silver–silver chloride wire immersed in a solution of the analyte ion.

❑ Examples of electrodes that utilize a **glass membrane** are those for **lithium** ions, **sodium** ions, potassium ions, and silver ions.

Cont...

- ❖ Varying percentages of Al_2O_3 and B_2O_3 , along with oxides of the metal analyte, are often found in the membrane, as well as other metal oxides.
- ❖ The selectivity and sensitivity of these electrodes vary.
- ❖ With **crystalline membranes**, the membrane material is most often an **insoluble ionic crystal** cut to a round, flat shape and having a thickness of 1 or 2 mm and a diameter of about 10 mm.
- ❖ This flat disk is mounted into the end of a Teflon or polyvinyl chloride (PVC) tube.
- ❖ **The most important of the electrodes with crystalline membranes is the fluoride electrode.**
- ❖ The membrane material for this electrode is **lanthanum fluoride**.
- ❖ The fluoride electrode is capable of accurately **sensing fluoride ion concentrations over a broad range and to levels as low as 10^{-6} M .**

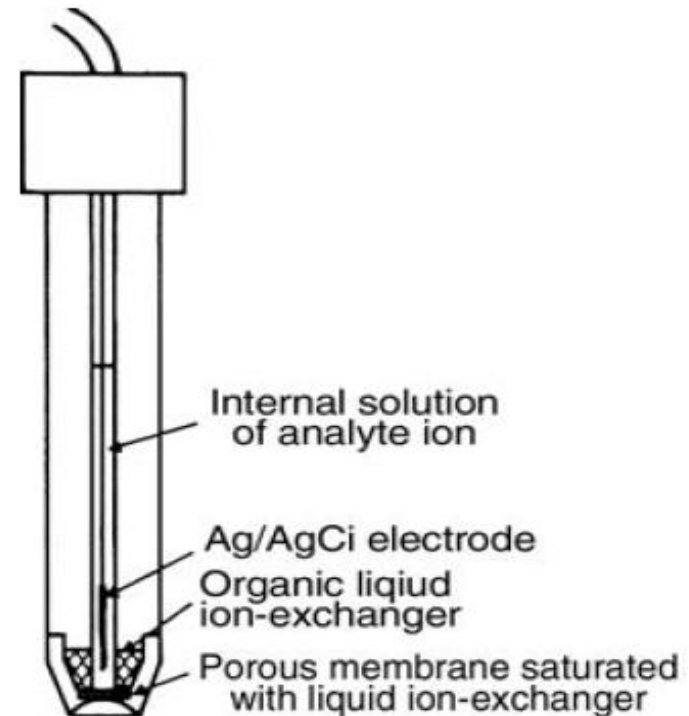
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- Other electrodes that utilize a crystalline membrane but with less impressive success records are chloride, bromide, iodide, cyanide, and sulfide electrodes.
- The main difficulty with these is problems with interferences.

Cont...

- **Liquid membrane electrodes** utilize porous polymer materials, such as PVC or other plastics.
- An organic liquid ion exchanger immiscible with H_2O contacts and saturates the membrane from a reservoir around the outside of the tube containing the water so/n of the analyte & the Ag–AgCl wire.
- Important electrodes with this design are the calcium and nitrate ion-selective electrodes.

- **Fig. 6.5.** A drawing of an ion-selective electrode with a liquid membrane.



- Finally, gas-permeable membranes are used in electrodes that are useful for dissolved gases, such as ammonia, CO_2 , & HCN .
- These membranes are permeated by the dissolved gases, but not by solvents or ionic solutes.
- Inside the electrode is a so/n containing the reference wire as well as a pH probe, the latter positioned to create a thin liquid film b/n the glass membrane of the pH probe and the gas permeable membrane.

Cont...

✓ As the gases diffuse in, the pH of the so/n constituting the thin film changes, and thus the response of the pH electrode changes proportionally to the amount of gas diffusing in.

➤ Calibration of ion-selective electrodes for use in quantitative analysis is usually done by preparing a series of standards as in most other instrumental analysis methods,

➤ since the measured **potential** is proportional to the **logarithm** of the **concentration**.

✓ The relationship is

$$E = E^* - \frac{0.0592}{z} \log[\text{ion}]$$

z is the signed **charge** on the ion.

Cont...

- The analyst can measure the potential of the electrode immersed in each of the standards and the sample (vs. the SCE or silver–silver chloride reference),
- plot E vs. $\log [\text{ion}]$, and find the unknown concentration from the linear regression procedures.

6.3 Other Details of Electrode Design

- The electrodes described in this section are **commercially available**.
- ❑ The body of these electrodes may be either glass or epoxy plastic.
- ❑ Epoxy plastic electrodes are unbreakable.
- ❑ Some electrodes are **gel-filled electrodes** and are sealed.
- ❑ This means that the KCl solution has a gelatin mixed with it.
- ❑ There is no vent hole, they cannot be refilled with saturated KCl, and solid KCl cannot be added.
- ❑ Some electrodes are **double-junction electrodes**.
- ❑ Such electrodes are encased in another glass tube and therefore have two junctions, or porous plugs.
- ❑ The purpose of such a design is to prevent contamination the contamination of the analyte so/n with the electrode solution, or both, by the diffusion of either so/n through the porous tip or plug.

6.4 Care and Maintenance of Electrodes

- ❖ While the SCE or Ag–AgCl electrode is dipped into the solution, there will be a slight leakage of the solutions through the porous tip.
- ❖ In order for these electrodes to be used accurately, the measurement must not be adversely affected by the slight contamination from these ions.
- ❖ It is a good idea to slide the moveable sleeve Fig. 6.1, for example downward so that the outer tube is vented while the electrode is in use so that the ions do indeed freely diffuse through the porous tip.
- ❖ Also, the electrode, under these circumstances, should not be immersed into the solution so deep that the level of solution in the external tube is lower than the level of the solution tested.
- ❖ This would cause the solution to diffuse into the reference electrode rather than the reverse, and thus would contaminate the solution inside and possibly damage the electrode.

Cont...

- ❖ The vent hole may also be used prior to the exp't to refill the outer tube with more fill so/n (often supplied by the manufacturer), as this so/n is lost with time or is sometimes drained out for long-term storage or cleaning.
- ❖ In addition, if the undissolved KCl in the SCE disappears, more solid KCl can be added through the vent hole.
- ❖ Proper storage of electrodes is important.
- ❖ For short-term storage (up to 1 week), the tip of the electrode should be immersed in a so/n to a level above the porous plug.
- ❖ Some manufacturers supply a solution to be used for this.
- ❖ Others recommend a particular so/n, such as a pH = 7 buffer so/n.
- ❖ Other details for such storage so/ns may be given in the manufacturer's literature.
- ❖ In any case, distilled water should *not* be used.

Cont...

- ❖ For long-term storage (longer than 1 week), the protective plastic sleeve provided with the electrode should be placed back on the tip and a small bit of cotton moistened with the storage so/n placed inside at the tip of the electrode.
- ❖ The **manufacturer's literature** usually contains the full recommendations for storage.

6.5 Potentiometric Titrations

- ❖ It is possible to monitor the course of a **titration** using potentiometric measurements.
- ❖ The **pH electrode**, for example, is appropriate for monitoring an acid–base titrⁿ and determining an **end point** instead of an indicator.
- ❖ The end point occurs when the measured pH undergoes a sharp change when all the acid or base in the titration vessel is reacted.
- ❖ The procedure has been called a **potentiometric titration** and the experimental setup is shown in Figure 6.5.

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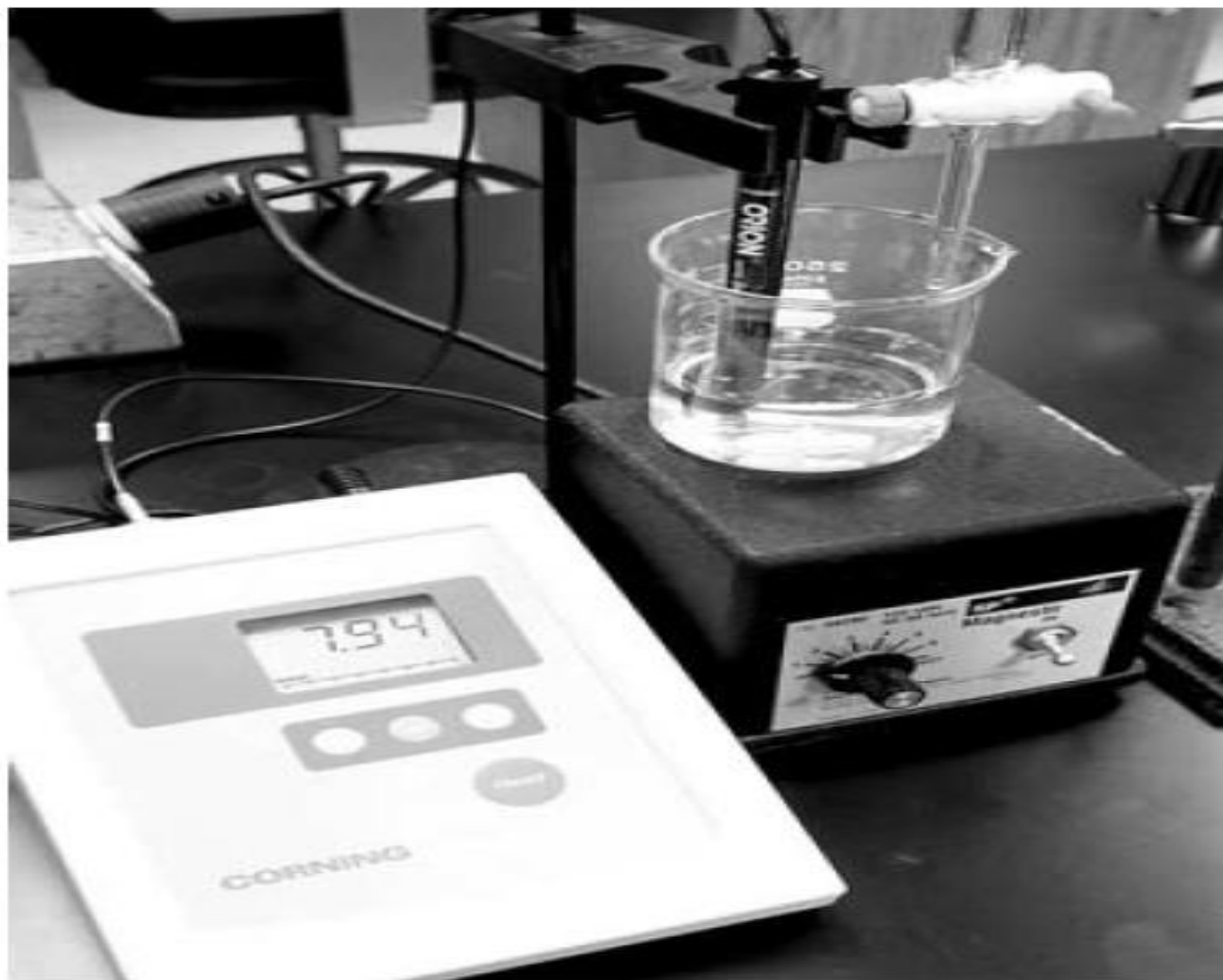
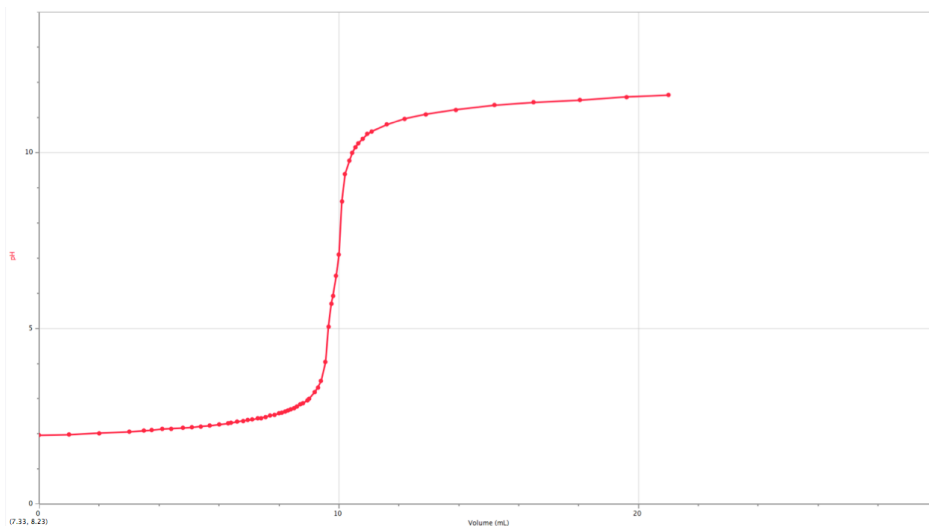


Fig. 6.5 A setup for a potentiometric titration.

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- ❑ The same procedure can be used for any ion for which an ion-selective electrode has been fabricated and for which there exists an appropriate titrant.
- ❑ In addition, potentiometric titration methods exist in which an electrode other than an ion-selective electrode is used.



➤ Make a graph of the
pH vs mL of NaOH added.

➤ $M_A V_A = M_B V_B$ to determine
the molarity of the base.

❑ **Figure:** Titration curve for the titration of a strong acid with a strong base.



THANK YOU