4/11

APPLICATIONS.

- Since the electrode potential is a constant it can be used as a secondary reference electrode.
- To determine electrode potential of other unknown electrodes.
- To determine the pH of a solution.

$Pt, H_2, H^+ // KCl, Hg_2Cl_2/Hg$

Electrode reaction: $H^+ + e^- \leftrightarrow 1/2\ H_2(g)$

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[H_2]^{1/2}}{[H^+]}$$

$$= 0 - 0.0592 \log 1/[H^+]$$

$$= -0.0592\ pH$$

$$E_{cell} = 0.2422 - (-0.0592\ pH)$$

$$\boxed{pH = \frac{[E_{cell} - 0.2422]}{0.0592}}$$

ADVANTAGES OF CALOMEL ELECTRODE

- It is simple to construct
- It can be used for a long time without much attention.
- Electrode potential is stable
- It has a low temperature coefficient of emf.
- It is less prone to contamination.

DISADVANTAGES OF CALOMEL ELECTRODE

- Calomel electrodes should not be used above 50°C.
- Mercury is toxic

Q. Write the cell scheme and determine the electrode potential of zinc immersed in 0.1 M $ZnSO_4$. Given EMF of cell = 1.0022 V and E° (Calomel electrode) = 0.2422 V.

Ans. $Zn/ZnSO_{4(0.1M)} \,||\, KCl; Hg_2Cl_2; Hg$

$$E_{cell} = E_{cathode} - E_{anode}$$

$$1.0022 = 0.2422 - E_{Zn^{2+}/Zn}$$

$$E_{Zn^{2+}/Zn} = -0.76\ V$$

Q. The emf of a cell consisting of a hydrogen and the normal calomel is 0.664 V at 25°C. Calculate the pH of the solution containing the hydrogen electrode.

$$E_{cell} = E_{cal(normal)} - (-0.0591\ pH)$$

Ans. $0.664 = 0.2810 + 0.0591\ pH$

$0.383 = 0.0591\ pH$

$pH = 6.48$.

Q. At 25°C, the EMF of the cell ~~Pt, H_2 (1 atm)~~ Pt, H_2 (1 atm) / H^+ // $KCl_{(satd)}$ / $Hg_2Cl_{2(s)}$, Hg is 0.445 V. Calculate the pH.

Ans. $0.445 = 0.2444 + 0.0591\ pH$.

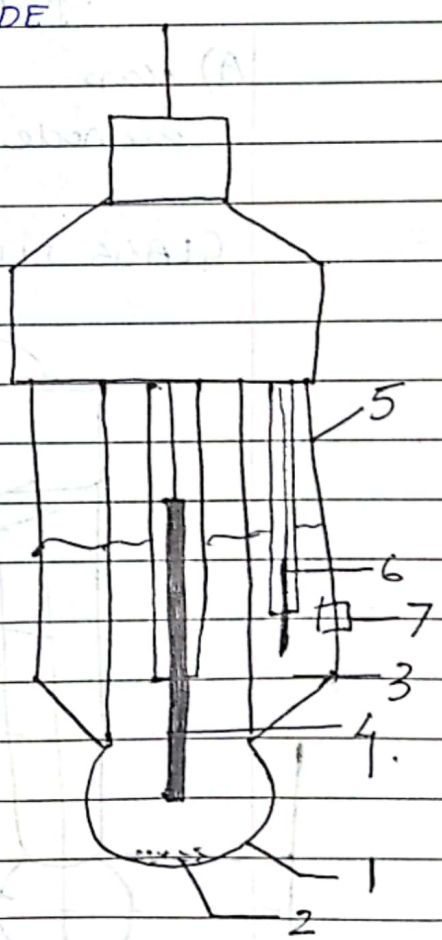
$pH = 0.2006 / 0.0591 = 3.3942$

ION SELECTIVE ELECTRODE

- It is sensitive to a specific ion present in an electrolyte
- The potential of this depends upon the activity of this ion in the electrolyte.
- Magnitude of potential of this electrode is an indicator of the concentration of the specific ion in the electrolyte.

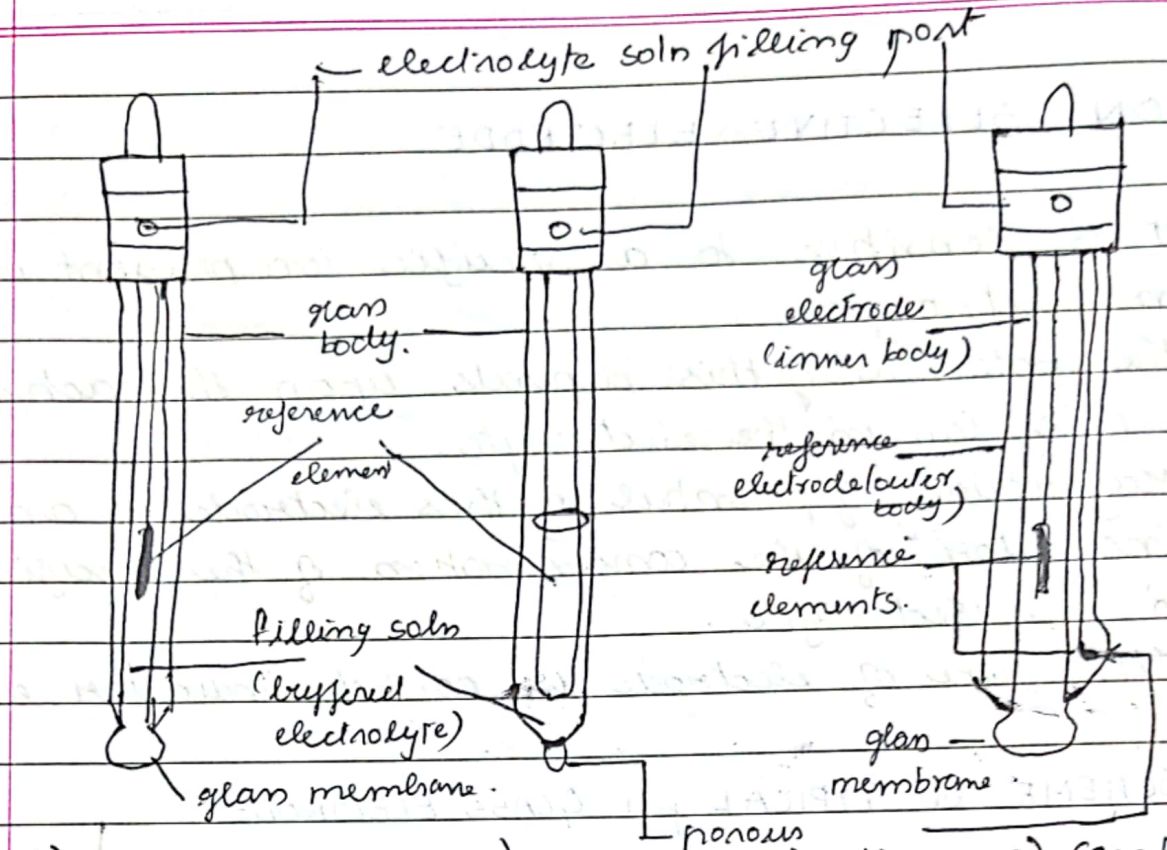
This type of electrode is called indicator electrode.

SCHEME OF TYPICAL pH GLASS ELECTRODE



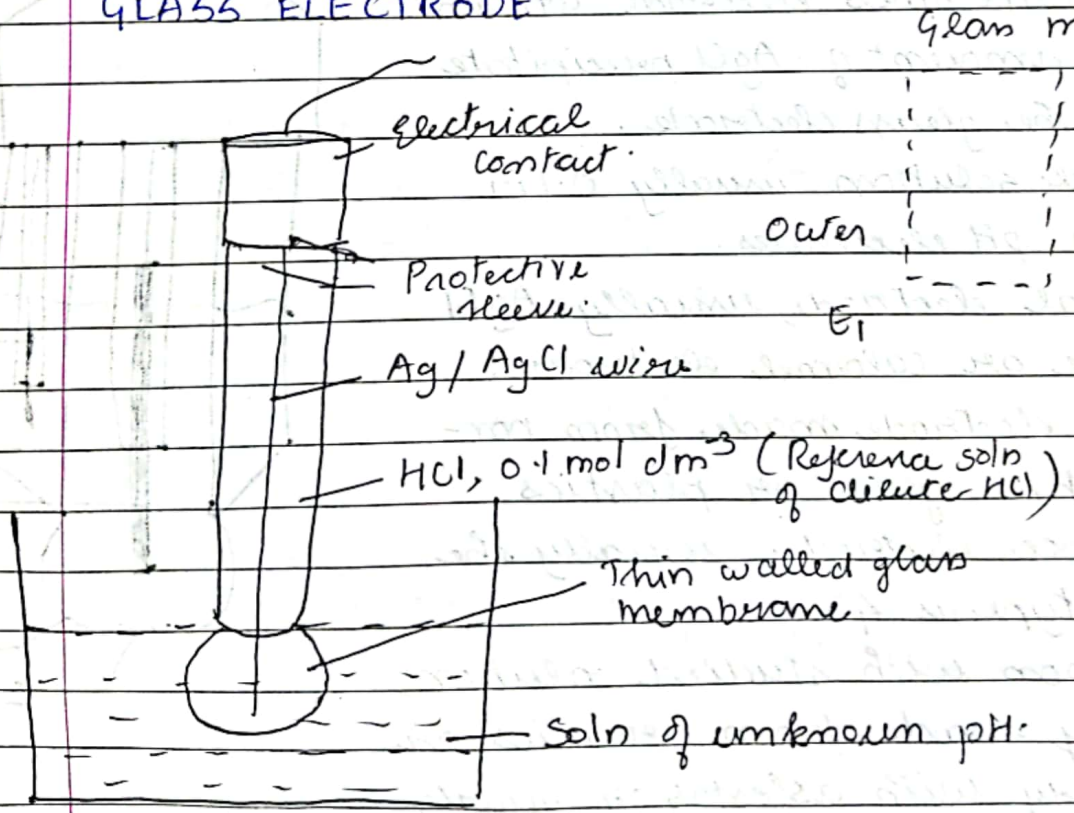
1. a sensing part of electrode
2. a bulb made from a specific glass sometimes electrode contain small amount of AgCl precipitate inside the glass electrode.
3. internal solution usually 0.1M HCl for pH electrodes.
4. internal electrode, usually AgCl electrode or calomel electrode.
5. body of electrode made from non-conductive glass or plastics.
6. reference electrode, usually the same type as 4.
7. junction with studied solution, usually made from ceramics or capillary with asbestos or quartz fiber.

Corning 015 glass.



A) glass electrode B) reference electrode C) combination electrode.

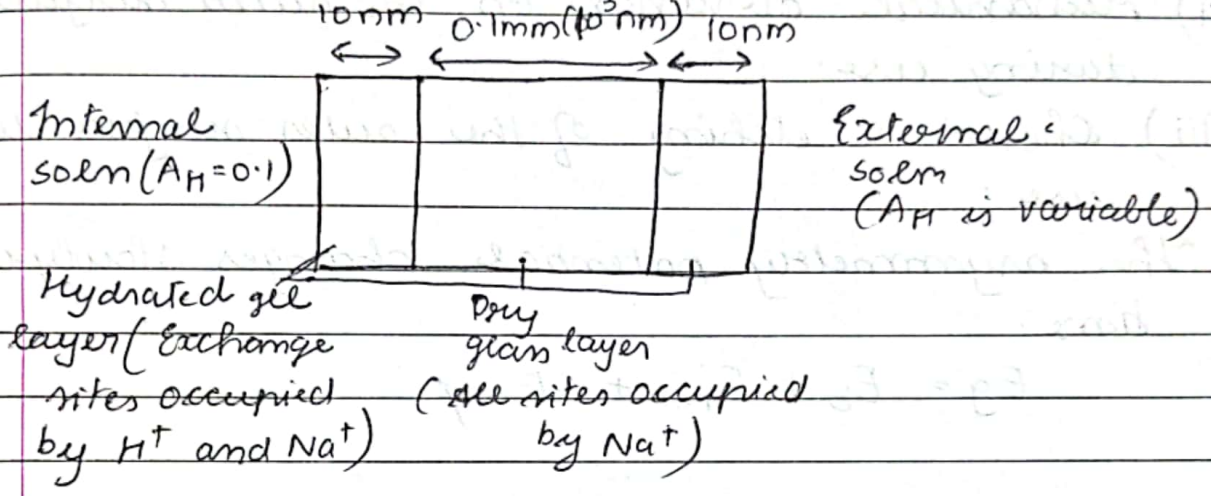
GLASS ELECTRODE



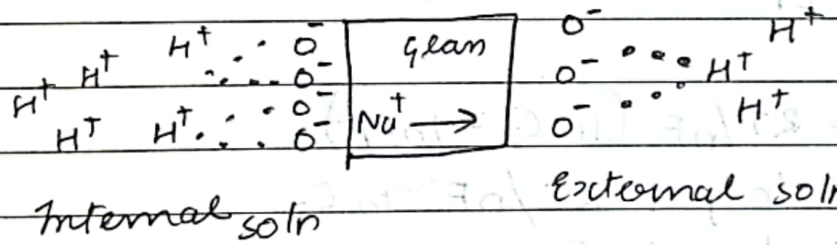
$$H^+_{(soln)} + Na^+_{(glass)} \longleftrightarrow Na^+_{(soln)} + H^+_{(glass)}$$

Structure of glass consists of an irregular network of SiO_4 tetrahedras connected through oxygen atoms.
Cations are coordinated to the oxygen atoms

CROSS SECTION OF THE GLASS MEMBRANE



Ion-exchange equilibria on the inner and outer surface of glass membrane.



ELECTRODE POTENTIAL OF GLASS ELECTRODE

$$E_g = E_b + E_{ref} + E_{asy}.$$

E_b - boundary potential.
E_{ref} - Internal reference electrode potential
E_{asy} - Asymmetric potential.

The sources of asymmetry potential include:

i) Differing conditions of stress in the two glass surfaces during manufacture - to the difference in response of the inner and outer surfaces of the glass bulb to changes in $[H^+]$

ii) Mechanical abrasion on the outer surface during use.

iii) Chemical etching of the outer surface during use.

The asymmetry potential changes slowly with time.

$$E_g = E_b + E_{ref} + E_{asy}$$

Solution to be analysed (C_2)	Membrane	0.1M HCl, Ag/AgCl (C_1) internal reference.
E_1		E_2.

$$E_b = E_1 - E_2 = RT/nF\ (\ln C_2 - \ln C_1)$$
$$= -RT/nF\ \ln C_1 + RT/nF\ \ln C_2$$
$$= L + RT/nF\ \ln C_2.$$

E_b depends on $[H^+]$ $\quad E_b = L - 0.0592\,pH.$

$$E_g = E_b + E_{Ag/AgCl} + E_{asy}$$
$$= L - 0.0592\,pH + E_{Ag/AgCl} + E_{asy}$$
$$(E^\circ_g = L + E_{Ag/AgCl} + E_{asy})$$

$$\boxed{E_g = E^\circ_g - 0.0592\,pH.}$$

APPLICATIONS

- Determination of pH.

Cell : SCE || Test solution / GE

$E_{cell} = E_g - E_{cal}$

$E_{cell} = (E^\circ_g - 0.0592pH) - E_{cal}$

$pH = E^\circ_g - E_{cell} - E_{cal} / 0.0592$.

ADVANTAGES.

1. Can be used without interference in solns containing strong oxidants/reductants, proteins, viscous fluids and gases.
2. pH range 2 to 10
3. Immune to poisoning and easy to use.
4. Equilibrium is reached quickly & rapid response
5. Can be used for very small quantity of solns.
6. Much more convenient to handle than SHE

DISADVANTAGES.

1. Bulb is fragile.
2. In presence of alkali ions, glass surface becomes responsive to both hydrogen and alkali ions. Measured pH values are low.
3. In highly acidic solns, measures pH values are high
4. Should be stored in aqueous soln.
5. Ordinary potentiometers can't be used to measure the potential of glass electrode.
6. The commercial version is expensive.
7. Standardization to be carried out frequently.