

Unit II : Instrumental Methods of Analysis

- **Content:**
- **Introduction:** Types of reference electrode(calomel electrode), indicator electrode (glass electrode), ion selective electrode: ion selective membranes such as solid membrane, enzyme based membrane and gas sensing membrane.
- **Conductometry:** Introduction, conductivity cell, conductometric titrations of acid versus base with titration curve.
- **pH metry:** Introduction, standardization of pH meter, pH metric titration of strong acid versus strong base with titration curve.

Lecture Plan

Lecture No.	Topics to be covered
1	Introduction, Types of reference electrode(calomel electrode)
2	indicator electrode (glass electrode), ion selective electrode: ion selective membranes such as solid membrane
3	enzyme based membrane and gas sensing membrane, Conductometry: Introduction, important terms with units
4	conductivity cell, conductometric titrations of acid versus base with titration curve (SA/SB, SA/WB)
5	conductometric titrations of acid versus base with titration curve (WA/SB, WA/WB)
6	pH metry: Introduction, Buffer solution, types, standardization of pH meter
7	pH metric titration of strong acid versus strong base with titration curve
8	Revision

➤ **Teaching Hours:** 08 Hours

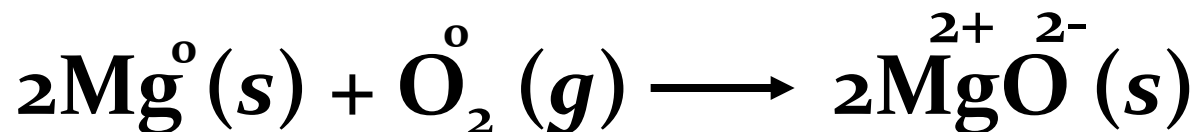
➤ **Weightage in Insem Exam (ISE):** 15 Marks

Questi on No.	Marks		Questi on No.	Marks
Q. 1 a	5	OR	Q. 2 a	5
Q. 1 b	4		Q. 2 b	4
Q. 1 c	3		Q. 2 c	3
Q. 1 d	3		Q. 2 d	3

- **Electroanalytical methods** are techniques that involve analysis of material (analyte) contained in an electrochemical cell by measuring the potential or current.
- **Electrochemistry:**
- Is the branch of chemistry that deals with the chemical changes produced by electricity and the production of electricity by chemical changes.

Electrochemical processes are oxidation-reduction reactions in which:

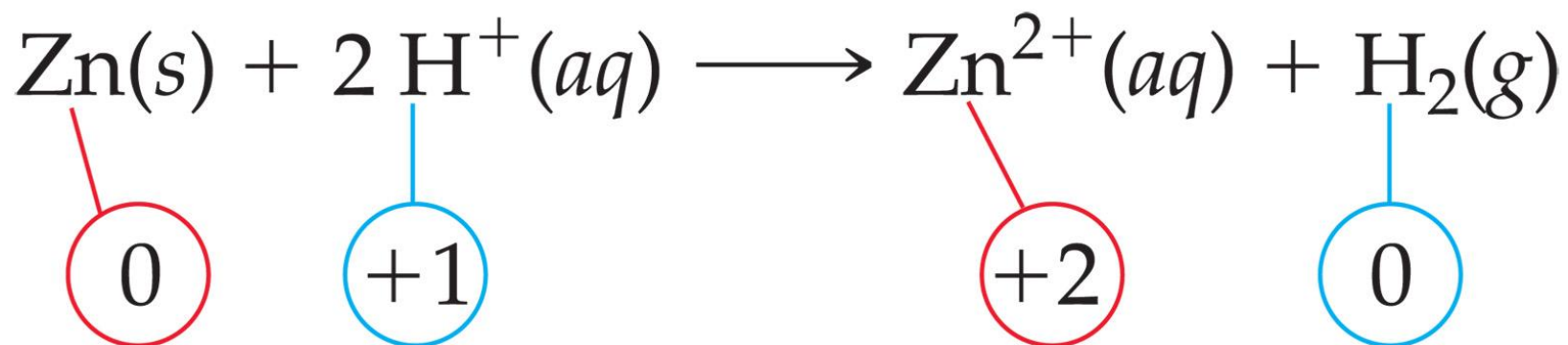
- the energy released by a spontaneous reaction is converted to electricity or
- electrical energy is used to cause a non-spontaneous reaction to occur



Oxidation-reduction

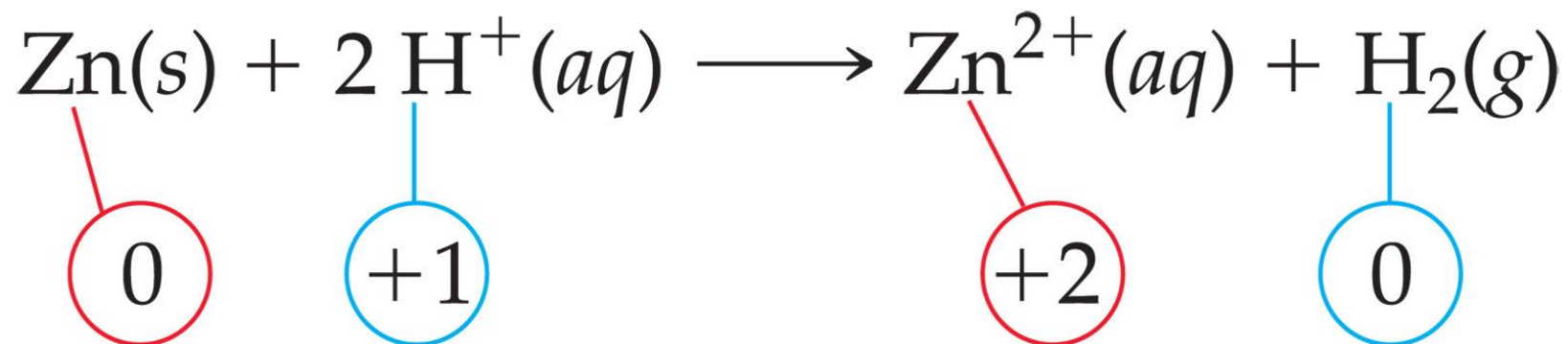
- Oxidation is loss of e^-
- O.N. increases (more positive)
- Reduction is gain of e^-
- O.N. decreases (more negative)
- Oxidation involves loss OIL
- Reduction involves gain RIG

Oxidation and Reduction



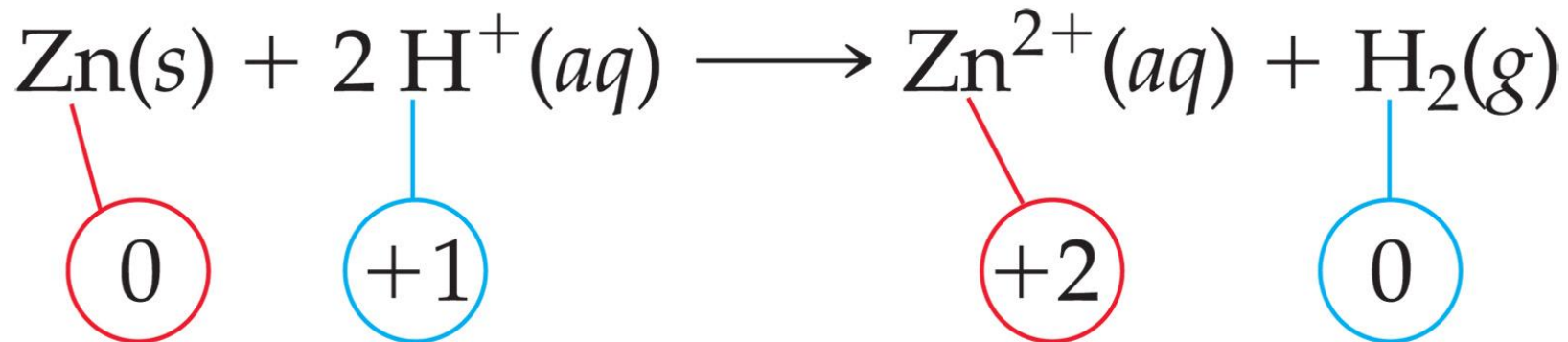
- A species is **oxidized** when it loses electrons.
 - Here, zinc loses two electrons to go from neutral zinc metal to the Zn^{2+} ion.

Oxidation and Reduction



- A species is **reduced** when it gains electrons.
 - Here, each of the H^+ gains an electron and they combine to form H_2 .

Oxidation and Reduction



- What is reduced is the **oxidizing agent**.
 - H^+ oxidizes Zn by taking electrons from it.
- What is oxidized is the **reducing agent**.
 - Zn reduces H^+ by giving it electrons.

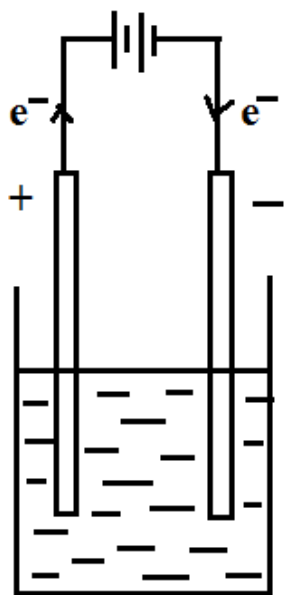
Cell

An **electrochemical cell** is a device capable of either deriving electrical energy from chemical reaction, or facilitating chemical reactions through the introduction of electrical energy.

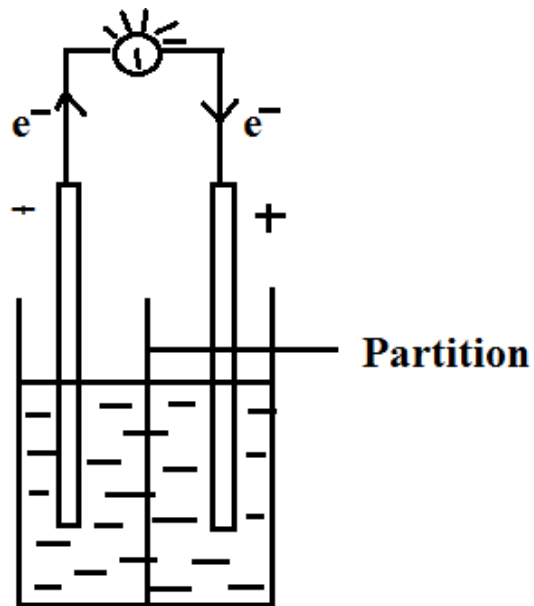
- A Cell consists of two electrodes (anode and cathode) in contact with an aqueous conducting medium.
- Half Cell : An electrode in contact with aqueous conducting medium is known a half cell.

Types of cells

- **Voltaic (galvanic) cells:**
 - a spontaneous reaction generates electrical energy
 - $\text{C. E.} \longrightarrow \text{E. E.}$
- **Electrolytic cells:**
 - absorb free energy from an electrical source to drive a non spontaneous reaction
 - $\text{E. E.} \longrightarrow \text{C. E.}$



Anode Cathode
Electrolytic Cell



Anode Cathode
Galvanic Cell

	Electrolytic Cell		Galvanic / Voltaic Cell	
	Anode	Cathode	Anode	Cathode
Sign	+	-	-	+
Electron Flow	Out	In	out	in
Half Reaction	Oxidation	Reduction	Oxidation	Reduction

Common Components

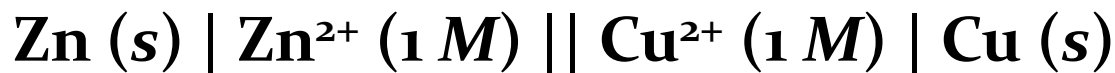
- **Electrodes:** conduct electricity between cell and surroundings
 - **Anode:** Oxidation occurs at the anode
 - **Cathode:** Reduction occurs at the cathode
- **Electrolyte:** mixture of ions involved in reaction or carrying charge
- **Salt bridge:** completes circuit (provides charge balance)

Galvanic Cells

The difference in electrical potential between the anode and cathode is called:

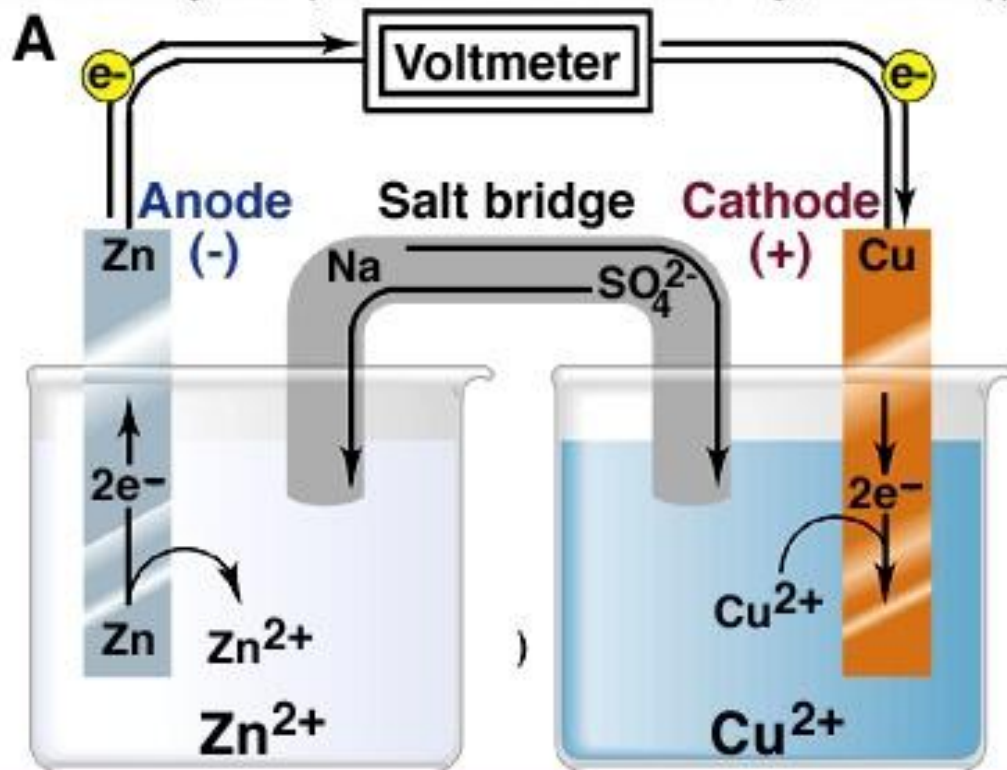
- *cell voltage/ electromotive force (emf)/ cell potential*

Cell setup

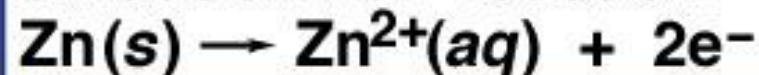


anode

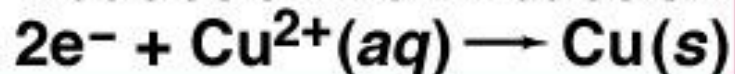
cathode



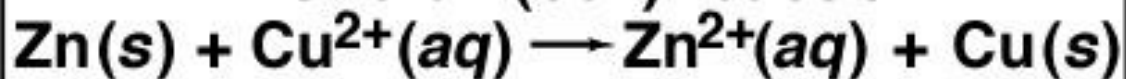
Oxidation half-reaction



Reduction half-reaction

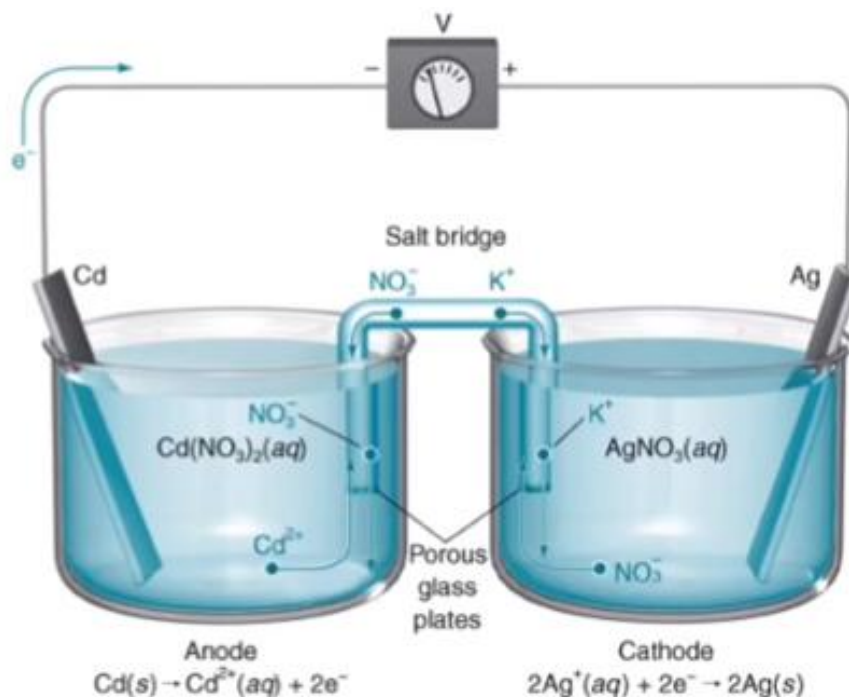


Overall (cell) reaction



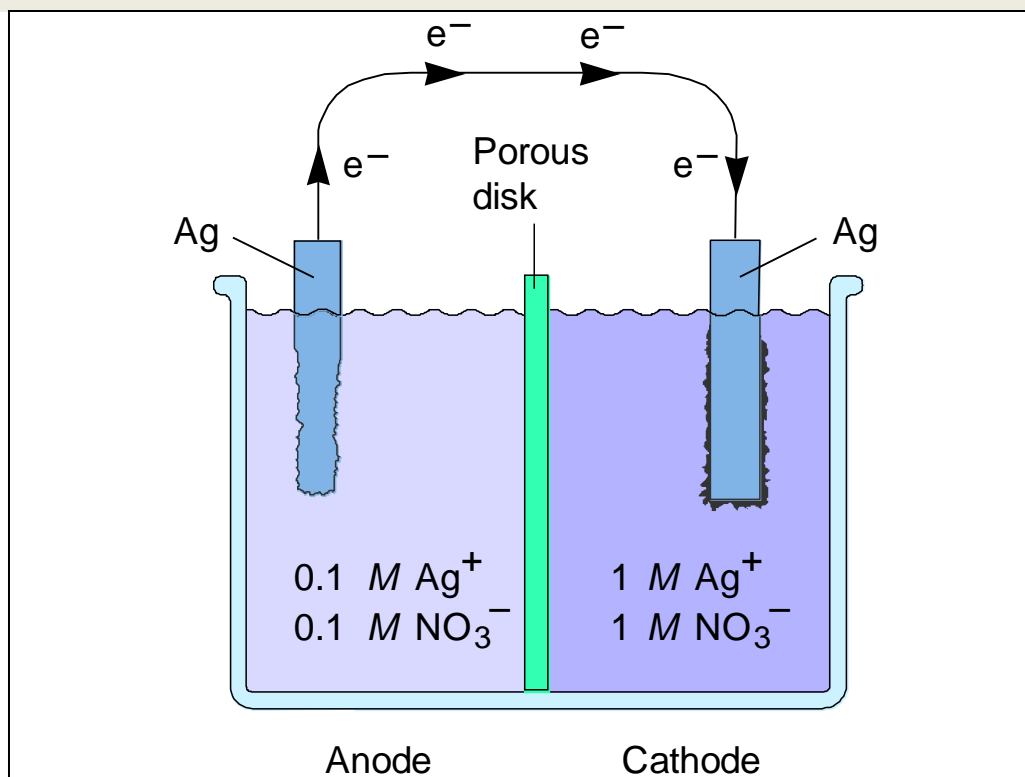
**Zinc-Copper
Reaction
Voltaic Cell**

- A *galvanic cell* (or *voltaic cell*) uses a spontaneous chemical reaction to generate electricity.
- The net reaction is composed of oxidation and reduction *half reactions*.
- Reduction occurs at the *cathode*.
- Oxidation occurs at the *anode*.



Concentration Cells

- A concentration cell is a cell where the two half cells are comprised of the same materials but differ in concentration.



- Representation of an electrochemical cell:

- 1) Anode (-ve electrode) is written on left hand side and cathode (+ve electrode) is written on right hand side.
- 2) Single vertical line (|) or semicolon (;) indicates direct contact between two phases



The molar concentration is written in brackets after the formula of ion



- 3) Double standing line represents salt bridge to connect two half cells.

4) Cell representation : $\text{Zn (s)} + \text{Cu}^{2+} (\text{aq}) \longrightarrow \text{Cu (s)} + \text{Zn}^{2+} (\text{aq})$



Electrode potential:

- **Electrode potential**, E , in chemistry or electrochemistry, according to a IUPSC definition, is the electromotive force of a cell built of two electrodes:
- on the left-hand side of the cell diagram is the standard hydrogen electrode (SHE), and
- on the right-hand side is the electrode in question.
- The SHE is defined to have a potential of zero Volt, so the signed cell potential from the above setup is
- $E_{\text{cell}} = E_{\text{left (SHE)}} - E_{\text{right}} = 0 \text{ V} - E_{\text{electrode}} = E_{\text{electrode}}$
- .SHE is cathode and electrode is anode
- $\Delta V_{\text{cell}} = E_{\text{red,cathode}} - E_{\text{red,anode}}$
- or, equivalently,
- $\Delta V_{\text{cell}} = E_{\text{red,cathode}} + E_{\text{oxy,anode}}$.

- **Reference electrode:**

Reference electrode is defined as the electrode which has **stable and reproducible potential** and completes the cell acting as half cell.

Purpose of reference electrode

1. to complete the cell
2. provide stable potential
3. returns to its original potential after being subjected to small currents

Types of Reference Electrodes

- 1) Standard hydrogen Electrode
- 2) Saturated Calomel Electrode

- Difficulties in use of Standard Hydrogen Electrode

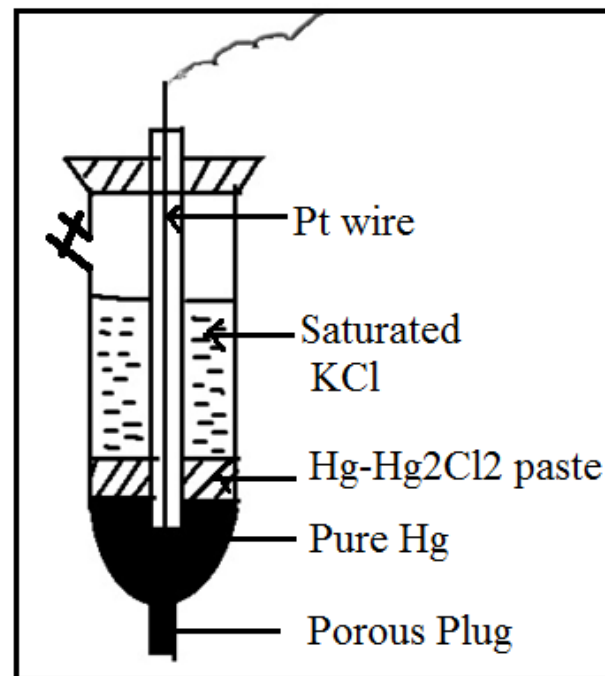
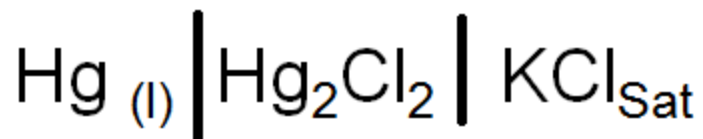
- 1) Platinum used in it get contaminated by impurities in solution and gases. Creates difficulty in attending equilibrium.
- 2) The presence of oxidising agents, unsaturated organic compounds etc in solution displaces the equilibrium and alters the potential.
- 3) It cannot be used frequently in presence of reducible ions or substances having +ve electrode potential such as Cu, Ag, Au etc.

Calomel Electrode

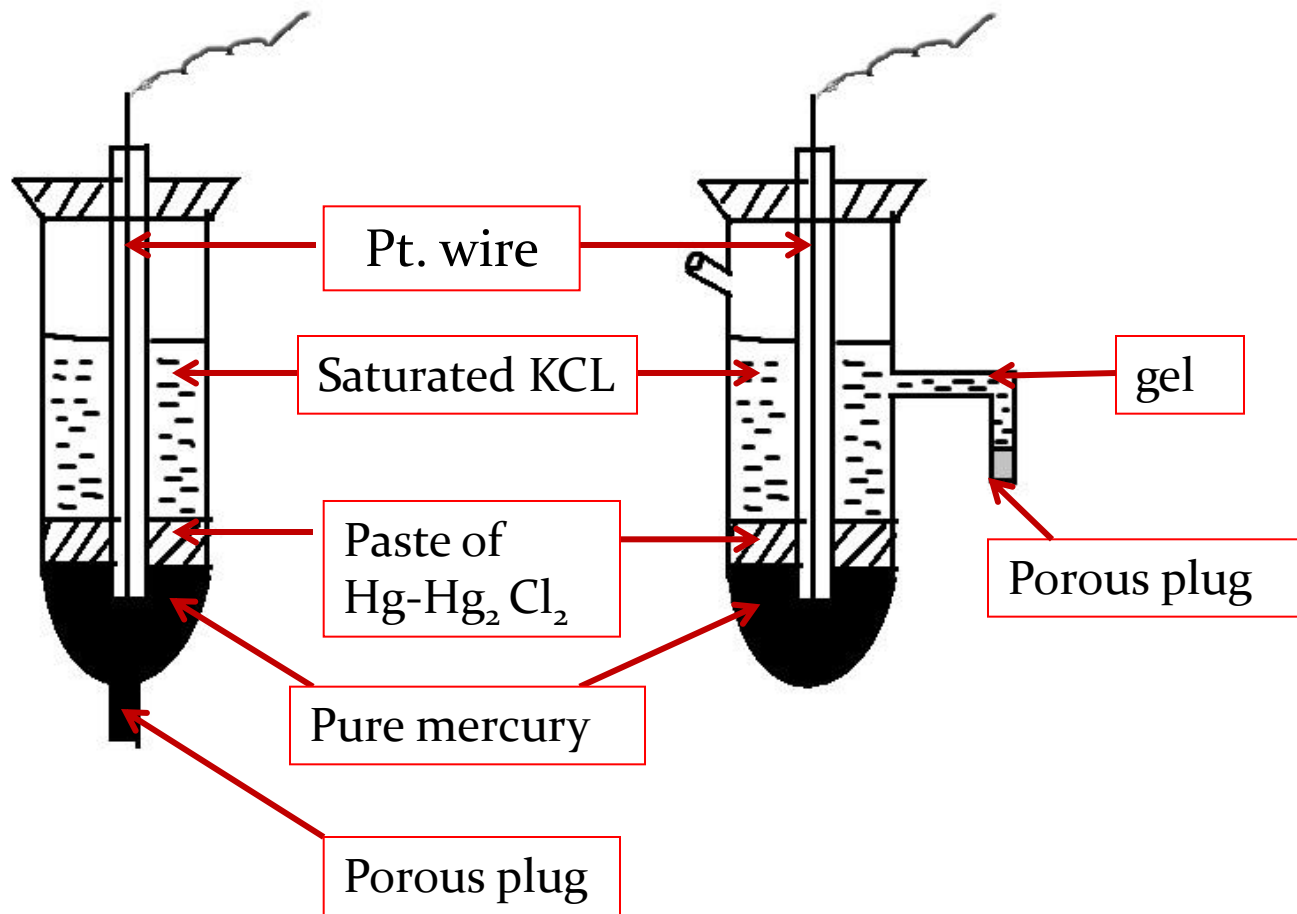
- **Construction :**

- Calomel electrode consist of narrow glass tube at the bottom of which pure Hg is placed, above this there is a paste of Hg-Hg₂Cl₂. A remaining portion of glass tube is filled with saturated KCl solution.
- Platinum wire is dipped in pure Hg to make electrical contact.
- In a direct dipping type of calomel electrode there is a porous plug at the bottom .

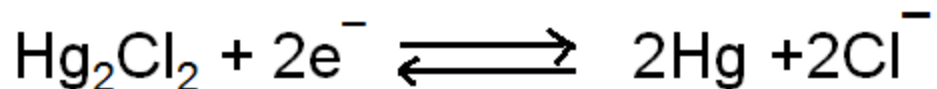
Electrode representation



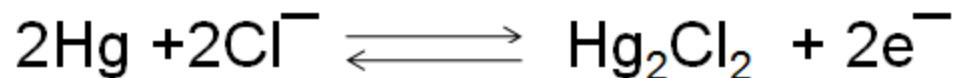
Calomel Electrode



- If calomel acts as cathode



- If calomel acts as anode



- The reduction electrode potential is given by equation $E_{\text{cal}} = E^\circ - 0.0591 \log [\text{Cl}^-]$

- Potential of calomel electrode dependant on concentration of KCL

Concentration of KCl	E ° calomel	Name
0.1 N	0.3334 volts	Desi normal calomel
1.0 N	0.2810 volts	Normal calomel
Saturated	0.2422 volts	Saturated calomel

- **Demerits of Calomel Electrode**

1. can not be use above 50°C as Hg_2Cl_2 starts decomposing
2. involves handling of poisonous Hg and Hg_2Cl_2

Advantages :

1. less prone to contamination as $\text{Hg} \mid \text{Hg}_2\text{Cl}_2$ interface is protected inside a tube and is not in direct contact with electrolyte.
2. Reproducibility of Calomel electrode is much better than $\text{Ag} \mid \text{AgCl}$

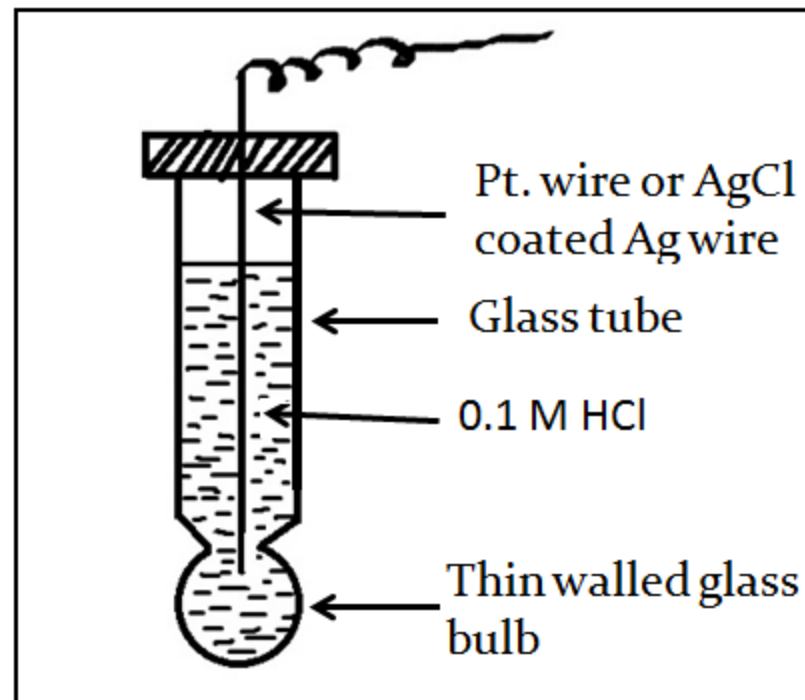
Calomel – mineral rarely found in nature . Mercurous (I) chloride, Hg_2Cl_2 .

Indicator Electrode-Glass Electrode

- **Indicator Electrode** – is the electrode of a cell in which the potential depends on the concentration of a particular ion .

Principle of Glass Electrode:

When two solution of different H^+ ions concentrations, are separated by a thin walled glass membrane, a potential difference developed is proportional to the difference in H^+ ion concentration of the two solutions.



- The glass electrode consists of a very thin walled glass bulb, made from a low melting glass having high electrical conductivity.
- Electrode is filled with 0.1M HCl solution.
- For external connection platinum (Pt) wire is insert.
- Cell set up of glass electrode



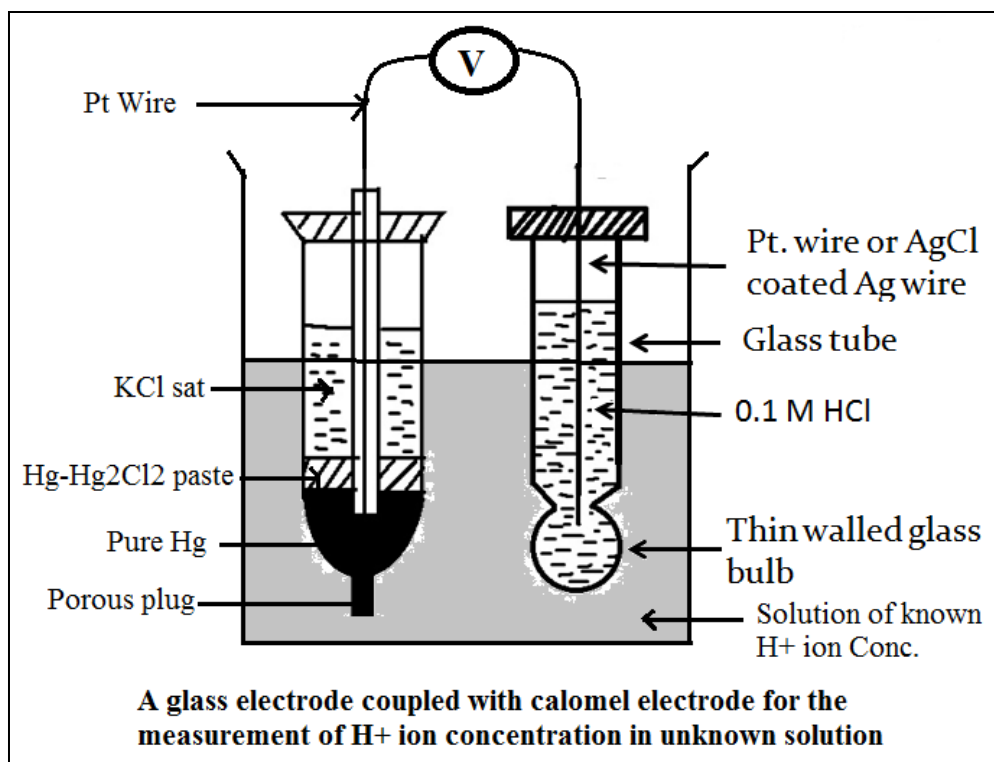
- The glass membrane acts as an ion exchanger i.e. exchange of Na^+ of glass with H^+ of solution.



$$E_G = E^\circ_G + 0.0591 \text{ pH}$$

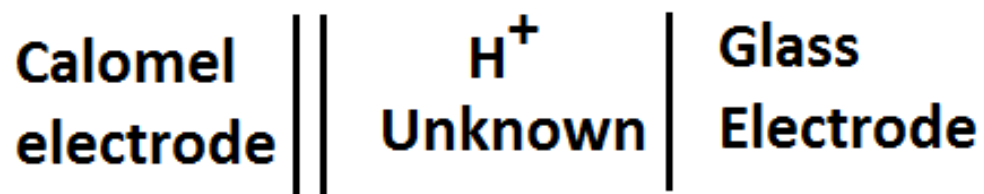
- Glass electrode require soaking of water for some hours before use so that –
- surface becomes active,
- hydrated layer developed on outer glass surface
- Ion exchange can take place easily.

- When glass electrode is placed in a sample solution containing unknown H^+ ion concentration, the potential development across the glass membrane as a result of a concentration difference of H^+ ions on both side of membrane.
- Potential is determine by using saturated calomel electrode.



Determination of pH of Solution

- A glass electrode is couple with the calomel electrode to determine the pH of the solution



$$E_{\text{cell}} = E_{\text{cal}} - E_{\text{G}}$$

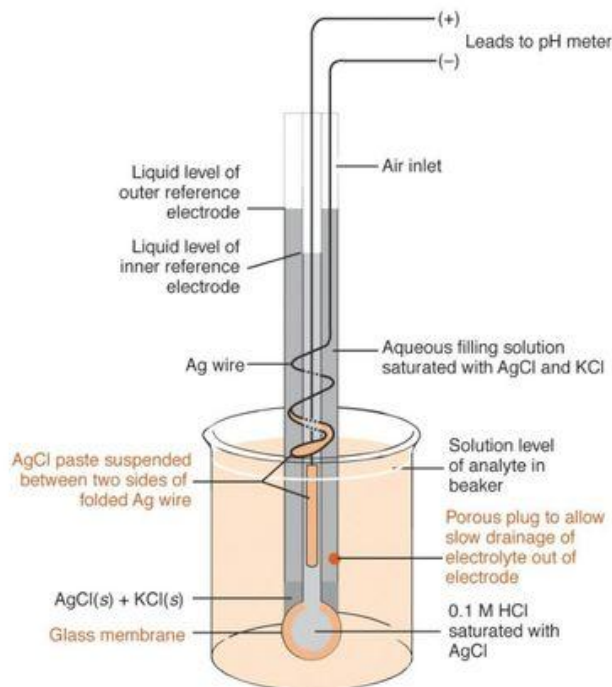
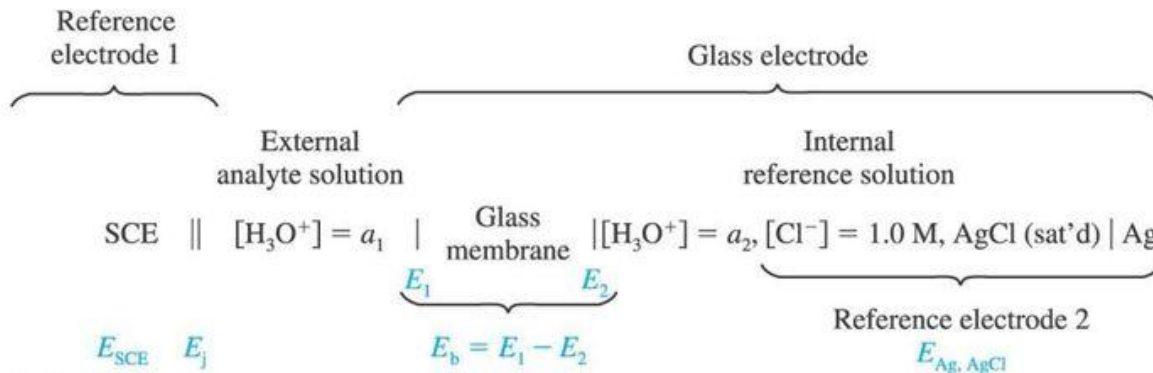
$$E_{\text{cell}} = 0.2422 - (E_{\text{G}}^0 + 0.0591\text{pH})$$

$$\text{pH} = \frac{0.2422 - E_{\text{cell}} - E_{\text{G}}^0}{0.0591}$$

- **Advantages of Glass Electrode**

1. It is stable electrode and can be used in presence of strong oxidizing and strong reducing agents.
2. It is compact and portable.
3. It can be used in presence of biological fluids/ proteins.
4. It attained equilibrium quickly.
5. It can detect and estimate H^+ ion in presence of other ions.

pH meter : A glass combination electrode



$$E = K - b (0.05916) \log (A_{in} / A_{out})$$

K : Asymmetry potential

b : electromotive efficiency (close to 1.00)

A : Activity of hydrogen ion

Ion-Selective Electrode (ISE)

- A membrane of a half cell is sensitive to particular ion in solution and ion exchange takes place between the membrane and the solution containing specific ions and develops a potential which depends upon the concentration of that ion.
- The potential develop at the ion sensitive sensor is a measure of concentration of the ions of interest.
- An **ion-selective electrode (ISE)**, also known as a specific **ion electrode (SIE)**, is a transducer (or sensor) that converts the activity of a specific **ion** dissolved in a solution into an electrical potential.

e.g. H^+ sensor (glass electrode) ;

Ca^{++} (sensor Calcium ISE)

- It is also called *chemical sensors*.

Ion selective electrode detect and measure the concentration of ion in the solution.

Advantages of Ion selective electrodes

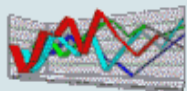
- 1) Relatively inexpensive and simple to use
- 2) Durable in field and laboratory environment.
- 3) Can be use for coloured and turbid samples.
- 4) Can be use over wide range of temperature.
- 5) Mechanically strong.
- 6) Show resistant to solvent and chemical attack.

ISEs widely used for chemical, environmental, clinical, pharmaceutical food analysis.

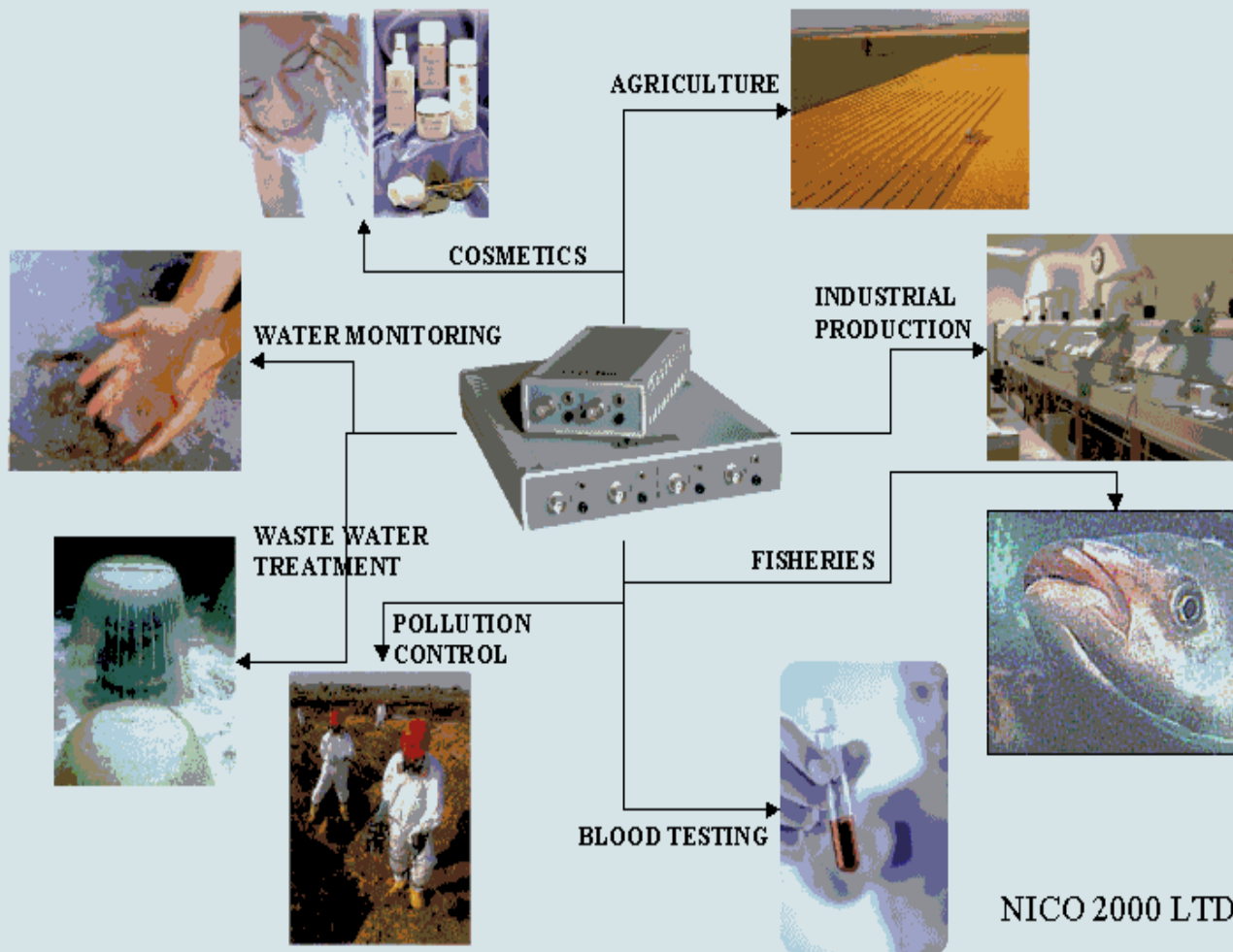
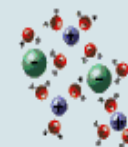
Based on type of membrane, Ion – selective electrodes can be classified into various types

- 1) Glass membrane electrode
- 2) Solid – State membrane Electrode
- 3) Enzyme based membrane / Biochemical electrode
- 4) Gas Sensing electrode
- 5) Liquid-liquid membrane electrode

- 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, fertilizers 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 and beer.
- K in fruit juices and wine making.
- 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 and recovery-cycle liquors.
- 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.



A Multitude of Applications for Ion Analysers



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1. Glass – Membrane electrode

These electrodes are formed by doping molten SiO_2 with various chemicals.

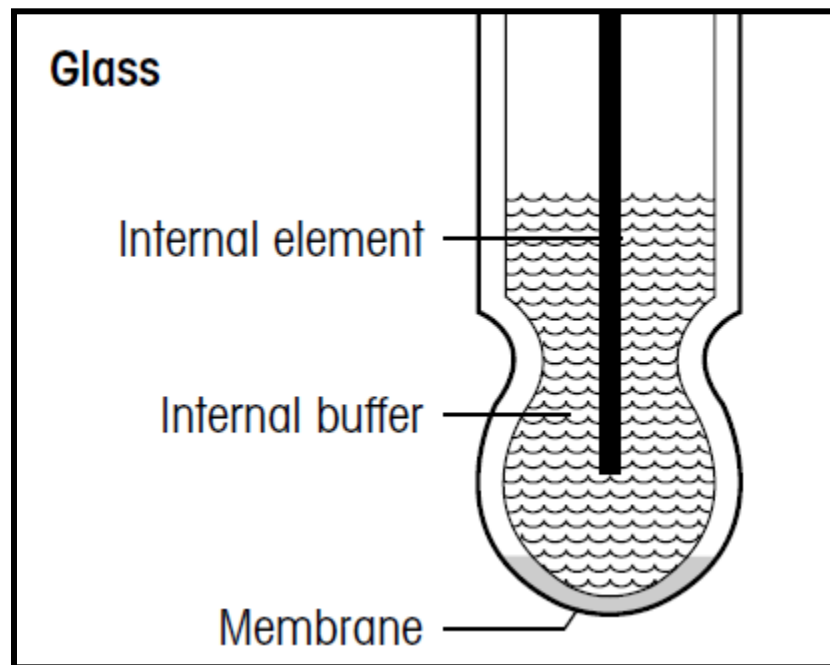
Most common such electrode is H^+ sensitive electrode or pH electrode



Different glass compositions can be made to measure Na^+ , Ag^+ , K^+ , NH_4^+

$$E_G = E^\circ_G + 0.0591 \text{ pH}$$

$$E_G = E^\circ_G - 0.0591 \log [M^{+n}]$$



Membrane indicator electrodes



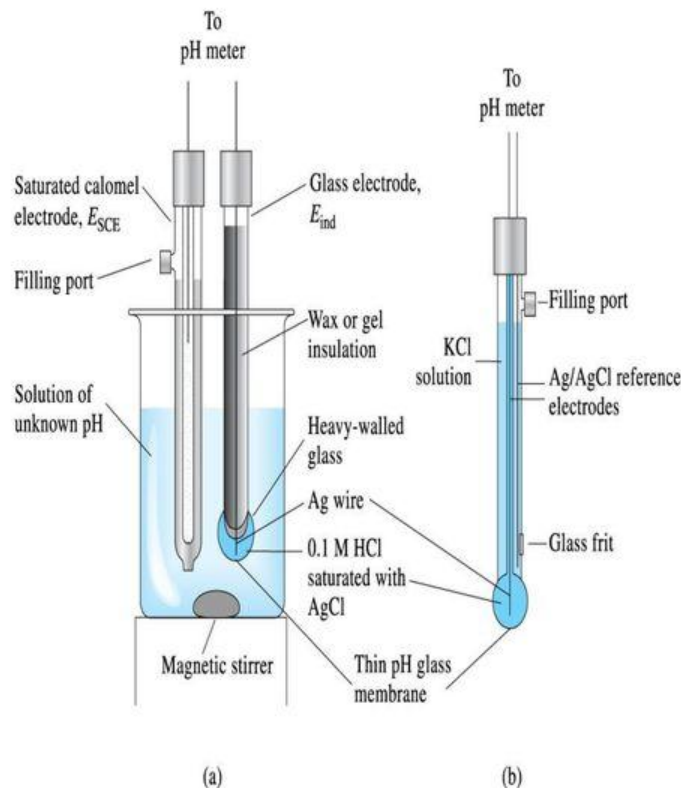
• Glass membrane pH electrodes

The internal element consists of silver-silver chloride electrode immersed in a pH 7 buffer saturated with silver chloride. The thin, ion-selective glass membrane is fused to the bottom of a sturdy, nonresponsive glass tube so that the entire membrane can be submerged during measurements. When placed in a solution containing hydrogen ions, this electrode can be represented by the half-cell :

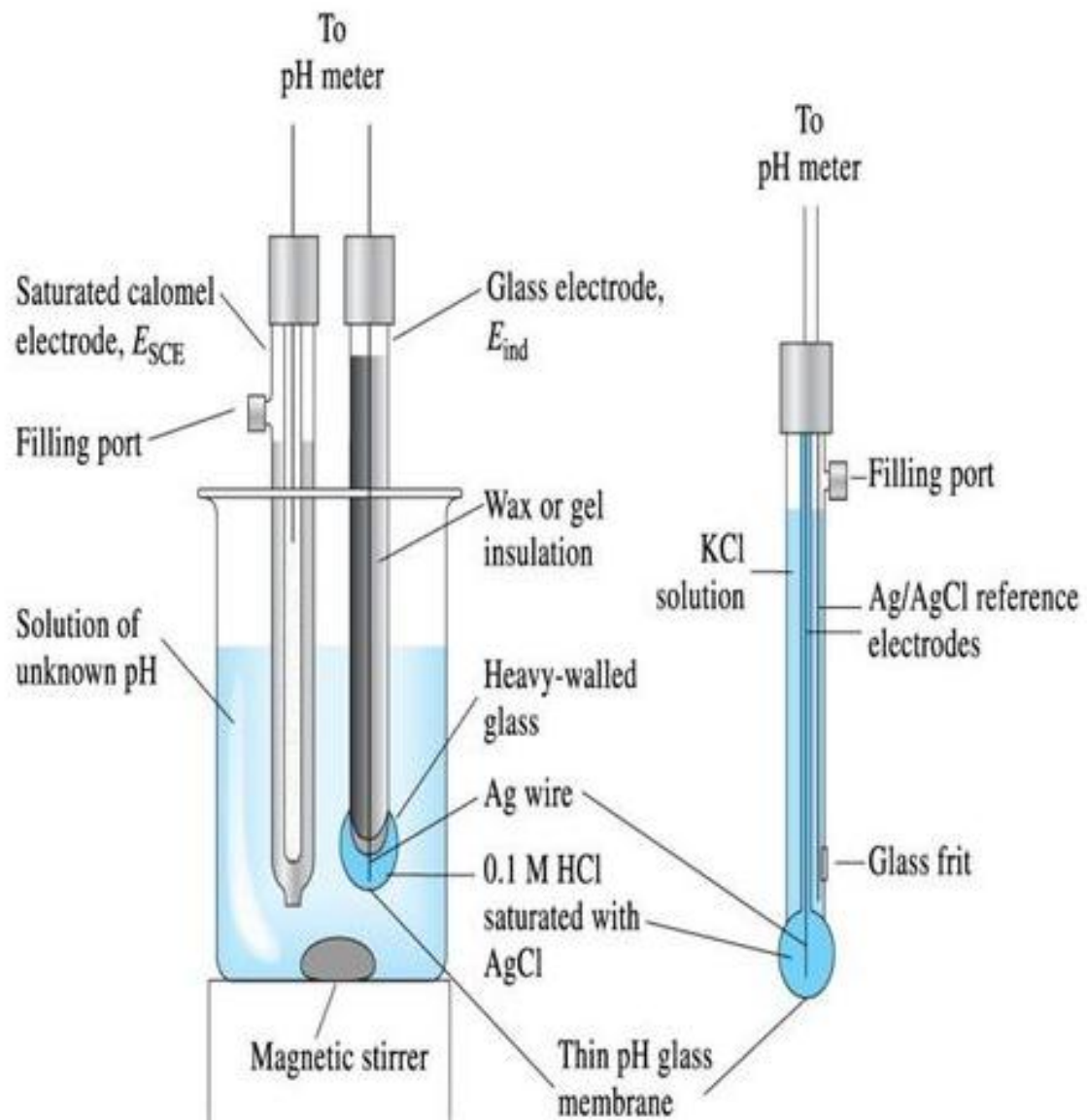
$\text{Ag(s)} \mid \text{AgCl[sat'd]}, \text{Cl}^-(\text{inside}), \text{H}^+(\text{inside}) \mid$
 glass membrane $\mid \text{H}^+(\text{outside})$

$$E = E^\circ - (0.05916/1) \log [\text{Cl}^-] + (0.05916/1) \log ([\text{H}^+(\text{outside})]/[\text{H}^+(\text{inside})])$$

$$E = Q + (0.05916/1) \log [\text{H}^+(\text{outside})]$$

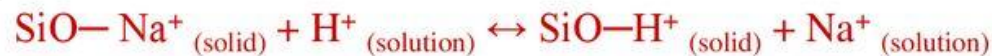


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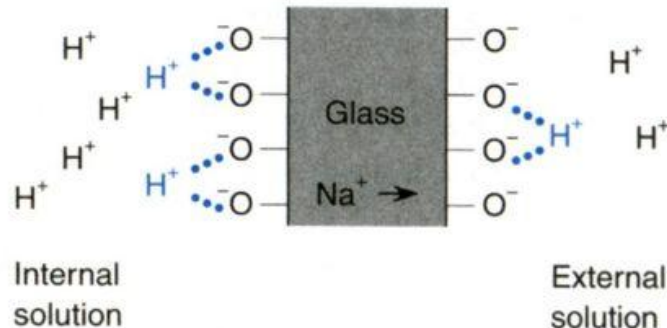


Theory of the glass membrane potential:

The pH electrode functions as a result of ion exchange on the surface of a hydrated layer. The membrane of a pH glass electrode consists of chemically bonded Na₂O and SiO₂. 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:



The protons are free to move and exchange with other ions.



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

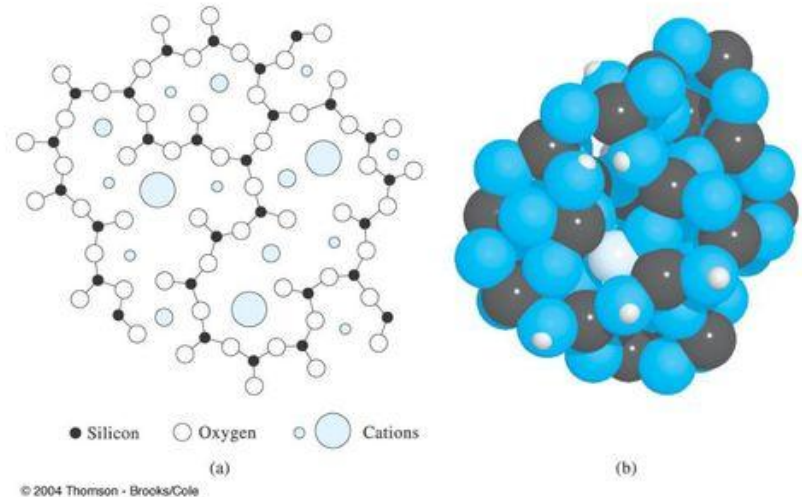
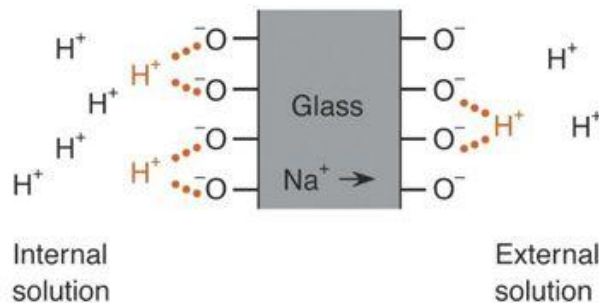
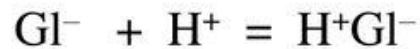
Potential is determined by external [H⁺]

Composition of glass membranes

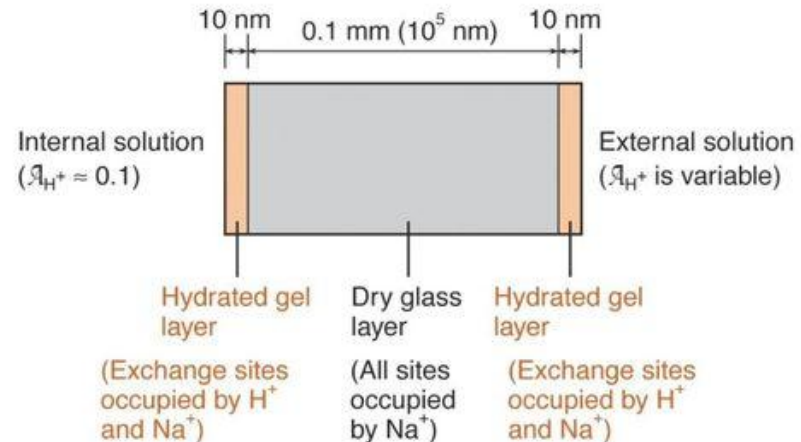
70% SiO_2

30% CaO , BaO , Li_2O , Na_2O ,
and/or Al_2O_3

Ion exchange process at glass membrane-solution interface:



(a) Cross-sectional view of a silicate glass structure. In addition to the three Si | O bonds shown, each silicon is bonded to an additional oxygen atom, either above or below the plane of the paper. (b) Model showing three-dimensional structure of amorphous silica with Na^+ ion (large dark blue) and several H^+ ions small dark blue incorporated.



2. Solid – State Electrode

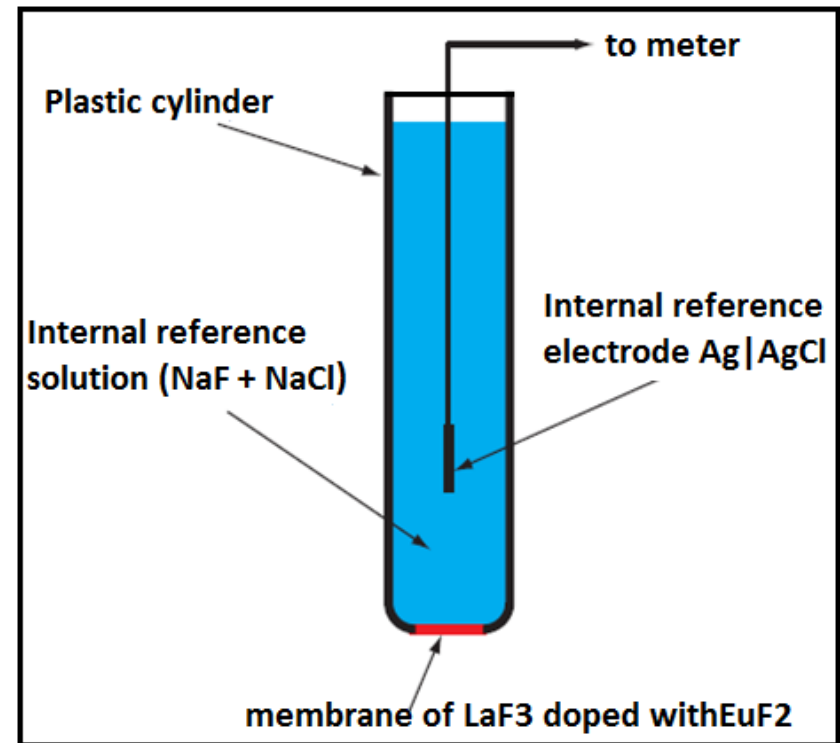
This is based on an inorganic crystal doped with a small amount of ions of a different vacancy to create vacant sites.

Examples 1) Fluoride ISE 2) Chloride ISE

1) Fluoride ISE -For instance, in a F^- ion electrode, a LaF_3 (Lanthanum fluoride) crystal is doped with EuF_2 (Europium fluoride) so that there are anion vacancies for the migration of F^- through the LaF_3 crystal.

Crystal is sealed at the bottom of the polymeric container containing internal reference solution ($NaF + NaCl$ or $KF + KCl$) and consisting of reference electrode

Use for the determination of F^- in water.



Working of Fluoride ion electrode

- EuF_2 produce holes in the crystal lattice of LaF_3 through which F^- ion can pass.
- When the electrode is in contact with the sample solution a potential develops across the membrane which depends on the differences of F^- concentration on either side of the membrane.
- Since the internal F^- ion conc. is fixed, the potential developed across the membrane is related to the F^- ion conc in the sample solution
- $\text{LaF}_3 \leftrightarrow \text{LaF}_2^+ + \text{F}^-$

Fluoride ion electrode: e.g.

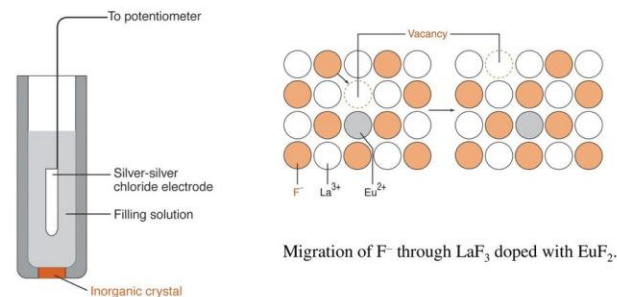
Internal electrode- Ag-AgCl electrode

Filling Solution – ($\text{NaCl} + \text{NaF}$) aqueous

Membrane – LaF_3 doped with EuF_2 crystal disc

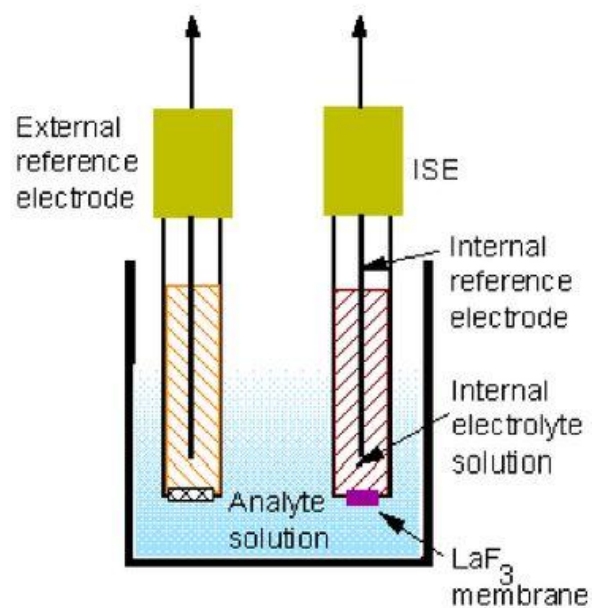
Application : Electroplating industry, water treatment, Toothpaste

Solid state crystalline membrane electrode



Instrumentation

ISEs consist of the ion-selective membrane, an internal reference electrode, an external reference electrode, and a voltmeter. A typical meter is shown in the document on the pH meter. Commercial ISEs often combine the two electrodes into one unit that are then attached to a pH meter.



Schematic of an ISE measurement

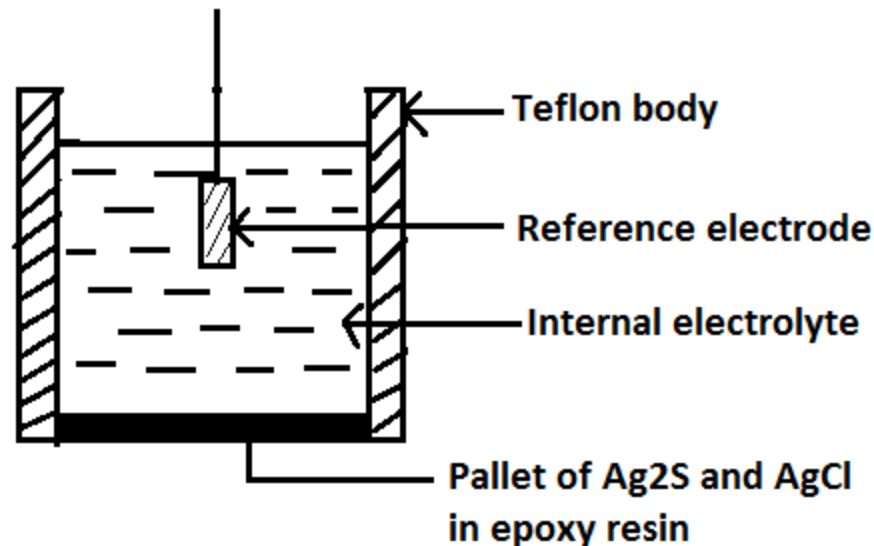


Picture of a commercial fluoride ISE

<http://www.chemistry.adelaide.edu.au/external/Soc-Rel/Content/ise.htm>

2) Chloride ion selective electrode — Solid state electrode

- Electrode is made up of teflon and the Pallet of Ag_2S and AgCl is attached using epoxy resin.
- When electrode membrane is in contact with a solution containing chloride ions, an electrode potential develops. This potential is measured using reference electrode.



2) Enzyme Based membrane electrode:

These electrodes use enzymes to convert substances in the solution into ionic products which are measured using ion selective electrodes. The enzyme is immobilized at the surface of the electrode.

Most common application – food industry

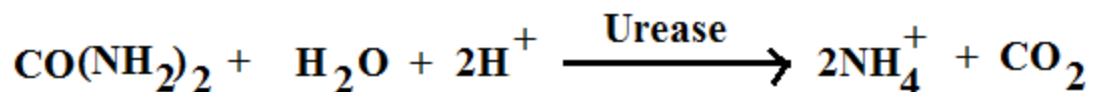
e.g. Enzyme based electrode for determination of urea.

Construction / composition :

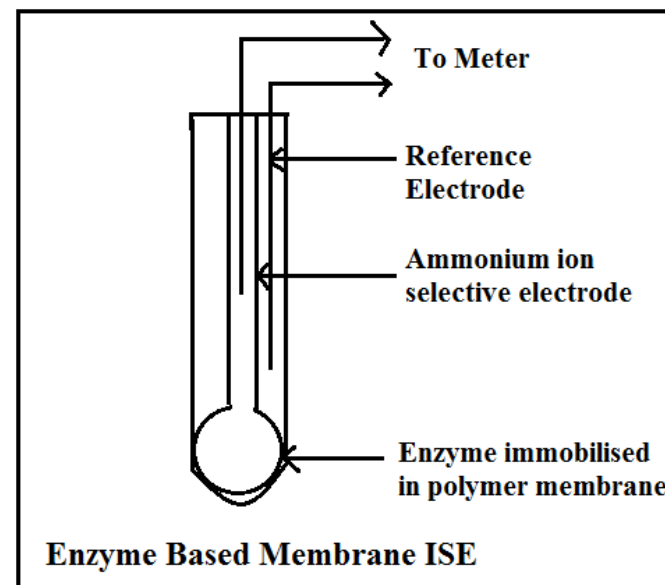
The enzyme **urease** is incorporated into a **polyacrylamide** gel which is allowed to set on the bulb of a glass electrode and is fixed in its position by nylon gauze.

Working:

- When electrode is immersed into a solution containing urea, NH_4^+ ions are produced which diffuse through the gel



- A boundary potential is developed due to difference in conc. of NH_4^+ on either side of the membrane.
- This potential developed is measured using a glass electrode as a reference electrode.



3) Gas-Sensing Membrane Electrode:

These electrode detect the ion into which the gas is converted after it passes through the outer membrane.

These electrodes are useful to analyze gases like NH_3 , NO_2 , SO_2 , CO_2 and H_2S .

A nitrate ion selective electrode is for NO_2 ,

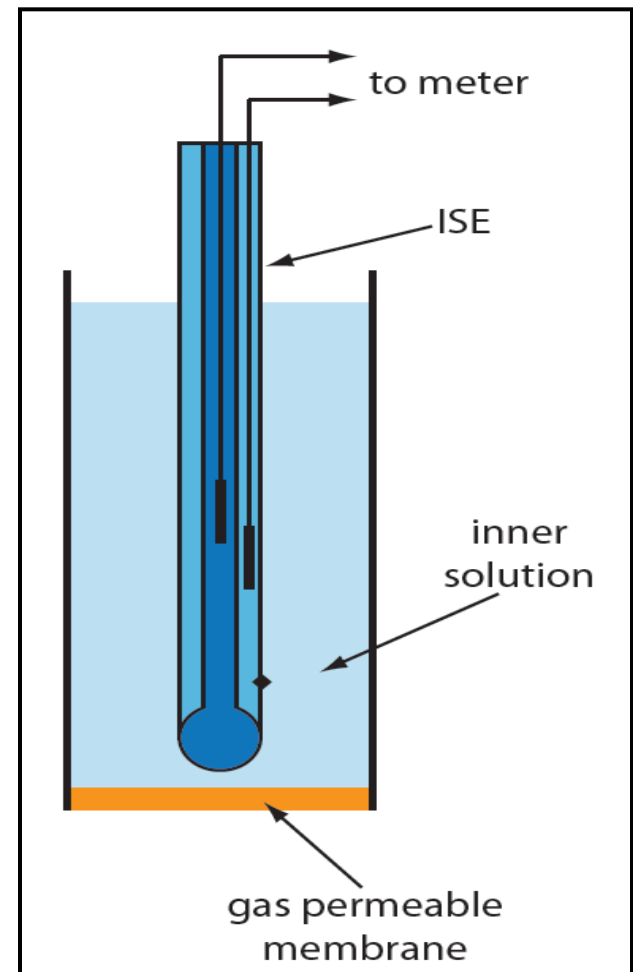
A sulphide ion selective electrode is for H_2S .

The micro porous membrane is hydrophobic, made from **polypropylene** or any other **fluoro-carbon** which allows only dissolve gases to pass through. The electrodes Ag/ AgCl and glass pH electrode are dipped in the inner solution.

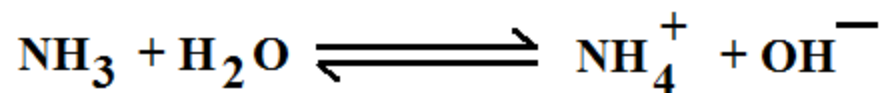
Area of electrode being small and volume of liquid being less, it reaches equilibrium with the test solution rapidly.

Construction and working:

- Monitor gaseous molecules dissolved in the solution
- The electrode does not detect the presence of molecular gas but rather an ion into which the gas is converted after passing through the membrane.
- The gas in the test solution diffuses through the membrane and react with internal filling solution to form the ions these ions are detected using gas sensing electrode.
- Membrane used in gas sensing electrode is hydrophobic gas-permeable porous polymer membrane (silicon rubber/teflon / polypropylene/fluorinated ethylene/ polyvinylidene fluoride) which allows the passage of dissolved gas but prevents the solution to pass through it.



- **Gas sensing membrane electrode for determination of ammonia**
- Hydrophobic Gas-permeable membrane separates sample solution and inner filling solution of ammonium chloride (NH₄Cl).
- When electrode is dipped in sample solution containing dissolved NH₃ (ammonium ions) from the sample solution diffuses through the membrane until the partial pressure of ammonium ions becomes equal on both sides of the membrane. The ammonia which diffuses through membrane dissolves in internal filling solution and react reversibly with water.



- The partial pressure of ammonium ions is directly proportional to its concentration.
- Boundary potential gets developed between the ammonium ion formed inside and outside ion selective electrode.
- Boundary potential formed due to difference in the concentration of ammonium ions is measured with the help of reference electrode.

Gas sensing membrane electrode for determination of ammonia

- Electrodes, including the ammonia ISE, use a gas sensing mode of operation. In the case of ammonia, a caustic solution is added to the sample solution to liberate ammonia. The gas permeates through a membrane and changes the pH of the filling solution. The change in pH is proportional to the ammonia concentration. This gives a quantitative measurement of the ammonia in the sample solution.

Conductometry

- The ability of any ion to transport charge depends on the mobility of the ion. Mobility of ion is affected by factors like- charge on ion, size and mass of ion , extent of solvation
- **Ohm's Law:**

Ohm's law state that the current (I) flowing through the conductor is directly proportional to the potential difference (V) applied across the conductor and inversely proportional to the electrode resistance (R) of the electrode.

$$I = \frac{V}{R}$$

Where I is the current in ampere

V – potential difference in volts

R – Resistance in ohm

Ohm's law is obeyed by metallic conductor and electrolyte solution

- **Electrolytes-**
 - substances on dissolution forms +ve and –ve ions
 - Substances whose solution in water conducts electric current.
 - Conduction takes place by the movement of ions.
Examples are salts, acids and bases.
- **Non electrolytes-** substances on dissolution does not forms +ve and –ve ions
 - Substances whose aqueous solution does not conduct electricity are called **non electrolytes.**
 - **Examples are solutions of cane sugar, glucose, urea etc.**

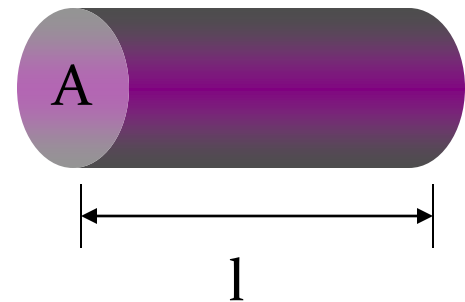
- **Conductance (C)** – is the ease with which current flows through the conductor or solution and is reciprocal of resistance

$$C = \frac{1}{R}$$

C - ohm⁻¹ or mho

- **Specific resistance (ρ)**- The resistance R of a conductor at a definite temperature, is directly proportional to its length (l) and inversely proportional to the area of cross section (A)
- Resistance of any uniform conductor is

$$R \propto \frac{l}{A} \quad R = \rho \frac{l}{A}$$



- ρ is specific resistance, if $l = 1\text{cm}$, and $A = 1\text{cm}^2$ then

- $R = \rho$

$$\text{Specific conductance, } \kappa = \frac{1}{\rho} = \frac{1}{RA/l} = \frac{l}{RA}$$

$$\text{Specific conductance, } K = \frac{\text{cm}}{\text{ohm} \times \text{cm}^2}$$

Specific conductance unit is $\text{ohm}^{-1}\text{cm}^{-1}$

- Unit of Sp. Conductance $\text{ohm}^{-1}\text{cm}^{-1}$
- SI unit is Sm^{-1} = Siemens m^{-1}
- **$1\text{S} = 1\text{ohm}^{-1} = 1\text{mho} = \Omega^{-1}$**
- **$1\text{Sm}^{-1} = 1\text{ohm}^{-1}\text{m}^{-1} = 1\Omega^{-1}\text{m}^{-1}$**
- **Specific conduction = Cell constant x Obs. Conductance**

- If $l = 1\text{cm}$ and $A = 1\text{cm}^2$
- $R = \rho$
- **Specific resistance** of a substance is defined as the resistance offered by a cube of length 1cm and area of cross section A , 1cm^2 , to passage of electricity through it.

$$\rho = R \frac{A}{l}$$

$$\rho = \text{ohm} \times \frac{\text{cm}^2}{\text{cm}} = \text{ohm} \cdot \text{cm}$$

- Hence unit of ρ is ohm.cm

- **Specific Conductance (K):**

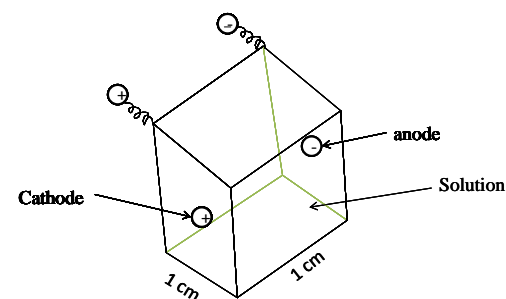
- The specific conductance of any conductor is the reciprocal of sp. Resistance.

$$K = \frac{1}{\rho}$$

- Sp. Conductance of a solution can be defined as the conductance of solution between two parallel electrodes which have cross section area 1 cm² and which are kept 1cm apart.

$$k = \frac{l}{A} \times \frac{1}{R}$$

- Unit of Sp. Conductance **ohm⁻¹.cm⁻¹**



- **Specific conductance depend on the number of ions present in unit volume (1 ml) of solution**

Cell Constant: The ratio of l/A is known as cell constant.

It depends upon the distance between the electrode (l) and the area of cross section (A) of the electrode.

From equation

$$\text{Cell constant} = \frac{l}{A} = \frac{\text{cm}}{\text{cm}^2} = \text{cm}^{-1}$$

$$K = \frac{1}{R} \times \frac{l}{A}$$

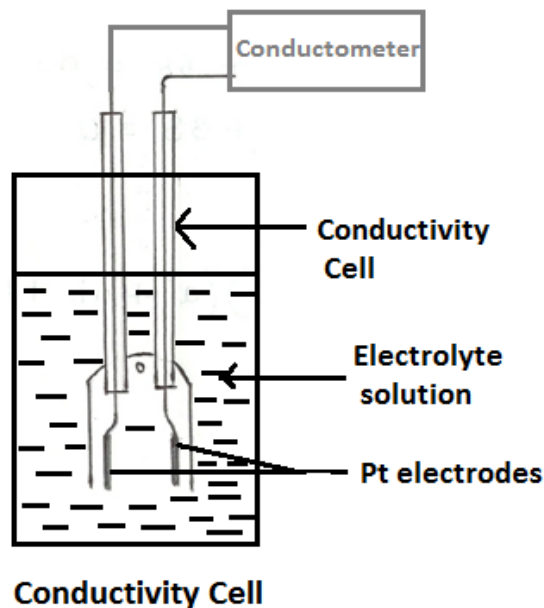
$$\frac{l}{A} = K \times R$$

$\text{Cell Constant} = \text{Sp. Conductance} \times \text{Obs. Resistance}$

$\text{Cell Constant} = \frac{\text{Sp. Conductance}}{\text{Observed Conductance}}$

- **Conductivity Cell:**

- In conductance measurement conductivity cell is used
- For conductance measurement AC current is used.
- Conductance is measure with the help of Wheatstone bridge circuit.
- Conductivity cell is made up of two Pt electrodes coated with Platinum black to avoid the polarization effect.



- Determination of cell constant:

$$\text{Cell Constant} = \frac{\text{Sp. Conductance}}{\text{Observed Conductance}}$$

- To determine the cell constant, a standard solution of KCl whose specific conductance at a given temperature is known is used. Then the standard KCl of same concentration is prepared and its conductance is measured at same temperature.
- **N/50 KCl** -0.372 gm KCl in 250 ml conductivity water, conductance at 25°C is 0.002765 mho.

- **Equivalent conductance:** is defined as the conductance of a solution containing one gram equivalent of an electrolyte at any particular concentration, when placed between two electrodes 1 cm apart.

$$\text{Equivalent conductance} = \text{Specific Conductance} \times \text{volume in ml per gm equivalent of the electrolyte}$$

$$\lambda_V = K \times V$$

- The volume per gram equivalent of electrolyte is called as dilution factor of the solution.
- If concentration of the solution is 'C' grams per lit, then the volume containing 1 gram equivalent of electrolyte will be

$$V = \frac{1000}{C}$$

$$\lambda_V = K \times \frac{1000}{C}$$

$$\lambda_V = (\text{ohm}^{-1} \text{cm}^{-1}) \frac{\text{cm}^3}{(\text{gm equiv})^{-1}}$$

$$\lambda_V = \text{ohm}^{-1} \text{cm}^2 (\text{gm equiv})^{-1}$$

- Molar Conductance:**

Molar conductance of an electrolyte is the conductance of solution containing 1 mole of the electrolyte, when placed between two electrode 1 cm apart.

$$\text{Molar conductance} = \text{Specific Conductance} \times \text{volume in ml per gm mole of the electrolyte}$$

$$\mu = K \times V$$

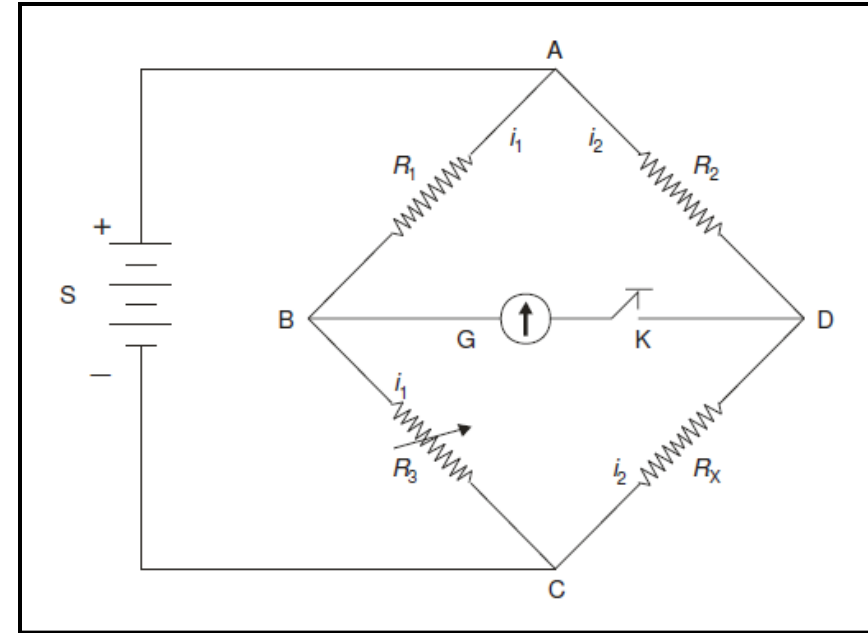
$$\mu = K \times \frac{1000}{M}$$

$$\text{Molar Conductance } (\mu) = \text{ohm}^{-1} \times \text{cm}^{-1} \times \frac{\text{cm}^3}{\text{gm mole}}$$

$$\text{Molar Conductance } (\mu) = \text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{gm}^{-1} \cdot \text{mole}^{-1}$$

MEASUREMENT OF ELECTROLYTIC CONDUCTANCE

Let R_x be an unknown resistor, R_1 and R_2 two standard resistors, R_3 an adjustable resistor and G a galvanometer. The bridge is connected to a source of power S, a battery, and a tapping key K is placed in the path to control the connections.



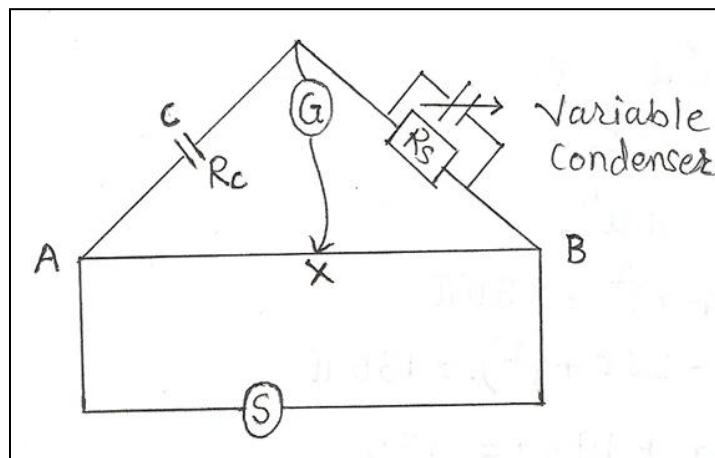
In the bridge the total current is divided into two paths: i_1 through R_1 and R_3 , and i_2 through R_2 and R_x . Under the balancing conditions, the potential at points B and D must be the same, i.e. the ohmic voltage drop through the resistors R_1 and R_2 must be the same. Hence, the potential at B (EB) must be equal to potential at D (ED).

$$EB = ED$$

$$\text{Or } i_1 R_1 = i_2 R_2$$

$$\text{Similarly, } i_1 R_3 = i_2 R_x$$

$$\frac{R_1}{R_3} = \frac{R_2}{R_x} \text{ therefore, } R_x = \frac{R_2 R_3}{R_1}$$



- Measured resistance can be converted to sp conductance

$$K = \frac{1}{R} \times \frac{l}{A}$$

- Knowing sp. Conductance Equivalent and Molar Conductance can be calculated.

$$\lambda_V = K \times \frac{1000}{C}$$

$$\mu = K \times \frac{1000}{M}$$

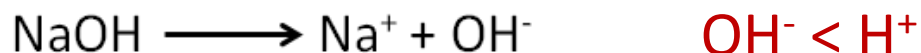
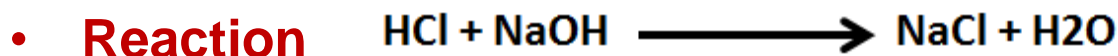
Factors affecting conductivity

- 1) **Number of ions per ml**- greater the number of ions per ml in a solution, greater is the specific conductance. At higher concentration of the solution, the number of ions per ml is higher.
- 2) **Concentration** – in case of weak electrolytes as concentration decreases i.e. is dilution increases the number of ions increases and equivalent conductance increases, although specific conductance decreases.
- 3) **Mobility of ions** – smaller the size of ion greater is its mobility e.g. H^+ ion.
- 4) **Charge on ion** – higher is the charge on ion greater is its mobility. e.g. $Mg^{++} > Na^+$; $SO_4^{-2} > NO_3^-$
- 5) **Temperature** – at higher temperature K.E. increases, viscosity decreases, interaction between ions decreases therefore conductance increases

Conductometric Titration Curves

- 1) Strong Acid with Strong Base

- e.g. HCl with NaOH (In burette NaOH and in conical flask HCl)

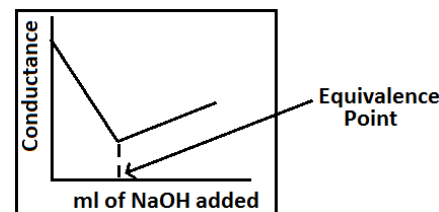


At the Initial Stage of Titration: Since HCl being strong acid, dissociate completely to produce H^+ and Cl^- . H^+ ions are small in size and shows highest mobility. Therefore in the beginning for zero ml addition of NaOH conductance is highest.

Before equivalence point: During titration on addition of NaOH from burette in HCl in beaker, HCl is under going neutralization, and concentration of H^+ decreases and therefore conductance decreases upto equivalence point.

At equivalence point conductance is minimum due the formation of salt NaCl, which is dissociating completely.

After equivalence point: On further addition of NaOH conductance increases due to OH^- ions

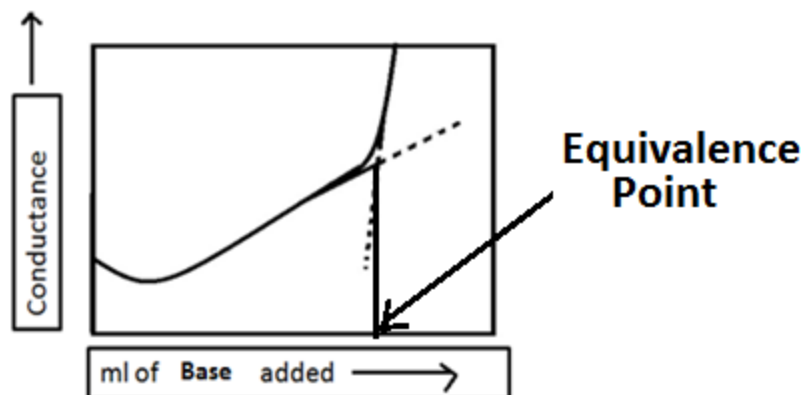
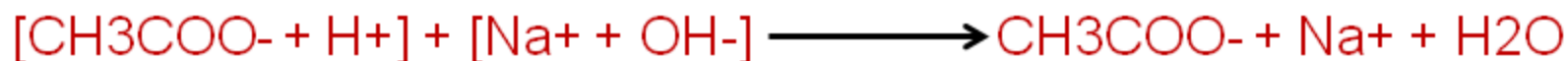
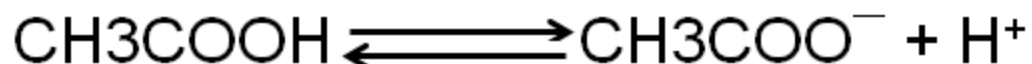


- **Calculation :**
- **1000 ml 1N NaOH = 36.5 gm HCl**
- **1 ml 1N NaOH = 36.5 mg HCl**

- **Curve Explanation:**
- **Initial stage**
- **Before equivalence point**
- **At the equivalence point**
- **After equivalence point**

2) Weak Acid with Strong Base

- e.g. CH_3COOH with NaOH

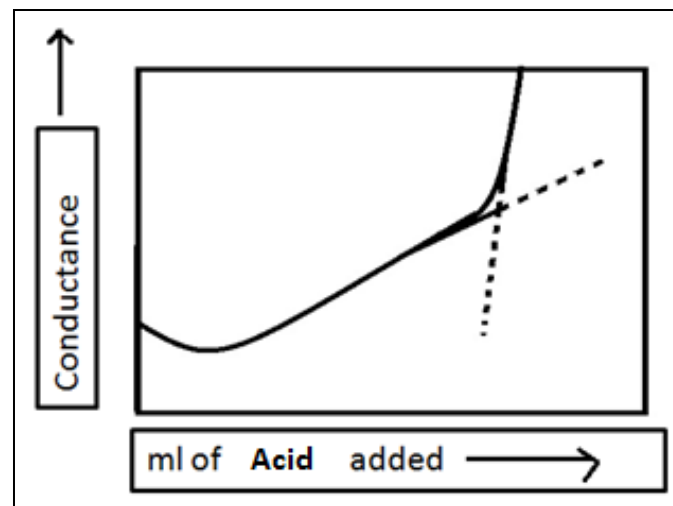


ml of NaOH added

- In the beginning conductance of acetic acid is low and it further decreases due to depression in the dissociation by the common ion formed during early stage of titration.
- After that conductance slowly increases due to formation of completely dissociated CH_3COONa upto equiv. point.
- After equiv. point conductance increases due to further addition of NaOH .
-
- **Calculation**
- $1000 \text{ ml } 1\text{N NaOH} = 60 \text{ gm of CH}_3\text{COOH}$
- $1 \text{ ml } 1\text{N NaOH} = 60 \text{ mg of CH}_3\text{COOH}$

3. Weak base with strong acid

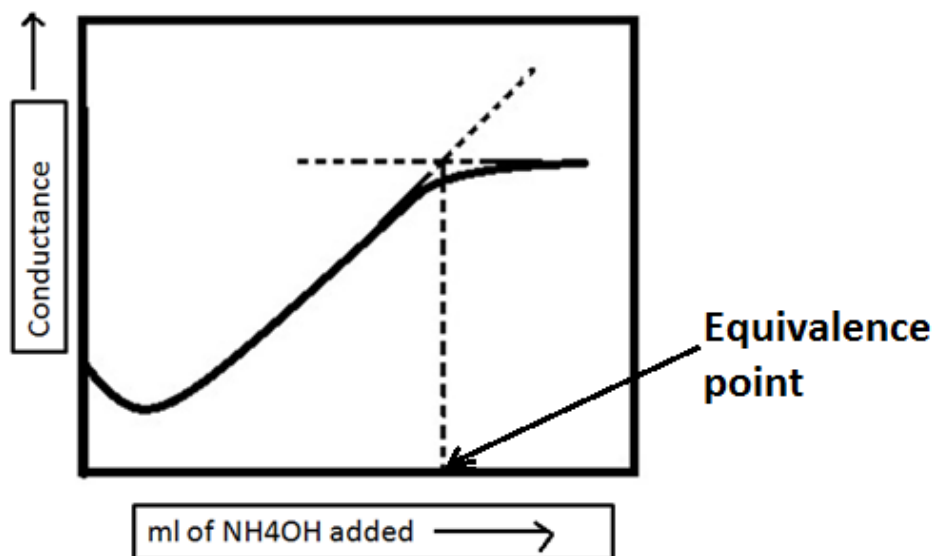
- e.g. NH_4OH with HCl
- Conical flask NH_4OH
- Burette standard known concentration HCl
- $\text{NH}_4\text{OH} + \text{HCl} \longrightarrow \text{NH}_4\text{Cl} + \text{H}_2\text{O}$



- Initially low conductance WB
- During titration due to formation of NH_4Cl conductance slowly increases
- After equiv. point conductance increases rapidly, fast moving H^+
- **Calculation**
- 1 ml 1N HCl = 35 mg of NH_4OH

4. Weak acid with Weak base

- e.g. CH_3COOH with NH_4OH
- In titration flask CH_3COOH
- In burette NH_4OH
- Neutralization reaction
- $\text{CH}_3\text{COOH} + \text{NH}_4\text{OH} \longrightarrow (\text{CH}_3\text{COO}^- + \text{NH}_4^+) + \text{H}_2\text{O}$



Conductometric Titration:

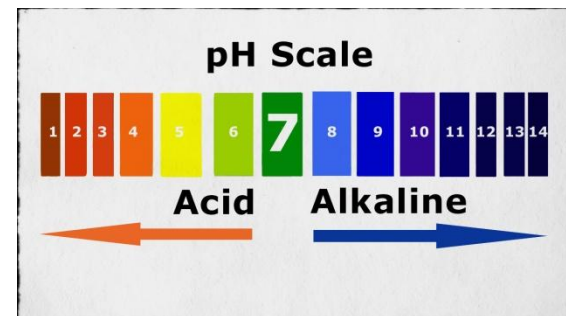
The titration in which conductance measurement are used to determine the equivalence point of the titration called as conductometric titration.

pH metry

- The term pH was introduced by Sorensen in 1909.
- $\text{pH} = -\log [\text{H}^+]$

$$\text{pH} + \text{pOH} = \text{pK}_w = 14$$

- **Buffer Solution** : two types
- **1. Acidic buffer** : WA with a salt of WA and SB
- e.g. $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
- $\text{Na}_2\text{HPO}_4 + \text{citric acid} [\text{C}_6\text{H}_8\text{O}_7]$
- **2. Basic Buffer**: WB with a salt of WB and SA
- e.g. $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$



From Handerson equation buffer solution can be prepared

- $pH \text{ of acidic buffer} = pK_a + \log \frac{[salt]}{[WA]}$
- $pK_a = -\log K_a$ K_a – dissociation constant of WA
- $pOH \text{ of basic buffer} = pK_b + \log \frac{[salt]}{[WB]}$
- $pK_b = -\log K_b$ K_b – dissociation constant of WB

The relationship between the pH of a solution and the concentrations of an acid and its conjugate base is easily derived.

$$[H^+] = K \frac{[HA]}{[A^-]}$$

Taking the negative log of each term

$$pH = -\log K + \log \frac{[A^-]}{[HA]}$$

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pH = pK + \log \frac{[A^-]}{[HA]} = pK + \log \frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$

This relationship known as the Henderson equation, that is often used to perform the calculations required in preparation of buffers for use in the laboratory, or other applications.

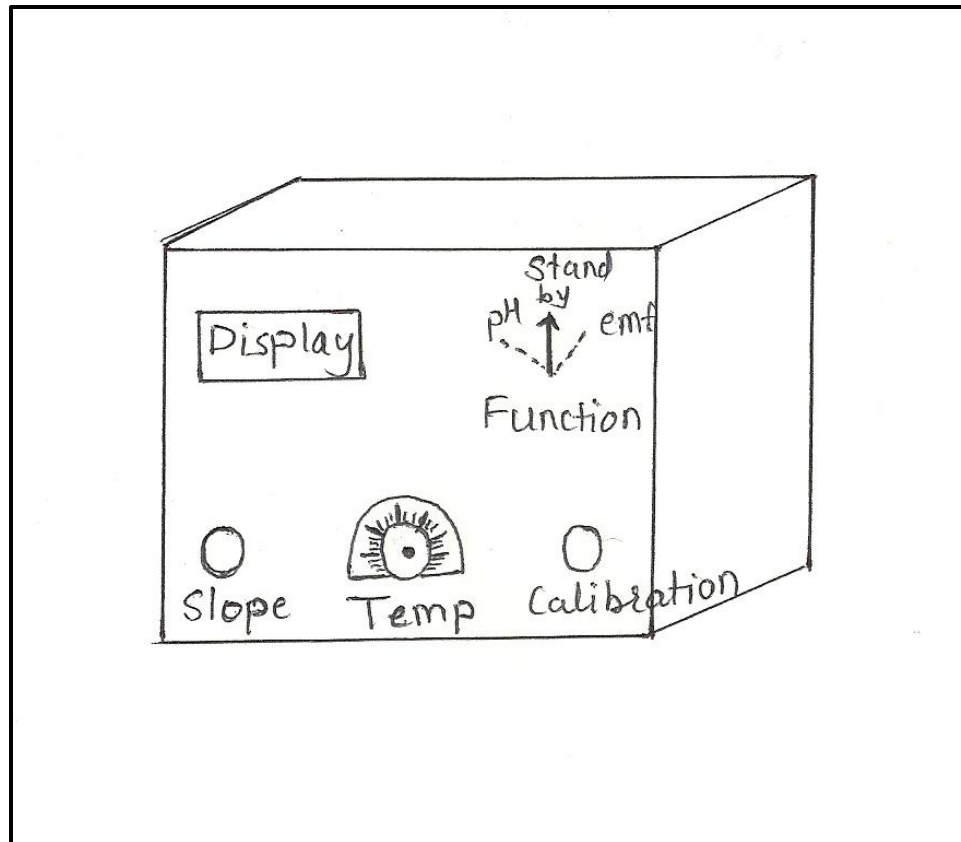
Applications of buffer solutions

- Used in quantitative inorganic analysis.
- Useful in electro-deposition of metals.
- In colorimetric determination of pK_a of indicator.
- Many life forms thrive only in a relatively small pH range so they utilize a buffer solution to maintain a constant pH. One example of a buffer solution found in nature is blood.
- Industrially, buffer solutions are used in fermentation processes and in setting the correct conditions for dyes used in colouring fabrics. They are also used in chemical analysis and calibration of pH meters.

Applications of buffer solutions

- Buffer solutions are necessary to keep the correct pH for enzymes in many organisms to work. Many enzymes work only under very precise conditions; if the pH moves outside of a narrow range, the enzymes slow or stop working and can denature. In many cases denaturation can permanently disable their catalytic activity. A buffer of carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) is present in blood plasma, to maintain a pH between 7.35 and 7.45.
- Industrially, buffer solutions are used in fermentation processes and in setting the correct conditions for dyes used in colouring fabrics. They are also used in chemical analysis and calibration of pH meters.

pH meter



- **Measurement of pH :**
- pH meter is used to determine pH of the solution
- Calomel electrode is used as reference electrode and glass electrode is used as indicator electrode.

- Importance of pH metric titration:
 - 1) Equivalence point of acid –base titration can be determine accurately by pH metric titration.
 - 2) In pH metric acid-base titration indicator is not needed.
 - 3) Instrument used is simple and easy to handle

pH metric titration between HCl and NaOH

Consider the titration between HCl and NaOH

As HCl is strong acid and NaOH is strong base, dissociates completely.



- **Procedure:**

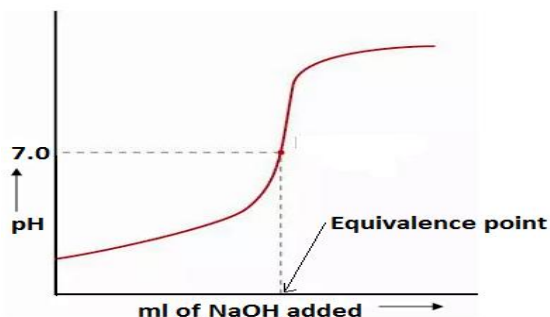
A) Standardization of pH meter: pH meter is standardized using buffer solutions with pH 4, 7 and 9.2.

HCl is taken in beaker and NaOH in burette.

B) Acid – Base Titration :

- 1) Take a known volume of HCl in a beaker.
- 2) Immerse the glass electrode (indicator electrode) and Calomel electrode (reference electrode) in it. Note the pH for zero mL addition of NaOH.
- 3) Fill the burette with known concentration of NaOH.
- 4) Every time add 0.5 ml NaOH in acid solution, stir the solution and note down the pH.
- 5) Continue the titration, at the equivalence point pH suddenly increases. After sudden increase in pH, do the few addition of NaOH till pH remains constant.

- **Graphs:** 1) Plot the graph of pH verses mL of NaOH added



Initial stage: at the initial stage of titration pH reading is between 1-2 pH due to complete dissociation of HCl. $\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-$

Before equivalence point: with the addition of NaOH from burette HCl is getting neutralization, and H^+ ion concentration decreases therefore slowly pH increases up to equivalence point.

At the equivalence point : at the complete neutralization of HCl, pH of solution is 7

After equivalence point: with further addition of NaOH pH increases, after that for the addition of NaOH it remains constant due to complete dissociation of NaOH.