Applications

(1) Since the electrode potential is a constant it can be used as a secondary reference electrode.
(2) To determine electrode potential of other unknown electrodes.
(3) To determine the pH of a solution.

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

oxidation → Test solution

Electrode Reaction – $H^+ + e^- \rightarrow \frac{1}{2} H_2(g)$

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[H_2]^{1/2}}{[H^+]}$$

$$0 - 0.0592 \log \frac{1}{[H^+]}$$

$$= -0.0592\, pH$$

$$E_{cell} = (0.2422 - (-0.0591\, pH)$$

$$pH = \frac{[E(cell) - 0.2422]}{0.0592}$$

Calomel Electrode

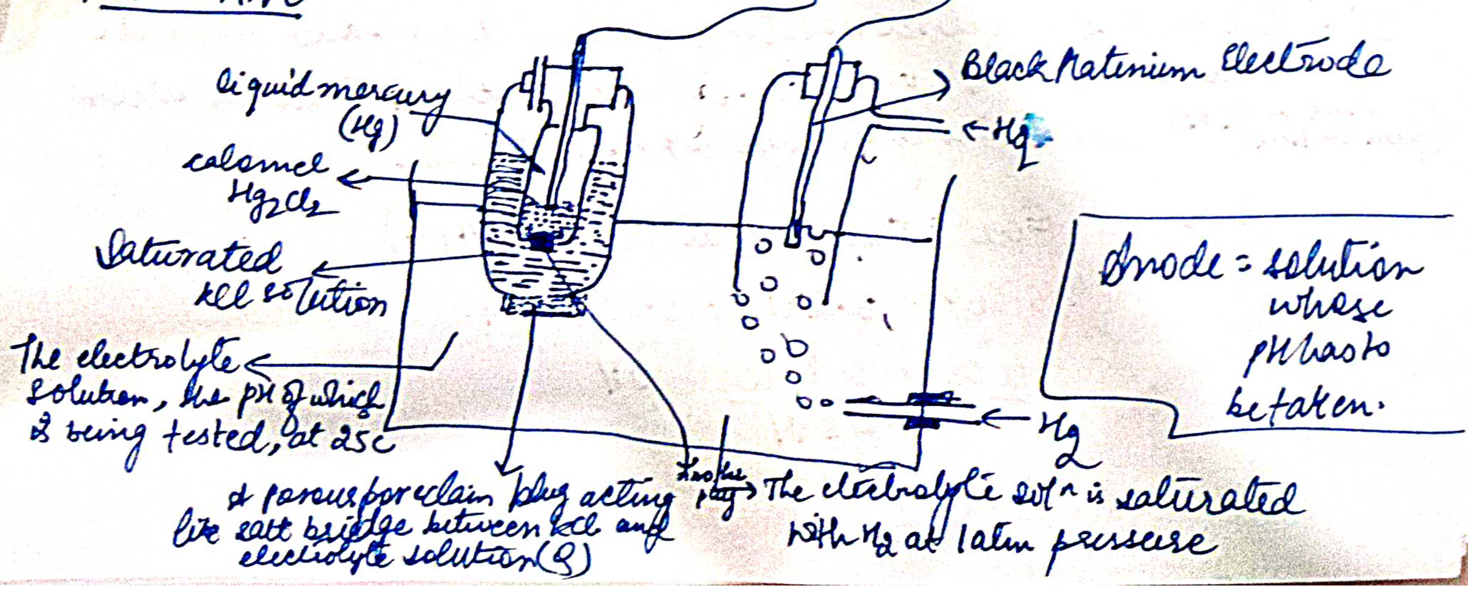
To determine the pH of a solution

$Pt [H_2] H^+(x) // KCl / Hg_2Cl_2 / Hg$

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

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

DIAGRAM



Advantages

(1) It is very simple and easy to construct
(2) It can be used for a long time without much attention
(3) Electrode potential is stable over a long period.
(4) It has low temp coefficient of emf
(5) It is less prone to contamination

Disadvantage

(decomposes above 50°C)

(1) Calomel electrodes should not be used above 50°C
(2) Mercury is being used which is toxic, should be handled properly
- Calomel electrode should be used with proper precaution as mercury compounds are toxic.

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

$$Zn / ZnSO_4\ (0.1M) \,//\, KCl ; Hg_2Cl_2 ; Hg$$

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

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

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

$$= -0.76V$$

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

(value from handbook) ← (1 N)

Ans

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

$$0.664 = 0.2810 + 0.0591\,pH.$$

$$\frac{0.664 - 0.2810}{0.0591} = pH$$

$$pH = 6.48$$

Q. At 25°c, the EMF of cell, Pt H_2 (1atm) / H^+ // KCl(sat) / $Hg_2Cl_{2(s)}$, Hg is 0.445V, calculate the pH of the solution

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

$$0.445 = 0.2444 + 0.0591\,pH$$

$$= \frac{0.445 - 0.2444}{0.0591} = pH$$

$$= \frac{0.2006}{0.0591} \rightarrow \underline{3.3942}$$

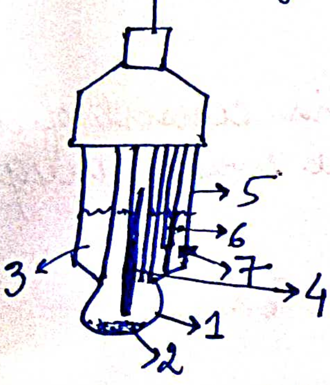
ION SELECTIVE ELECTRODE

(glass electrode sensitive towards H^+ ions)

- 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 is known as indicator electrode)

- The electrode which is sensitive to a specific ion present in an electrolyte whose potential depends upon the activity of specific ion in the electrolyte is called ion selective electrode.
- The magnitude of potential of this electrode is an indicator of the activity of specific ion in the electrolyte. Example for this type of electrode is the glass electrode.



Combined glass → calomel + glass (6)

<u>scheme of typical pH glass electrode</u>

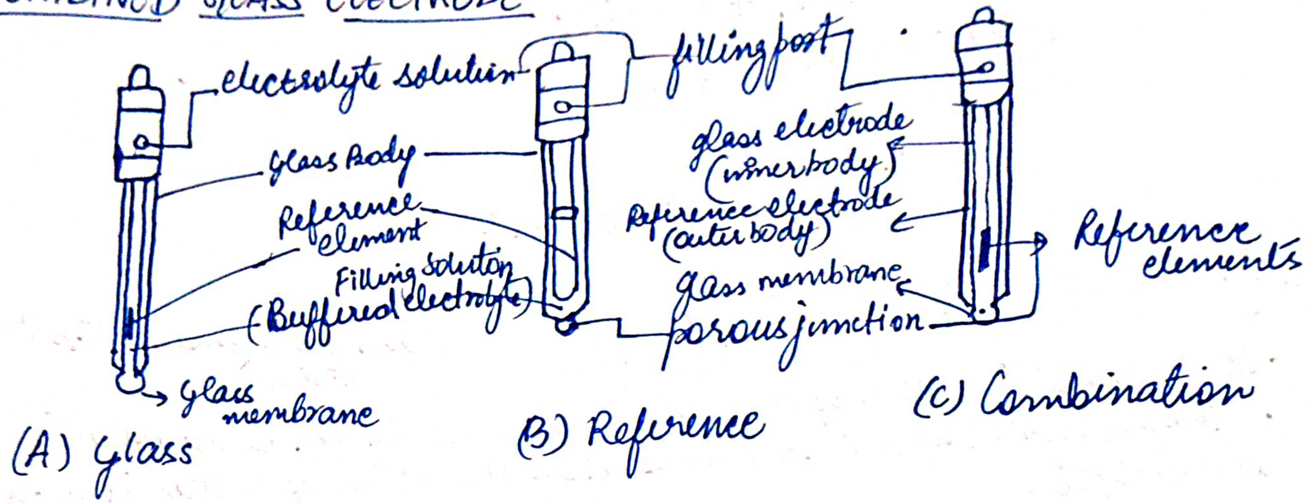
1) A sensing part of electrode
2) A bulb made from a specific glass sometimes electrode contain small amount of AgCl precipitate inside the glass electrode
3) Internal solution, usually 0.1M HCl for pH electrodes.
4) Internal electrode, usually silver chloride electrode or calomel electrode

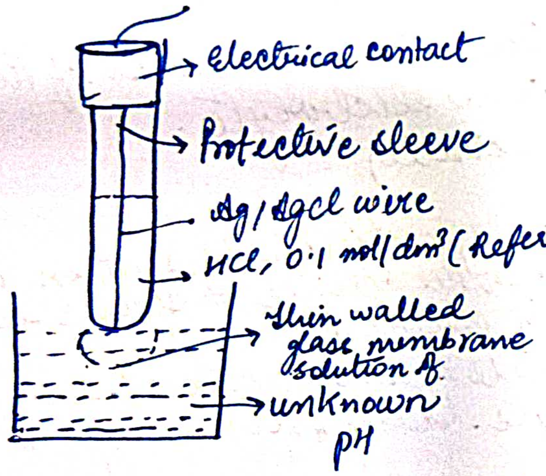
5) Body of electrode, made from non conductive glass or plastics

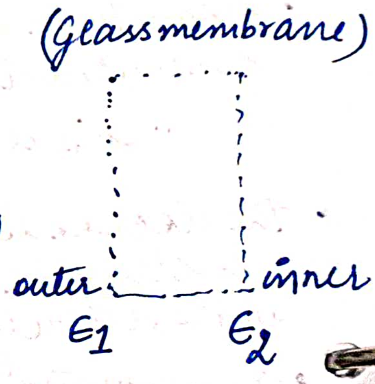
6) Reference electrode, usually the same type as 4

7) Junction with studied solution, usually made from ceramics or capillary with asbestos or quartz fibre.

COMBINED GLASS ELECTRODE



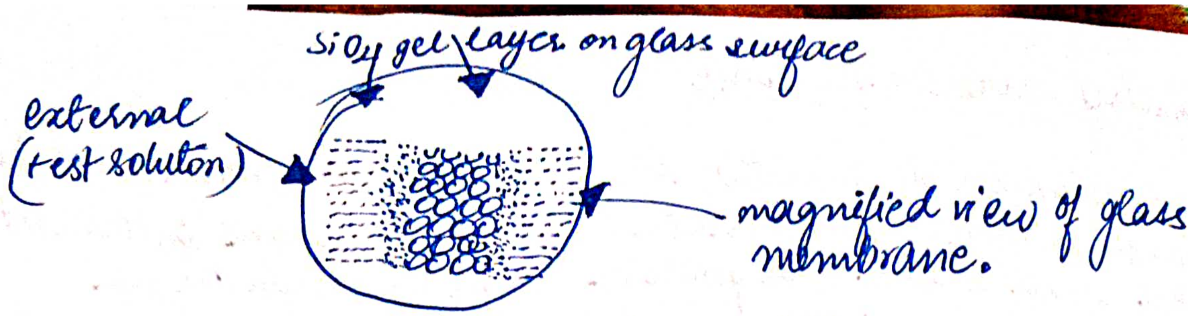




$$\underset{(soln)}{H^+} + \underset{(glass)}{Na^+} \leftrightarrow \underset{(soln)}{Na^+} + \underset{(glass)}{H^+}$$

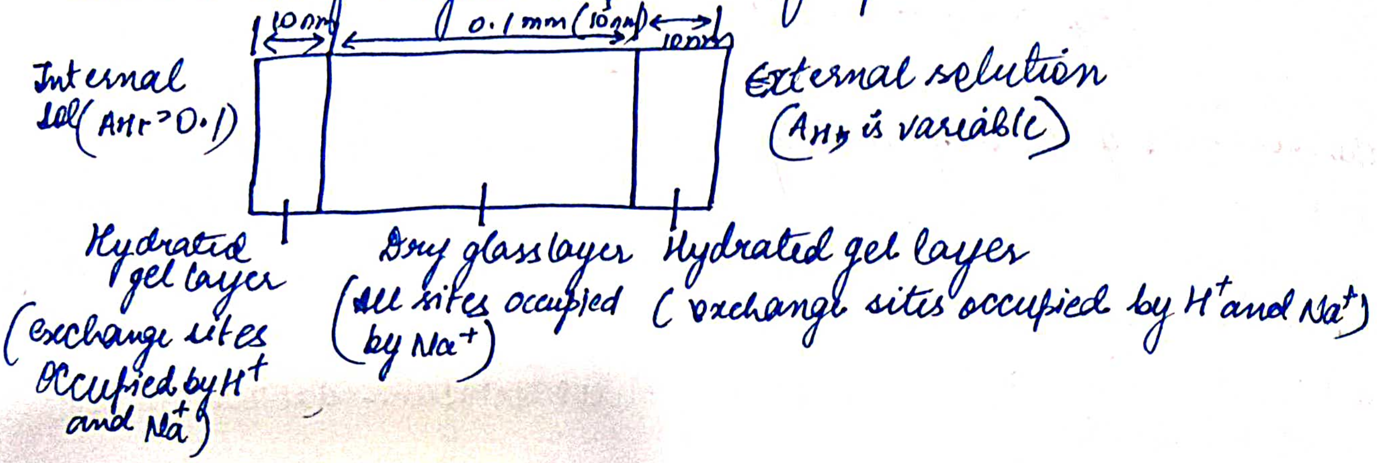
Schematic diagram of the structure of glass, which consist of an irregular network of SiO_4 tetrahedra connected through oxygen atoms.

cations are coordinated to the oxygen atoms.

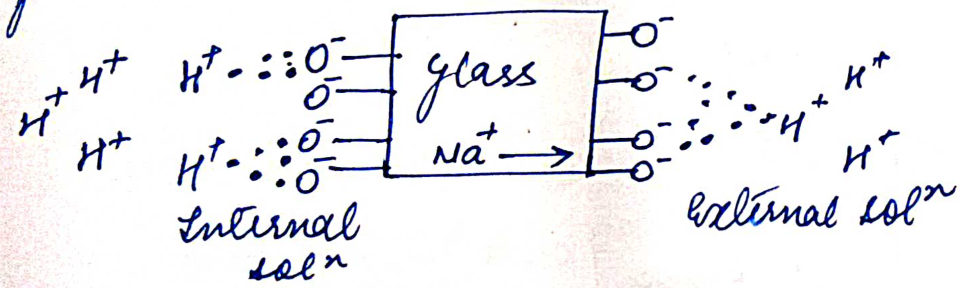


0.1 mm glass membrane width

A cross section of the glass membrane of a pH electrode



Ion exchange Equilibria on the inner and outer surfaces of the glass membrane.



ELECTRODE POTENTIAL OF GLASS ELECTRODE

The overall potential of the glass electrode is given by:

$$E_g = \underbrace{E_b}_{\text{boundary potential}} + \underbrace{E_{ref}}_{\text{reference}} + \underbrace{E_{asy}}_{\text{asymmetry potential}}$$

Three Components

- → The boundary potential E_b.
- → Internal reference electrode potential E_{ref}
- → Assymetric potential E_{asy}.

Asymmetry varies with time

- The hydration of a pH sensitive glass membrane involves in ion exchange reaction between singly charged cations in the interstices of the glass lattice and protons from the solutions.

$$H^+ + MGl \rightleftharpoons M^+ + HGl$$

soln. membrane soln membrane

$$\boxed{E_g = E_g^{\circ} - 0.0592\,pH}$$

origin
causes
The sources of the asymmetry potential include the following:

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

(ii) mechanical abrasions on the outer surface during use ~~of electrodes~~.

(iii) Chemical etching of the outer surface during use.

The Asymmetry potential changes slowly with time

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

Expression for E Boundary (Potential of Glass electrode)

solution to be analysed (C_2) | membrane (glass bulb) | 0.1 M HCl, Ag / AgCl (C_1) internal reference

E_1 (outer side) E_2 (inner side)

$$E_b = E_1 - E_2 = \frac{RT}{nF}\left(\log C_2 - \log C_1\right)$$

$$= -\frac{RT}{nF}\log C_1 + \frac{RT}{nF}\log C_2$$

$$= L + \frac{RT}{nF}\log C_2 \qquad C_2 = (H^+ \text{ ion concentration})$$

E_b depends upon (H^+) $\quad E_b = L - 0.0592\,pH$

Application of glass electrode

(By convention GE is cathode)

Determination of pH :

cell: SCE / test solution || GE

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

$E_{cell} = (E_g^0 - (0.0592\, pH)) - E_{cal}$

$$\boxed{pH = \frac{E_g^0 - E_{cell} - E_{cal}}{0.0592}}$$

$E_g = E_b + E_{Ag/AgCl} + E_{asy}$

$L - 0.0592\, pH + E_{Ag/AgCl} + E_{asy}$

★ $\left(E_g^0 = L + E_{Ag/AgCl} + E_{asy}\right)$

$$\boxed{E_g = E_g^0 - 0.0592\, pH}$$

constant for particular glass electrode, Not for universal constant.
(Asy is varying)

When $C_1 = C_2$, $E_b = 0$ (should be) but E_b is not 0, some potential still exists

Advantages of Glass Electrode

(1) Can be used without interference in solutions, containing strong oxidants / reductants, proteins, viscous fluids & gases, as the glass is Chemically Robust
(2) Can be used for solution having pH values 2 to 10.
(3) Immune to poisoning and is simple to operate
(4) Eq^m is reached quickly & the response is rapid
(5) Can be used for very small quantities of the solutions.
(6) Much more convenient to handle than the inconvenient hydrogen electrode.

for pH for than 10

Another type of glass Al_2O_3 + Corning 015 glass + B_2O_3 incorporated interstices of glass matrix.

Disadvantages of glass electrode.

* The bulb is very fragile and has to be used with great care.
* Imp. In the presence of alkali ions, glass surface becomes responsive to both hydrogen and alkali ions. Measured pH values are low than actual
* Imp. In highly acidic solutions measured pH values are high
* When not in use, the electrode should be stored in an aqueous solution, to prevent membrane from drying out.
* Ordinary potentiometers can not be used to measure the potential of glass electrode.
* The commercial version is moderately expensive.
* Standardization has to carried out frequently

[Acid Error] (pH < 2)

[Alkali Error] * pH > 10

[Influence of anions destroying the glass matrix.]

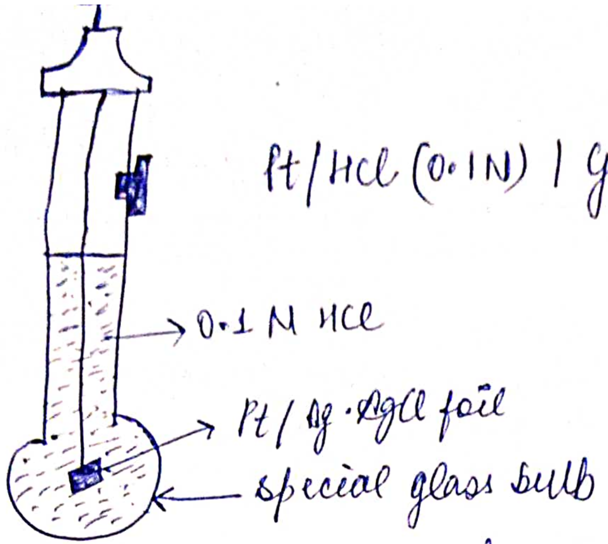
→ higher than actual

Q Why the glass electrode has to be standardized before use everytime?

Ans Assymmetric potential varies with time. (mention sources also)

Q Why ordinary potentiometers cannot be used to measure potential of GE. (electronic potentiometers have to be used)

Ans The type of glass used in making GE is Corning 015. [Low melting point and high electrical resistance] It won't draw any current. Those fitted with amplifiers have to be used which will not require any current.



Pt / HCl (0.1N) | glass or Ag / AgCl(s) / HCl (0.1N) / Glass

(Construction of GE)

The electrode consists of a thin glass membrane (about 50mm thick), sealed into one end of a heavy walled glass tube.
A special variety of glass (Corning 015 glass) with app. composition 20% Na_2O, 6% CaO & 72% SiO_2) is used.
It has low melting point and high electrical resistance

Silver / $AgCl_2$ reference electrode which is connected to one of the terminals of a potential measuring device.
Note that internal reference electrode is a part of the glass electrode and it is not the pH sensing element.

Only the potential that occurs between the outer surface of the glass bulb and the test ~~surface~~ solution responds to pH changes.

WORKING

A silicate glass used for membranes consist of an infinite 3D-network of SiO_4^{4-} group. There are sufficient cations to balance the negative charge of the silicate groups within the interstices of this structure.
Singly charged cations such as sodium and lithium are mobile in the lattice and are responsible for electrical conduction within the membrane.

Imp

The glass is a partially hydrated aluminosilicate containing sodium or calcium ions.

Imp → divalent are more strongly held.. The silica glass structure is shaped in such a way that it allows Na^+ ions some mobility. The metal cations in the hydrated gel diffuse out of the glass and into the solution while H^+ from solution can diffuse into the hydrated gel.

[The process involves univalent cations exclusively because divalent cations are too strongly held within the silicate structure to exchange with ions in the solution and hence immobile.

Cont.... disadvantages

(1) It can be used for very small quantities of the solutions. Small electrodes can be used for pH measurement in one drop of solution in a tooth cavity or in the sweat of the skin (micro determinations) using microelectrodes.

(2) If recently caliberated, the glass electrode gives an accurate response

(3) The glass electrode is much more convenient to handle than the inconvenient hydrogen gas electrode.

(4) Glass electrodes which are selective for Li^+, Na^+, Cs^+, Ag^+ and NH_4^+ ions are commercially available, and these special electrodes are useful for measuring the above ions.

Q The cell SCE || 0.1 M HCl | AgCl(s) | Ag gave EMF of 0.24 V and 0.26 V with buffer having pH 2.8 and unknown value pH respectively calculate pH of unknown pH solution.

Ans

given $E_{SCE} = 0.2422$ V.

$$E_{cell} = E_g^\circ - 0.0591\,pH$$

$$0.24 = E_g^\circ - 0.0591 \times 2.8$$

$$0.24 + 0.0591 \times 2.8 = E_g^\circ$$

$$\Rightarrow 0.24 + 0.16548 = E_g^\circ$$

$$E_g^\circ = 0.4054$$

$$pH = \frac{E_g^\circ - E_{cell} - E_{cal}}{0.0591}$$

$$pH = \frac{0.4054 - 0.26 - 0.2422}{0.0591}$$

$$pH = \frac{0.1454 - 0.2422}{0.0591}$$

$$pH = \frac{-0.0968}{0.0591}$$

$$pH = \underline{1.63}$$