

Measurement of pH

In its most common interpretation, pH is used to specify the **degree of acidity or basicity** of an aqueous solution.

Definition of pH

Historically, pH was first defined as the negative logarithm of the hydrogen ion concentration [H⁺]

i.e $\text{pH} = -\log [\text{H}^+]$

More rigorous definition of pH as the negative logarithm of the hydrogen ion activity in solution,

$$\text{pH} = -\log a_{\text{H}^+} = -\log \gamma [\text{H}^+]$$

where a_{H^+} is the hydrogen ion activity and γ is the activity coefficient.

pH is a measure of hydrogen ion concentration in aqueous solution. It is an important parameter to determine the quality of water. The pH value is expressed as:

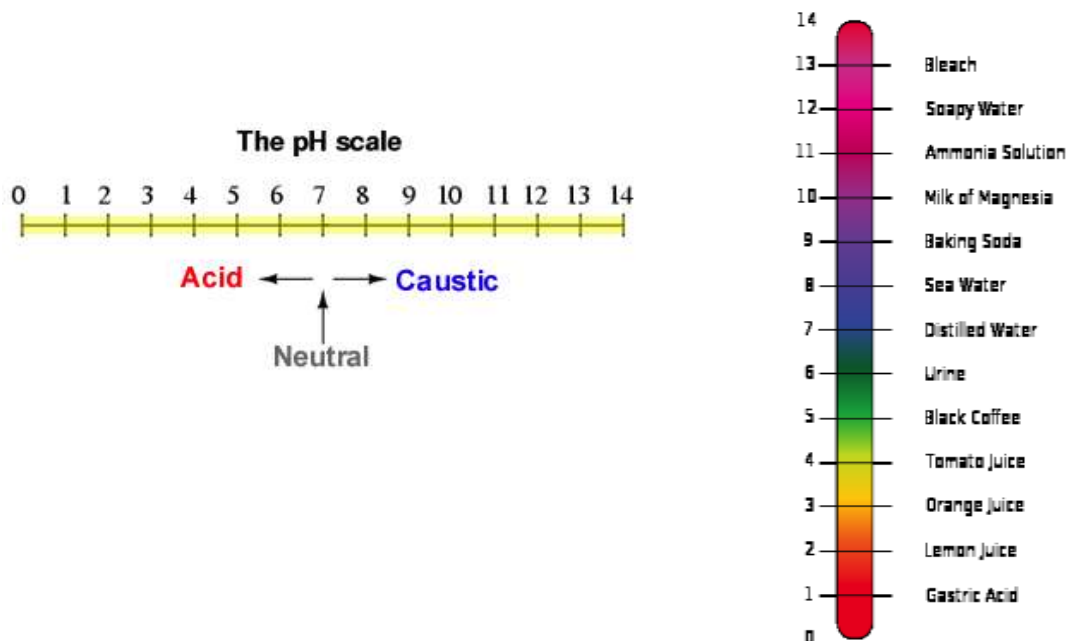
$$\text{pH} = \frac{1}{\log_{10} C}$$

Where C is the concentration of H⁺ ions in a solution. In pure water, the concentration of H⁺ ions is 10⁻⁷ gm/ltr at 25° C. So the pH value is

$$\text{pH} = \frac{1}{\log_{10} 10^{-7}} = 7.$$

The advantage of using pH scale is that the activities of all strong acids and bases can be brought down to the scale of 0-14. The pH value of acidic solutions is in the range 0-7 and alkaline solutions in the range 7-14.

pH Scale



Note : As pH value changes by 1 unit , then acidity and alkalinity values changes by factor of 10 .

Why pH measurements are important ?

1. Measurement of pH of a solution is necessary to judge whether the **liquid is acidic , alkaline or neutral** .
2. The application areas are food and beverage industry , aquarium , gardening, medicine, biology, chemistry, agriculture, forestry, food science , environmental science, oceanography, civil engineering and many other applications.
3. Measurement of pH of liquids is necessary in many condensate systems as a **check on corrosion** , in **pharmaceuticals and drug production** for maximum yield , in food manufacturing to reduce spoilage and improve taste and in innumerable chemical processes .
4. The **continuous monitoring of blood pH** is essential for proper treatment of patients suffering from metabolic and respiratory problems .

pH in nature

pH-dependent plant pigments that can be used as pH indicators occur in many plants, including hibiscus, red cabbage ,and red wine.



Hydrangea macrophylla blossoms vary from pink to blue, according to a pH-dependent mobilization and uptake of soil aluminium into the plants.

Seawater

The pH of seawater plays an important role in the ocean's carbon cycle, and there is evidence of ongoing ocean acidification caused by carbon dioxide emissions.

pH in living systems

The **pH of blood** is usually slightly basic with a value of pH **7.365**. This value is often referred to as physiological pH in biology and medicine.

The pH of different cellular compartments, body fluids, and organs is usually tightly regulated in a process called acid-base homeostasis.

The most common disorder in acid-base homeostasis is acidosis, which means an acid overload in the body, generally defined by pH falling below 7.35.

Compartment	pH
Gastric acid	1
Lysosomes	4.5
Granules of chromaffin cells	5.5
Human skin	5.5
Urine	6.0
Neutral H ₂ O at 37 °C	6.81
Cytosol	7.2
Cerebrospinal fluid (CSF)	7.3
Blood	7.34–7.45
Mitochondrial matrix	7.5
Pancreas secretions	8.1

How do you Measure pH ?

pH Electrode

The pH value of a solution is measured by using **pH electrode**. It essentially consists of a pair of electrodes: **measuring and reference electrode**, both dipped in the solution of unknown pH. These two electrodes essentially form two *half-cells*; the total potential developed is the difference between the individual electric potential developed in each half cell. **While the potential developed in the reference cell is constant, the measuring cell potential is dependent on the hydrogen ion concentration of the solution** and is governed by *Nernst's equation*:

$$E = E_0 + \frac{RT}{nF} \ln(aC)$$

where ,

E = e.m.f of the half cell

E_0 = e.m.f of the half cell under saturated condition

R = Gas constant (8.314 J/°C)

T = Absolute temperature (K)

N = valance of the ion

F = Faraday Constant = 96493 C

a = Activity co-efficient ($0 \leq a \leq 1$); for a very dilute solution, $a \rightarrow 1$

C = molar concentration of ions.

Measuring Electrode

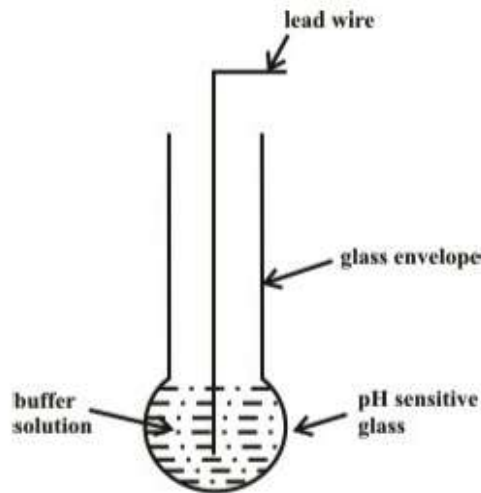


Fig. 7 Measuring Electrode

The measuring electrode is made of *thin sodium ion selective glass*. A potential is developed across the surface of this glass bulb, when dipped in aqueous solution. **This potential is sensitive to the H^+ ion concentration, having a sensitivity of 59.2 mv/pH at 25°C .** Fig. 7 shows the basic schematic of a measuring probe. The buffer solution inside the glass bulb has a constant H^+ ion concentration and provides electrical connection to the lead wire.

Reference Electrode (common use is Calomel electrode)

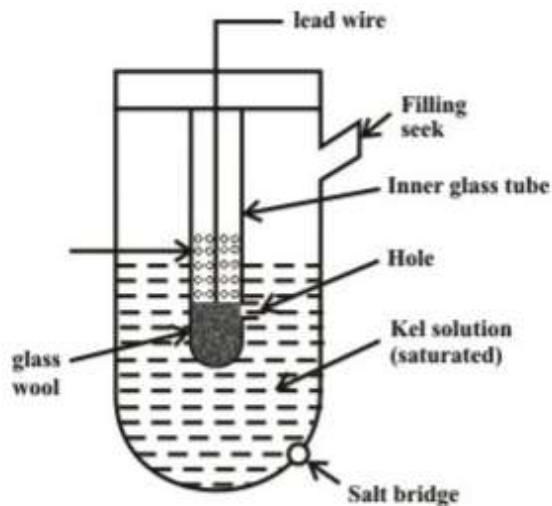


Fig. 8 Reference Electrode

Calomel (mercury and mercurous chloride)

The basic purpose of a reference electrode is to provide continuity to the electrical circuit, since the potential across a single half cell cannot be measured. With both the measuring and reference cells dipped in the same solution, the potential is measured across the two lead wires. A reference electrode should satisfy the following basic requirements:

1. The potential developed should be independent of H^+ ion concentration.
2. The potential developed should be independent of temperature
3. The potential developed should not change with time.

Considering all these requirements, two types of reference electrodes are commonly used: (i) Calomel (Mercury-Mercurous Chloride) and (ii) Silver-Silver Chloride. The construction of a Calomel reference electrode is shown in Fig. 8. The electrical connection is maintained through the *salt bridge*.

Combination type pH Electrode (common form of pH measurement)

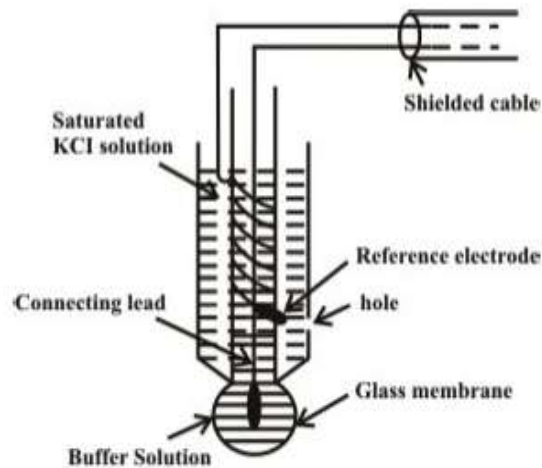
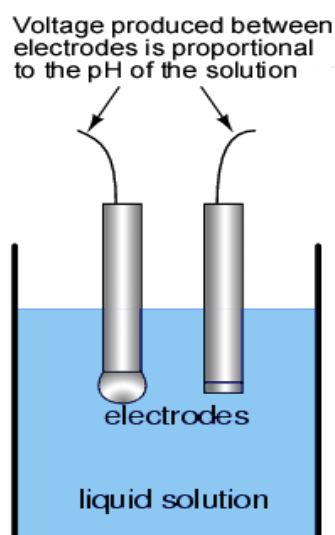


Fig. 9 Combination type pH electrode

Sometimes the reference and measuring electrodes are housed together, as shown in Fig. 9. This type of electrode is known as *Combination Electrode*. The reference electrode used in this case is Silver-Silver Chloride. The combination is dipped in the solution whose pH is to be measured and the output voltage is the difference between the e.m.f.s generated by the measuring glass electrode and the reference electrode.



Measuring scheme

The sensitivity of pH probe is around 59.2mv/pH at 25°C. This sensitivity should be sufficient for measurement of voltage using ordinary electronic voltmeters. But, that is not the case; special

measuring circuits are required for measurement of pH voltage. This is because of the fact that the internal resistance of the pH probe as a voltage source is very high, in the order of 10^{10} - $10^{12} \Omega$. This is because of the fact; the electrical path between the two lead wires is completed through the glass membrane.

As a result, the input resistance for of the measuring device must be at least ten times electrode resistance of the electrode. FET-input amplifier circuits are normally used for amplifying the voltage from the pH probe. Not only that, the insulation resistance between the leads must also be very high. They are normally provided with moisture resistance insulation coating.

The voltage in the pH probe is temperature dependent, as evident from Nernst equation. As a result suitable temperature compensation scheme should also be provided in the measuring scheme.

Electrochemical Methods of pH Measurement

The Glass Membrane Indicator Electrode

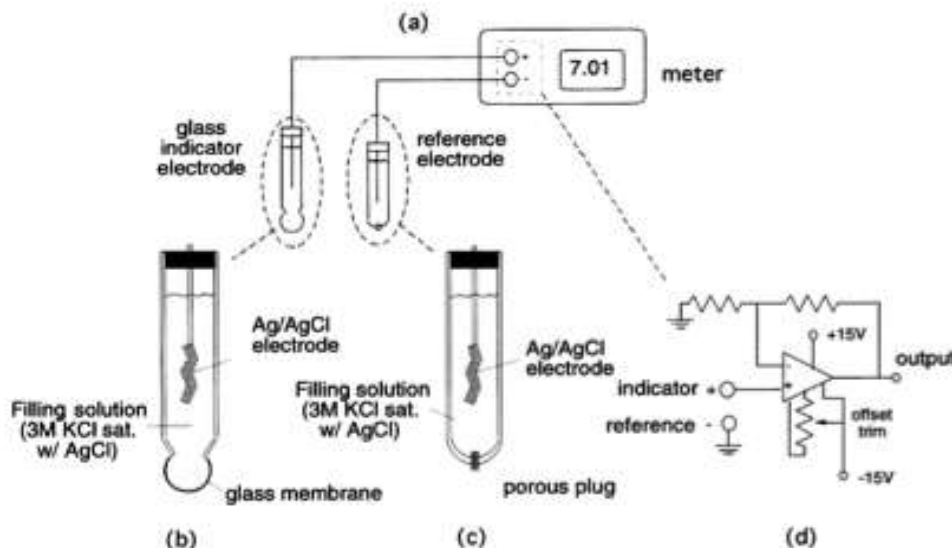


FIGURE 71.1 pH measurement using a glass membrane electrode: (a) measurement system comprising a pH meter, indicator, and reference electrodes; (b) indicator electrode construction; (c) reference electrode construction; and (d) amplifier circuit.

1. The most widely used method for measuring pH is the glass membrane electrode. As illustrated schematically in Figure 71.1(a), a pH meter measures the electrical potential difference (voltage) that develops between a glass membrane pH *indicator / measuring* electrode and a *reference* electrode immersed in the sample to be tested.
2. The indicator and reference electrodes are commonly combined into a single, functionally equivalent, probe, referred to as a combination electrode. The glass membrane of the indicator electrode develops a pH-dependent potential.
3. The construction of a typical pH indicator electrode is illustrated in Figure 71.1(b). The glass membrane at the tip of the electrode, which acts as the transducer of pH, is approximately 0.1 mm thick.
4. One side of the membrane contacts the sample while the other contacts the electrode filling

solution, an electrolyte of defined composition and pH. A reference element (e.g., a silver chloride coated silver wire) immersed in the filling solution makes a stable electrical contact between the potential measuring circuitry of the pH meter and the electrolyte in contact with the inner side of the glass membrane.

5. The reference electrode illustrated in Figure 71.1(c) provides a means of making electrical contact between the meter and the sample that is in contact with the external side of the indicator electrode's pH-sensitive glass membrane. Like the indicator electrode, the body of the reference electrode is filled with an electrolyte into which a reference element is immersed.
6. **The electrical potential difference between the pH indicator electrode and the reference electrode provides a measure of pH.**
7. The main function of the pH meter of Figure 71.1(a) is to measure this difference, with a precision of 0.1 mV or better. The amplifier circuit of Figure 71.1(d) illustrates how this may be done. Due to the high electrical resistance of the indicator electrode's glass membrane, the meter must have a correspondingly high input impedance.