

Unit-II
Potentiometry
and
Ion-Selective Electrode

Electrochemical Methods

- Electrochemical methods are divided into static methods and dynamic methods.
- In static methods **no current passes** between the electrodes, and **the concentrations** of species in the electrochemical cell **remain unchanged**, or static. Eg. Potentiometry.
- In dynamic methods, in which **current flows and concentrations change** as the result of a redox reaction. Eg. Stripping voltammetry, Polarography, Cyclic voltammetry.
- Although all different electrochemical methods of analysis are based on **Ohm's law**.
- The **statement** that the current moving through a circuit is proportional to the applied potential and inversely proportional to the circuit's resistance

Electrodes

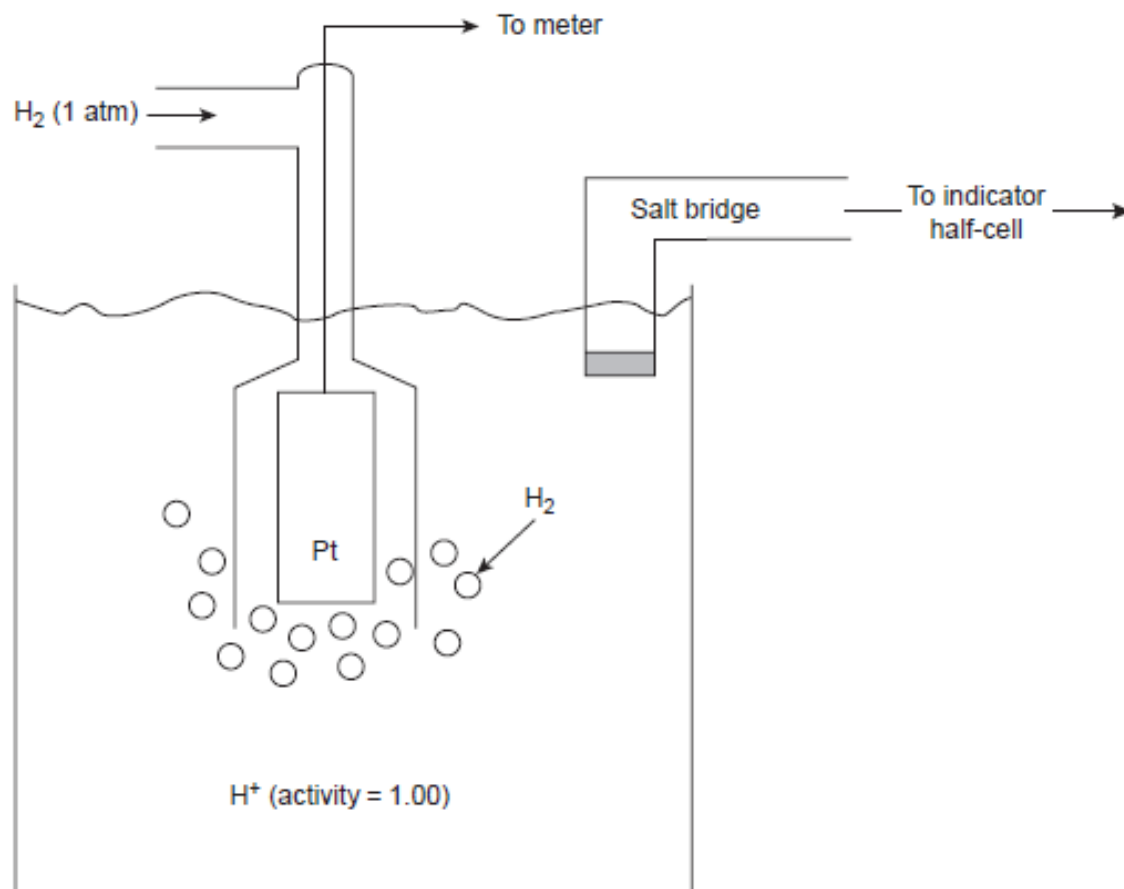
- Electrochemical measurements are made in an electrochemical cell, consisting of two or more electrodes.
- **Indicator electrode:** The electrode whose potential is a function of the analyte's concentration (also known as the working electrode).
- **Counter electrode:** The second electrode in a two-electrode cell that completes the circuit.
- **Reference electrode:** An electrode whose potential remains constant and against which other potentials can be measured.
- If the potential of counter electrode remains constant it is act as reference electrode.
- If counter electrode only complete the circuit it also called auxiliary electrode

Reference Electrodes

- Potentiometric electrochemical cells are constructed such that 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
- and the cell potential is
- $E_{cell} = E_{ind} - E_{ref} + E_{lj}$

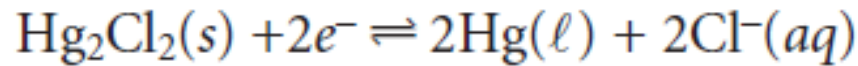
Standard Hydrogen Electrode

- The standard hydrogen electrode (SHE) 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.
- The SHE consists of a Pt electrode immersed in a solution in which the **hydrogen ion activity is 1.00** and in which **H₂ gas** is bubbled at a **pressure of 1 atm**.
- A conventional salt bridge connects the SHE to the indicator half-cell. The shorthand notation for the standard hydrogen electrode is
- $\text{Pt}(s), \text{H}_2(g, 1 \text{ atm}) / \text{H}^+(aq, a = 1.00) //$



Calomel Electrodes

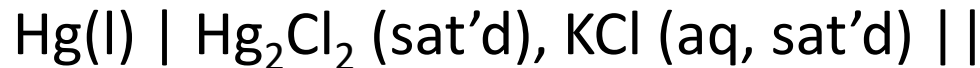
- Calomel reference electrodes are based on the redox couple between Hg_2Cl_2 and Hg (calomel is a common name for Hg_2Cl_2).

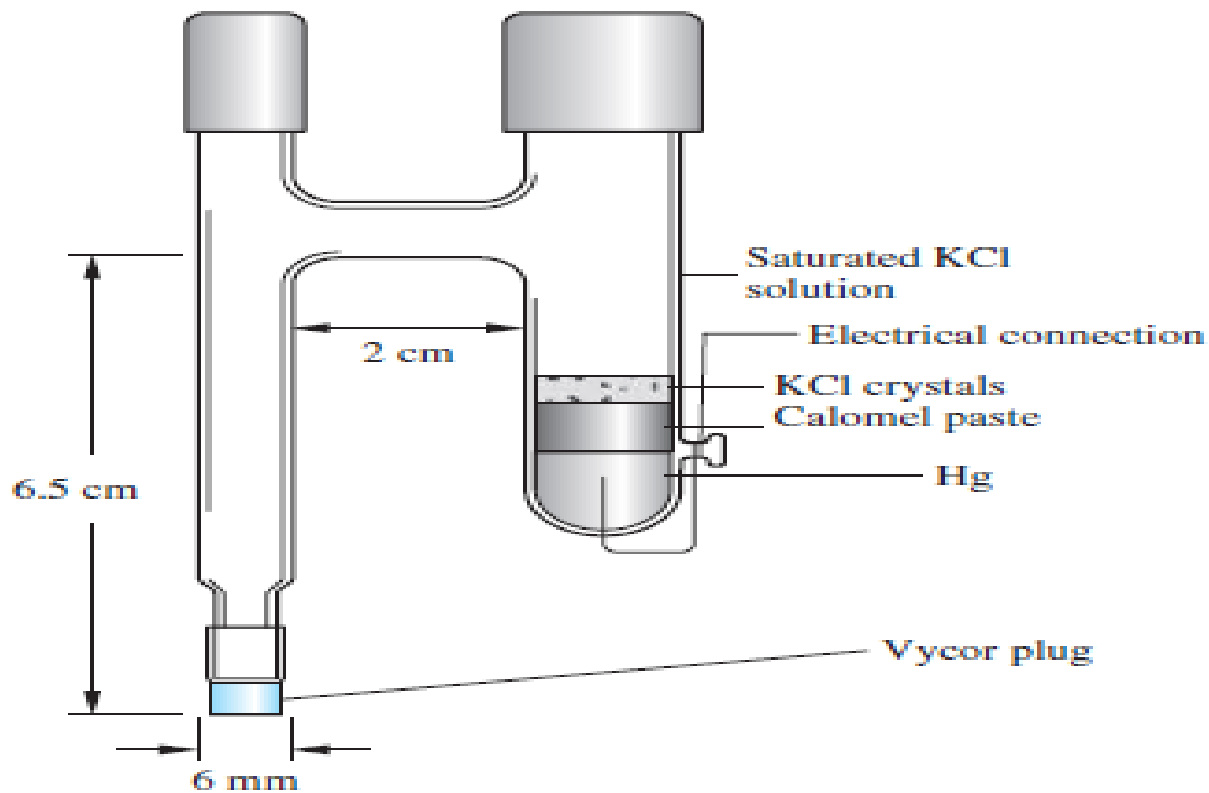


The Nernst equation for the calomel electrode is

$$E = E_{\text{Hg}_2\text{Cl}_2/\text{Hg}}^\circ - \frac{0.05916}{2} \log[\text{Cl}^-]^2 = +0.2682 - \frac{0.05916}{2} \log[\text{Cl}^-]^2$$

- The potential of a calomel electrode, therefore, is determined by the concentration of Cl^- .
- The shorthand notation for this cell is





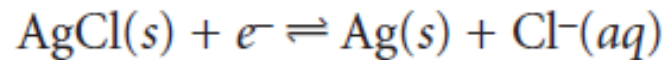
The H-shape body of the electrode is made of glass of dimensions shown in the diagram. The right arm of the electrode contains a platinum electrical contact, a small quantity of mercury/mercury(I) chloride paste in saturated potassium chloride, and a few crystals of KCl.

The tube is filled with saturated KCl to act as a salt bridge through a piece of porous Vycor (“thirsty glass”) sealed in the end of the left arm.

- Standard potential of Calomel electrode is at **25 °C of +0.2444 V.**
- The SCE has the **advantage** that the **concentration of Cl⁻**, and, therefore, **the potential of the electrode, remains constant** even if the KCl solution partially evaporates.
- On the other hand, a significant **disadvantage** of the SCE is that the **solubility of KCl is temperature sensitive.**
- At higher temperatures the concentration of Cl⁻ increases, and the electrode's potential decreases. For example, the potential of the SCE at 35 °C is +0.2376 V.
- Another disadvantage to calomel electrodes is that they cannot be used at temperatures above 80 °C.

Silver/Silver Chloride Electrodes

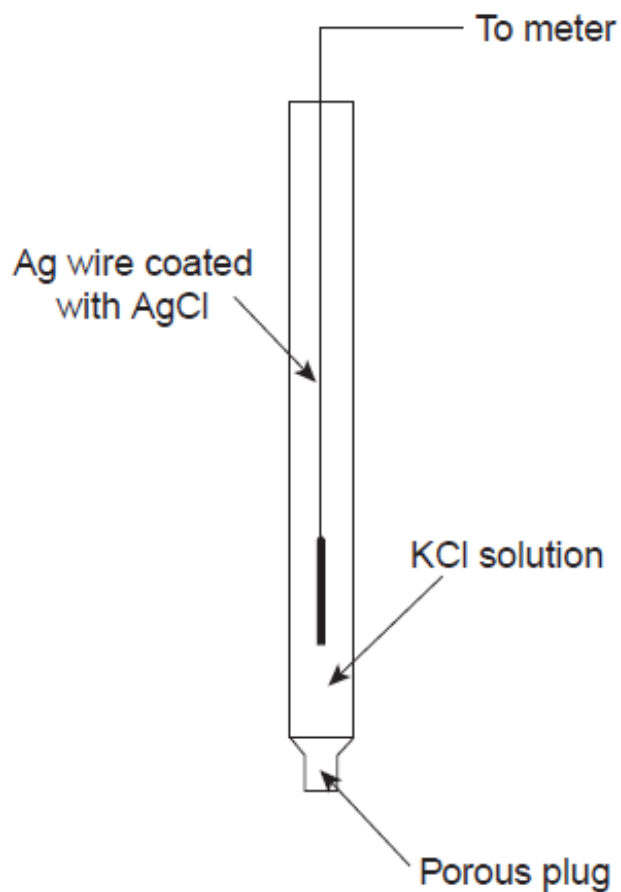
- Silver/silver chloride electrode, which is based on the redox couple between AgCl and Ag.



As with the saturated calomel electrode, the potential of the Ag/AgCl electrode is determined by the concentration of Cl⁻ used in its preparation.

$$E + E_{\text{AgCl/Ag}}^\circ - 0.05916 \log [\text{Cl}^-] = +0.2223 - 0.05916 \log [\text{Cl}^-]$$

- When prepared using a saturated solution of KCl, the Ag/AgCl electrode has a potential of +0.197 V at 25 °C.
- Another common Ag/AgCl electrode uses a solution of 3.5 M KCl and has a potential of +0.205 at 25 °C.
- The Ag/AgCl electrode prepared with saturated KCl, of course, is more temperature-sensitive than one prepared with an unsaturated solution of KCl.



- A typical Ag/AgCl electrode is shown in Figure and consists of a silver wire, the end of which is coated with a thin film of AgCl.
- The wire is immersed in a solution that contains the desired concentration of KCl and that is saturated with AgCl.
- A porous plug serves as the salt bridge.
- The shorthand notation for the cell is

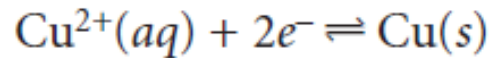


- Ag/AgCl electrode has the **advantage** of being useful at higher temperatures.
- Ag/AgCl electrode is more reactive with solutions to form insoluble silver complexes that may plug the salt bridge between the electrode and the solution. (**Disadvantage**)

Metallic Indicator Electrodes

- The potential of a metallic electrode is determined by the position of a redox reaction at the electrode–solution interface.
- Three types of metallic electrodes are commonly used in potentiometry, each of which is considered in the following discussion.
- Electrodes of the First Kind
- Electrodes of the Second Kind
- Inert Redox electrode

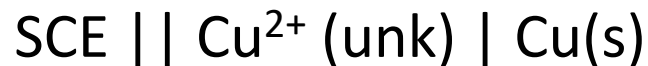
- **Electrode of the first kind:** A metallic electrode whose potential is a function of the concentration of M^{n+} in an M^{n+}/M redox half-reaction.
- When a copper electrode is immersed in a solution containing Cu^{2+} , the potential of the electrode due to the reaction



is determined by the concentration of copper ion.

$$E = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - \frac{0.05916}{2} \log \frac{1}{[\text{Cu}^{2+}]} = +0.3419 - \frac{0.05916}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

If the copper electrode is the indicator electrode in a potentiometric electrochemical cell that also includes a saturated calomel reference electrode



- The cell potential can be used to determine an unknown concentration of Cu^{2+} in the indicator half-cell

$$E_{\text{cell}} = E_{\text{ind}} - E_{\text{ref}} + E_{\text{Ij}} = +0.3419 - \frac{0.05916}{2} \log \frac{1}{[\text{Cu}^{2+}]} - +0.2444 + E_{\text{Ij}}$$

- Metallic indicator electrodes in which a metal is in contact with a solution containing its ion are called **electrodes of the first kind**. **In general, for a metal M, in a solution of M^{n+} , the cell potential is given as**

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

Limitations of “electrode of the first kind”

- **Slow kinetics for electron transfer.** Hence show response time.
- **Not selective:** For example, a copper electrode cannot be used for the determination of copper(II) ions in the presence of silver(I) ions because the electrode potential is also a function of the Ag^+ concentration.
- **pH sensitive:** Zn, Cd cannot be used in acidic solutions where they are easily oxidized (dissolve) by H^+ .
- The existence of **surface oxides and interfering reactions.**
- Electrodes of the first kind are limited to used in potentiometry are Ag/Ag^+ and Hg/Hg^{2+} in neutral solutions and Cu/Cu^{2+} , Zn/Zn^{2+} , Cd/Cd^{2+} , Bi/Bi^{3+} , Tl/Tl^+ , and Pb/Pb^{2+} in de-aerated solutions (to remove access oxygen).

Electrode of the second kind

- **Electrode of the second kind:** A metallic electrode whose potential is a function of the concentration of X in an MX_n/M redox half-reaction.
- Metals not only serve as indicator electrodes for their own cations but also respond to the activities of **anions that form sparingly soluble precipitates or stable complexes** with such cations.
- For example, the potential of a silver electrode in a solution of Ag^+ is given by

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

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



- To determine the concentration of Ag^+ ; thus

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

- where $K_{\text{sp, AgI}}$ is the solubility product for AgI.

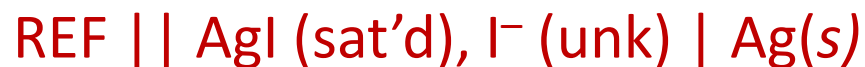
$$E = +0.7996 - 0.05916 \log \frac{[\text{I}^-]}{K_{\text{sp, AgI}}}$$

- shows that the potential of the silver electrode is a function of the concentration of I^- .

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

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

- When this electrode is incorporated into a potentiometric electrochemical cell, its shorthand notation is -



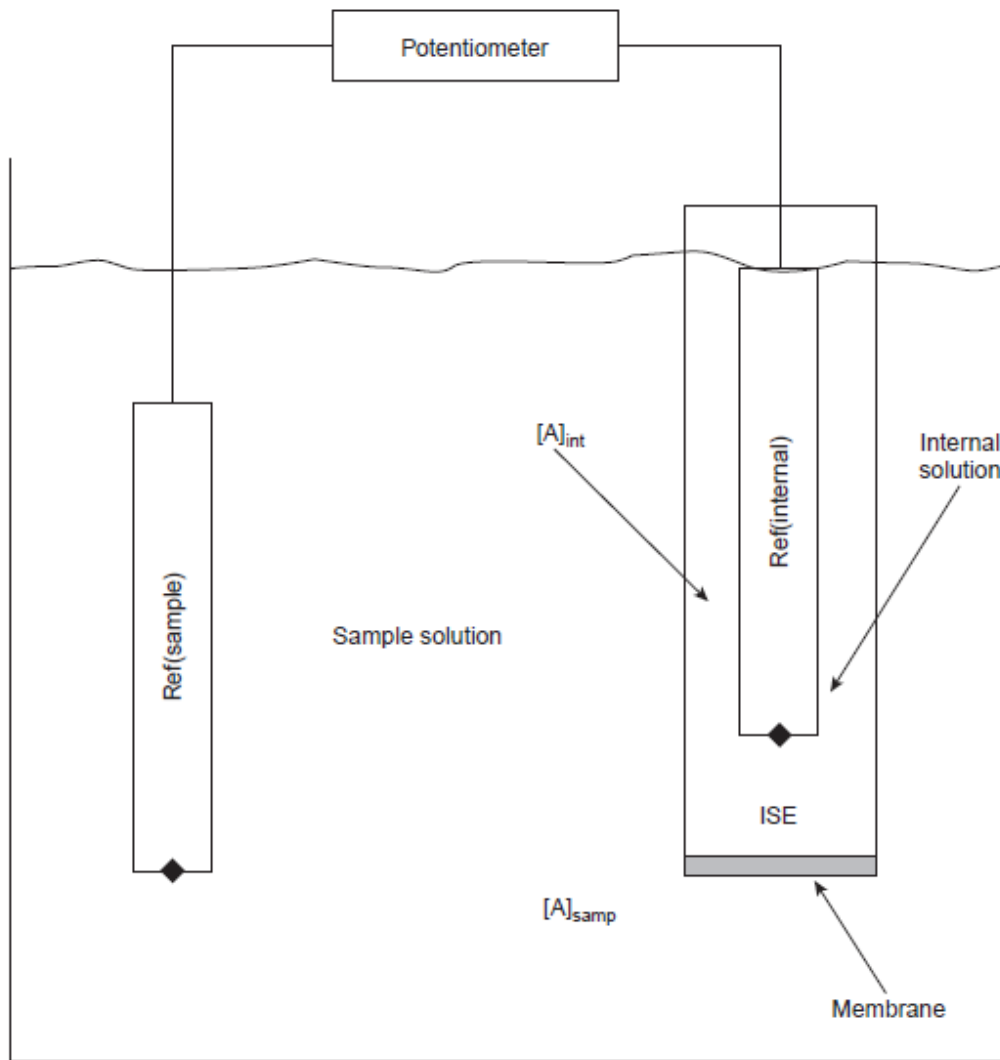
- When the potential of an electrode of the first kind responds to the potential of another ion that is in equilibrium with Mn^+ , it is called an ***electrode of the second kind***.
- **Two common electrodes of the second kind are the calomel and silver/silver chloride electrodes.**
- Electrodes of the second kind also can be based on complexation reactions.
- For example, an electrode for EDTA is constructed by coupling of Hg^{2+}/Hg electrode of the first kind to EDTA by taking advantage of its formation of a stable complex with Hg^{2+} .

Inert redox electrode

- **Inert redox electrode** : An inert electrode that serves as a source or sink for electrons for a redox halfreaction.
- Several relatively inert conductors (metal) respond to redox systems.
- Such materials as platinum, gold, palladium, and carbon can be used to monitor redox systems.
- For example, the potential of a platinum electrode immersed in a solution containing cerium(III) and cerium(IV) or solution of Fe^{2+} and Fe^{3+} .
- Note that the potential of a redox electrode generally responds to the concentration of more than one ion, limiting their usefulness for direct potentiometry.

Membrane Electrodes / Ionselective Electrode

- In 1906, a concept of membrane electrode has been developed in which, thin glass membrane that separates two solutions with different hydrogen ion concentrations (pH) use to determining pH of solution through **membrane potential**.
- This phenomena led to the eventual development of a whole new class of indicator electrodes called **ionselective electrodes (ISEs)**.
- **Membrane potential**: A potential developing across a conductive membrane whose opposite sides are in contact with solutions of different composition.
- **Ion-selective electrode**: An electrode in which the membrane potential is a function of the concentration of a particular ion in solution.



- Ion selective electrode function by membrane that react selectively with a concentration of single ion.
- Two reference electrodes are used; one positioned within the internal solution, and one in the sample solution. The cell potential, therefore, is
- $E_{cell} = E_{Ref(int)} - E_{Ref(samp)} + E_{mem} + E_{ij}$

where E_{mem} is the potential across the membrane.

The shorthand notation for this cell is -
 Ref(samp) || $[A]_{samp}$ | $[A]_{int}$ || Ref(int)

- 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 a Nernst-like equation

$$E_{\text{mem}} = E_{\text{asym}} - \frac{RT}{zF} \ln \frac{[A]_{\text{int}}}{[A]_{\text{samp}}}$$

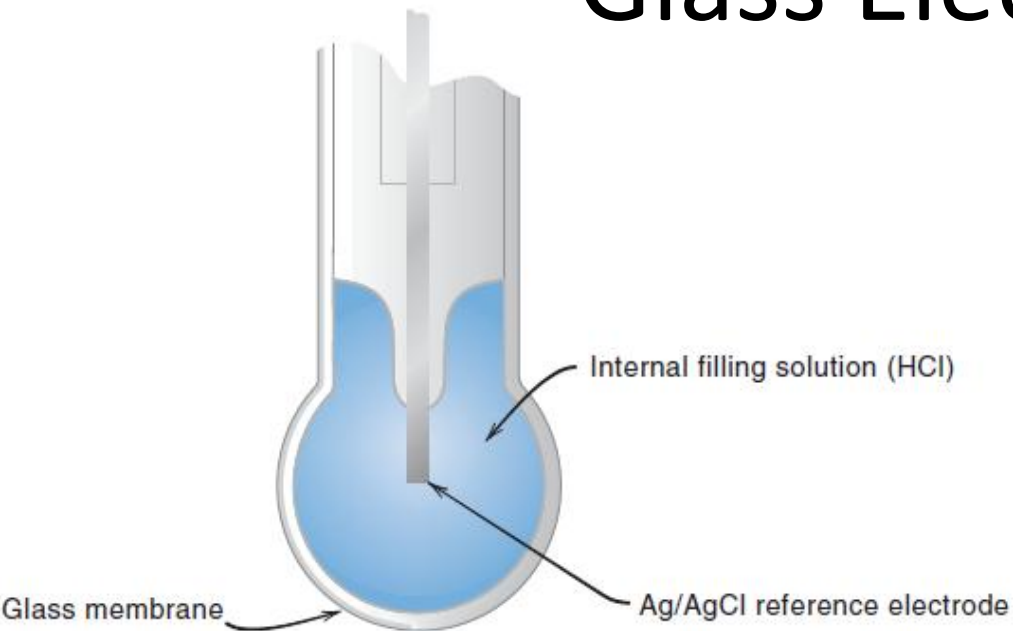
- where $[A]_{\text{samp}}$ and $[A]_{\text{int}}$ are the concentrations of analyte in the sample and the internal solution, respectively, and z is *the analyte's charge*.
- If the concentrations of analyte on both sides of the membrane are equal *Emem should* be zero but practically it is not happen.
- This phenomena is due to **asymmetry potential (Easym)**.

- **Asymmetry potential:** The asymmetry potential is a small potential across the membrane that is present even when the solutions on both sides of the membrane are identical.
- Practically a nonzero potential is observed.
- If we put this value of E_{mem} in to E_{cell} formula....

$$E_{cell} = K + \frac{0.05916}{z} \log [A]_{samp}$$

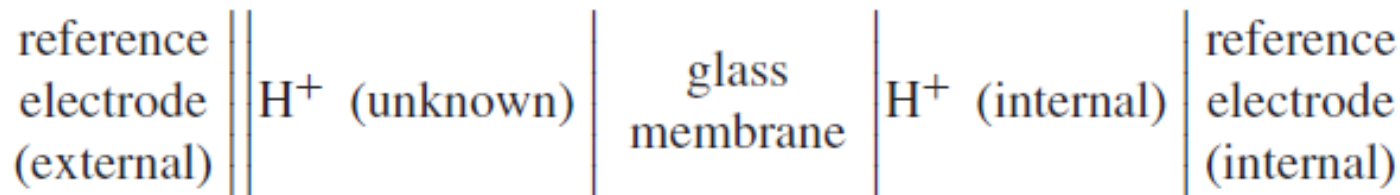
- where K is a constant accounting for the potentials of the reference electrodes, any liquid junction potentials, the asymmetry potential, and the concentration of analyte in the internal solution.
- Above formula is general equation, and applies to all types of ion-selective electrodes.

Glass Electrode



A complete cell, then, can be represented by

- There is an internal reference electrode ($Ag/AgCl/Cl^-$) and electrolyte HCl for making electrical contact with the glass membrane.
- The potential of this system remain constant by the fix concentration of HCl.
- For measurement, only bulb need to be submerged in sample solution.



- The potential of the glass membrane is given by

$$E_{\text{cell}} = k + \frac{2.303RT}{F} \log a_{\text{H}^+ \text{ unk}}$$

where k is a constant that includes the potentials of the two reference electrodes, the liquid-junction potential, a potential at the glass membrane due to H^+ (internal), and a term known as the **asymmetry potential**.

Asymmetry potential is depended on following factors such as

Composition of the membrane

Strains within the membrane,

Mechanical and chemical attack of the external surface,

The degree of hydration of the membrane.

It slowly changes with time, especially if the membrane is allowed to dry out.

For this reason, a glass electrode must be calibrated at least once a day.

- Since $\text{pH} = -\log a\text{H}^+$,

k must be determined by calibration with a **standard buffer** (see below) of known pH:

$$E_{\text{cell}} = k - \frac{2.303RT}{F} \text{pH}_{\text{unk}}$$

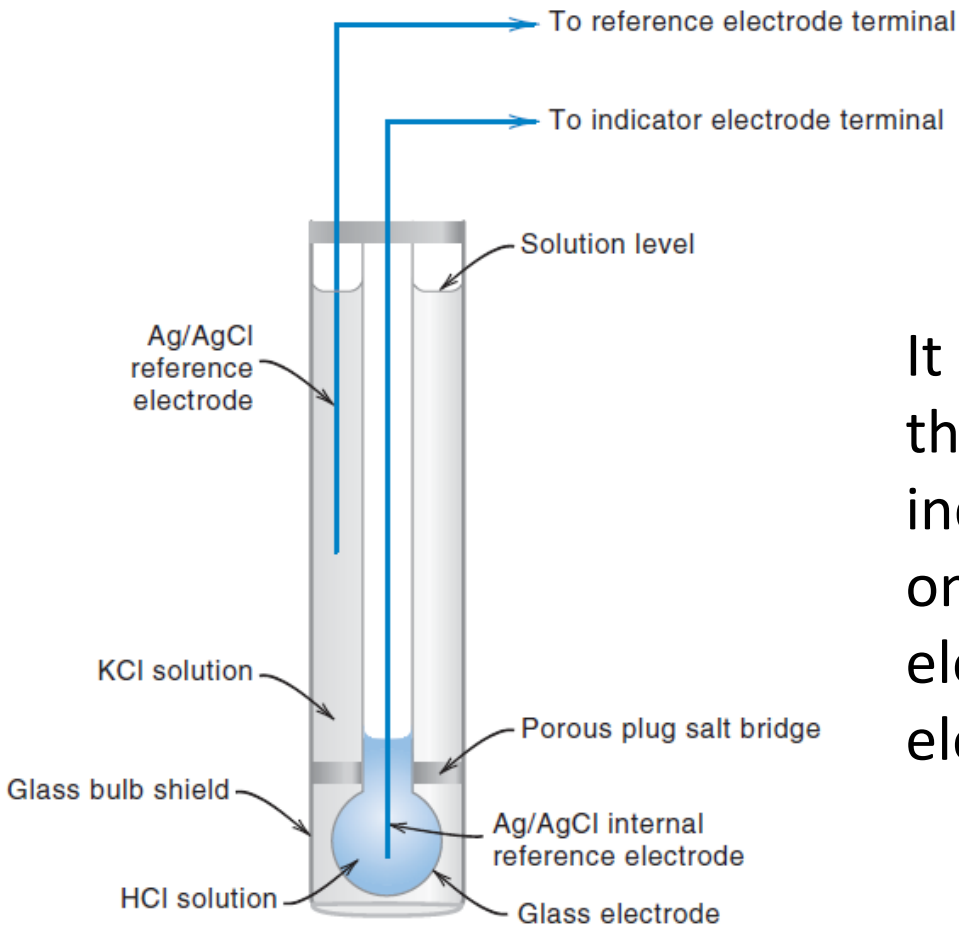
$$\text{pH}_{\text{unk}} = \frac{k - E_{\text{cell}}}{2.303RT/F}$$

$$k = E_{\text{cell}} + \frac{2.303RT}{F} \text{pH}_{\text{std}}$$

After putting the value of *k* from above equation the final formula to calculate pH of unknown solution is

$$\text{pH}_{\text{unk}} = \text{pH}_{\text{std}} + \frac{E_{\text{cell std}} - E_{\text{cell unk}}}{2.303RT/F}$$

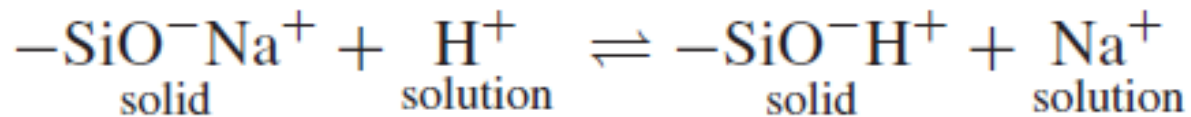
COMBINATION pH ELECTRODES—A COMPLETE CELL



It consists of a tube within a tube, the inner one housing the pH indicator electrode and the outer one housing the reference electrode (e.g., a Ag/AgCl electrode) and its salt bridge.

Working Mechanism of Glass Membrane Electrode

- The pH glass electrode depends on the ion exchange on the surface of a hydrated layer.
- The membrane of a pH glass electrode consists of chemically bonded Na_2O and $-\text{SiO}_2$.
- The surface of a new glass electrode contains fixed silicate groups associated with sodium ions, $-\text{SiO}-\text{Na}^+$.
- For the electrode to work properly, it must first be soaked in water. During this process, the outer surface of the membrane becomes *hydrated*



The $-\text{SiO}-$ sites are fixed, but the protons are free to move and exchange with other ions.

- The potential of the membrane depends on the hydrogen ion activity only.
- H-ion activity is depend on the boundary potential and the diffusion potential of glass membarane.
- The **boundary potential** resides at the surface of the glass membrane, that is, at **the interface between the hydrated gel layer and the external solution**.
- When the electrode is dipped in an aqueous solution, a boundary potential is built up, which is determined by the activity of hydrogen ions in the external solution and the activity of hydrogen ions on the surface of the gel.
- The ions will tend to migrate in the direction of lesser activity

- For example if the sample solution is more acidic, protons migrate toward the surface of the gel, building up a positive charge.
- Hence, the potential of the electrode increases, as indicated by following equations.

$$E_{\text{cell}} = k + \frac{2.303RT}{F} \log a_{\text{H}^+ \text{ unk}}$$

Or

$$E_{\text{cell}} = k - \frac{2.303RT}{F} \text{pH}_{\text{unk}}$$

Rearrange

$$\text{pH}_{\text{unk}} = \frac{k - E_{\text{cell}}}{2.303RT/F}$$

- The **diffusion potential depends on the activity protons in the inner part** of the gel layer to diffuse toward the dry membrane, which contains $-\text{SiO}-\text{Na}^+$
- A tendency of the sodium ions in the dry membrane to diffuse to the hydrated layer.
- But a similar phenomenon occurs on the other side of the membrane, only in the opposite direction.
- These in effect cancel each other, and so the net diffusion potential is very small.
- Hence, the potential of the membrane is determined largely by the boundary potential.

Errors in potential measurement

- ALKALINE ERROR: Such error is due to the capability of the membrane for responding to other cations besides the hydrogen ion.
- When the hydrogen ion activity becomes very small, these other ions can compete successfully in the potential-determining mechanism.
- Although the hydrated gel layer prefers protons, sodium ions will exchange with the protons in the layer when the hydrogen ion activity in the external solution is very low.
- Hence, the potential depends partially on the ratio of $a^{Na+}_{external}/a^{Na+}_{gel}$; that is, the electrode becomes a **sodium ion electrode**.

- The error is negligible at pH less than about 9; but at pH values above this, the H^+ concentration is very small relative to that of other ions,
- So, the electrode response to the other ions such as Na^+ , K^+ , and so on, becomes appreciable.
- In effect, the electrode appears to “see” more hydrogen ions than are present, and the pH reading is too low.
- By a change in the composition of the glass, the affinity of the glass for sodium ion can be reduced. If the Na_2O in the glass membrane is largely replaced by Li_2O ,
- This is the so-called lithium glass electrode, high-pH electrode, or full-range electrode (0 to 14 pH range).

- **Acidic Error** : At very low pH values ($\text{pH} < 1$), *the gel layer of the pH-sensitive glass membrane* absorbs acid molecules.
- This absorption decreases the activity of hydrogen ions and results in a lower potential at the outer membrane phase boundary.
- The pH measurement therefore shows a higher pH value than the actual pH value of the sample solution.
- This phenomena is called **Acidic Error**.
- This kind of error occurs when high concentration of dissolved salt in aqueous solution
- By addition of nonaqueous solvent such as ethanol.
- Acid error, in general, is smaller than alkaline error.

Crystalline solid-state ion-selective electrode

- **Solid-state ion-selective electrode:** An ion-selective electrode based on a sparingly soluble inorganic crystalline material.
- Polycrystalline ion-selective electrodes are made by forming a thin pellet of Ag_2S , or a mixture of Ag_2S and either a second silver salt (AgCl , AgBr , AgI) or another metal sulfide (CdS , CuS , PbS).
- The pellet, which is 1–2 mm in thickness, is sealed into the end of a nonconducting plastic cylinder, and an internal solution containing the analyte and a reference electrode are placed in the cylinder.
- Charge is carried across the membrane by Ag^+ ions.

- The membrane potential for a Ag_2S pellet develops as the result of a difference in the equilibrium position of the solubility reaction



- When used to monitor the concentration of Ag^+ ions, the cell potential is

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

- The membrane also responds to the concentration of S^{2-} , with the cell potential given as

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

- Thus, pellets made from a mixture of Ag_2S and AgX can serve as a X^- ion-selective electrode, with a cell potential of

$$E_{\text{cell}} = K - 0.0591 \log [\text{X}^-]$$

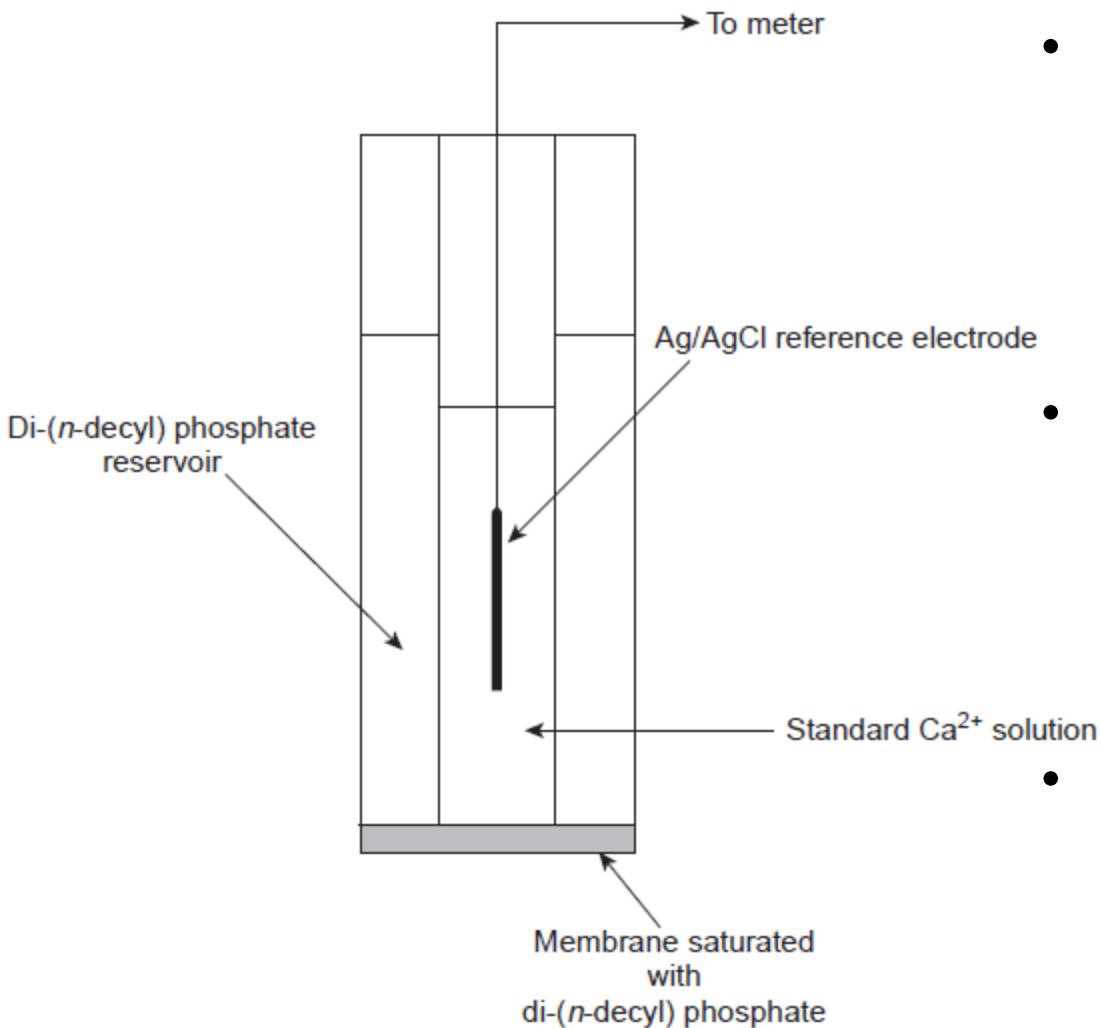
Where, $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{F}^-$ ions.

- Membranes fashioned from a mixture of Ag_2S with CdS , CuS , or PbS are used to make ion-selective electrodes that respond to the concentration of Cd^{2+} , Cu^{2+} , or Pb^{2+} . In this case the cell potential is

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

liquid-based ion-selective electrode

- **liquid-based ion-selective electrode** : An ion-selective electrode in which a chelating agent (liquid) is incorporated into a hydrophobic membrane.
- Three types of organic liquids have been used: cation exchangers, anion exchangers, and neutral **ionophores**.
- **Ionophore**: A neutral ligand whose exterior is hydrophobic and whose interior is hydrophilic. Eg. di-(*n-decyl*) *phosphate*, Valinomycin, Nonactin and monactin, tetradodecyl ammonium nitrate.
- These ionophores are supported by PVC while making membrane.
- One example of a **liquid-based ion-selective electrode** is that for **Ca²⁺**, which uses a porous plastic membrane saturated with di-(*n-decyl*) *phosphate*



- As shown in Figure, the membrane is placed at the end of a nonconducting cylindrical tube and is in contact with two reservoirs.
- The outer reservoir contains di-(*n*-decyl) phosphate in di-*n*-octylphenylphosphonate, which soaks into the porous membrane.
- The inner reservoir contains a standard aqueous solution of Ca²⁺ and a Ag/AgCl reference electrode.

Calcium ion-selective electrodes are also available in which the di-(*n*-decyl) phosphate is immobilized in a polyvinyl chloride (PVC) membrane, eliminating the need for a reservoir containing di-(*n*-decyl) phosphate.

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

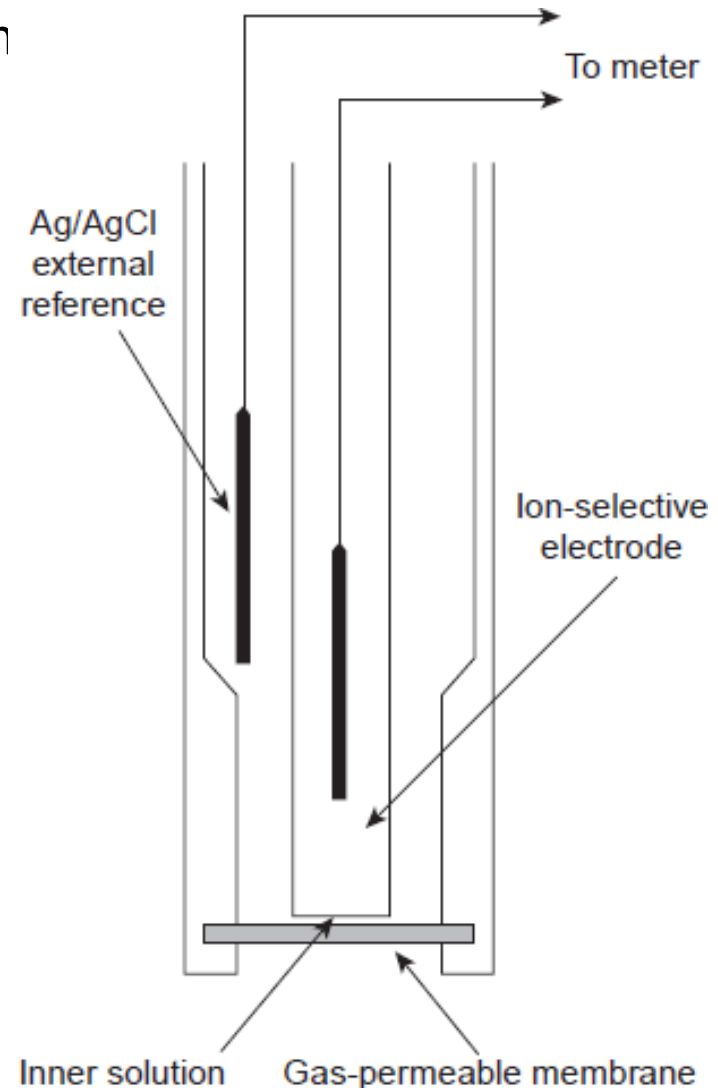


- on the two sides of the membrane, where *(m)* indicates that the species is present in the membrane. The cell potential for the Ca^{2+} ion-selective electrode is

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

Gas-Sensing Electrodes

- A number of membrane electrodes have been developed that respond to the concentration of dissolved gases.
- The basic design of these electrodes is shown in Figure
- It consists of a thin membrane separating the sample from an inner solution containing an ion-selective electrode.
- The membrane is permeable to the gaseous analyte, but is not permeable to nonvolatile components in the sample matrix.
- Once the gaseous analyte passes through the membrane, it reacts in the inner solution, producing a species whose concentration can be monitored by an appropriate ion-selective electrode.



- For example, in the CO₂ electrode, CO₂ reacts in the inner solution to produce H₃O⁺.



- The change in the concentration of H₃O⁺ is monitored with a pH ion-selective electrode, for which the cell potential is given by equation

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

- The relationship between the concentration of H₃O⁺ and CO₂ is given by rearranging the equilibrium constant expression for reaction.

$$[\text{H}_3\text{O}^+] = K \frac{[\text{CO}_2]}{[\text{HCO}_3^-]}$$

- where K is the equilibrium constant. If the amount of HCO₃⁻ in the internal solution is sufficiently large, then its concentration is unaffected by the presence of CO₂ and remains constant.

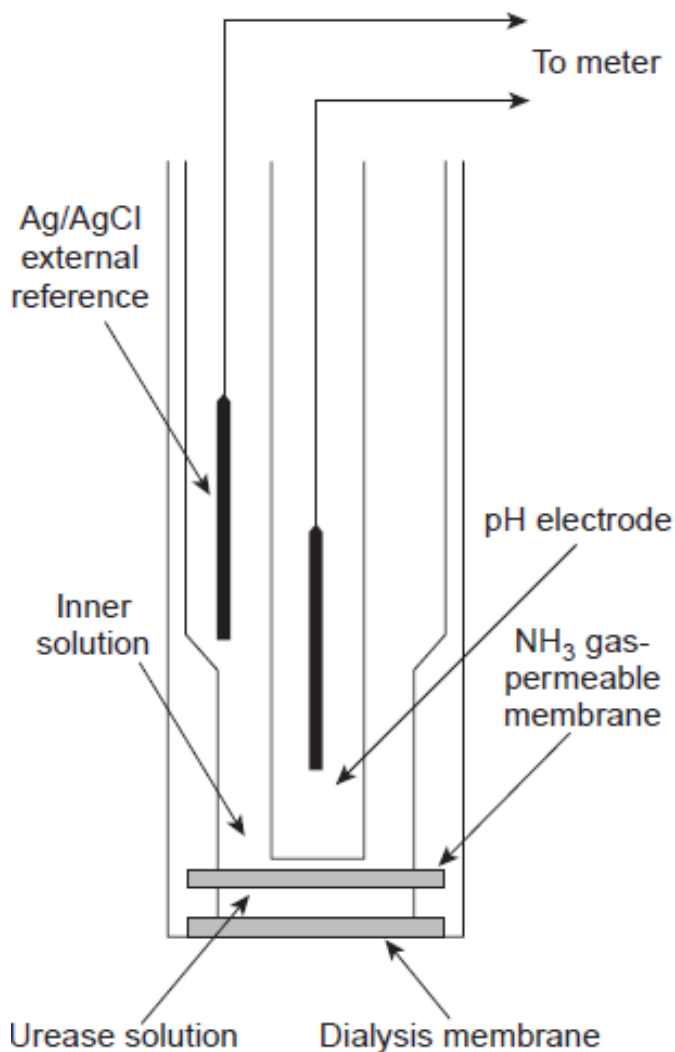
$$E_{\text{cell}} = K' + 0.05916 \log [\text{CO}_2]$$

- where K'' is a constant that includes the constant for the pH ion-selective electrode, the equilibrium constant for reaction and the concentration of HCO_3^- .
- To analyse other gas, the composition of the inner solution changes with use, and both it and the membrane must be replaced periodically according to analyte gas.
- Gas-sensing electrodes are stored in a solution similar to the internal solution to minimize their exposure to atmospheric gases.

Enzyme electrodes/ Potentiometric Biosensors

- **Enzyme electrodes** : An electrode that responds to the concentration of a substrate by reacting it with an immobilized enzyme, producing an ion that can be monitored with an ion-selective electrode.
- In this electrode an enzyme is trapped or immobilized at the surface of an ion-selective electrode. Reaction of the analyte with the enzyme produces a product whose concentration is monitored by the ion-selective electrode.
- One example of an enzyme electrode is the urea electrode, which is based on the catalytic hydrolysis of urea by urease





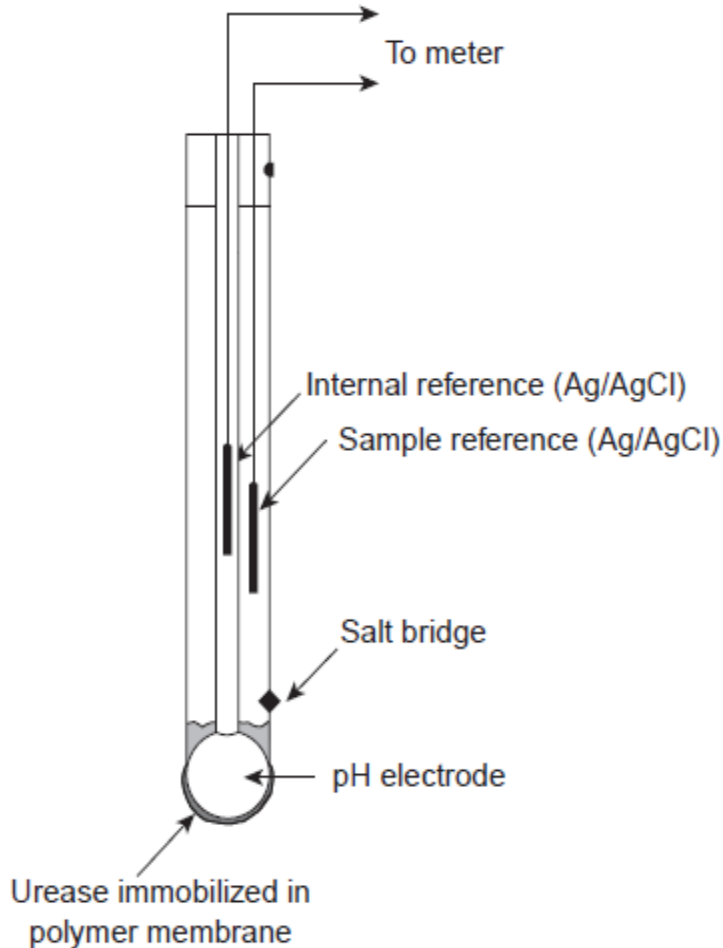
- NH₃ electrode is modified by adding a dialysis membrane that physically traps a pH 7.0 buffered solution of urease between the dialysis membrane and the gas-permeable membrane.
- The NH₄⁺ that is produced is in equilibrium with NH₃



- The produces NH₃ diffuses through the gas-permeable membrane, where it is detected by a pH electrode.

- The response of the electrode to the concentration of urea is given by

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



Another version of the urea electrode immobilizes the enzyme in a polymer membrane formed directly on the tip of a glass pH electrode. In this case, the electrode's response is

$$\text{pH} = K [\text{urea}]$$

Few potentiometric biosensors are commercially available for biologically active species, including antibodies, bacterial particles, tissue, and hormone receptors.