

$$\text{E}_{\text{Hg}} = \text{E}'_{\text{Hg}} - 0.0592 \log [\text{H}^+]_{\text{aq}}$$

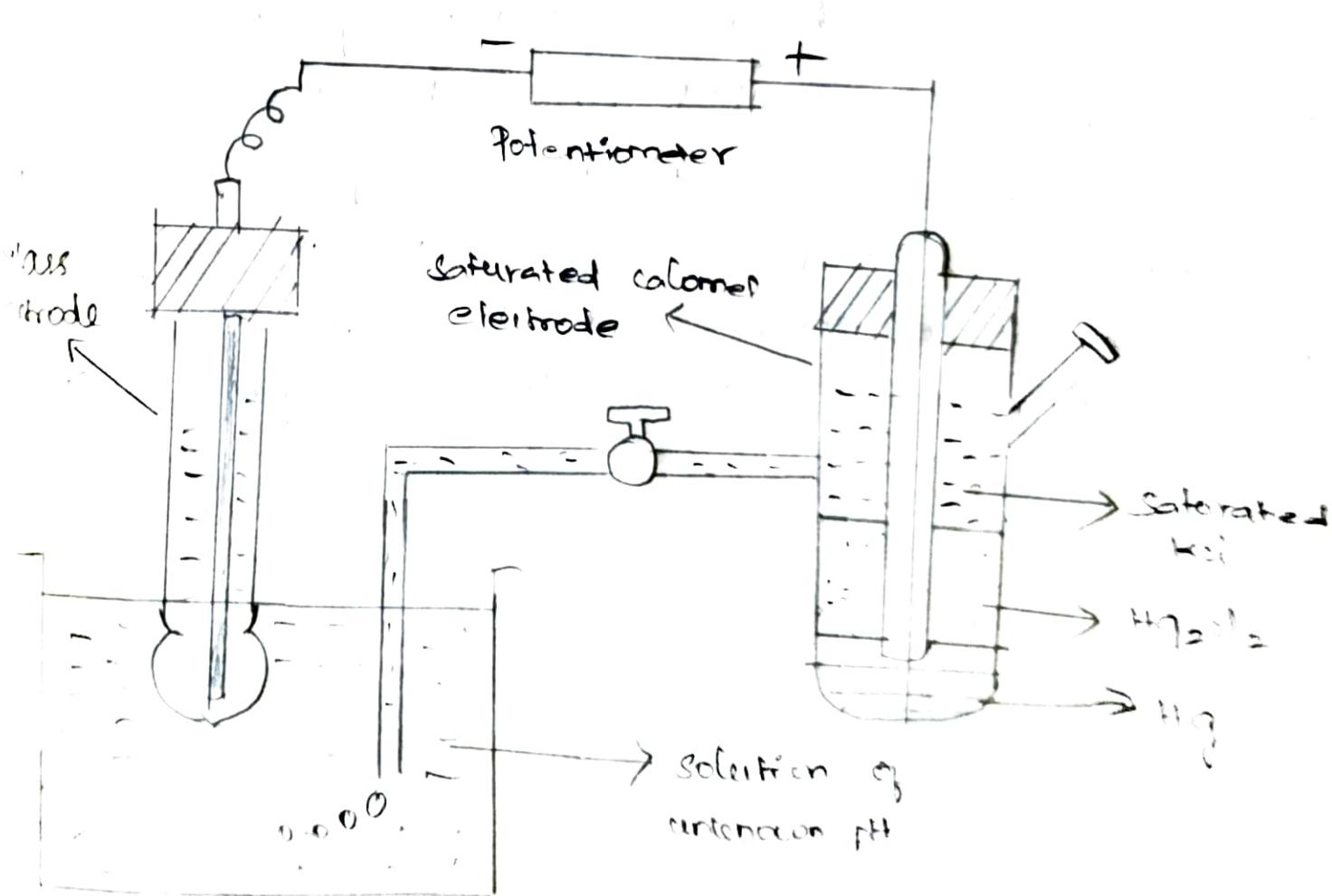
(or)

$$\text{E}_{\text{Hg}} = \text{E}'_{\text{Hg}} + 0.0592 \text{ pH}, \quad [(\text{pH} = -\log [\text{H}^+])]$$

from the equation it is clear that the pH of a solution is a direct measure of emf of a glass electrode.

Determination of pH of a solution using glass electrode.

The glass electrode is placed in the solution under test and is coupled with saturated calomel electrode as.



The emf of the cell is measured. From the emf, the pH of the solution is calculated as follows,

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

$$\begin{aligned}E_{\text{cell}} &= E_{\text{cal}} - E_{\text{in}} \\&= E_{\text{cal}} - (E_{\text{in}}^{\circ} + 0.0592 \text{ pH}) \\&= E_{\text{cal}} - E_{\text{in}}^{\circ} - 0.0592 \text{ pH}\end{aligned}$$

$$\text{pH} = \frac{E_{\text{cal}} - E_{\text{in}}^{\circ} - E_{\text{cell}}}{0.0592}$$

$$\therefore E_{\text{cal}} = 0.2422 \text{ V}$$

$$\therefore \text{pH} = \frac{0.2422 - E_{\text{in}}^{\circ} - E_{\text{cell}}}{0.0592}$$

Advantages of Glass Electrode :-

- i) It can be easily constructed and readily used.
- ii) The results are accurate.
- iii) It is not easily poisoned.
- iv) Equilibrium is rapidly achieved.

Disadvantages (Limitations)

Since the resistance is quite high, special electronic potentiometers are employed for measurement. The glass electrode can be used in solutions

only with pH range of 0 to 10. However above the pH 12 (high alkalinity), cations of the solution affect the glass and make the electrode useless.

Applications of ISES:

- i) ISES are used in determining the concentrations of cations like H^+ , Na^+ , K^+ , Ag^+ , U^+ .
- ii) ISES are used for the determination of hardness (Ca^{2+} and Mg^{2+} ions)
- iii) Concentrations of anions like NO_3^- , Cl^- , S^{2-} , halides (X^-) can be determined.
- iv) ISES are used in the determination of concentration of a gas by using gas-sensing electrodes.
- v) pH of the solution can be measured by using gas-sensing electrode.

Electrolysis:

The chemical decomposition of an electrolyte caused by the passage of electricity is called electrolysis.

Consider the electrolysis of an aqueous solution of HCl between two platinum electrodes. It is seen that hydrogen is evolved at the cathode and chlorine is evolved at the anode.