

# Analytical Instrumentation

## UNIT – 4 NOTES

# Principle of pH measurement

- pH measurement is done by checking the voltage (potential) in an electrochemical setup. This setup includes two electrodes: a **measuring electrode** (which responds to pH) and a **reference electrode** (which maintains a stable voltage). Both electrodes are placed in the test solution and connected to a measuring device. The measuring electrode's voltage changes based on the pH of the solution, while the reference electrode provides a constant voltage for comparison. The difference between these voltages is used to determine the pH of the solution.

- The potential of the measuring electrode may be written using the Nernst equation:

$$E = E_0 + 2.3026 \frac{RT}{F} \log C_H$$

where  $E_0$  = standard potential

$R$  = gas constant

$T$  = absolute temperature

$F$  = Faraday constant

- The factor  $-2.3026 \frac{RT}{F}$  is called the slope factor and is dependent upon the solution temperature. It is clear that with  $1^\circ\text{C}$  change in temperature, the emf changes by 0.2 mV

# Glass electrode for pH measurement

## □ Principle –

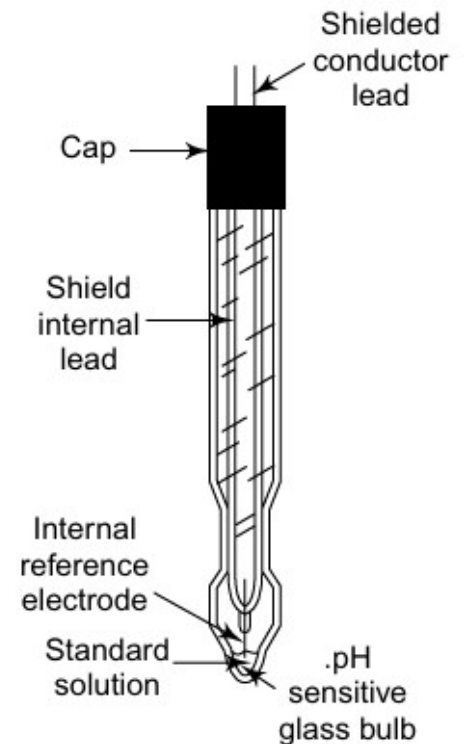
- When a thin membrane of glass is interposed between two solutions, a potential difference is observed across the glass membrane, which depends on the ions present in the solutions.

## □ Construction –

- The glass electrode consists of a thin walled bulb of pH-sensitive glass sealed to a stem of non-pH-sensitive high resistance glass. The pH response is limited entirely to the area of the special glass membrane, thus making the response independent of the depth of immersion.
- Glass pH electrodes are made from a special type of glass that acts as an **ion-selective barrier**, allowing only **hydrogen ions ( $H^+$ ) to pass through** while blocking other ions in the solution. To enable this selective response, the glass is **chemically doped with lithium ions**, which make it sensitive to **electrochemical reactions with hydrogen ions**.

# Glass electrode for pH measurement (cntd...)

- Since glass is an **excellent insulator**, it does not easily conduct electricity. This creates a challenge when trying to measure the voltage between the two electrodes. The electrical path starts from **one electrode, passes through the glass membrane, travels through the solution, and returns through the second electrode**, resulting in **very high resistance**.
- Inside the glass membrane, there is a **stable pH reference system**, typically made up of a **silver-silver chloride (Ag/AgCl) or calomel electrode** immersed in **hydrochloric acid (HCl)**. The changes in **electrical potential on the outer membrane** (which interacts with the test solution) are detected using an **external reference electrode** connected through a **salt bridge**, allowing accurate pH measurement.



# Glass electrode for pH measurement (cntd...)

## □ Measurement of output -

- The complete pH cell is represented as follows:

Internal Reference Electrode	Internal Electrolyte	Glass Membrane	Test Solution	External Reference Electrode
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- The ideal pH response of a glass electrode behaving exactly in the same manner as a hydrogen electrode is given by

$$E_2 - E_1 = 2.3026 \frac{RT}{F} (\text{pH}_2 - \text{pH}_1)$$

where  $E_1$  &  $E_2$  are the values of the emf of cell 1 in test solutions pH equal  $\text{pH}_1$  and  $\text{pH}_2$  respectively. The equation shows that ideal pH response is 54.2 mV at 0°C, 59.16 mV at 25°C and 73.04 mV at 95°C.

- Glass electrodes are typically effective within a **pH range of 1 to 11**. When measuring **pH values below 1**, **acid errors** can occur, making frequent calibration necessary using a **buffer solution with a pH close to the actual test solution**. Similarly, at **pH levels above 11**, **alkaline errors** may appear. The extent of these **alkaline errors** depends on the **composition of the glass membrane**.

# Glass electrode for pH measurement (cntd...)

## □ Advantages –

- A faster response
- More reliable measurements
- A long lifetime

## □ Disadvantages –

- Measuring solutions containing particulate can damage the glass membrane.
- The glass membrane is easily broken. There are alternatives to the glass membrane, though they are used seldom due to other drawbacks, such as limited pH range or long response time.

# Factors affecting the accuracy of pH readings

## ❑ Temperature:

- The Nernst equation includes a temperature-dependent term indicating that the electrode's response varies with temperature.
- Temperature fluctuations can affect both the electrode's sensitivity and the actual pH of the solution.
- Compensation mechanisms or temperature-controlled environments are often employed to mitigate these effects.

## ❑ Calibration:

- Regular calibration with standard buffer solutions is essential to ensure accurate measurements. Deviations can occur due to electrode aging or changes in the glass membrane properties.

## ❑ Ionic Strength and Composition of the Test Solution:

- Solutions with low ionic strength (e.g., distilled water) can lead to unstable readings.
- High concentrations of interfering ions, such as sodium ( $\text{Na}^+$ ) or potassium ( $\text{K}^+$ ), especially at high pH levels, can cause "alkaline error," leading to inaccurate readings.

# Factors affecting the accuracy of pH readings

## ❑ Electrode Condition:

- The glass membrane must remain hydrated to function correctly. Drying out can impair its response.
- Contamination or coating of the glass membrane with substances like oils, proteins, or other deposits can hinder its interaction with hydrogen ions, affecting accuracy.

## ❑ Reference Electrode Junction Potential:

- The liquid junction potential can vary if there's a difference in ionic composition between the reference electrolyte and the test solution, introducing errors.



# Working principle of Dissolved oxygen (DO) analysers

Dissolved oxygen analysers measure the amount of oxygen dissolved in a liquid, which is critical for water quality and biological processes. The two common methods used for DO measurement are:

## ❑ Electrochemical (Membrane-Based) Method:

- Uses an **electrochemical sensor** with **two electrodes (anode and cathode)** inside an electrolyte solution.
- A **semi-permeable membrane** allows only oxygen to pass through.
- Oxygen undergoes **reduction at the cathode**, generating a current proportional to the oxygen concentration.
- The output is calibrated to display the dissolved oxygen level in mg/L or ppm.

## ❑ Optical (Luminescence-Based) Method:

- Uses a **fluorescent dye** that emits light when exposed to oxygen.
- The intensity and decay time of fluorescence change based on oxygen concentration.
- This method is **more stable, requires less maintenance**, and **eliminates membrane fouling issues**.

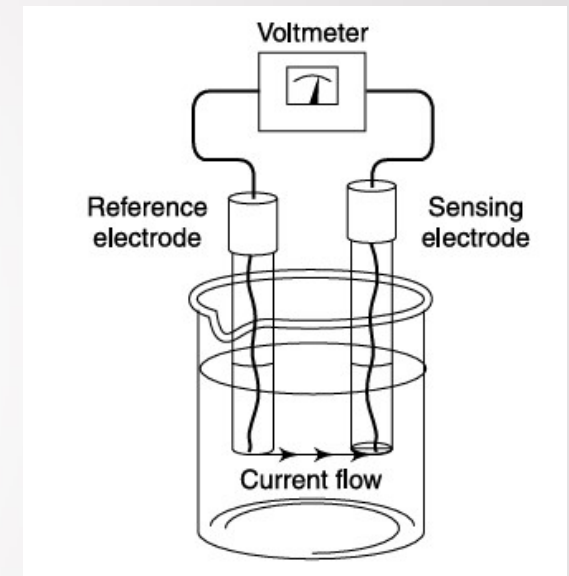


# Applications of Dissolved oxygen (DO) analysers

- ❑ **Environmental Monitoring:** Ensures proper oxygen levels in rivers, lakes, and oceans for aquatic life.
- ❑ **Wastewater Treatment:** Monitors oxygen levels in aeration tanks to optimize bacterial activity for organic matter breakdown.
- ❑ **Food & Beverage Industry:** Controls oxygen levels in fermentation processes (e.g., beer brewing).
- ❑ **Power Plants:** Prevents corrosion by monitoring oxygen in boiler feed water.

# Working principle of Sodium analysers

- ❑ Sodium analysers are used for measuring trace amounts of sodium ions in water, particularly in power plants and industrial processes. These instruments use **ion-selective electrodes (ISEs)**, which work on the basic principle of the galvanic cell based on the following principle:
- ❑ A **sodium-selective glass electrode** is placed in the sample solution along with a **reference electrode**.
- ❑ The electrode generates a **potential difference** (voltage) based on sodium ion concentration.
- ❑ The **Nernst equation** is used to calculate sodium concentration, which is displayed in ppb (parts per billion) or ppm (parts per million).



# Applications of Sodium analysers

- ❑ **Power Plants:** Ensures ultra-pure water in boilers to prevent scaling and corrosion.
- ❑ **Water Treatment Plants:** Monitors sodium levels in desalination and purification processes.
- ❑ **Pharmaceutical Industry:** Ensures purity in drug manufacturing.
- ❑ **Semiconductor Industry:** Maintains high-purity water for chip fabrication.



# Role in Water Quality Monitoring and Industrial Process Control

Both **DO and sodium analyzers** play vital roles in maintaining **water quality and efficiency in industrial processes**:

## ☐ Water Quality Management:

- DO analyzers help in maintaining **aquatic life balance** and detecting **pollution**.
- Sodium analyzers prevent **contamination** in drinking water supplies.

## ☐ Industrial Process Optimization:

- DO analyzers ensure proper aeration in wastewater treatment and prevent corrosion in power plants.
- Sodium analyzers protect **steam turbines and boilers** from sodium-induced damage.

## ☐ Environmental Compliance:

- Industries must **meet regulatory standards** (e.g., EPA, WHO) for water discharge.
- These analyzers help industries avoid **fines and environmental damage**.



**Thank you**