ENGINEERING CHEMISTRY

Department of Science and Humanities

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Electrochemical equilibria

Class content:

- ***Glass electrode***
  - ***Construction***
  - ***Working***
  - ***Determination of pH***

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Electrochemical equilibria

Ion selective electrodes (ISE)

- Selectively respond to a **specific ion** in a mixture
- Potential developed is a function of concentration of that ion
- Have a membrane which is capable of exchanging the specific ion with solution with which it is in contact
- **Membrane electrodes**
  e.g., glass electrode

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Electrochemical equilibria

Glass electrode

- Ion-selective electrode
- Responds to Hydrogen ion
- pH sensitive; can be used to determine pH of a solution
- Consists of a glass membrane which is capable of exchanging H^+ ions

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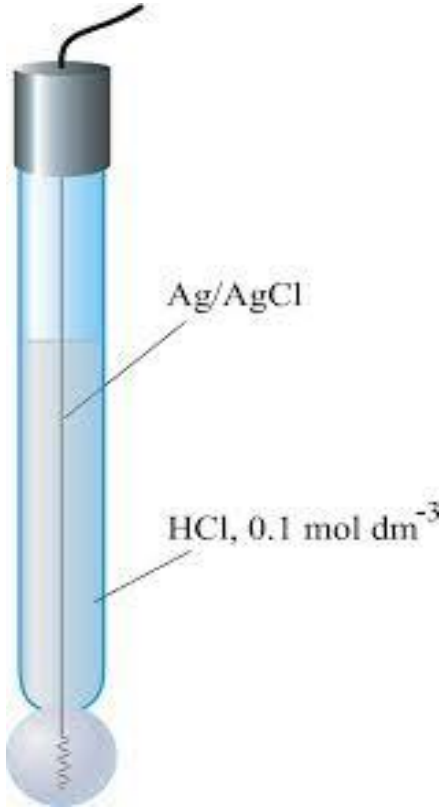
Electrochemical equilibria

- **Construction:**
- Glass tube , the end of which is a bulb of **very thin glass membrane**
- Glass bulb is made up of special type of glass, CORNING 015
- The glass bulb is filled with **solution of known pH** which is the reference solution
- A **silver - silver chloride electrode** is dipped inside the reference solution serves as internal reference electrode and also provides external electrical contact
- The electrode is immersed in a **solution containing H^+** which is the analyte
- **Ag/AgCl/HCl/glass**



Source:https://glossary.periodni.com/glossary.php?en=glass+electrode

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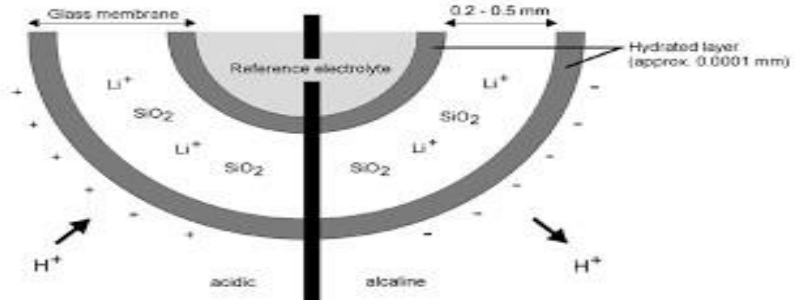
Working:

analyte solution | reference solution | Ag-AgCl electrode

$[H^+] = C_1$ | $[H^+] = 0.1M\ HCl = C_2$

$$H^+_{\text{solution}} + Na^+Gl^- \rightleftharpoons Na^+_{\text{solution}} + H^+Gl^-$$

- The inner and outer surfaces of the glass membrane can exchange H^+ ions with the solution they are in contact with



Source:http://www.metrohmsiam.com/teachingresearch/TRL_25/TRL25_955207_80155013.pdf

- The hydrated glass membrane brings about ion exchange reaction between singly charged cations in the interstices of glass lattice and protons from the solution
- A potential is developed, which is a function of H^+ of the solution

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Electrode potential of a glass electrode :

analyte solution
$[H^+] = C_1$

reference solution
$[H^+] = 0.1M\ HCl = C_2$

Ag-AgCl electrode

boundary potential is $E_b = \frac{2.303RT}{nF} \log\left(\frac{C_1}{C_2}\right)$

since concentration of reference solution, C_2 is constant

$$E_b = L' + \frac{2.303RT}{nF} \log C_1$$

where $L' = -\frac{2.303RT}{nF} \log C_2$

At 298K, $E_b = L' + \frac{0.0591}{n} \log[H^+]$ since for H^+, n = 1

$$E_b = L' - 0.0591 pH$$

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The glass electrode potential has 3 components

1. **The boundary potential**
2. **The potential of internal reference electrode**
3. **Asymmetric potential**

$$E_G = E_b + E_{ref} + E_{asymmetric}$$

- Asymmetric potential arises due to difference in responses of inner and outer surfaces of the glass bulb, due to differing conditions of stress on two glass surfaces

$$E_G = E_b + E_{ref} + E_{assymmetric} \quad ; \quad E_b = L' + \frac{0.0591}{n}\log[H^+]$$

$$= L' + \frac{0.0591}{n}\log[H^+] + E_{ref} + E_{assymmetric}$$

$$= E^0_G + 0.0591\log[H^+] \quad \text{where } E^0_G = L' + E_{ref} + E_{asymmetric}$$

$$E_G = E^0_G - 0.0591pH$$

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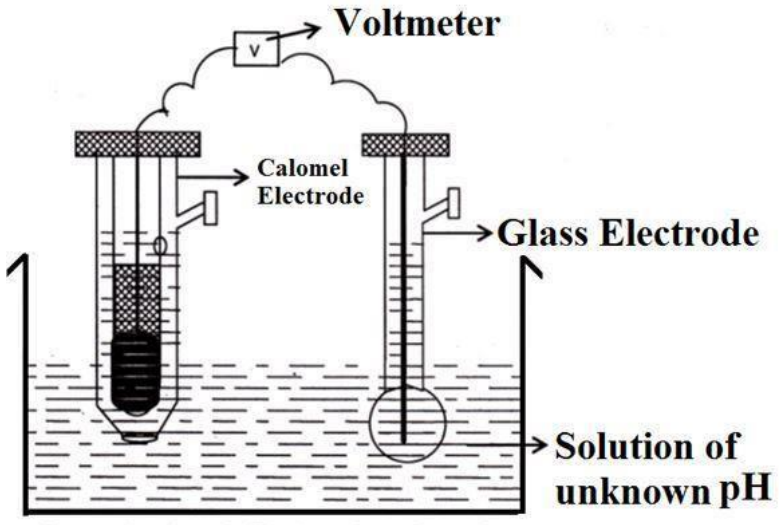
Determination of pH using glass electrode:

- Glass electrode is combined with an external reference electrode

$Hg/Hg_2Cl_2/Cl^-$//analyte solution/glass/0.1N HCl/AgCl/Ag



Determination of pH using glass electrode

Source:https://utkarshiniedu.wordpress.com/2016/12/22/lecture-1-108-ion-selective-electrodes/

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Determination of pH using glass electrode:

- The emf of the cell is determined potentiometrically

$$E_{cell} = E_G - E_{calomel} \; ; \qquad E_G = E^0_G - 0.0591pH$$

$$= E^0_G - 0.0591pH - E_{calomel}$$

$$pH = \frac{E^0_G - E_{calomel} - E_{cell}}{0.0591}$$

- To evaluate E^0_G the glass electrode is dipped in a **solution of known pH(buffer solution)** and combined with calomel electrode, the emf of the cell is measured from which **E^0_G can be evaluated**

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Applications of glass electrode:

Used extensively in chemical, industrial, agricultural and biological labs

Advantages of glass electrode :

- Can be used in oxidizing and reducing environments and metal ions
- Does not get poisoned
- Can be used for very small volumes
- Accurate results can be obtained between pH 1 to 9 by ordinary electrodes. However by using special glass electrodes pH 1 to 14 can be measured with accuracy
- Simple to operate and can be used with portable instruments

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Disadvantages of glass electrode:

- Because of high resistance of glass, a simple potentiometer cannot be used. It requires sensitive potentiometer for emf measurements

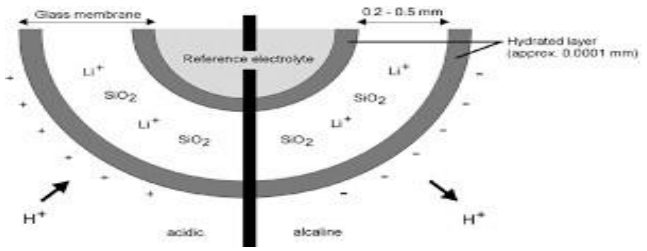
- Glass membrane is very delicate, hence has to be handled carefully

- At very high pH levels usually over a pH of 9 , **Alkaline error** is observed

$$H^+_{\text{solution}} + Na^+Gl^- \rightleftharpoons Na^+_{\text{solution}} + H^+Gl^-$$

When the Sodium ion level is relatively high, some of the H^+ ions in the gel layer around the sensitive electrode membrane are replaced by Na^+ ions

The electrode may eventually respond to Na^+ instead of H^+ ions, giving a false lower pH value than the actual value



THANK YOU

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