4. Ion selective electrodes

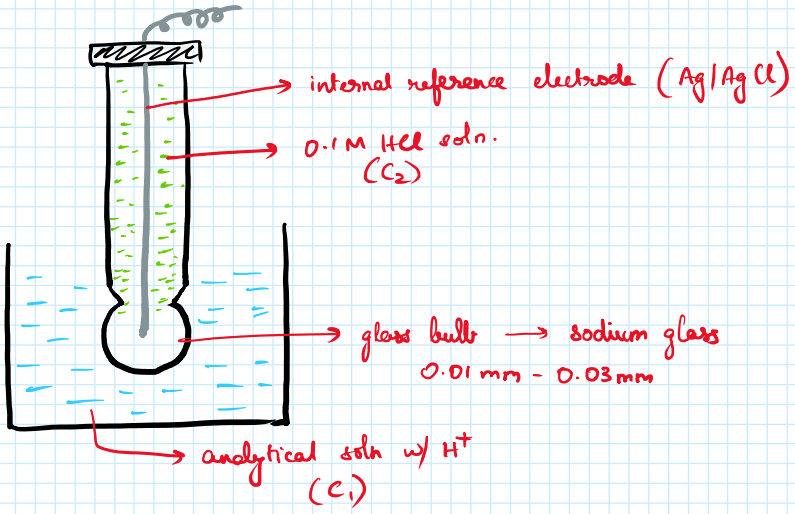
12 October 2023 09:52

Ion Selective Electrode

The electrode which selectively detects a particular ion (quantitatively measure?)

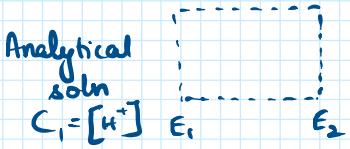
Eg: glass electrode

Glass Electrode



- pH sensitive electrode
- detects H^+ ions
- internal reference electrode : Ag | AgCl
- membrane electrode

$H^+_{(soln)} + NaCl \rightleftharpoons HCl + Na^+_{(soln)}$



$E_b = E_1 - E_2$

Note: Boundary potential
Potential diff. b/w analytical and standard solution

$$E_b = \frac{0.0591}{n} \log \frac{C_1}{C_2}$$

$$E_b = \frac{0.0591}{n} \log C_1 - \frac{0.0591}{n} \log C_2$$

$$E_b = K + \frac{0.0591}{n} \log C_1 \quad [\because C_1 = [H^+], n = 1]$$

$$E_b = K + 0.0591 \log [H^+] \quad [\because pH = -\log[H^+]]$$

$$\boxed{E_b = K - 0.0591\ pH}$$

Calculation of Glass Electrode Potential (E_g)

$$E_g = E_b + E_{\text{reference electrode}} + E_{AP}$$

E_{AP} → Assymetric potential

Note: Assemetric potential
The potential difference b/w

$E_G = K - 0.0591\,pH + E_{RE} + E_{AP}$

$\because E^\circ_G = K + E_{RE} + E_{AP}$,

$$\boxed{E_G = E^\circ_G - 0.0591\,pH}$$

NOTE: Assemetric potential
The potential difference b/w curvature of glass bulb of analytical soln and standard soln.

APPLICATIONS OF GLASS ELECTRODE

- Industrial
- Agriculture
- Laboratories

ADVANTAGES OF GLASS ELECTRODE

- Can work in both oxidising and reducing environments
- Construction is easy

DISADVANTAGES OF GLASS ELECTRODE

- Sensitive potentiometer since glass bulb is extremely thin
- Alkaline error: Glass electrodes using sodium glass bulb (Na$_2$O)
  ↓
  Detects only 1-9 pH accurately
  ↓
  10-14 is not detected properly } Alkaline error

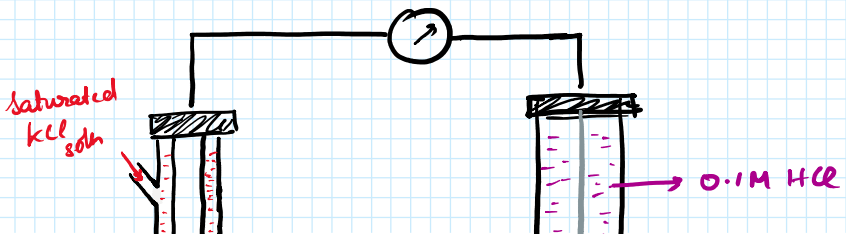
How to reduce alkaline error?

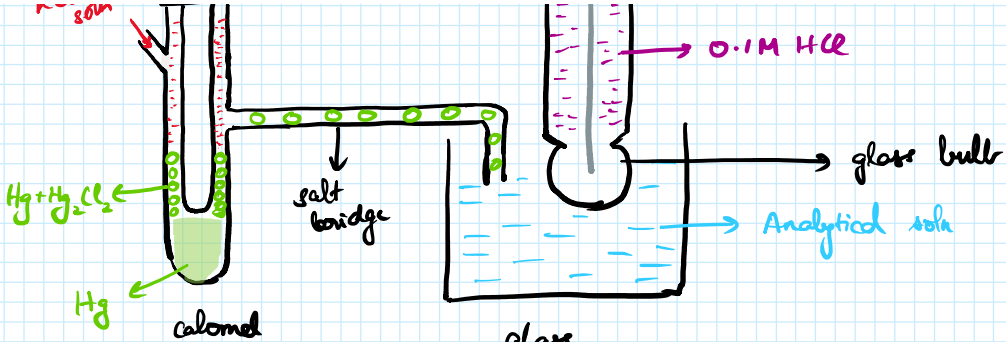
Use lithium glass bulb instead of sodium glass bulb
↓
Accurately detects 1-14 pH but is more expensive

CALCULATION OF pH USING GLASS ELECTRODE

Calomel electrode || Glass electrode

$$\boxed{Hg \mid Hg_2Cl_2 \mid Cl^- \,||\, \underset{soln\ (H^+)}{Analytical} \mid Glass \mid HCl\,(0.1M) \mid AgCl \mid Ag}$$





$E_{calomel}$

$E_G = E^\circ_G - 0.0591\,pH$

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

$E_{cell} = E^\circ_G - 0.0591\,pH - E_{calomel}$

$$E^\circ_G = 0.0591\,pH + E_{cell} + E_{calomel}$$

$$pH = \frac{E^\circ_G - E_{cell} - E_{calomel}}{0.0591}$$

PROBLEMS

Q. A glass electrode is dipped with a solution (pH = 4) offered a potential of 0.284 V at 298 K. With a solution of unknown pH at same temperature, E = 0.38 V.

$E_{calomel} = 0.2422$

Soln

known values → E°_G

unknown → pH

$E^\circ_G = 0.0591(4) + 0.284 + 0.2422$

$= 0.7626$

$$pH = \frac{E^\circ_G - E_{cell} - E_{calomel}}{0.0591}$$

$$= \frac{0.7626 - 0.38 - 0.2422}{0.0591}$$

$= 2.38$

Q Same question: ① pH = 4.066, E = 0.209 at 298 K

② pH = ?, E = 0.1162

$E_{calomel} = 0.2422$

Soln. $E^{\circ}_{G} = 0.0591(4.066) + 0.209 + 0.2422$

$= 0.6915\ V$

$pH = \dfrac{E^{\circ}_{G} - E_{calomel} - E_{cell}}{0.0591}$

$= \dfrac{0.6915 - 0.2422 - 0.1162}{0.0591}$

$= 5.64$