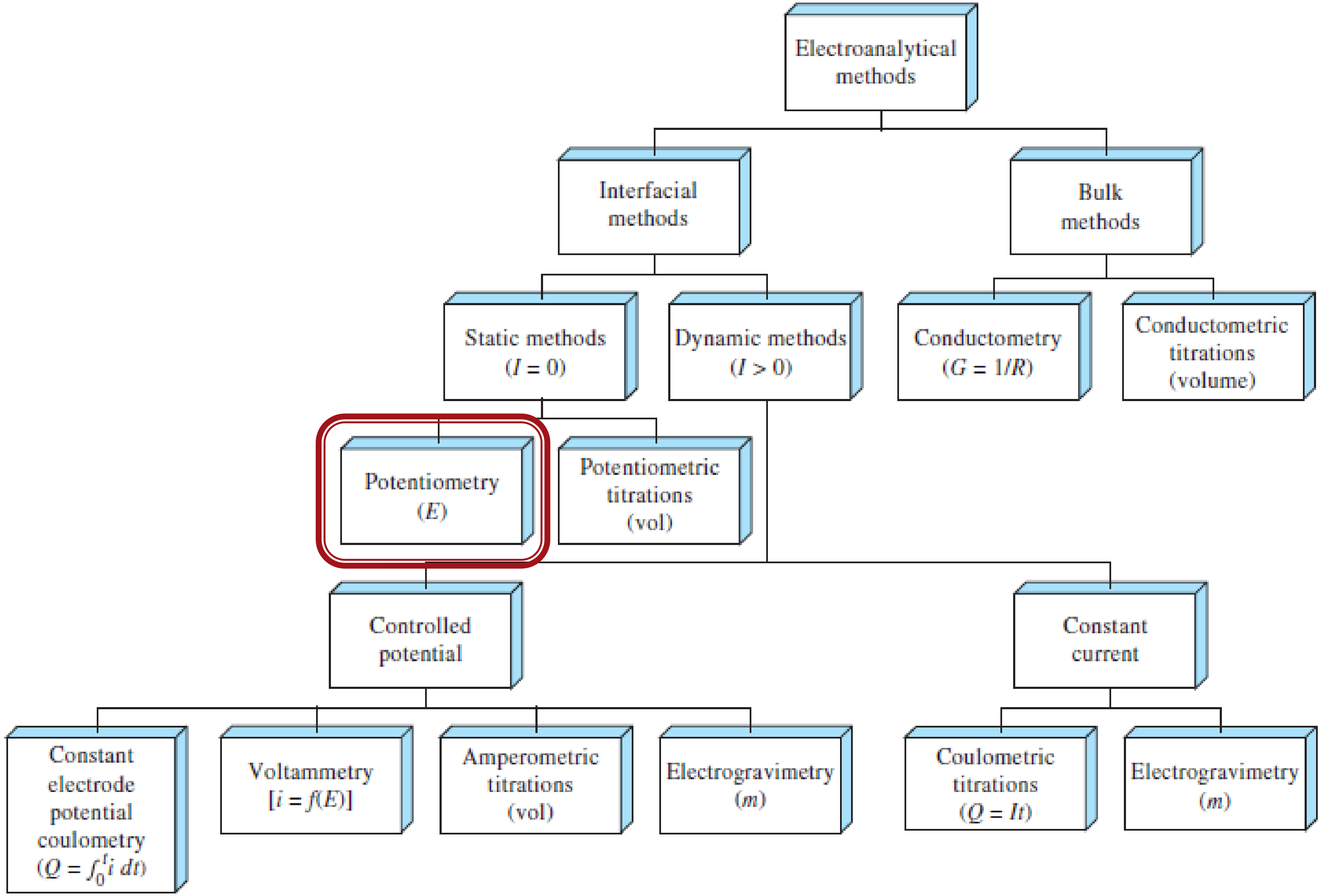
FDE 301
INSTRUMENTAL ANALYSIS

Potentiometric pH Measurement, pH Meter



Electroanalytical methods

Interfacial methods

Bulk methods

Static methods ($I = 0$)

Dynamic methods ($I > 0$)

Conductometry ($G = 1/R$)

Conductometric titrations (volume)

Potentiometry (E)

Potentiometric titrations (vol)

Controlled potential

Constant current

Constant electrode potential coulometry ($Q = \int_0^t i\,dt$)

Voltammetry [$i = f(E)$]

Amperometric titrations (vol)

Electrogravimetry (m)

Coulometric titrations ($Q = It$)

Electrogravimetry (m)

Electrochemical Methods-Potentiometry

- **Electroanalytical methods** are a class of **techniques** in analytical chemistry which study an analyte by measuring the potential (volts) and/or current (amperes) in an electrochemical cell containing the analyte.

- Electroanalytical chemistry encompasses a group of qualitative and quantitative analytical methods based on the electrical properties of an analyte solution when it is made part of an electrochemical cell.

- Electrochemistry studies the interconversion of chemical energy and electrical energy.

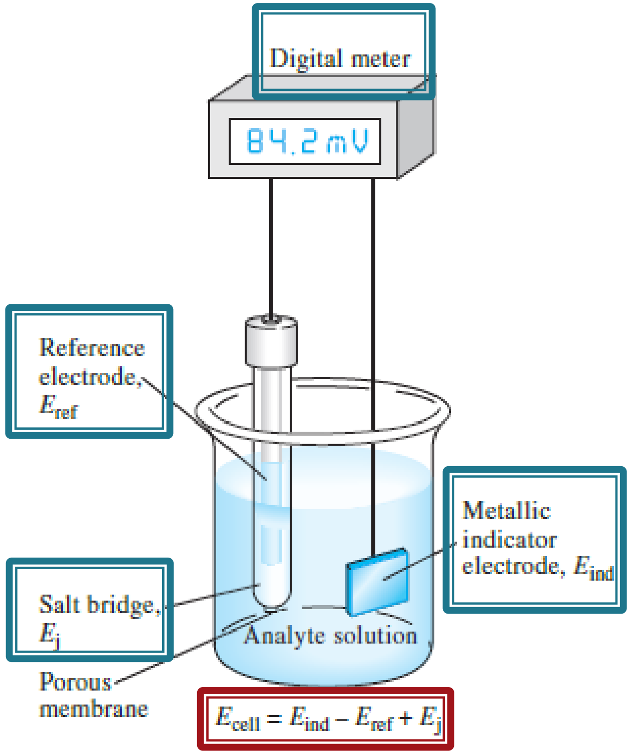
- Potentiometry is one type of electrochemical analysis methods.

- Potentiometric methods of analysis are based on measuring the potential of electrochemical cells without drawing significant current.

A typical potentiometric electrochemical cell

The equipment required for potentiometric methods;

- reference electrode: has a potential that is known, constant and completely insensitive to the composition of the solution under study.
- indicator electrode: which is immersed in a solution of the analyte, develops a potential, $\mathbf{E_{ind}}$, that depends on the activity of the analyte. Most indicator electrodes used in potentimetry are selective in their responses.
- **salt bridge**: prevents the components of the analyte solution from mixing those of the reference electrode. (potassium chloride is the ideal electrolyte for the salt bridge).
- potential measuring device

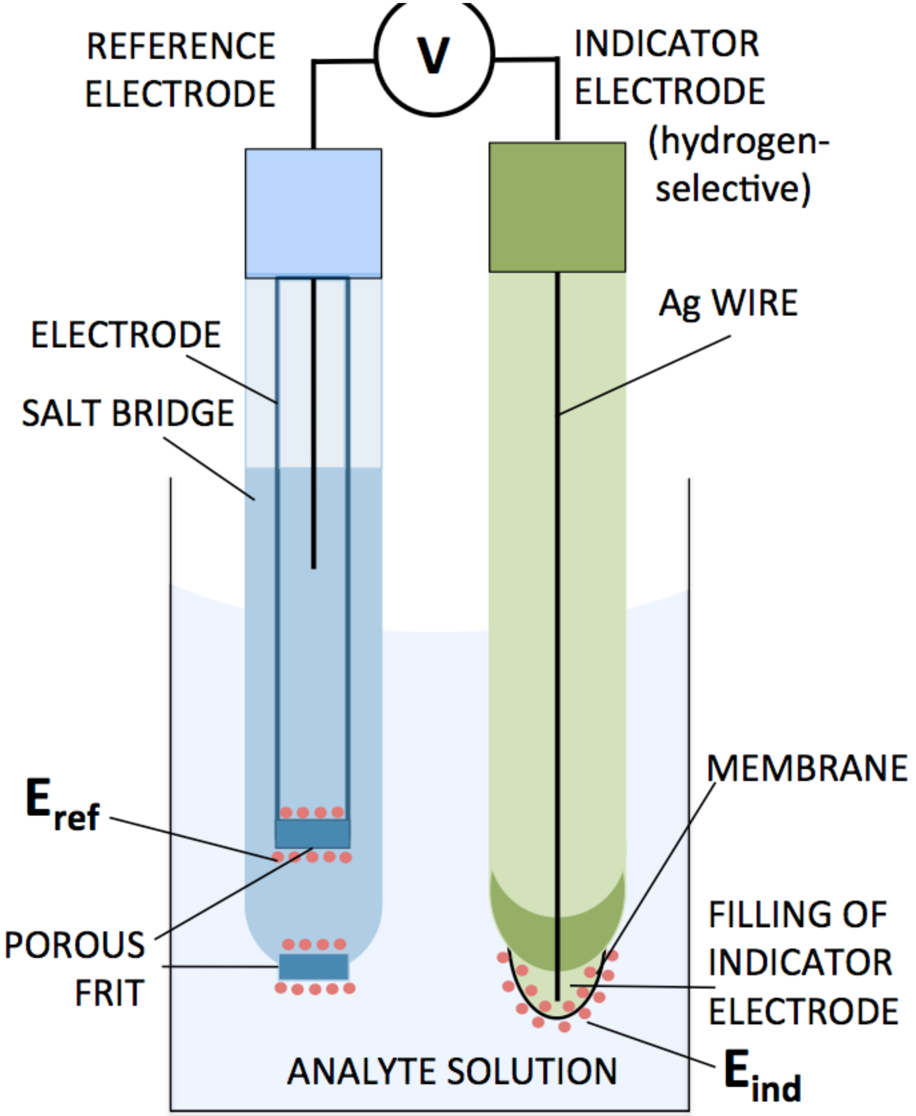


A cell for potentiometric determinations

$$\underbrace{\text{reference electrode}}_{E_{ref}} | \underbrace{\text{salt bridge}}_{E_j} | \text{analyte solution} | \underbrace{\text{indicator electrode}}_{E_{ind}}$$

Potentiometric measurement system

- Potentiometry is based on the measurement of the potential of an electrode system (e.g. electrochemical cell).
- Potentiometric measurement system consists of two electrodes called reference and indicator electrode, potentiometer and a solution of Analyte.
- Reference electrode is an electrode with potential which is independent of concentration of analyte (or other) ions in solution.
- Potential of an indicator electrode depends mainly on the concentration of the analyte ions (in this case hydrogen ions).
- Potentiometric measurements enable selective detection of ions in presence of multitude of other substances.
- In case of this figure, the potential of the indicator electrode is sensitive to hydrogen ions. In a system like this, the potential is measured in reference to a calomel electrode, e.g. Calomel electrode functions as the reference electrode.



Potentiometric measurement system (for pH measurement)

The Sorensen definition of pH as hydrogen ion concentration (Notional definition)

- The original concept of pH was developed by the Danish scientist Søren Peder Lauritz Sørensen, and involved the concentration rather than the activity of hydrogen ions.
- Sorensen first proposed the term pH as an abbreviation of "pondus hydrogenii (the power of Hydrogen)" in 1909 to express very small concentrations of hydrogen ions.
- The pH value was defined as, by the Sørensen equation, as the negative logarithm of the **hydrogen ion $[H^+]$ concentration** in the solution.
- **$pH = - \log_{10}[H^+]$**
- **pH** is defined as the logarithm of the reciprocal of the hydrogen ion concentration.
- **$pH = 1 / \log_{10}[H^+]$**

Therefore, a $[H_3O^+]$ concentration of 1×10^{-6} is expressed simply as pH 6.0.

Activity vs. Concentration

- **Activity** is a measure of expressed chemical reactivity, while **concentration** is a measure of all forms (free and bound) of ions in solution.

- Because of the interactions of ions between themselves and with the solvent, the effective concentration or activity is, in general, lower than the actual concentration, although activity and concentration tend to approach each other at infinite dilution.

- Activity and concentration are related by the following equation:

$$\boxed{A = \gamma C}$$

A = activity
γ = activity coefficient
C = concentration

- **The activity coefficient is a function of ionic strength.**
- **Ionic strength is a function of the concentration of, and the charge on, all ions in solution.**
- **Activity issues can become significant for hydronium ions below pH 1 and for hydroxyl ions at pH 13 and above.**

- As a greater understanding of the behavior of ionic solutes in solution developed, chemists recognized that the measurement techniques used to determine hydrogen ion concentration were in fact measuring the hydrogen ion activity, often referred to as the "effective concentration".

- This led to the adoption of the more rigorous definition of pH as **the negative logarithm of the hydrogen ion activity in solution**.

$$\mathrm{pH} = -\log \underset{A}{\boxed{a_{\mathrm{H}^+}}} = -\log \gamma \underset{C}{\boxed{[\mathrm{H}^+]}}$$

a_{H+}= Hydrogen ion activity
γ = the activity coefficient

- The two definitions expressed in Equations written with respect to hydrogen ion concentration and hydrogen ion activity are equivalent in dilute solution where concentration approximates activity, a_{H+}.

Operational Definition of pH

- Sørensen’s equation can only be notional definition of pH, since it is defined in terms of a quantity that can not be measured by thermodynamically valid method.

- In practice, the routine measurement of pH is not accomplished by the direct determination of the hydrogen ion activity. Rather, pH is determined relative to one or more standard solutions of known pH.

- The operational definition of pH endorsed by the National Institute of Standards and Technology (NIST), similar organizations in other countries, and the International Union of Pure and Applied Chemistry (IUPAC) is based on the direct calibration of the meter with carefully prescribed standard buffers followed by potentiometric determination of the pH of unknown solutions.

Instrument	Energy source (stimulus)	Analytical information	Information sorter	Input transducer	Data domain of transduced information	Signal processor/ readout
Photometer	Tungsten lamp	Attenuated light beam	Filter	Photodiode	Electrical current	Amplifier, digitizer, LED display
Atomic emission spectrometer	Inductively coupled plasma	UV or visible radiation	Monochromator	Photomultiplier tube	Electrical current	Amplifier, digitizer, digital display
Coulometer	Direct-current source	Charge required to reduce or oxidize analyte	Cell potential	Electrodes	Time	Amplifier, digital timer
pH meter	Sample/glass electrode	Hydrogen ion activity	Glass electrode	Glass-calomel electrodes	Electrical voltage	Amplifier, digitizer, digital display
Mass spectrometer	Ion source	Mass-to-charge ratio	Mass analyzer	Electron multiplier	Electrical current	Amplifier, digitizer, computer system
Gas chromatograph with flame ionization	Flame	Ion concentration vs. time	Chromatographic column	Biased electrodes	Electrical current	Electrometer, digitizer, computer system

Nernst Equation

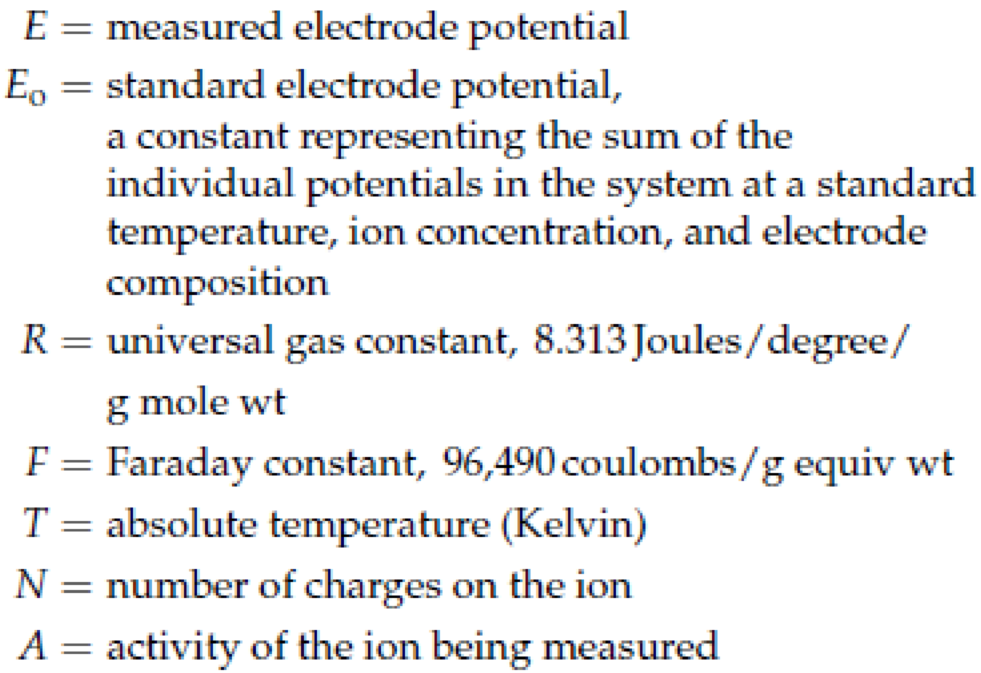
- The principle of potentiometric pH measurement can be explained by Nernst's law.
- The relationship between the potential and hydrogen ion activity in the sample is described by the Nernst equation.
- Hydrogen ion concentration (or more accurately, activity) is determined by the voltage that develops between the two electrodes.

- The **Nernst equation** relates the electrode response to the activity.

$$\boxed{E = E_0 + 2.303\frac{RT}{NF}\log A}$$

$\parallel$

$$\boxed{E = E^0 + 2.3\frac{RT}{F} \bullet \log a_{H+}}$$



E = measured electrode potential

E_0 = standard electrode potential, a constant representing the sum of the individual potentials in the system at a standard temperature, ion concentration, and electrode composition

R = universal gas constant, 8.313 Joules/degree/g mole wt

F = Faraday constant, 96,490 coulombs/g equiv wt

T = absolute temperature (Kelvin)

N = number of charges on the ion

A = activity of the ion being measured

Nernst Equation

$$\boxed{E = E_o + \boxed{2.303\frac{RT}{NF}}\log A}$$

NERNST POTENTIAL (E_N)
NERNST FACTOR
SLOPE FACTOR
IDEAL SLOPE FACTOR

- Change in potential per pH unit
- Depends on absolute temperature

- For monovalent ions (such as the hydrogen ions, n=1), THE SLOPE FACTOR at 25°C (298 K) is calculated to be **0.0591 V** or **59.16 mV**, as follows:

$$\boxed{\frac{2.303 \times 8.316 \times 298}{96,490} = 0.0591}$$

- Thus, **voltage produced by the electrode system is a linear function of the pH, the electrode potential being essentially +59mV (0.059 V) for each change of one pH unit.**

pH meter

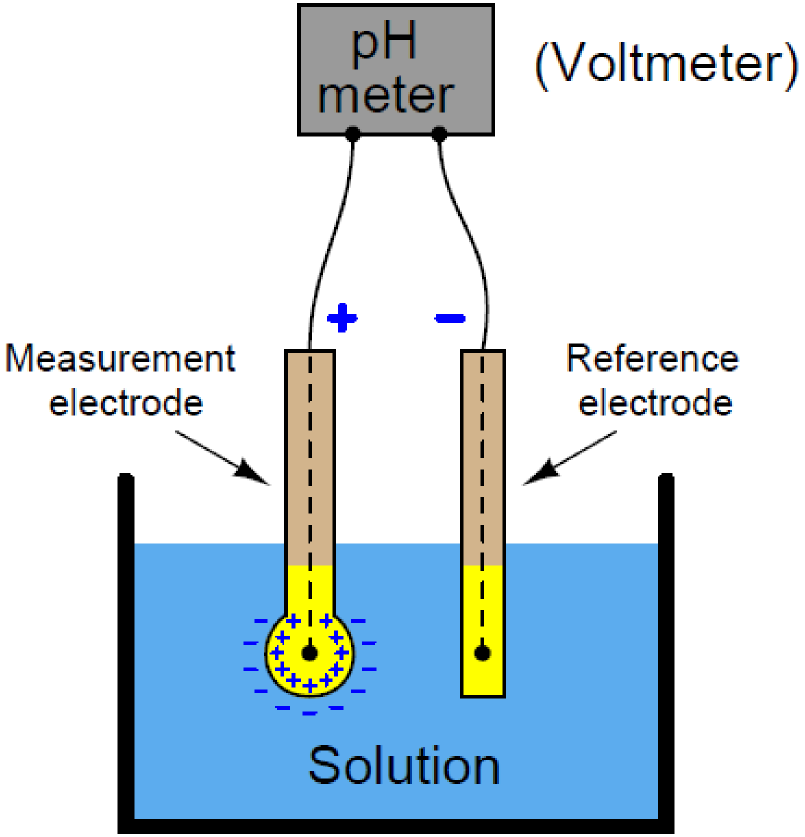
Four major parts of the pH system

(1) reference electrode,

(2) indicator electrode (pH sensitive),

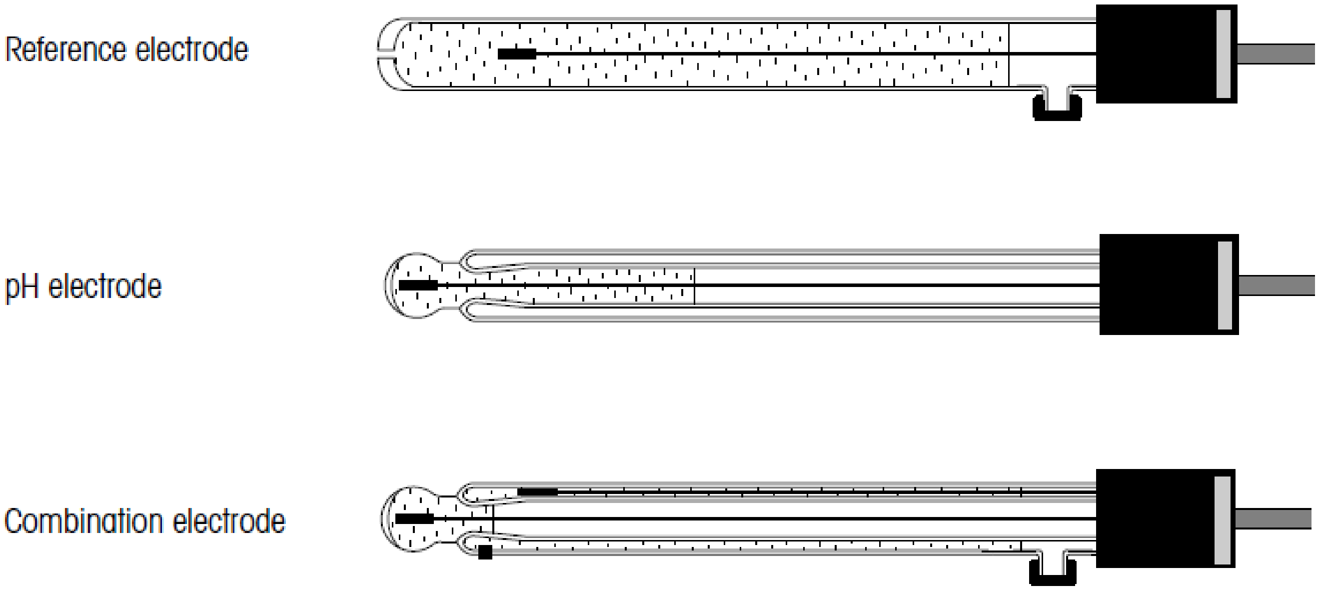
(3) voltmeter or amplifier that is capable of measuring small voltage differences in a circuit of very high resistance

(4) the sample being analyzed



Electrodes

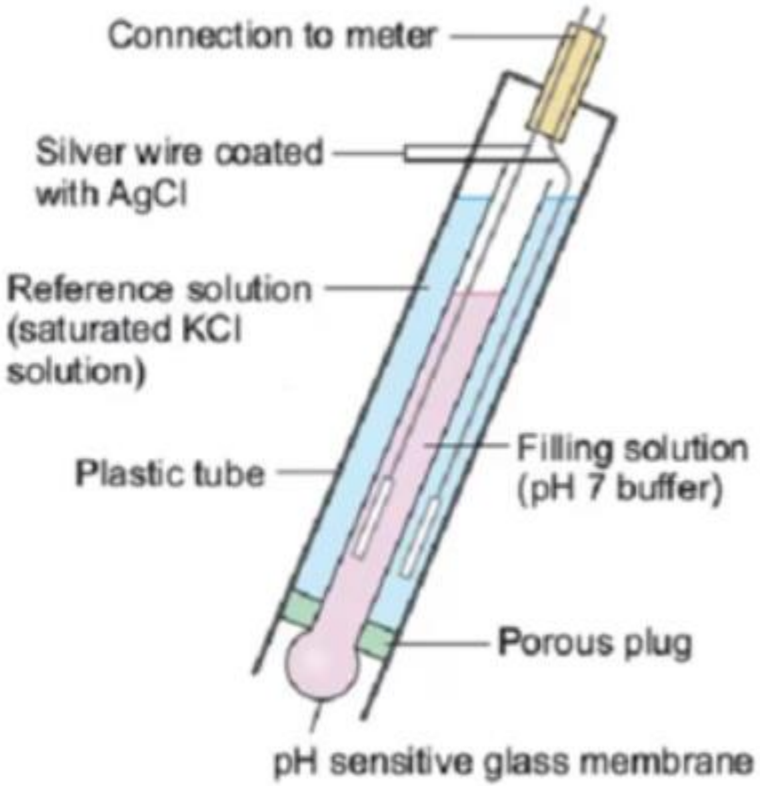
- There are 3 types of electrodes used in the pH determination:



pH and reference electrode in one sensor.

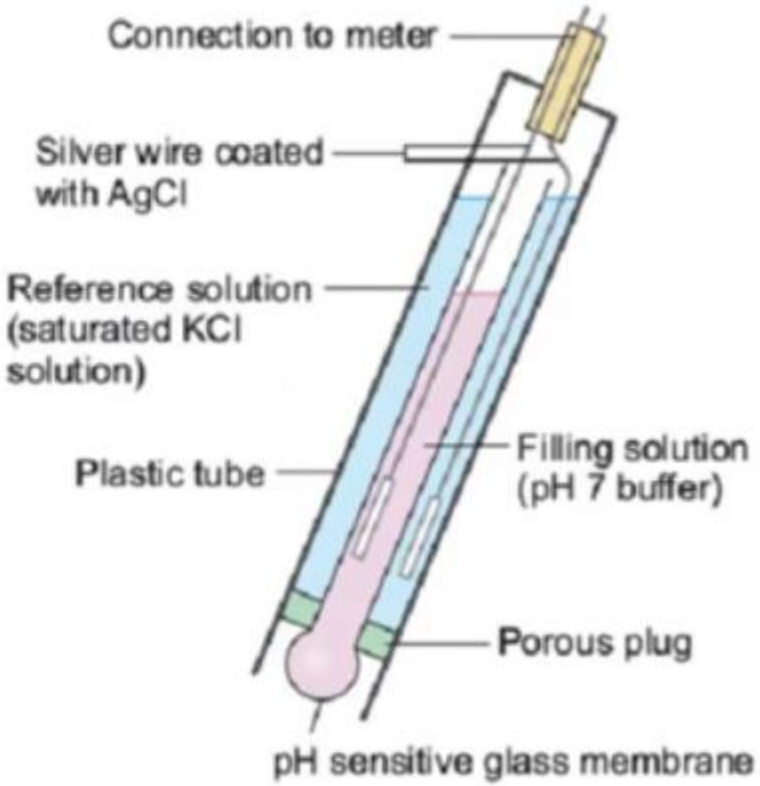
Working principle of pH meter

- In a typical combination electrode, the glass pH probe contains 2 electrodes , an indicator electrode an reference electrode.
- These electrodes are in the form of glass tubes one contains pH 7 buffer and other contains saturated potassium chloride solution. The sensor electrode bulb is made up of porous glass or permeable glass membrane coated with silica and metal salts.
- A silver wire coated with silver chloride (AgCl) is immersed in pH 7 buffer in the bulb.
- Another silver wire coated with silver chloride (AgCl) is immersed in the saturated potassium chloride solution in reference electrode as shown in the figure.



Working principle of pH meter-continued

- When the probe is dipped in a solution to measure the pH, the hydrogen ions accumulate around the bulb and replace some of the metal ions from the bulb. (Since the hydrogen ions are much smaller in size than the metal ions, they have a much greater drift velocity). This exchange of ions generates some electric flow that is captured by the silver wire.
- The voltage of this electric flow is measured by the pH meter by converting it into pH value by comparing the generated voltage with the reference electrode.
- This increase or decrease in hydrogen ion concentration depending on the acidity or alkalinity of the solution changes the voltage measured.
  - An increase in acidity in the solution has greater concentration of hydrogen ions that increases the voltage. This increased voltage decreases the pH reading in pH meter.
  - An increase in alkalinity decreases the hyrogen ions or increases in hydroxyl ions concentration also decreases the voltage and increase the pH value in pH meter.



- **The overall working principle of pH electrode/pH meter depends on the exchange of ions from sample solution to the inner solution (pH 7 buffer) of glass electrode through the glass membrane.**

Access link: https://www.youtube.com/watch?v=P1wRXTl2L3I