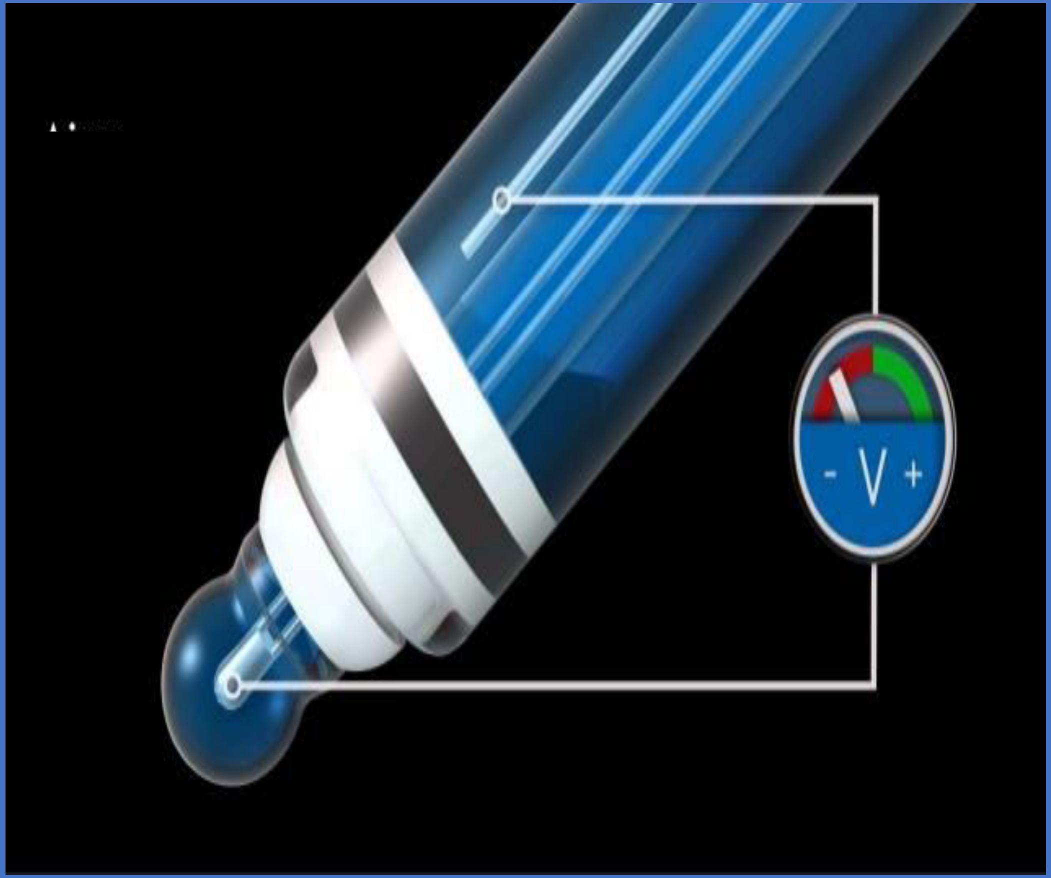
Ph Meter



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UNIT - 1

pH

- pH is a unit of measure which describes the degree of acidity or alkalinity (basic) of a solution.
- It is measured on a scale of 0 to 14.
- The formal definition of pH is the negative logarithm of the hydrogen ion activity.
- pH = -log[H+]

- **pH was originally an acronym for French clause Pouvoir hydrogene, which can be translated into the English as power of hydrogen or potential of hydrogen. Hence the name pH.**

pH value

- The pH value of a substance is directly related to the ratio of the hydrogen ion and hydroxyl ion concentrations.
- If the H+ concentration is higher than OH- the material is acidic.
- If the OH- concentration is higher than H+ the material is basic.
- 7 is neutral, < is acidic, >7 is basic

pH Measurement

- A pH measurement system consists of three parts: a pH measuring electrode, a reference electrode, and a high input meter.
- The pH measuring electrode is a hydrogen ion sensitive glass bulb.
- The reference electrode output does not vary with the activity of the hydrogen ion.

Introduction

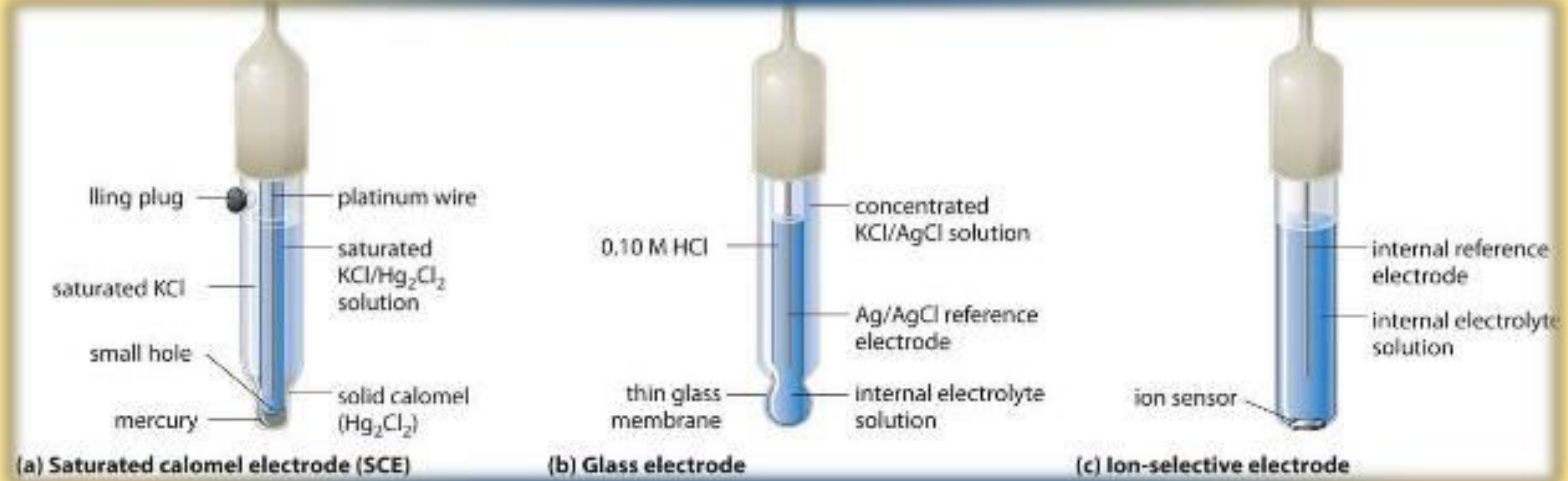
- The pH meter was invented in 1934 by the American chemist **Arnold O. Beckman** (1900-2004) to measure the sourness of lemons.
- A simple and speedy device to measure acidity or alkalinity.

- A sample is placed in a cup and the glass probe at the end of the retractable arm is placed in it.
- The probe is connected to the main box.
- There are two electrodes inside the probe that measure voltage.
- One is contained in liquid with fixed pH.
- The other measures the acidity of the sample through the amount of H+ ions.

pH Meter

- A voltmeter in the probe measures the difference between the voltages of the two electrodes.
- The meter then translates the voltage difference into pH and displays it on the screen.
- Before taking a pH measurement the meter must be calibrated using a solution of known pH.

Types of Electrode:



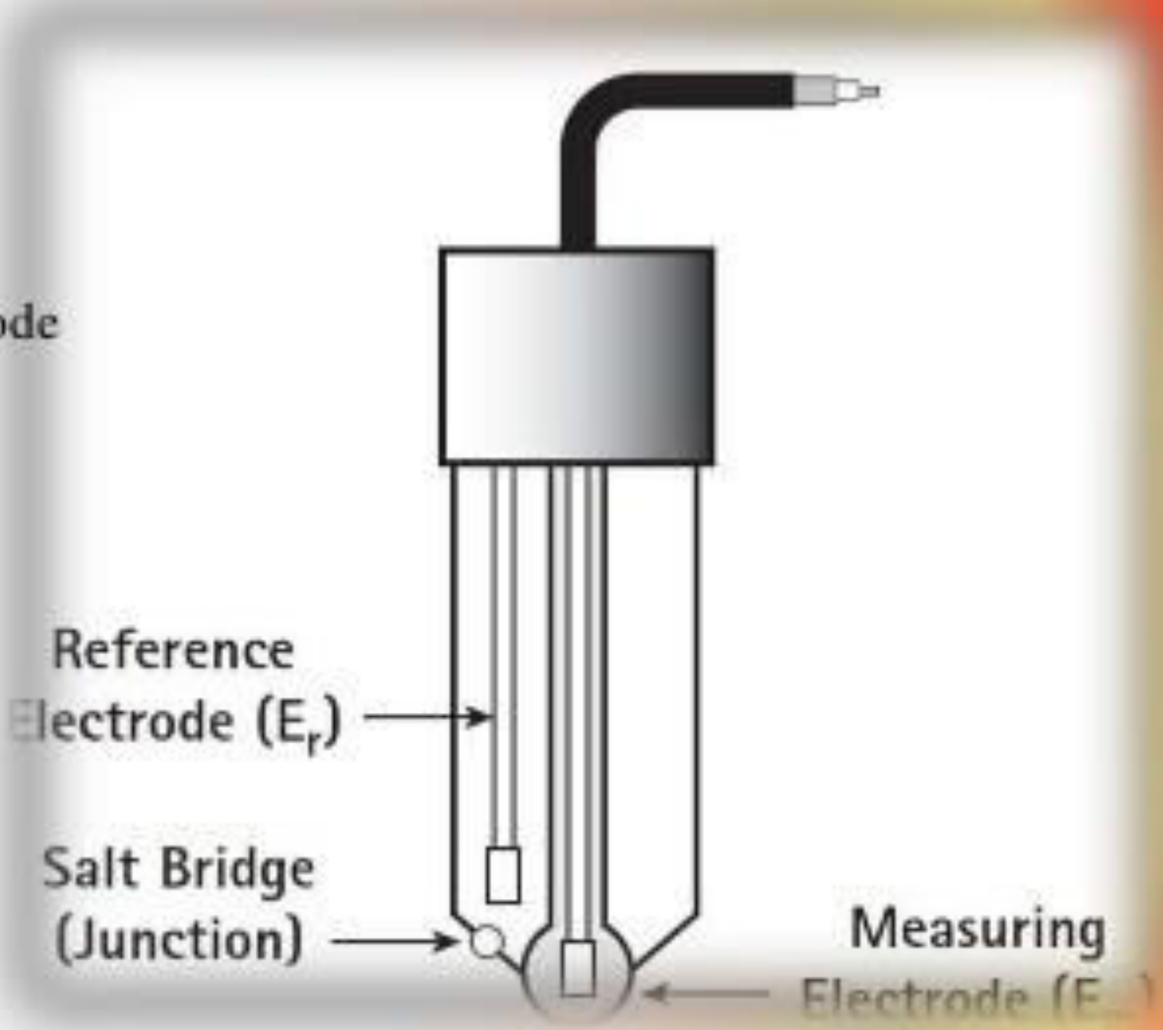
a. Calomel electrode: It consists of a glass tube containing saturated KCL connected to platinum wires through mercury (mercury chloride)

b. Glass electrode: It consists thin bulb of special glass blown(lithium) at the end of the glass tube,and the bulb is filled with dilute acid for example decinormal HCL acid connected to a silver chloride electrode

c. Reference junction: typically made of porous ceramic or porus teflon

Combined Electrode:

- It is easier to handle one electrode instead of two.
- The indicating glass electrode and the reference electrode are simply built into a single physical entity.
- This helps to ensure that the two electrodes have the same temperature during operation.



WORKING PRINCIPLE OF pH METER

- The magnitude of this potential is given by the following equation

$$E = 2.303 \frac{RT}{F} \log \frac{[H^+]_1}{[H^+]_2}$$

- E is the potential
- R is the gas constant
- F is Faraday constant
- $[H^+]_1$ is molar concentration on the inside of the glass
- $[H^+]_2$ is molar concentration on the outside of the glass

If H^+ concentration of one solution is fixed, the potential will be proportional to the pH of the other solution.

WORKING PRINCIPLE OF pH METER

Since **glass electrode(one half cell)** contains silver, silver chloride and 0.1MHCl solution, their dissociation constants are as follows(fig1),

c) $Ag \rightarrow Ag^{+} + e^{-}$

$$K_c = \frac{[Ag^{+}][e^{-}]}{[Ag]}$$

d) $AgCl \rightarrow Ag^{+} + Cl^{-}$

$$K_d = \frac{[Ag^{+}][Cl^{-}]}{[AgCl]}$$

fig 1

Reference electrode(other half cell) contains mercury, mercury chloride, and saturated solution of potassium chloride. each of these compound exists in ionized state although the extent of ionization may vary widely, their dissociation constants are given in fig 2

a) $Hg \rightarrow Hg^{+} + e^{-}$

$$K_a = \frac{[Hg^{+}][e^{-}]}{[Hg]}$$

b) $Hg_2Cl_2 \rightarrow 2Hg^{+} + 2Cl^{-}$

$$K_b = \frac{[2Hg^{+}][2Cl^{-}]}{[Hg_2Cl_2]}$$

fig2

Following reactions take place in the electrodes

The glass electrode contains Ag, AgCl, and HCL. All these remain in the ionized state.

$Ag \longleftrightarrow Ag^+ + e^-$

$AgCl \longleftrightarrow Ag^+ + Cl^-$

$HCL \longleftrightarrow H^+ + Cl^-$

All the above three equilibrium reactions are balanced. In the glass electrode, H+ is generated.

The calomel electrode contains Hg, Hg_2Cl_2 , and KCL.

Here also the following series of ionizations take place.

$Hg \longleftrightarrow Hg^+ + e^-$

$Hg_2Cl_2 \longleftrightarrow 2Hg^+ + 2Cl^-$

$KCL \longleftrightarrow K^+ + Cl^-$

The above equilibrium reactions are balanced. In the calomel electrode, H^+ is not generated.

WORKING PRINCIPLE OF pH METER

- The electromotive force(emf) of the complete cell(E) is given by

$$E=E_{ref}-E_{glass}$$

Electromotive force is a difference in potential that tends to give rise to an electric current.

E_{ref} is the potential of the reference electrode, which at normal temperature is +0.250V and E_{glass} is the test electrode which depends on the pH of the test solution.

Then the pH of the solution (at 25°C)can be determined by the following equation

.

$$pH=\frac{E_{glass}-E_{ref}}{0.0591}$$

At 25°C,substituting the value for E_{ref}

$$pH=\frac{E_{glass}-0.250V}{0.0591}$$

Working Principle of instrument

- When a pair of electrodes or a combined electrode(glass &calomel electrode) is dipped in an aqueous solution, a potential is developed across the thin glass of the bulb. The e.m.f of complete cell(E) formed by linking of this two electrodes at a given solution temperature is therefore,

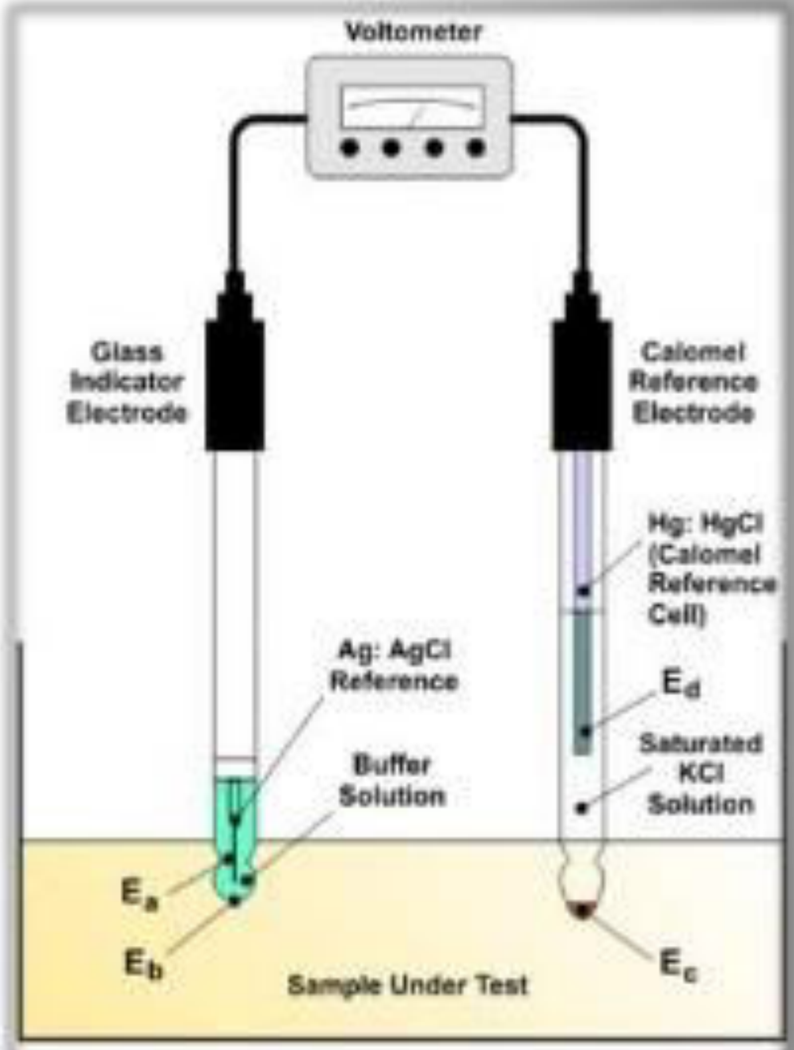
$$E = E_{ref} - E_{glass}$$

E_{ref} = The potential of stable calomel electrode which at normal room temp is +0.250V.

E_{glass} = The potential of glass electrode which depends on the pH of the solution under test.

A pH meter acts as a volt meter that measures the electrical potential difference between a pH electrode and a reference electrode and displays the result in terms of the pH value of the solution in which they are immersed.

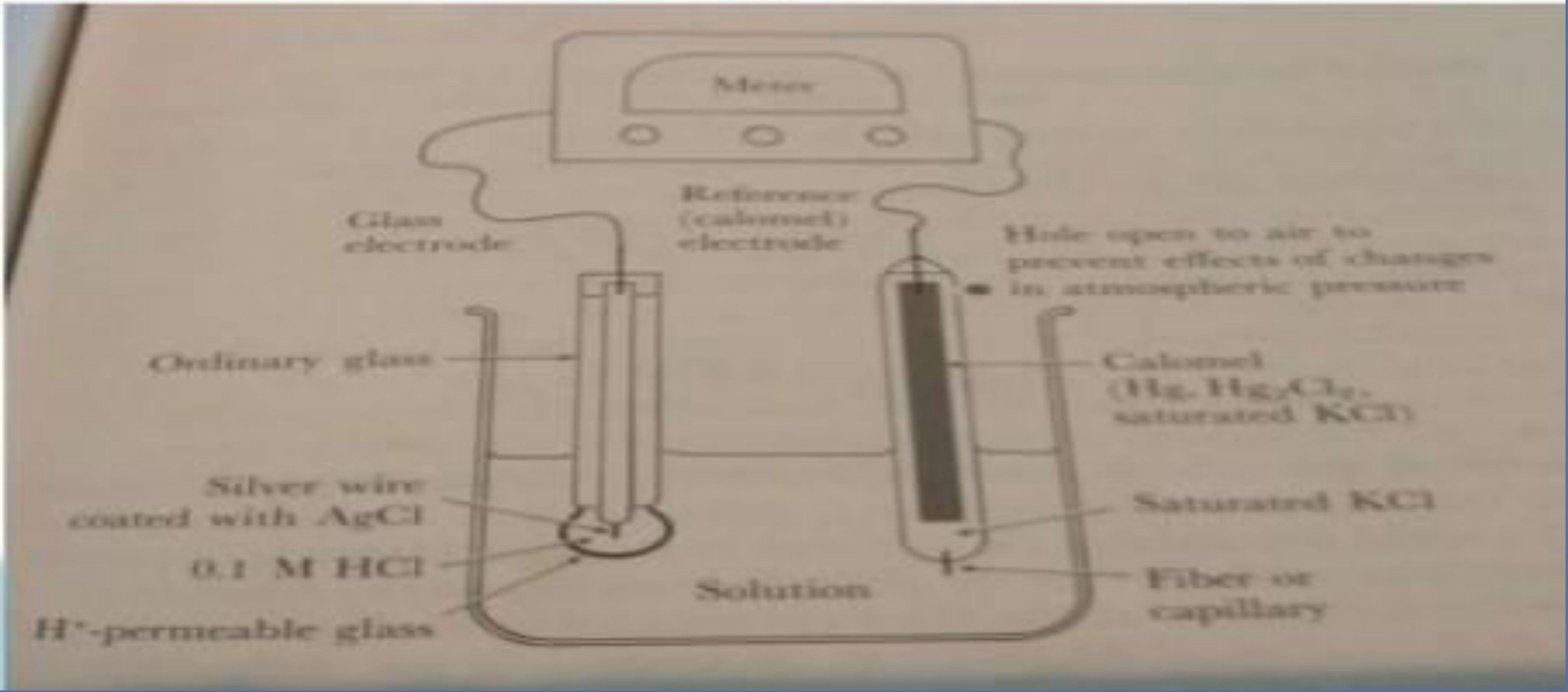
An electrical potential develops when one liquid is brought into contact with another one ,but a membrane is needed to keep such liquid apart.



WORKING PRINCIPLE OF pH METER

- The pH of a solution measures the degree of acidity or alkalinity relative to the ionization of water.
- Measuring pH involves comparing the potential of solutions with unknown [H+] to a known reference potential. pH meters convert the voltage ratio between a reference half-cell and a sensing(pH electrode) half-cell to pH values.
- At 25°C:
- pH 0 = +414.120mV (Acidic)
- pH 4 = +177.480mV (Acidic)
- pH 7 = 0.000mV (Neutral)
- pH 10 = -177.480mV (Basic)
- pH 14 = -414.120mV (Basic)
- The voltage on the outer glass surface changes proportionally to changes in [H+].

PICTURE OF GLASS AND REFERENCE ELECTRODES OF A pH meter



Instrumentation of pH meter

In the picture -

- **The Glass electrode(pH electrode)** contains 0.1 M HCl in contact with the H^+ permeable glass. Connection to the potentiometer is by means of a silver wire coated with silver chloride, which is immersed in the HCl.
- The circuit is completed by immersing into the solution a **reference electrode** that has been selected to be pH-independent. The type most commonly used contains a Hg-Hg2Cl2 paste in saturated KCl; this is called *calomel* electrode. If a high temperature operation is required, Ag-AgCl is used instead of Hg-Hg2Cl2 . In both cases KCl makes contact between this unit and the solution being measured.
- A saturated potassium chloride solution is normally used as a salt bridge in the **reference electrode** because many **ions** diffuse from the salt bridge against which the sample **ions** must diffuse.

INSTRUMENTATION OF pH METER

- Reference electrode is encased in a tube made of glass that is impermeable to H^+ ions(so that its potential is pH-independent).
- Electrical contact between the KCl within the electrode and the solution is by means of a fine fiber or capillary in the glass casing.(The KCl slowly flows into the sample. In cases in which the Cl^- ion is not required, a Hg-HgSO4 *reference electrode* can be used)
- Voltage measured by such a system is primarily the difference between that of the glass and the reference electrode. This can be written as follows-

$$V = \text{constant} - \frac{2.303RT}{F} \text{pH}$$

- Thus, voltage generated is linearly related to the pH of the solution.

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Q.What are electrochemical cell and electrolytic cell?

- **A-Electrochemical cell** is a device which converts chemical energy into electrical energy. On the other hand, **electrolytic cell** is a device which converts electrical energy into chemical energy. For example, in **electrochemical cell** anode is negative whereas in **electrolytic cell**, the anode is positive.

Q. What is galvanic cell or voltaic cell?

- A **galvanic cell**, or **voltaic cell**, named after Luigi Galvani, or Alessandro Volta respectively, is an electrochemical cell that derives electrical energy from spontaneous redox reactions taking place within the cell. It generally consists of two different metals connected by a salt bridge, or individual half-cells separated by a porous membrane.

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Q. Explain properties of salt bridge and its use?

- A **salt bridge**, in electrochemistry, is a laboratory device used to connect the oxidation and reduction half-cells of a galvanic cell (voltaic cell), a type of electrochemical cell. It maintains electrical neutrality within the internal circuit, preventing the cell from rapidly running its reaction to equilibrium.
- **Without** the **salt bridge**, the solution in the anode compartment **would** become positively charged and the solution in the cathode compartment **would** become negatively charged, because of the charge imbalance, the electrode reaction **would** quickly come to a halt, therefore It helps to maintain the flow of electrons from the oxidation half cell to a reduction half cell.
- Thus, the purpose of a salt bridge is not to move electrons from the electrolyte, rather to maintain charge balance because the electrons are moving from one half cell to the other.

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Q. Why is KCl used?

- A-KCl is a salt in nature which shows that it has a cation of strong base and anion of strong acid and they both have no effect on the pH paper and it is has a standard value which shows that its pH is **7.0** which is a neutral figure.
- **KCl is used** as **salt bridge** because it provides positive K+ ions and negative Cl- ions. The **salt bridge** is required to maintain the neutrality in the system by providing enough negative ions equal to the positive ions during oxidation.

Q. How to maintain pH meter?

- A-Always keep **pH electrode** moist. It is better to store **electrode** in a **solution** of 4 M **KCl**. If 4 M **KCl** is not available, **use** a **pH** 4 or 7 buffer **solution**. DO NOT store **electrode** in distilled or deionized water—this will cause ions to leach out of the glass bulb and render **electrode** useless.

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Q. What is pH calibration?

Calibration is measurement technology. **It** is the process of configuring an instrument to provide a result for a sample within an acceptable range, and metrology is the comparison of measurement values delivered by a device under test with those of a **calibration** standard of known accuracy.

The pH meter measures the difference in electrical potential between a pH electrode and a reference electrode. For pH meters to work efficiently and to be **accurate**, they have to be properly calibrated (the meter is accurately translating voltage measurements into pH measurements), so they usually need testing.

Temperature and Buffers

- Temperature compensation is contained within the instrument because pH electrodes are temperature sensitive.
- Temperature compensation only corrects for the change in the output of the electrode, not for the change in the actual solution.
- Buffers are solutions that have constant pH values and the ability to resist changes in pH.
- They are used to calibrate the pH meter.

•Applications:

- To measure the ph of biological fluids such as blood, urine, gastric acid etc to ascertain , type of biological conditions.
- Useful in determination of concentration of substances by pH measurement
- To know the pH of buffer solution
- To maintain the pH of reaction conditions
- If the pH value of a soil sample is found to be in an optimal range, it is considered to be the To measure the pH of soil, which will helpful in maximizing the yields and returns from the soil.
- To measure the pH of rainwater
- Maintaining perfect and accurate pH levels helps in several daily activities like keeping the milk from turning sour.
- pH meters are employed chemical industry, neutralization of effluent in steel, pulp and paper, pharmaceutical manufacturing, biotechnology and petrochemical industries.
- Hence, pH meter helps in analyzing the exact pH value of chemical substances and food grade products, thus ensuring high levels of safety and quality.

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STANDARD OPERATING PROCEDURE(SOP) of pH meter.

Calibration of pH meter-

- Rinse the electrode with deionized water and blot dry using a piece of tissue.
- Place the electrode in the solution of **pH 7** buffer, allow the display to stabilize and, then, set the display to read 7 by adjusting calibration knob. Remove the electrode from the buffer.
- Rinse and blot dry as before and put the electrodes in the buffer of either **4** or **10** pH whichever is near to the desired pH of the solution to be used for experiment.
- Allow the display to stabilize and, then, set the display to read 4 or 10 by adjusting calibration knob.

Adjustment of pH of experimental solution

- Rinse and blot dry the electrode and put it in experimental solution, allow the display to stabilize and adjust the pH of the solution by adding buffer components.

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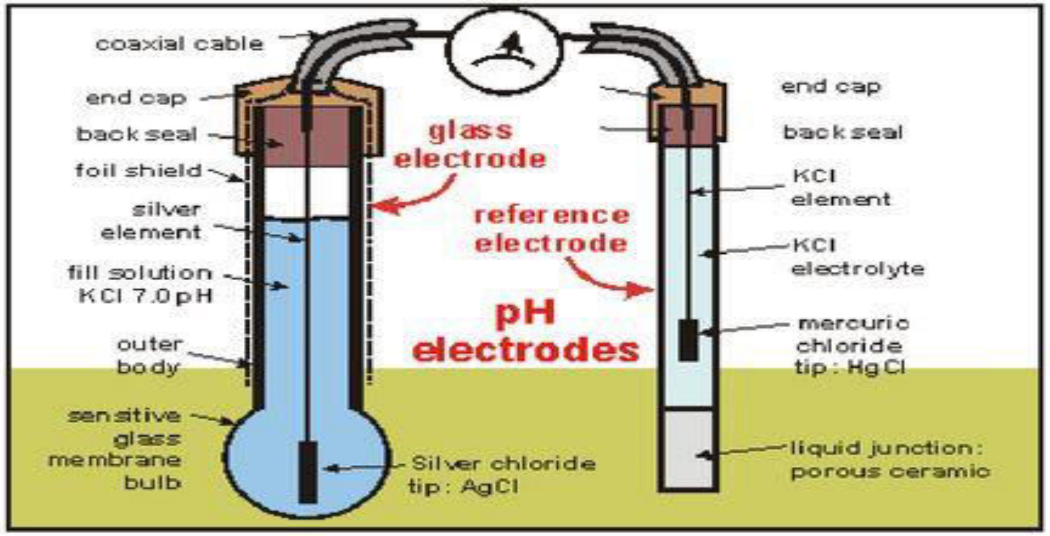
Q. What type of solutions are used for pH calibration?
A-pH calibration solutions, also called **pH** buffers, are a high-grade buffers and are used to **calibrate** pH meter before each use is to get the most accurate results every time. **Buffer solutions are used** to **calibrate pH meters** because they resist changes in **pH on addition of small amounts of acid or base.** They **are** easily prepared for a given **pH**. They **are** stable for long periods of time.

Q. What is a pH indicator?
A-A **pH indicator** is a halochromic chemical compound added in small amounts to a solution so the **pH** (acidity or basicity) of the solution can be determined visually. Hence, a **pH indicator** is a chemical detector for hydronium ions (H_3O^+) or hydrogen ions (H^+) in the Arrhenius model.

Table showing different pH values

Samples	pH value
Gastric juice	1.5 – 3.5
Lemon juice	2
Thums up	2.68
Appy fizz	3.58
Milk	6.7
RO drinking water	7.02
Blood	7.35 – 7.45
Distilled water	7.42
Normal tap water	7.45
Pond water	8.24


coaxial cable
end cap
back seal
foil shield
silver element
fill solution KCl 7.0 pH
outer body
sensitive glass membrane bulb
glass electrode
reference electrode
pH electrodes
Silver chloride tip: AgCl
end cap
back seal
KCl element
KCl electrolyte
mercuric chloride tip: HgCl
liquid junction: porous ceramic

THANK YOU