DEPTH OF BIOLOGY

UNIT-V

- **Electrochemical methods of analysis**
  - **Conductometry**- Introduction, Conductivity cell, Conductometric titrations, applications.
  - **Potentiometry** - Electrochemical cell, construction and working of reference (Standard hydrogen, silver chloride electrode and calomel electrode) and indicator electrodes (metal electrodes and glass electrode), methods to determine end point of potentiometric titration and applications.
  - **Polarography** - Principle, Ilkovic equation, construction and working of dropping mercury electrode and rotating platinum electrode, applications

Potentiometry

- Similar to direct titration. It is a technique which is used in analytical chemistry.
- Used to find the concentration of solute in solution.
- No use of chemical indicator takes place.

This, potentiometric titration is done using 2 electrodes

1. Indicator electrode
2. Reference electrode

a) Hydrogen electrode

b) Silver chloride electrode

Potentiometry

- One of the Volumetric Techniques in Electro Analytical chemistry.
- Potentiometry involves measurement of potential difference of a solution between a reference electrode and indicator electrode.
- Potential of a solution depends on nature and concentration of ions of the drug substance.
- The measured potential is proportional to the concentration of the analyte.

Potentiometric Analysis

- A typical cell for potentiometric analysis consists of

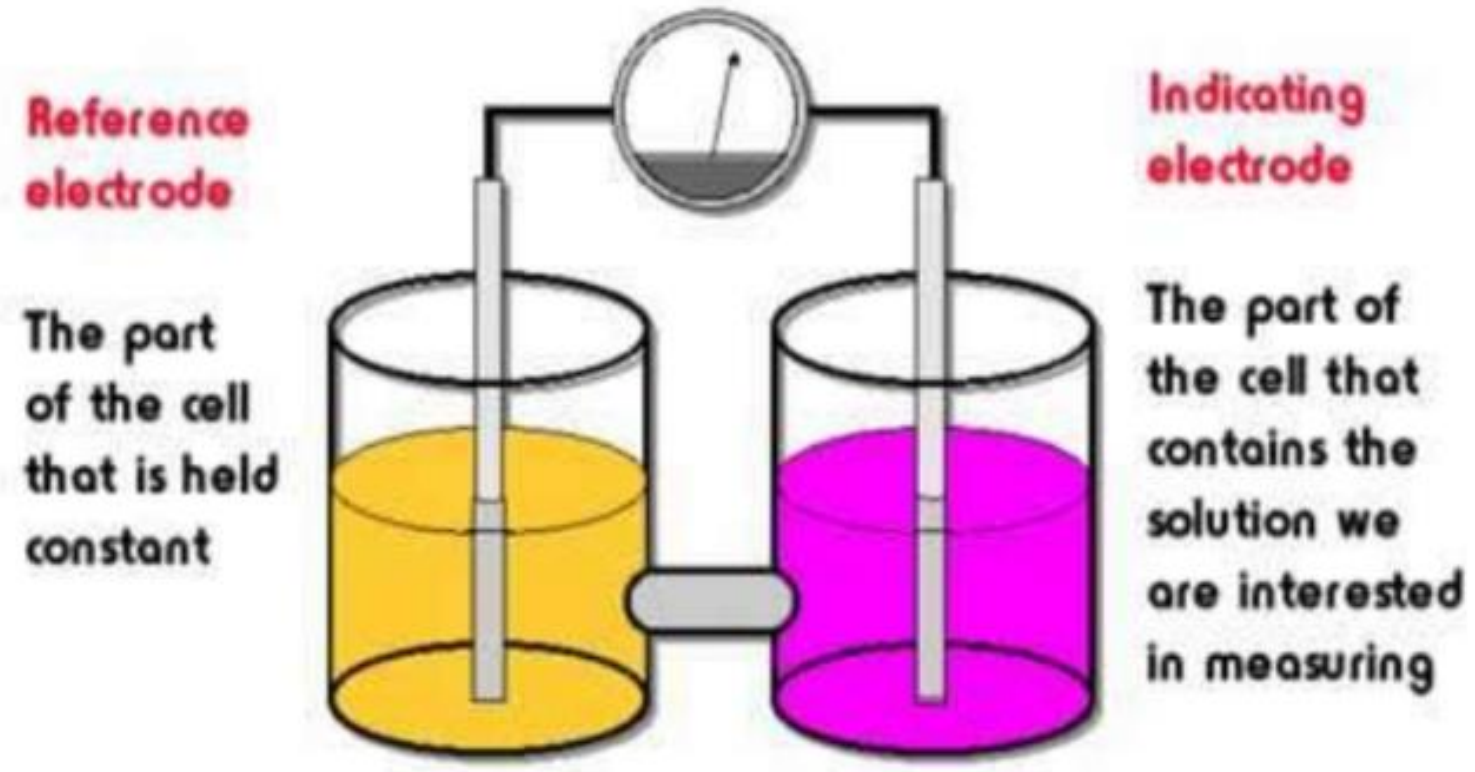
- ❑ reference electrode
- ❑ indicator electrode
- ❑ salt bridge.

- The Cell can be represented as

Reference electrode | salt bridge | analyte solution| indicator electrode

E ref **E j** **E ind**

Potentiometric Methods



Principle

Reference electrode

- Eref is a half-cell having a known potential (standard Potential) that remains constant at constant temperature and independent of the
- composition of the analyte solution.

Indicator electrode

- Responds to changes in emf or pH of solution.
- Eind has a potential that varies with variations in the concentration of an analyte.

Salt bridge that prevents the components of the analyte solution from mixing with those reference electrode.

Electrochemical Cell

- The potential of the cell is given by the equation

Ecell= Eind +Eref + Ej

- Eind= gives the measure of potential of solution in which it is dipped (depends on concentration).
- Eref = Standard or known potential. (constant)
- Ej= liq junction potential (negligible): eliminated by salt bridge

Eind measure the potential of solution.

- Represented by 2 half cell reactions.

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

Electrode Potentials

- The potential (E) of a metal electrode at 25^0C immersed in a solution of its own ions follows Nernst Equation:

$E = E^0 + (RT/nF) \ln Q$

- E = Potential Observed
- E^0 = Standard potential of metal electrode
- R is gas law constant, T is Absolute temperature, F is the Faraday, and n is number of electrons transferred in redox reaction , Q is the activity quotient (ions).
- On substituting Constants :

$E = E^0 + 0.0591/n \ln Q$

The above equation is used for calculating the potential of any electrode (half cell) from the electrode potential of standard at 25^0C. **E^0 = zero**

Reference Electrode

- Known half-cell potential
- Insensitive to solution under examination
- ➢ Reversible and obeys Nernst equation
- ➢ Constant potential
- ➢ Returns to original potential

Egs of Reference electrode

- Hydrogen electrode
- Saturated calomel Electrode
- Silver-Silver Chloride Electrode

Hydrogen Electrode

Consist of Platinum wire

- Coated with platinum black (increase the Surface area and catalyse electrode reaction.)
- Inert: does not participate in many chemical reactions
- Simply used to transfer of electrons

Hydrogen Electrode

Hydrogen electrode (SHE)

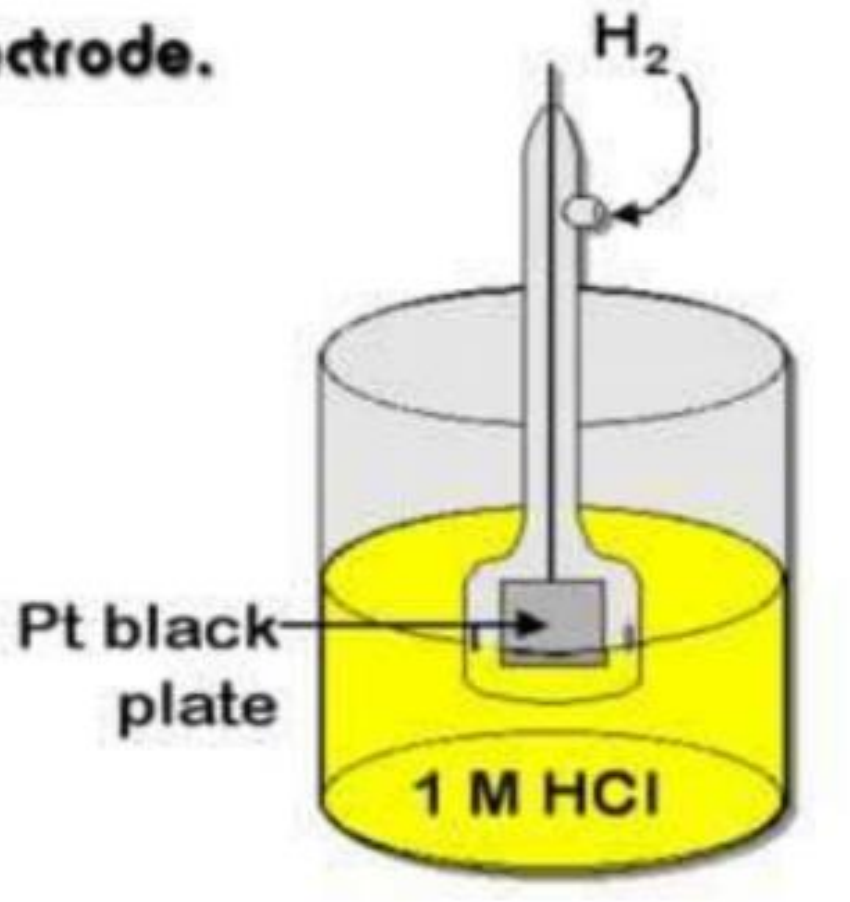
The ultimate reference electrode.

Difficult to work with.

H_2 is constantly bubbled into a 1 M HCl solution

Pt / H_2 (1atm), 1M H^+ //

E° = 0.000000 V



Hydrogen Electrode

- Transmission of current across the interface is given by half cell reaction:

$$H_2 \rightleftharpoons 2H^+ + 2e^- \quad E^0 = 0.000V$$

When coupled with proper half cell, hydrogen electrode behave as anode or cathode.

As Anode

Hydrogen gas is oxidized to hydrogen ions.

As cathode

Hydrogen ion is reduced to hydrogen gas.

Hydrogen Electrode

The Potential of the electrode is given as:

$E = E_H^0 + 0.0591 \log [H+]$

$E = E_H^0 - 0.0591\ pH$ (since $pH = -\log [H+]$

$E = -\ 0.0591\ pH$

E_H^0 = Standard potential of hydrogen electrode and taken as zero

By measuring the EMF of the cell, pH value can be determined.

Advantage

1. Primary reference electrode against which pH or potential of other electrodes can be measured
2. Can be used over the entire pH range.
3. Can be used as a reference electrode when dipped in standard acid solution and as indicator electrode when dipped in sample solution.

Demerits

1. Purity and pressure of hydrogen affects the potential of this electrode.
2. Affected by presence of oxidising and reducing substance.
3. Potential is affected due to poisoning of platinum surface (due to cyanides, arsenic etc.)
4. Not easy to get pure H_2.
5. Difficult to maintain pressure of H_2 gas

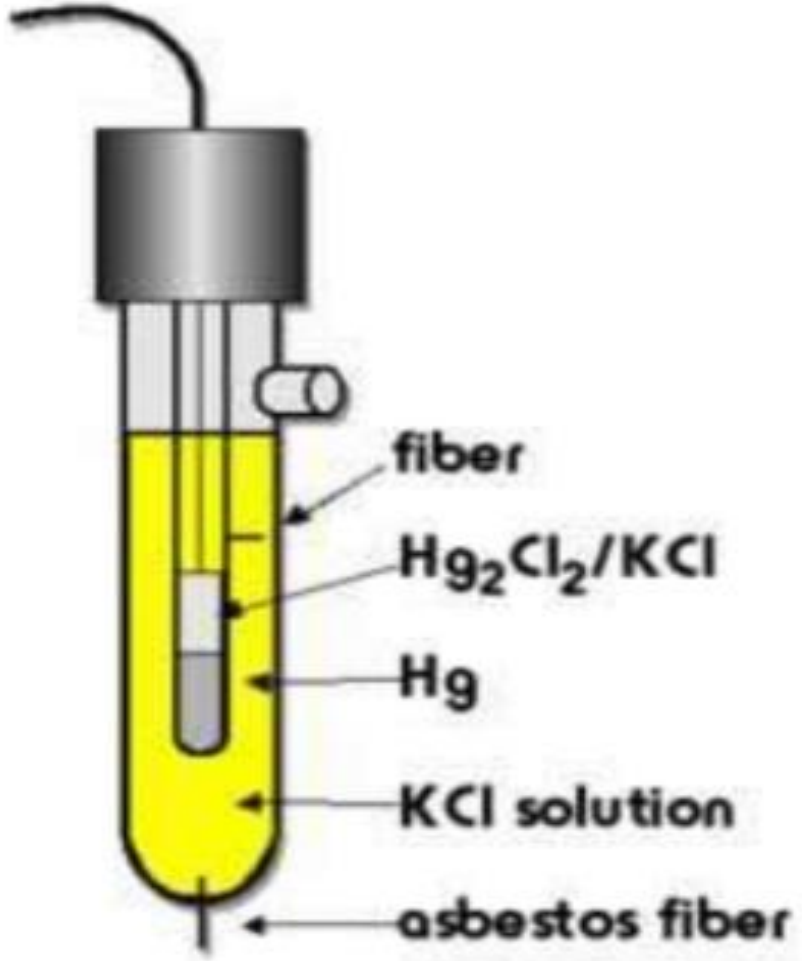
Reference Electrode

Calomel electrode (SCE)

A much more common reference electrode.

$Hg / Hg_2Cl_{2(sat)}, KCl //$

Chloride is used to maintain constant ionic strength.



Calomel Electrode

- Consist of 2 tubes
- Inner tube: Hg-Hg2Cl2/KCl
- Outer Tube: KCl Solution
- Pin hole in inner tube connects 2 tubes.

Calomel Electrode is rep as:

$$\mathbf{Hg\text{-}Hg_2Cl_2\ /\ Cl^-\ (xM)}$$

Calomel Electrode reaction is rep as:

$$\mathbf{Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-}$$

Conc of Cl - determines the potential of the electrode.

Calomel Electrode

- Conc of Cl - used are : 0.1M, 1 M and saturated KCl.
- Std oxidation potential of 3 reference electrode w.r.t S.H.E at 25^0C - 0.334v, -0.280 v, -0.242 v resp.
- SCE (saturated calomel electrode) is popular bcos of suppressive effect of saturated KCl on the liquid potential.
- This electrode behave as a cathode when used with respect to hydrogen electrode.

Advantage:-

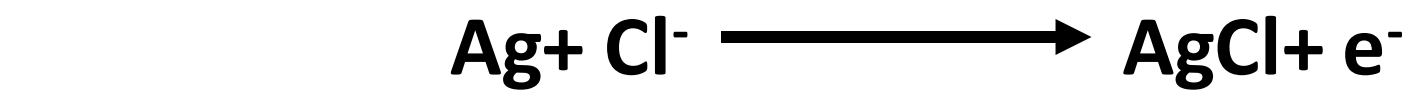
- Easy to construct
- Stability of potential.

Silver-silver Chloride Electrode

- Consist of Ag wire/ Ag plated platinum wire.
- Dipped in KCl soln of known conc saturated with AgCl.
- Potential of the electrode is governed by the activity of chloride ions
- Calomel Electrode is rep as:

$Ag/ AgCl / Cl^{-} (xM)$

Electrode reaction is rep as:



Std oxidation potential of this electrode w.r.t S.H. E at

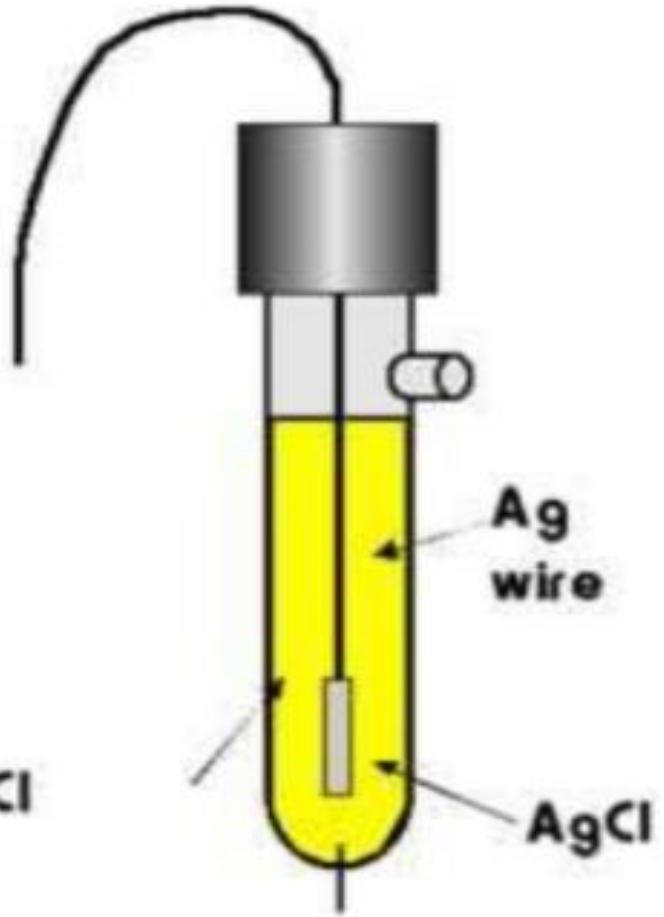
25^0C is -0.197volt.

Reference Electrode

Ag/AgCl

Another common reference electrode.

Easier to produce a combination electrode.



Indicator Electrode

- Respond directly to changing activity of electrode ion
- Direct equilibrium with solution

- Glass electrode
- Metal electrode

Glass Electrode

- Commonly used cell for measuring pH consist of a **glass indicator electrode** and a **saturated calomel reference electrode** immersed in the solution whose pH is unknown.
- The indicator electrode consists of a thin, pH sensitive glass membrane sealed onto one end of a heavy-walled glass tube.
- A small volume of **hydrochloric acid saturated** with **silver chloride** is contained in the tube.
- **Ag-AgCl wire** in this solution forms a silver/silver chloride **inner-reference electrode**, which is connected to one of the terminals of the potential-measuring device, pH-meter.

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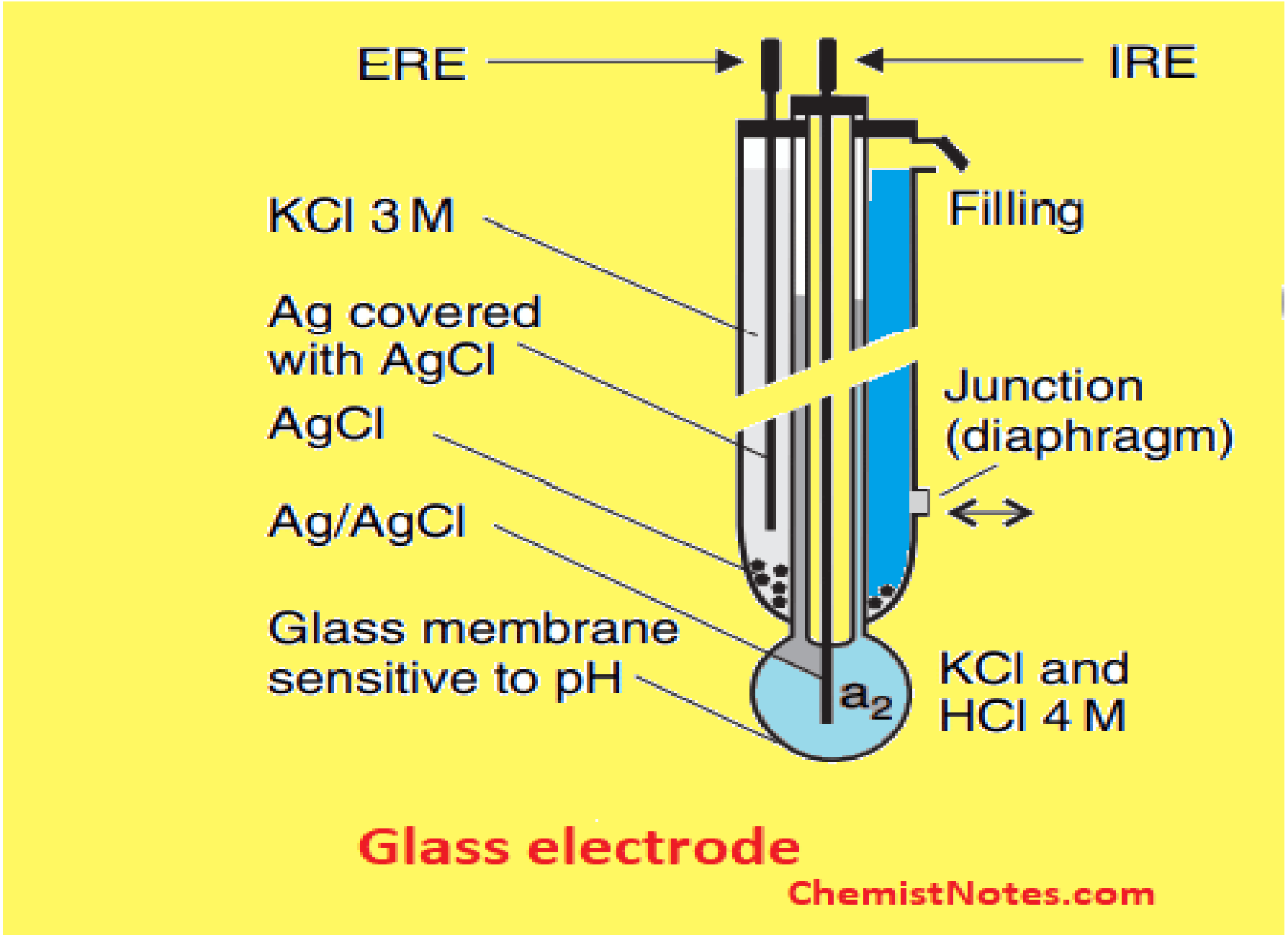
- Glass bulb containing solution is dipped in the beaker containing the solution whose pH has to be determined. Assembly act as indicator electrode.
- The calomel electrode is connected to the other terminal (which acts as reference electrode).
- Only potential which vary is the potential b/w outer surface of the glass and test solution in which it is immersed.
- Overall potential of the electrode depend on hydrogen ion conc of test solution.
- Cell is represented as
- Ag-AgCl,0.1 M HCl / Glass / Unknown Solution / KCl salt . Hg2Cl2 /Hg.


ERE
IRE
KCl 3 M
Filling
Ag covered with AgCl
AgCl
Junction (diaphragm)
Ag/AgCl
Glass membrane sensitive to pH
a_2
KCl and HCl 4 M
Glass electrode
ChemistNotes.com

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- Potential of glass electrode is given by:
- $E = k + 0.0592 (pH_1 - pH_2)$ at 25^0C

pH_1 = pH of solution inside the bulb

pH_2 = pH of test solution outside

$E = k + 0.0592\ pH_1 - 0.0592\ pH_2)$

$E = k - 0.0592\ pH_2$

pH_1= constant.

Advantages of Glass Electrode

- Gives a rapid response
- Chemically resistant to oxidising and reducing agents, dissolved gases.
- When lithia silica glass is used , can be used over the entire pH range.

Disadvantage

- Fragile
- Unsatisfactory in more alkaline solution above pH 10 range.