# STUDY MATERIAL

# VIVEKANANDA COLLEGE THAKURPUKUR

NAAC ACCREDITED GRADE—'A'

# Subject: Chemistry

## Topic: Calibration of pH meter

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# Defining pH

**Sørensen defined pH as :** $$pH = -\log_{10}[H^+]$$

**This was later revised, as further research demonstrated that pH is more related to hydrogen ion activity than hydrogen ion concentration. In 1920, pH was redefined as follows**

$$pH = -\log_{10} a_{H^+}$$

$$a_{H^+} = f \times [H^+]$$

**f =activity coefficient.**

**Practical pH measurement uses methods based on this definition.**

## Measurement of pH

# The glass-electrode

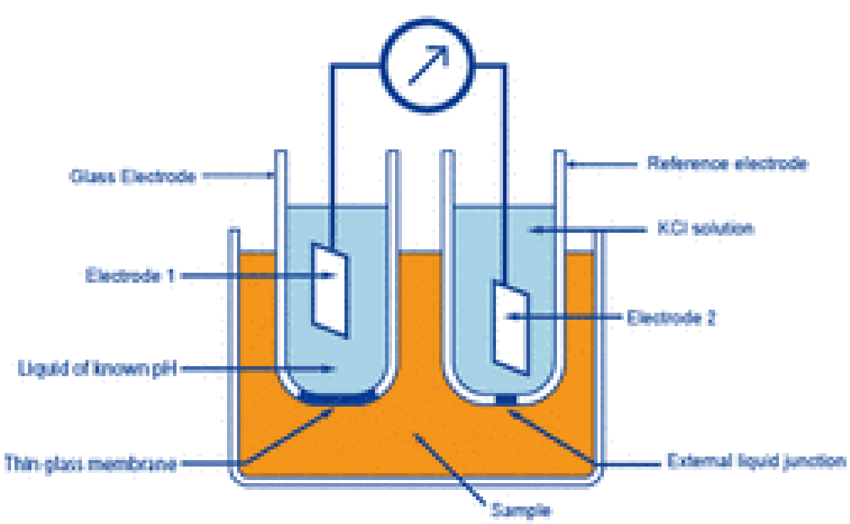
**In the glass-electrode method, the pH of a test solution is determined by combining two electrodes to form a cell, and measuring the potential difference generated between them. The electrodes are:**

- **Glass electrode**

  **(An ion-selective membrane electrode kept in contact with the test solution)**

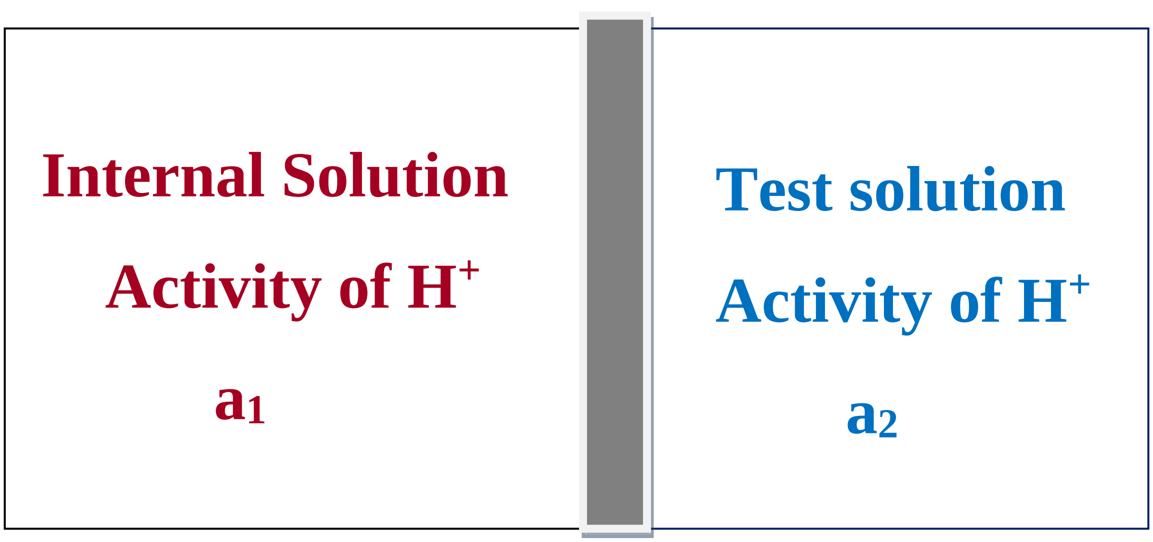
- **A reference electrode**

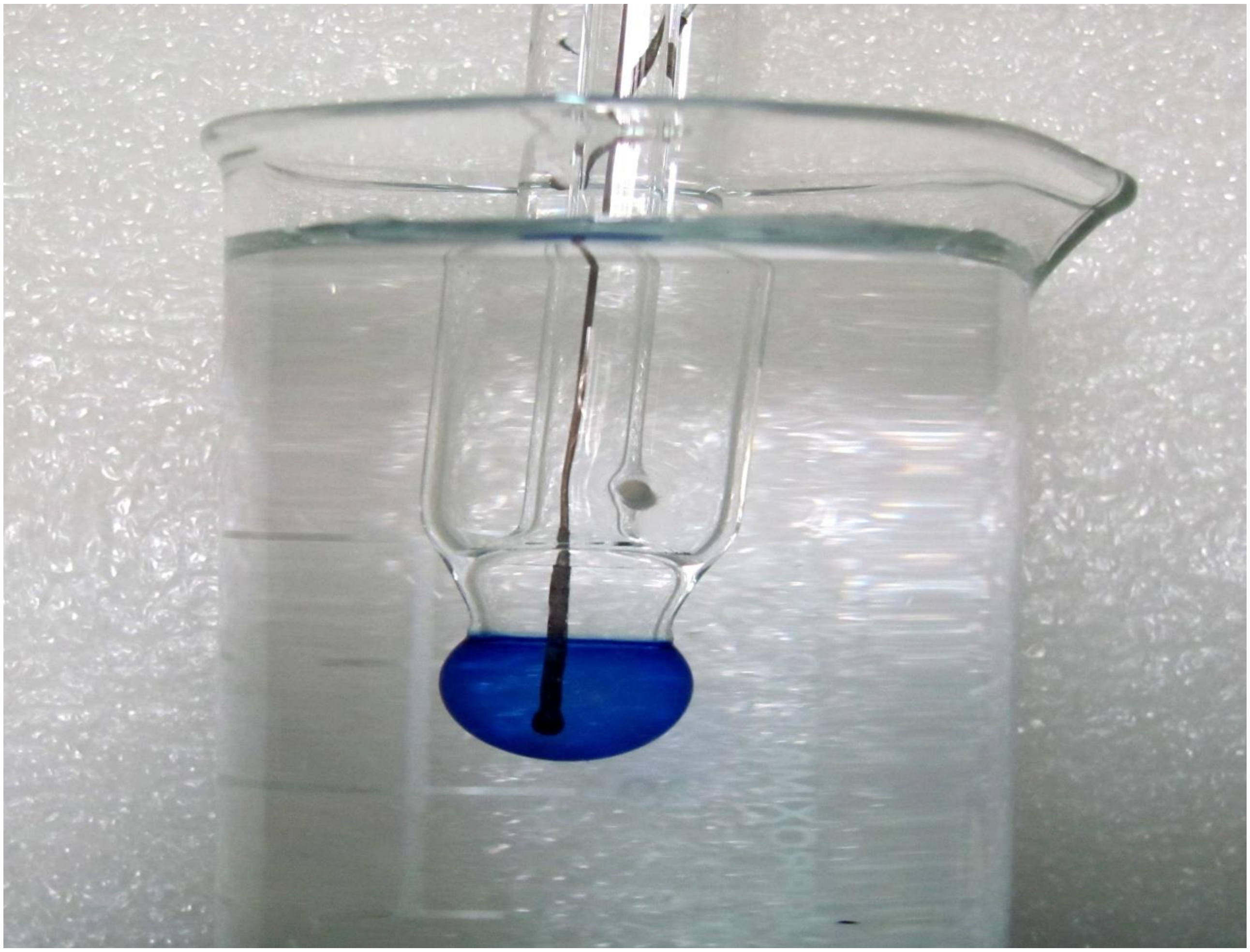
  **(Saturated Calomel or $Ag/\,AgCl\,/\,Cl^{-}$electrode)**



If two solutions of different activities are placed on two sides of a thin selectively-permeable glass membrane, an electrical potential difference will form across the membrane, called the

# Asymmetry potential





If a bulb-shaped electrode is made with such special glass, containing a solution of constant pH, which is dipped in an external test solution of different pH, an asymmetry potential will be generated which is proportional to this difference in pH.

- When there is a change in the pH of the external solution (test solution), this potential difference will change. This is the principle of measurement of pH in this method.

**The liquid inside the glass electrode has a known constant pH. If one can measure the potential of the glass electrode, the pH of the test solution can be found out by calculation.**

$$E_{Glass} = E^{o}{}_{Glass} - \frac{RT\times 2.303}{F}\log\frac{a_{H^+}(internal\ solution)}{a_{H^+}(test\ solution)}$$

$$E_{Glass} = E^{o'}{}_{Glass} + \frac{RT\times 2.303}{F}\log a_{H^+}(test\ solution)$$

$$E_{Glass} = E^{o'}{}_{Glass} - \frac{RT\times 2.303}{F}pH(test\ solution)$$

**A second electrode is necessary to measure the potential generated at the glass electrode. This electrode, which contributes a very stable potential, is paired with the glass electrode to form a cell. It is called the reference electrode. The electromotive force generated by the cell is measured by the pH meter, which is essentially a digital potentiometer, capable of measuring small potentials (usually much less than 1 volt).**

## $E_{Glass}$ depends on pH.

**Therefore, glass electrode functions as left hand or right hand electrode depending on the pH of the test solution and the potential of the reference electrode.**

**When glass electrode is combined with saturated calomel electrode (SCE) at pH less than 7 (acidic solution), $E_{Glass}$ is greater than the electrode potential of SCE. So glass electrode serves as the right hand electrode. The cell is**

***Pt / Hg(l) / $Hg_2Cl_2$ (s) / KCl (saturated) // Test solution/ Glass electrode***

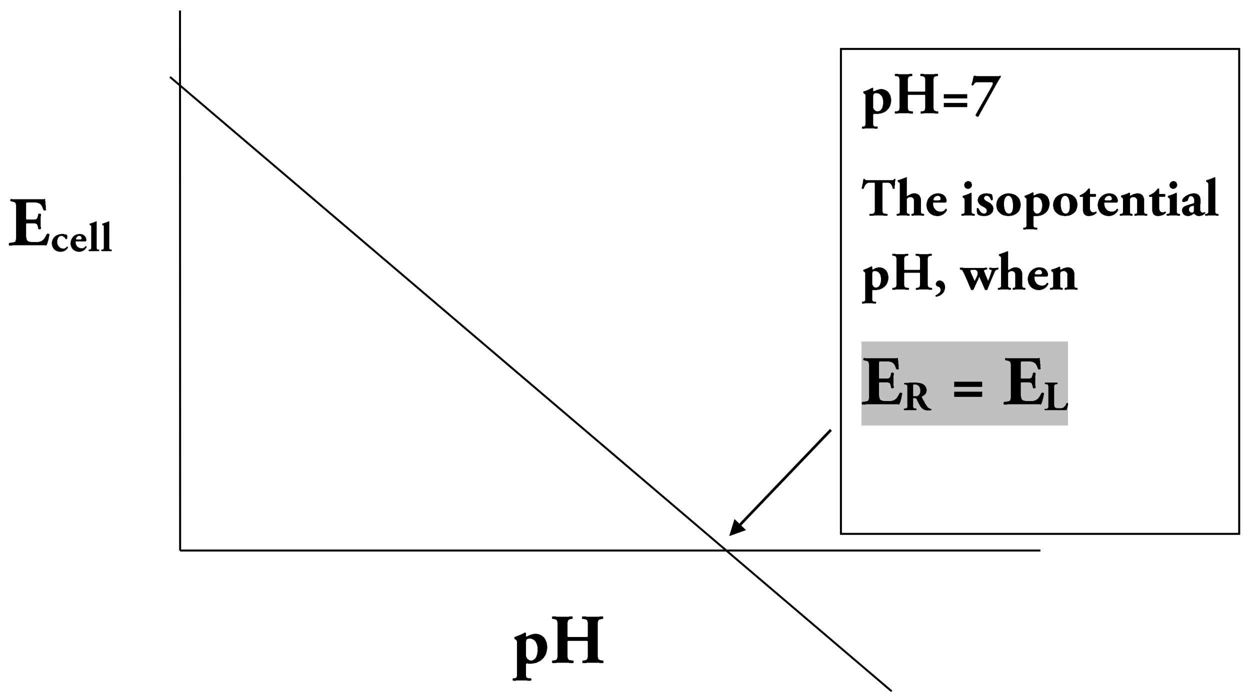
The cell EMF is: $E_{Cell} = E_{Glass} - E_{SCE}$

$$E_{Cell} = (E^{o'}_{Glass} - E_{SCE}) - \frac{RT \times 2.303}{F} pH(test\ soln)$$

$$E_{Cell} = K - \frac{RT \times 2.303}{F} pH(test\ solution)$$

At 25°C The value of $\frac{RT \times 2.303}{F}$ is 0.0591 V= 59.1 mV

So, the plot of $E_{cell}$ *vs* pH will be a straight line with a negative slope (equal to 59.1 mV at 25°C) and a positive intercept on the Y axis (K, which includes the potential of SCE, the 'standard potential' of the glass electrode as well as any small amount of liquid junction potential generated in spite of a salt bridge)




Calibration of a glass electrode essentially amounts to drawing this straight line $E_{cell}$ *vs* pH.

**At 25 °C, for a decrease of 1 pH unit, the increase in $E_{cell}$ value should be 59.1 mV. So, for a buffer of pH 4 (drop of pH=3 units from 7) we should expect an $E_{cell}$ value of 59.1× 3 = 177.3 mV at 25 °C.**

**For other temperatures, slope will be different**. Calibration of a glass electrode is essentially setting the correct slope and the intercept at the experimental temperature. We need at least two points to do this. **Usually they are at pH 7 and pH 4. Sometimes we use another point at pH 9.2.**

**When glass electrode is combined with saturated calomel electrode (SCE) at pH greater than 7 (alkaline solution), $E_{Glass}$ is less than the electrode potential of SCE. So glass electrode serves as the left hand electrode. The cell is**

***Glass electrode / test solution // KCl (saturated) / $Hg_2Cl_2$ (s) / Hg(l)) / Pt***

The cell EMF is: $E_{Cell} = E_{SCE} - E_{Glass}$

$$E_{Cell} = (E_{SCE} - E^{o'}_{Glass}) + \frac{RT \times 2.303}{F} pH(test\ solution)$$

$$E_{Cell} = K' + \frac{RT \times 2.303}{F} pH(test\ solution)$$

**When the test solution has pH greater than 7, $E_{cell}$ increases with pH. At 25 °C, for an increase of 1 unit of pH, the increase in the value of $E_{cell}$ value should be 59.1 mV. So, for a buffer of pH 10, we should expect an $E_{cell}$ value of 59.1× 3 = 177.3 mV**