

UNIT I ELECTROCHEMISTRY & APPLICATIONS

Conductance, Factors affecting conductance, Specific conductance, molar conductance, equivalent conductance, effect of dilution, conductometric titrations

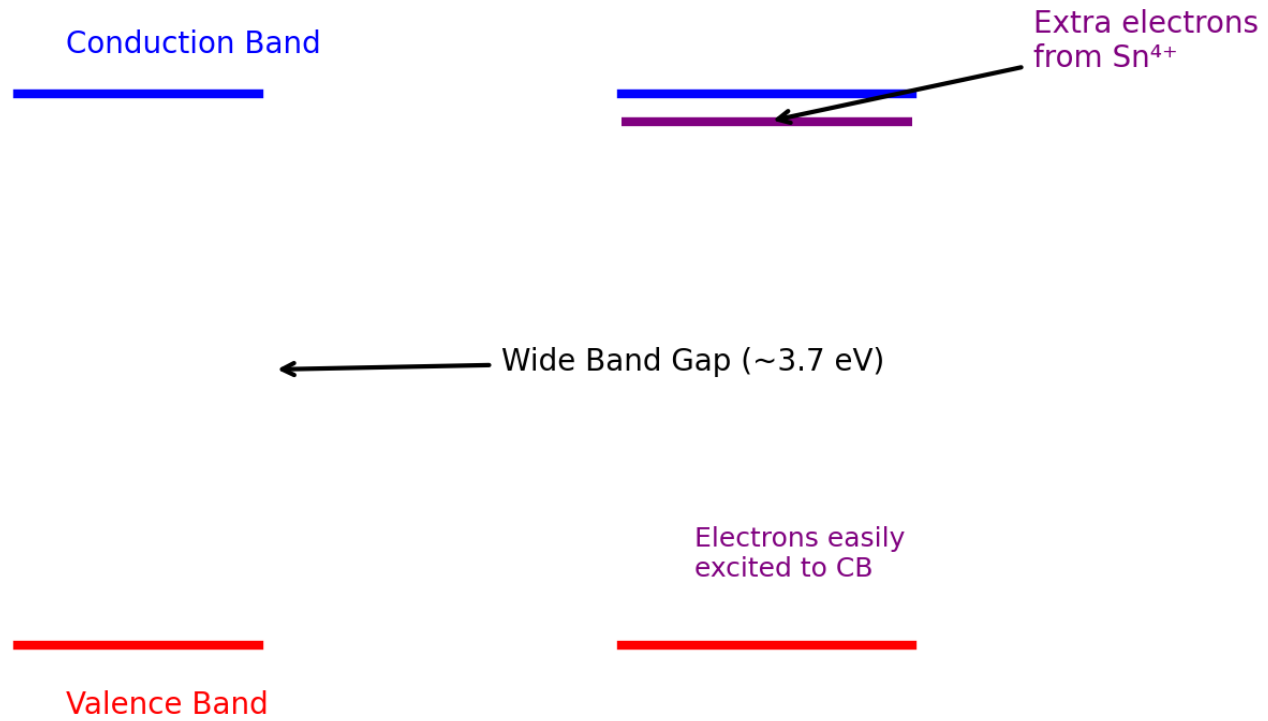
Electrode potential- Nernst Equation, Galvanic cells, Reference electrode- Calomel electrode, Quinhydrone electrode, potentiometric titrations, Fuel cells

1. Conductance & Types of Conductivity

Applications in Engineering

- **Water treatment plants:** Engineers monitor **conductivity** to assess water purity.
- **Semiconductor industry:** Conductivity of doped materials determine electronic properties. (Tin-doped Indium Oxide | Used in flat-panel displays, solar panels, and OLEDs)
- **Battery and sensor design:** Engineers evaluate electrolyte conductivity for optimal performance.
- **Corrosion monitoring:** Conductance helps assess metal ion concentration in corrosion studies.

Chemistry of Tin-doped Indium Oxide (ITO): Band Structure

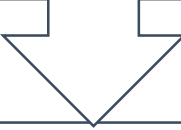


Electrode Potential & Nernst Equation

Corrosion engineering: Used to predict corrosion tendency of metals (by calculating electrode potential).



Sensors: pH meters, redox sensors and gas sensors work on Nernst-based electrochemical principles.



Battery design: Voltage prediction and optimization.

Galvanic Cells

Battery systems: Primary (non-rechargeable) and secondary (rechargeable) battery design.

Cathodic protection: Used in **pipelines, ships, and storage tanks** to prevent corrosion.

Biomedical implants: Small galvanic cells used for power in implantable devices.

Potentiometric Titrations

Applications in Engineering

- **Automated titration systems** for **quality control** in chemical and pharmaceutical industries.
- **Food engineering:** Estimation of acidity, preservatives, and salts in food processing.
- **Mining and metallurgy:** Determination of metal ion concentration.

Fuel Cells

Applications in Engineering

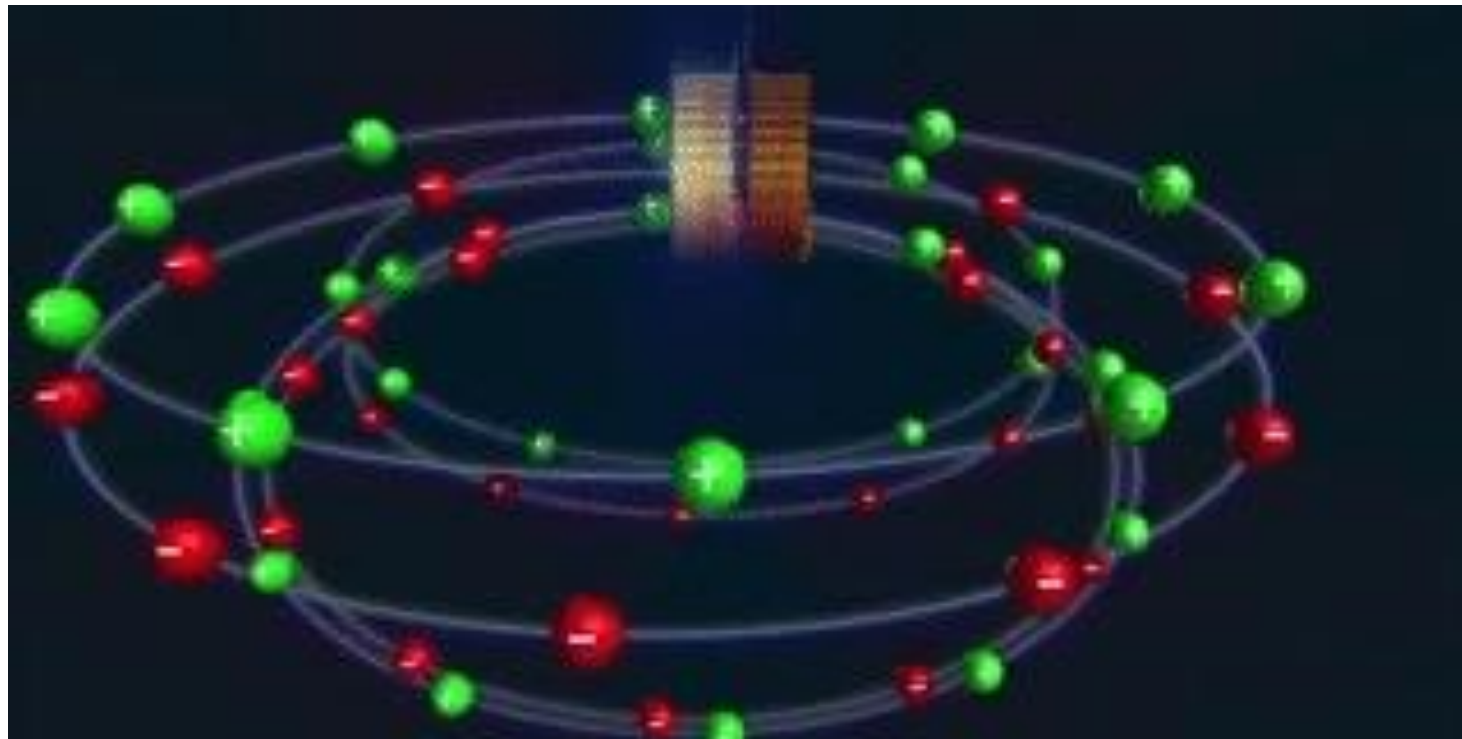
- **Sustainable energy:** Hydrogen and methanol fuel cells for **electric vehicles, drones, and backup power systems.**
- **Portable power:** Military and remote communication devices.
- **Building-integrated energy systems:** Fuel cells used in green buildings for decentralized electricity generation.

Content

- Conductance
- Specific conductance
- Equivalent conductance
- Molar conductance
- Factors affecting conductance
- Effect of dilution
- Conductometric titration

Conductance

- Conductance is the measure of how easily electricity can pass through a conductor or electrolyte due to the movement of electrons or ions.



Conductance of a solution of an electrolyte is its capacity to conduct electricity through it. It is reciprocal of resistance

- The resistance R of a solution is directly proportional to the distance between the electrodes and inversely proportional to the area of cross section of the electrodes.

$$R \propto \frac{l}{a}$$

- Conductance is defined as reciprocal of resistance.

$$C \propto \frac{a}{l} \qquad C = \kappa \frac{a}{l}$$

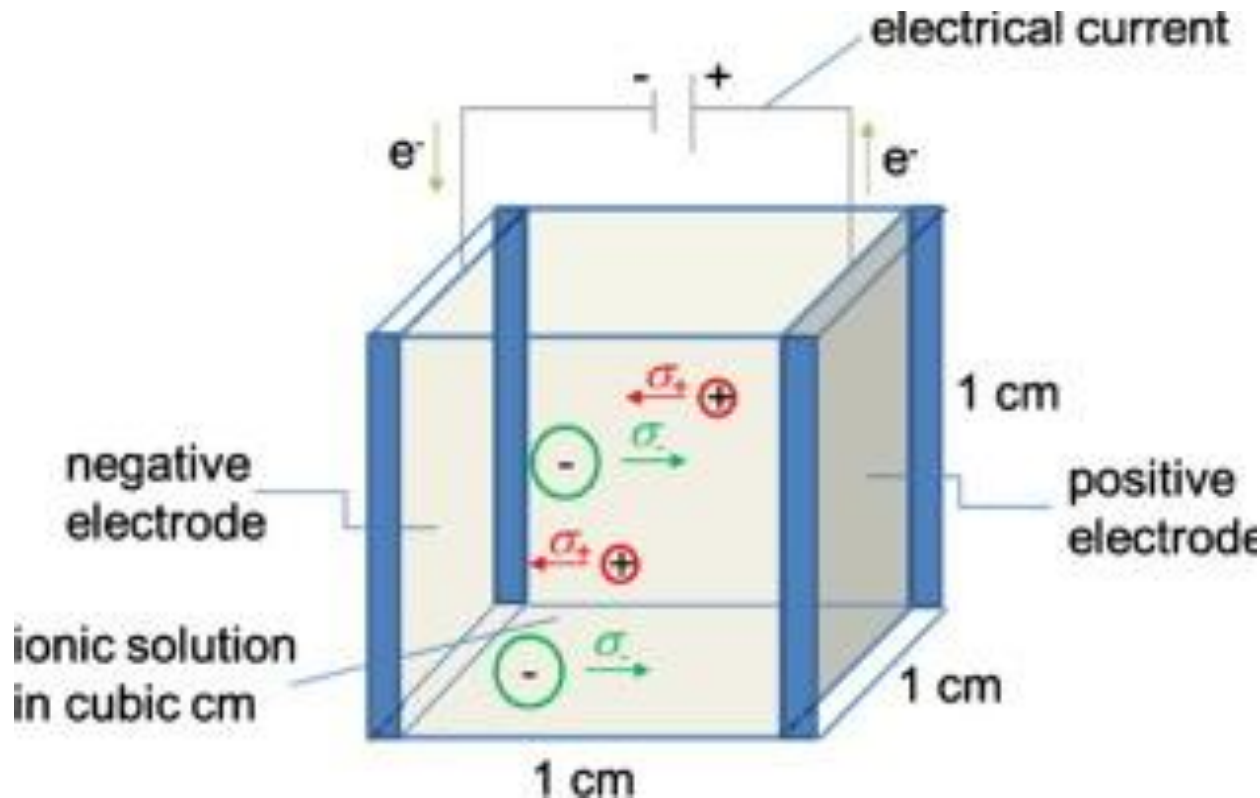
- Where κ (kappa) is called specific conductance

$$\kappa = C \frac{l}{a}$$

- If $l = 1\text{m}$ & $a = 1\text{m}^2$, then $\kappa = C$

Specific Conductance (κ)

- Also called **conductivity**, it is the conductance of **1 cm³ of a solution** placed between two electrodes **1 cm apart**.



$$\kappa = \frac{1}{\rho}$$

- Unit: S cm⁻¹
- Depends on: concentration, temperature, nature of ions
- ◆ It measures the total conducting power of the solution per unit volume.

Equivalent conductance(Λ_{eq})

- It is the **conductance of all the ions** produced by **1 gram equivalent** of an electrolyte in a given volume.

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N}$$

Where:

- N = Normality of the solution
- Unit: $S\ cm^2\ eq^{-1}$

Molar conductance(Λ_m)

It is the **conductance of all the ions** produced by **1 mole** of an electrolyte **in a given volume** of solution.

$$\Lambda_m = \frac{\kappa \times 1000}{C}$$

Where:

- Λ_m = molar conductance ($\text{S cm}^2 \text{ mol}^{-1}$)
- κ = specific conductance (S cm^{-1})
- C = concentration in mol/L

◆ Increases with dilution due to more ion mobility.

Factors affecting conductance

- **Nature and concentration of the electrolyte**
- **Temperature**
- **Solvent polarity and viscosity**
- **Ion size and mobility**

Conductance is not just a chemistry topic—it's a tool engineers use daily: civil engineers in water quality, electrical engineers in batteries, mechanical engineers in boilers, and biomedical engineers in sensors.

Factors Affecting Conductance

- **Nature of Electrolyte**
 - **Strong electrolyte:** Completely ionizes → High conductance
 - **Weak electrolyte:** Partially ionizes → Low conductance
- **Concentration of Solution**
 - **Dilute solution:** Ion mobility increases → Conductance increases
 - **Concentrated solution:** Ion pairing and reduced mobility → Conductance decreases

Temperature

- Increase in temperature
 - Increases ion mobility
 - Decreases viscosity of solvent
 - Increases conductance

Solvent

- Polarity of the solvent:
 - More polar solvent facilitates ionization
 - Higher conductance
- Viscosity of the solvent also affects ion movement

Interionic Attraction

- Strong interionic forces (e.g., in concentrated solutions)
 - Decrease in mobility
 - Decrease in conductance

Size of Ions

- Smaller ions move faster → Higher conductance
- Larger ions face more resistance → Lower conductance

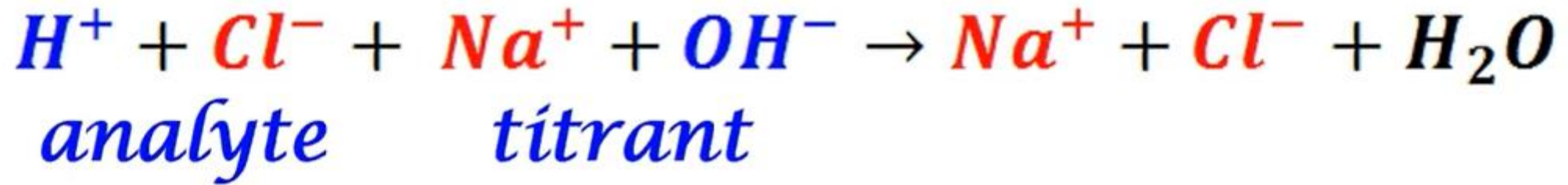
CONDUCTOMETRIC TITRATION : PRINCIPLE

Conductometric titration is a titration used to measure the amount of an analyte present in the given solution by measuring the change in the conductance as a function of volume of titrant.

- ❖ conductance is due to the movement of ions in the solution*
- ❖ one ion replaces with another ion of different ionic conductivity during the titration*
- ❖ equivalence point is determined graphically.*

CONDUCTOMETRIC TITRATION (STRONG ACID VS STRONG BASE)

(HCl Vs NaOH)



High ionic conductivity – $\begin{cases} H^+ \\ OH^- \end{cases}$
Low ionic conductivity – $\begin{cases} Na^+ \\ Cl^- \end{cases}$

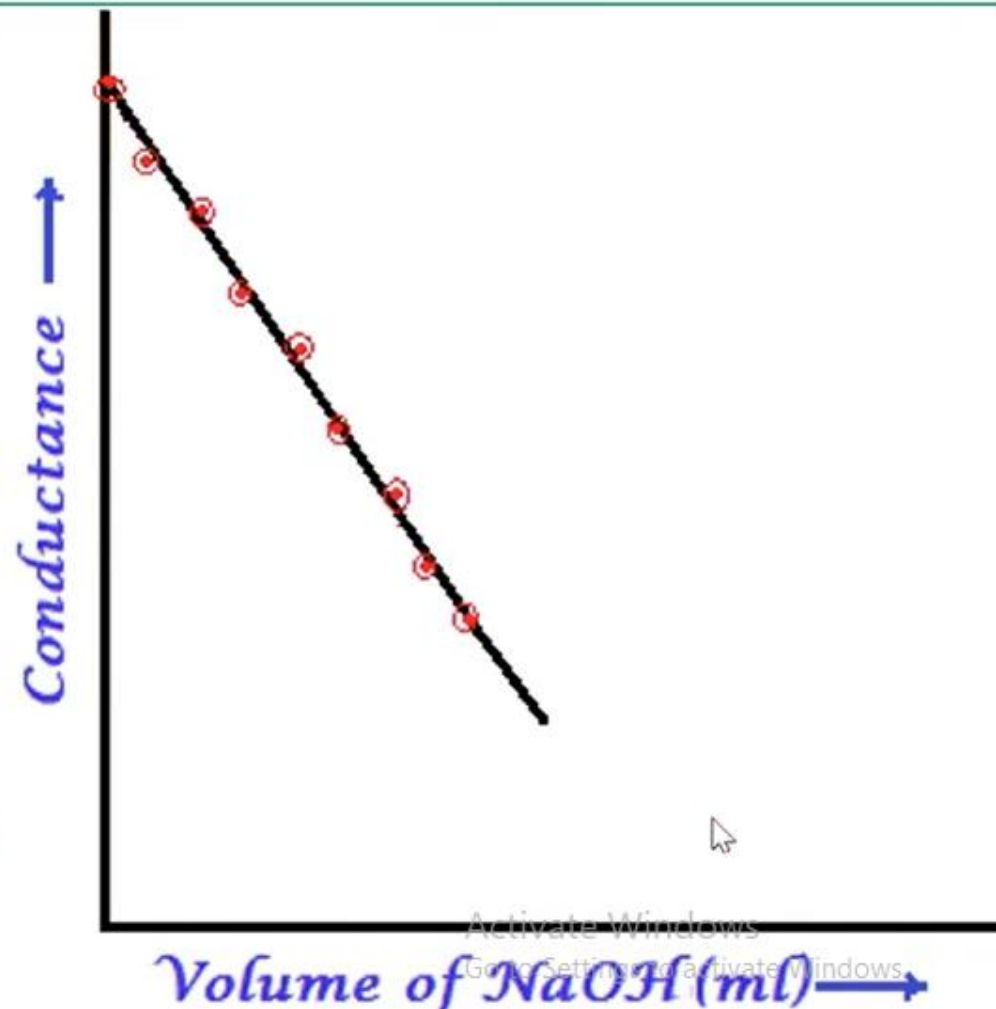


❖ Before titration - only HCl present.

➤ Presence of H^+ with high ionic conductivity - high conductance

❖ During titration till equivalence point / neutralisation point-

➤ H^+ with high ionic conductivity is replaced by Na^+ with low ionic conductivity - conductance decreases



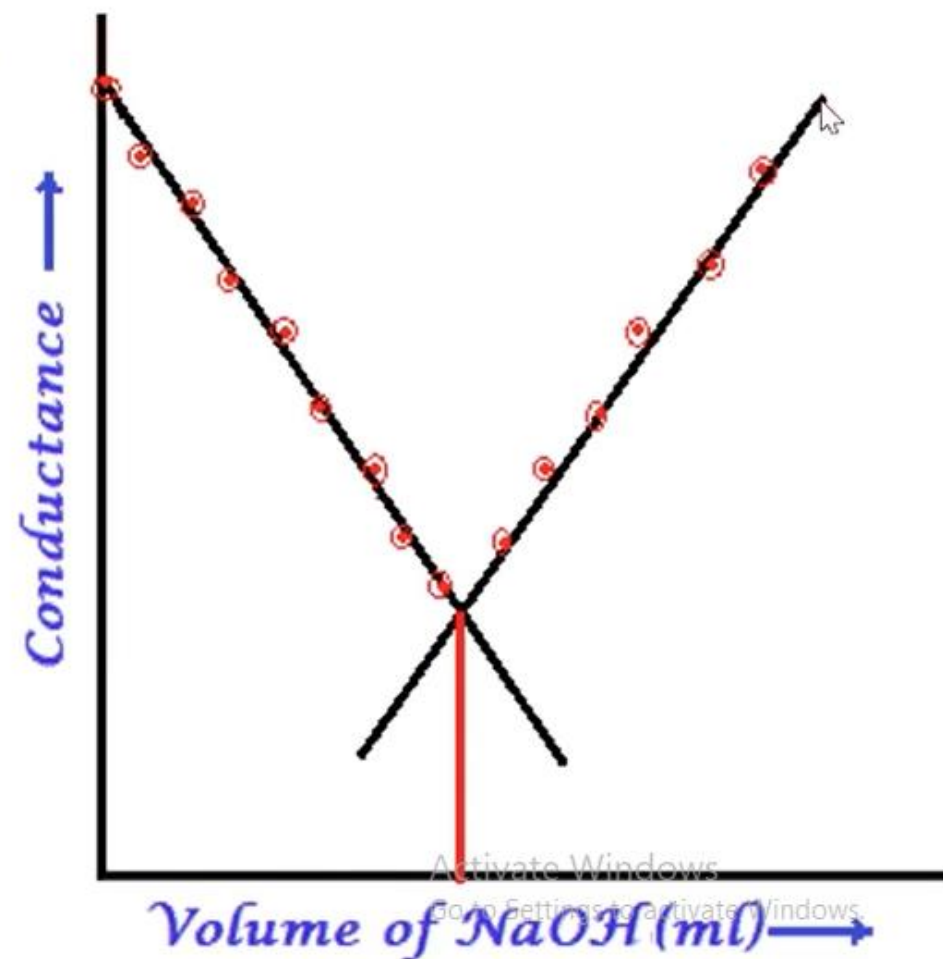


❖ At equivalence point/neutralisation point - $NaCl$ and H_2O are present

➤ least conductance

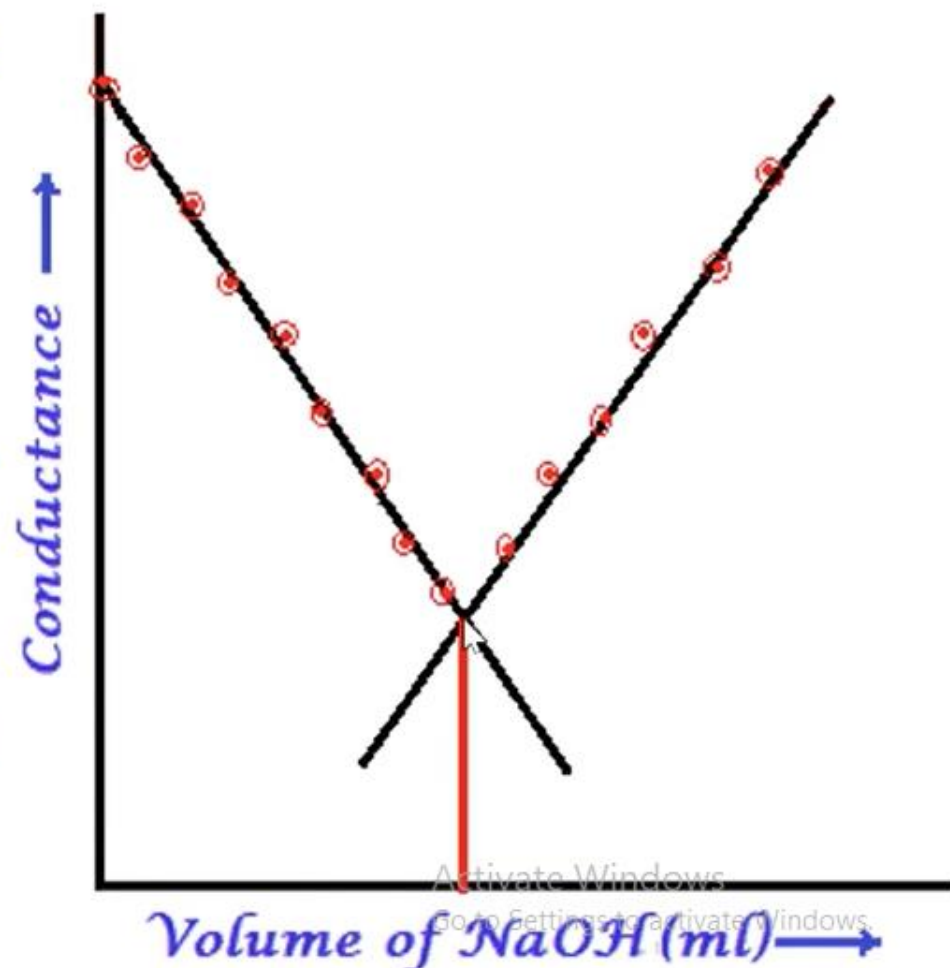
❖ After equivalence point - excess $NaOH$ is added

➤ accumulation of OH^{-} with high ionic conductivity - conductance increases

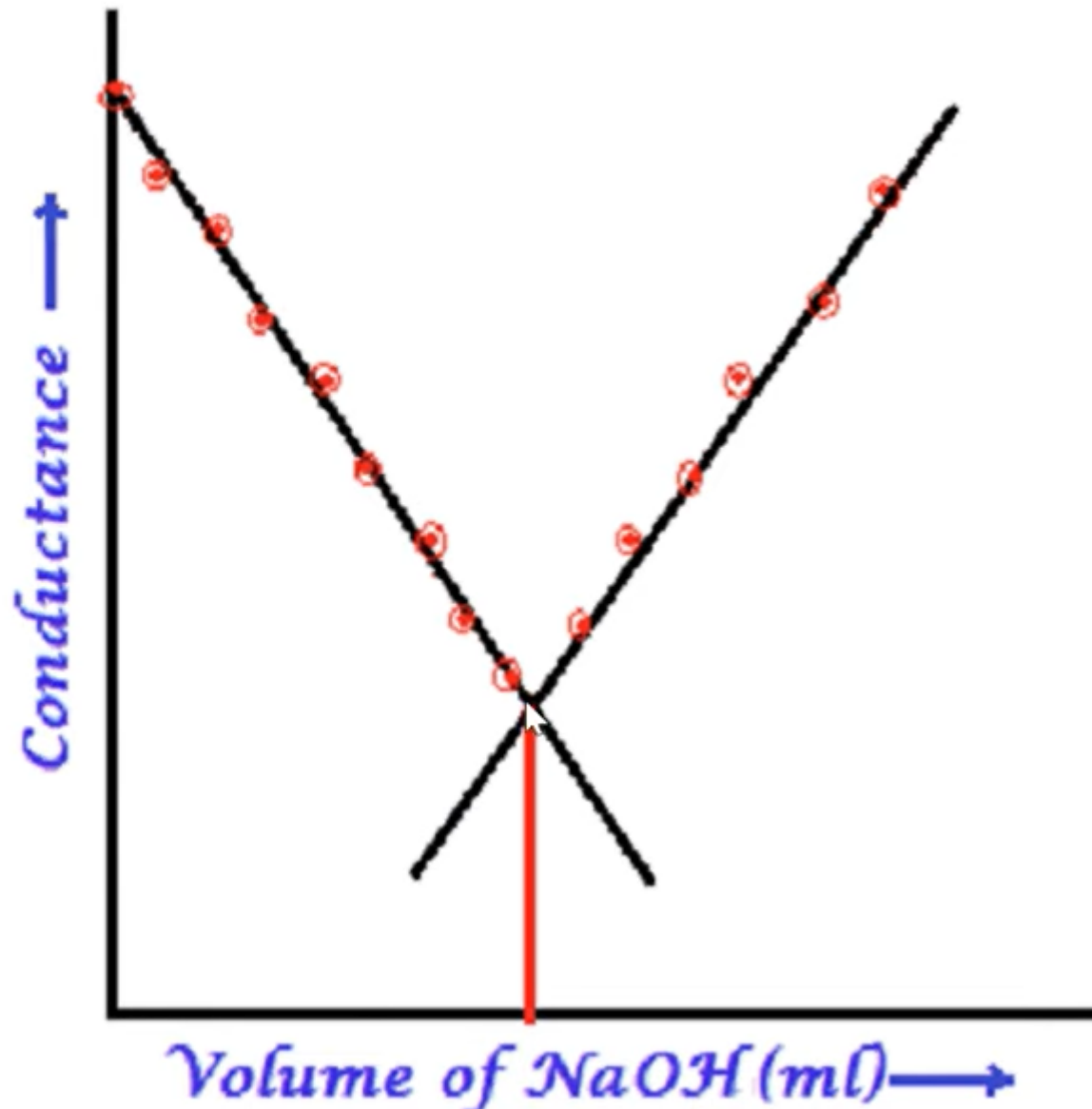




- ❖ At equivalence point/neutralisation point - $NaCl$ and H_2O are present
 - least conductance
- ❖ After equivalence point - excess $NaOH$ is added
 - accumulation of OH^{-} with high ionic conductivity - conductance increases



TITRATION CURVE



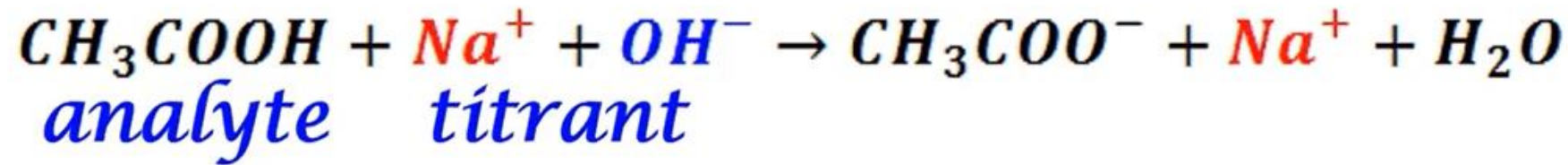
❖ *equivalence point/neutralisation point is determined graphically*

ADVANTAGES

- Used for *coloured* solutions
- Suitable for *turbid* solutions
- Suitable for *dilute* solutions
- System with *incomplete reactions*
- Used for determining the concentration of *weak bases and weak acids or mixture of acids*
- *Special care is not required at the end point, as it is determined graphically*
- *Does not require indicators.*

CONDUCTOMETRIC TITRATION (WEAK ACID VS STRONG BASE)

$(CH_3COOH \text{ Vs } NaOH)$



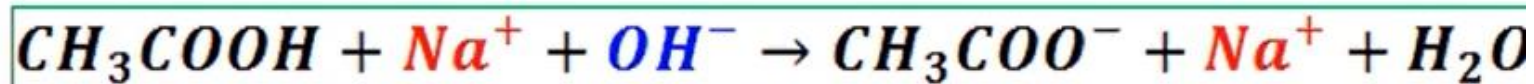
CH_3COOH - *does not dissociate easily*

$NaOH$ - *dissociates immediately*

CH_3COONa - *dissociates better than CH_3COOH*

Na^+ - *has low ionic conductivity*

High ionic conductivity - $\begin{cases} H^+ \\ OH^- \end{cases}$

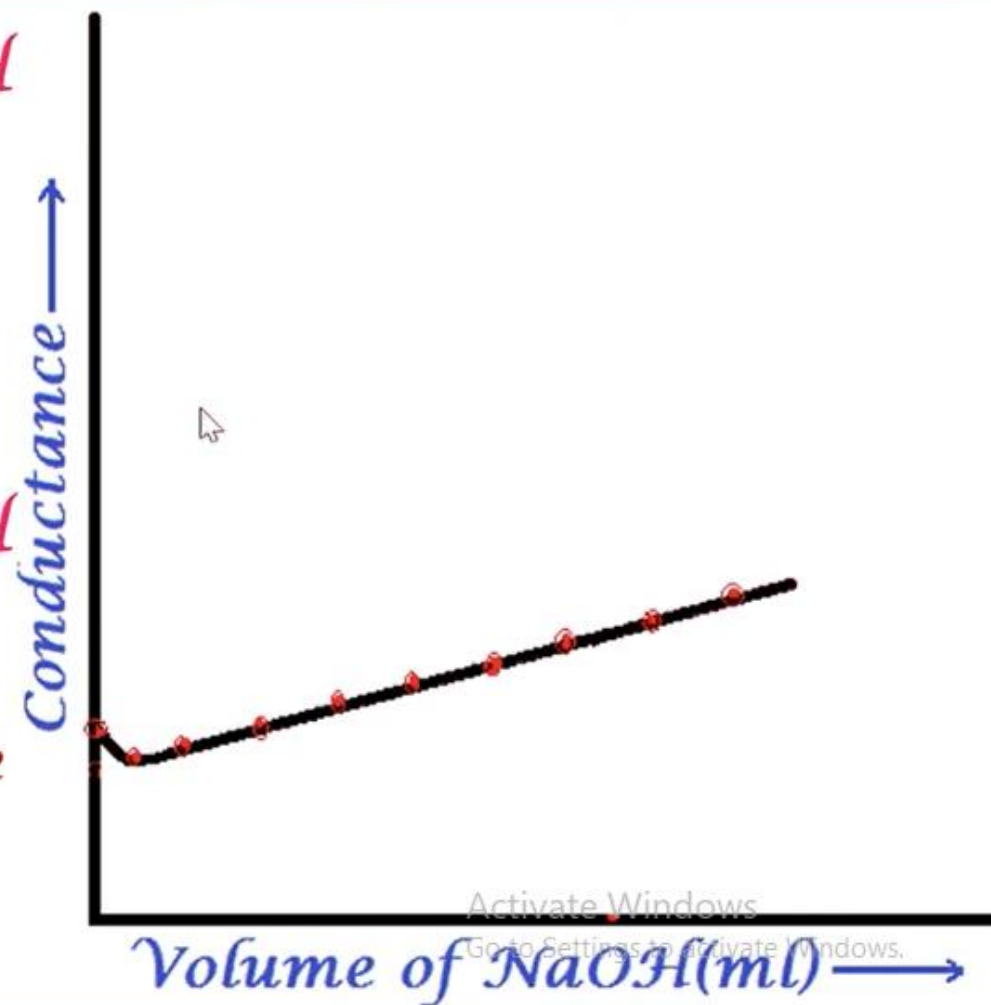


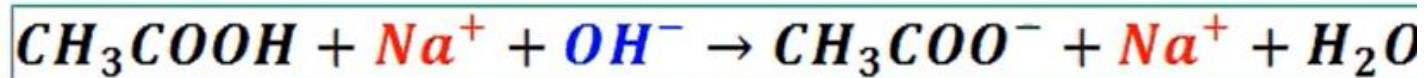
❖ Before titration - only CH_3COOH present

➤ CH_3COOH does not dissociate easily - low conductance

❖ Initial addition of NaOH - CH_3COOH and small amount of CH_3COONa

➤ CH_3COOH does not dissociate easily due to common ion effect of CH_3COO^- - slight decrease in conductance



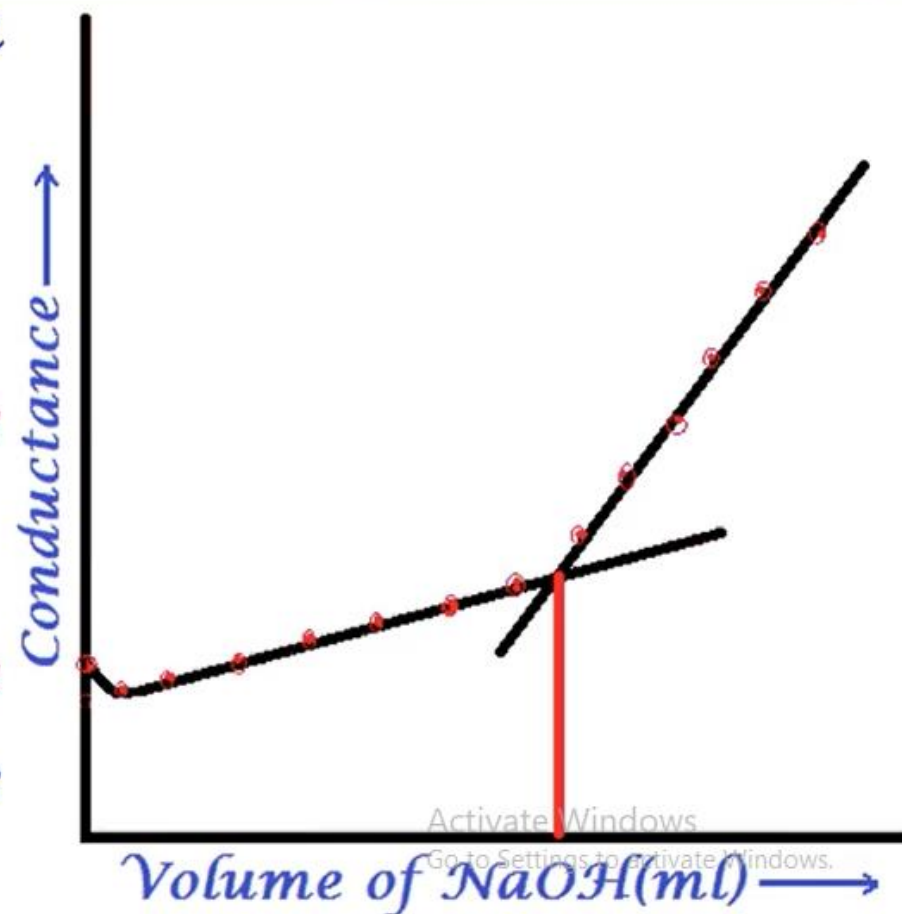


❖ At equivalence point/neutralisation point - CH_3COO^- and Na^+ are present

➤ Conductance increases

❖ After equivalence point - excess NaOH is added

➤ accumulation of OH^- with high ionic conductivity - conductance increases drastically

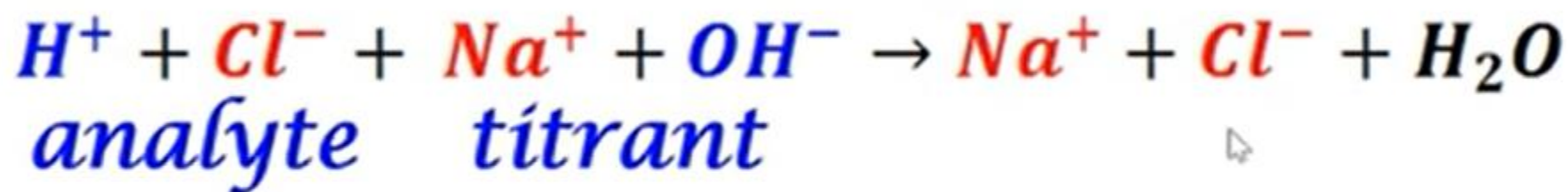


Analytical techniques/ Electrochemistry

*Conductometric titration
(Mixture of acids vs Strong base)*

CONDUCTOMETRIC TITRATION

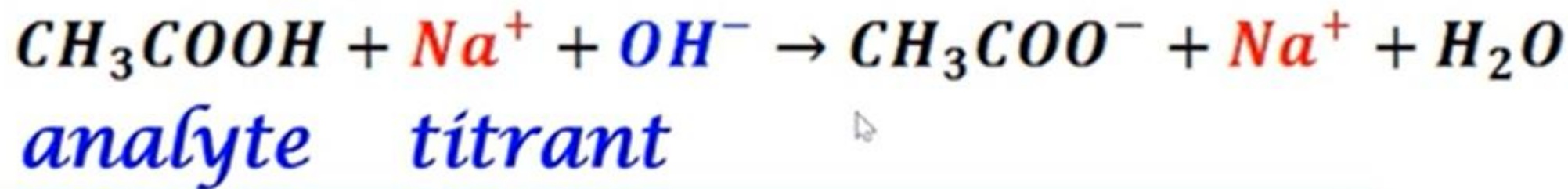
(MIXTURE OF ACIDS VS STRONG BASE)



High ionic conductivity – $\begin{cases} H^+ \\ OH^- \end{cases}$

Low ionic conductivity – $\begin{cases} Na^+ \\ Cl^- \end{cases}$

$(\text{HCl} + \text{CH}_3\text{COOH}) \text{ Vs } \text{NaOH}$



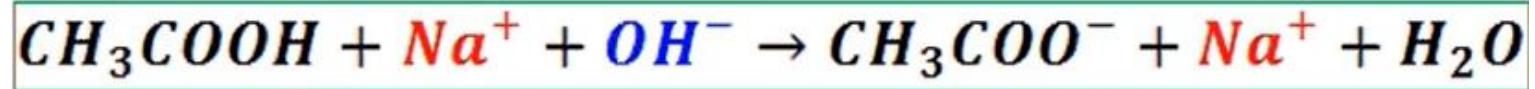
CH_3COOH - *does not dissociate easily*

CH_3COONa - *dissociates better than CH_3COOH*

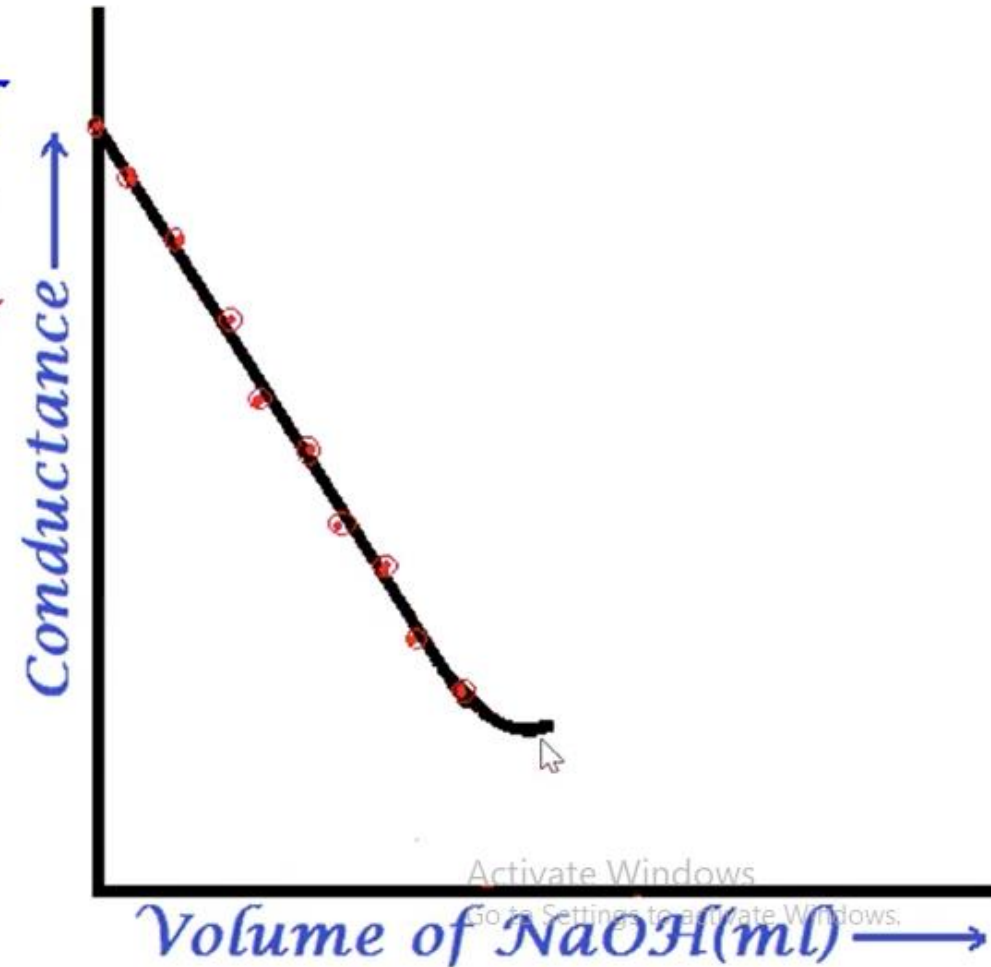
NaOH - *dissociates immediately*

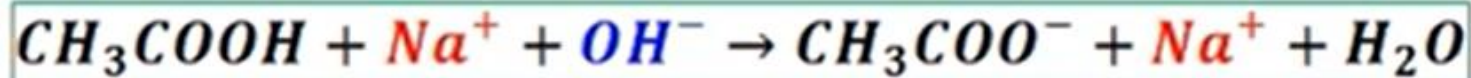
Na^+ - *has low ionic conductivity*

High ionic conductivity - $\begin{cases} \text{H}^+ \\ \text{OH}^- \end{cases}$



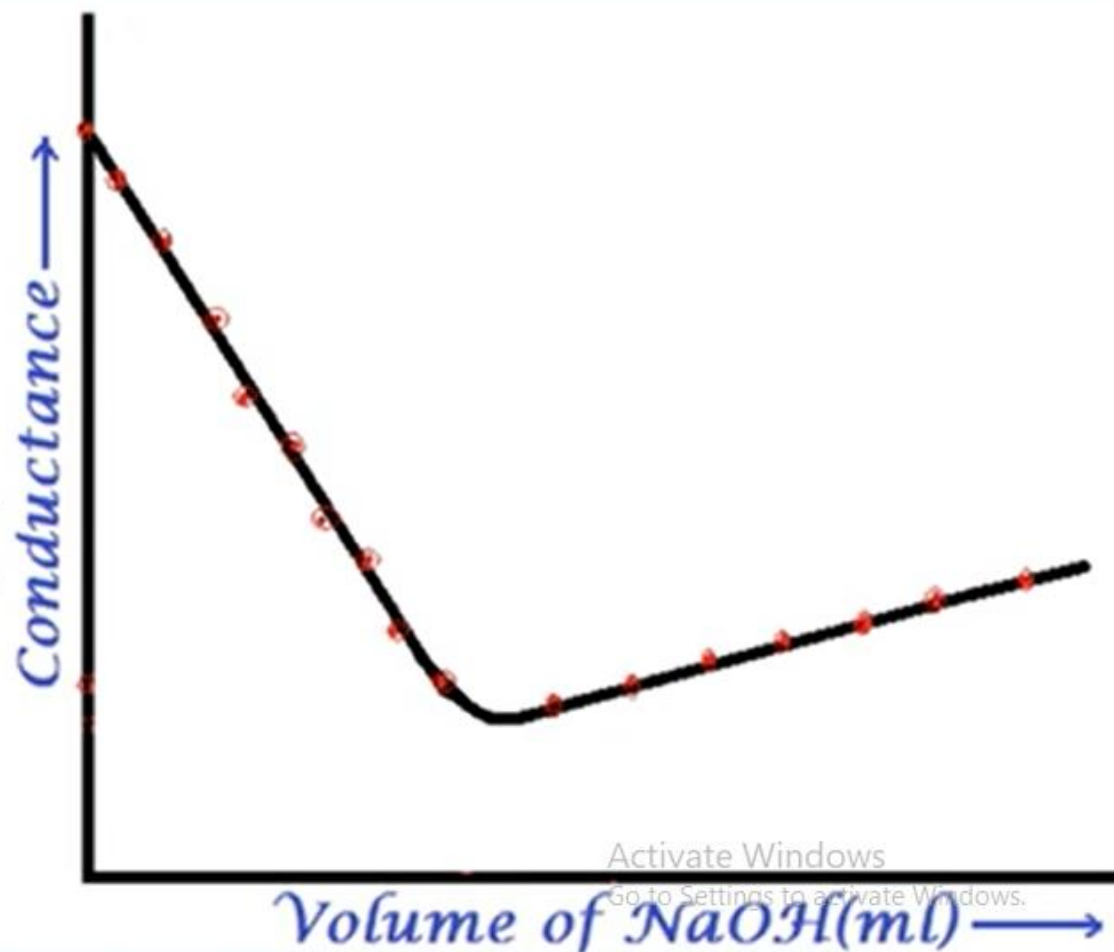
- ❖ After complete neutralisation of HCl - initial addition of NaOH - NaCl , CH_3COOH and small amount of CH_3COONa
- CH_3COOH does not dissociate easily due to common ion effect of CH_3COO^- - slight decrease in conductance

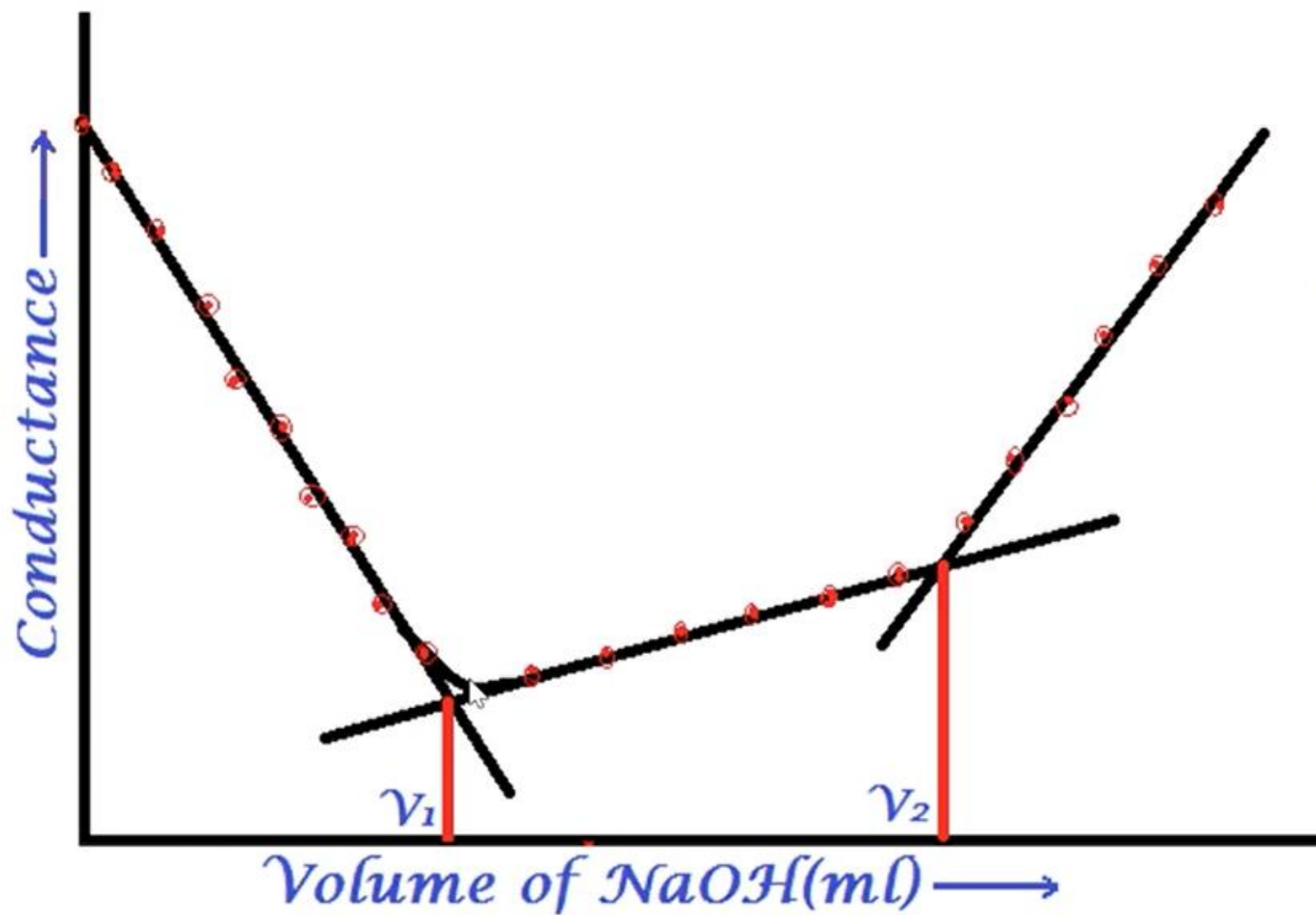




❖ During titration till equivalence point/neutralisation point of CH_3COOH -

➤ CH_3COONa ionises better than CH_3COOH - conductance increases slowly



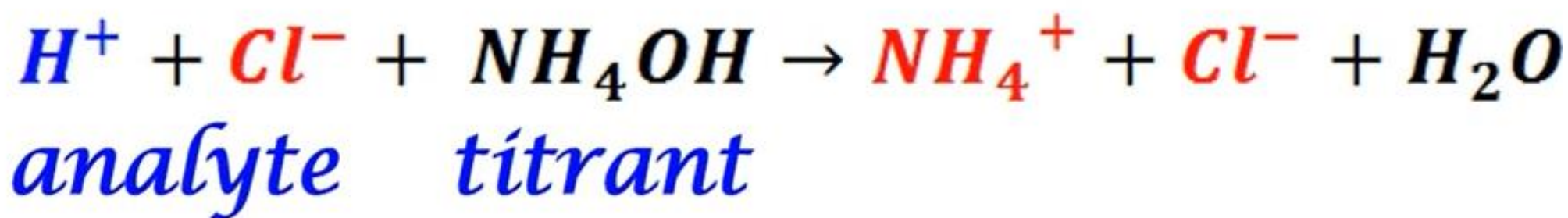


V_1 - neutralisation point
of HCl

V_2 - neutralisation point
of CH_3COOH

*Conductometric titration
(Strong acid vs Weak base)*

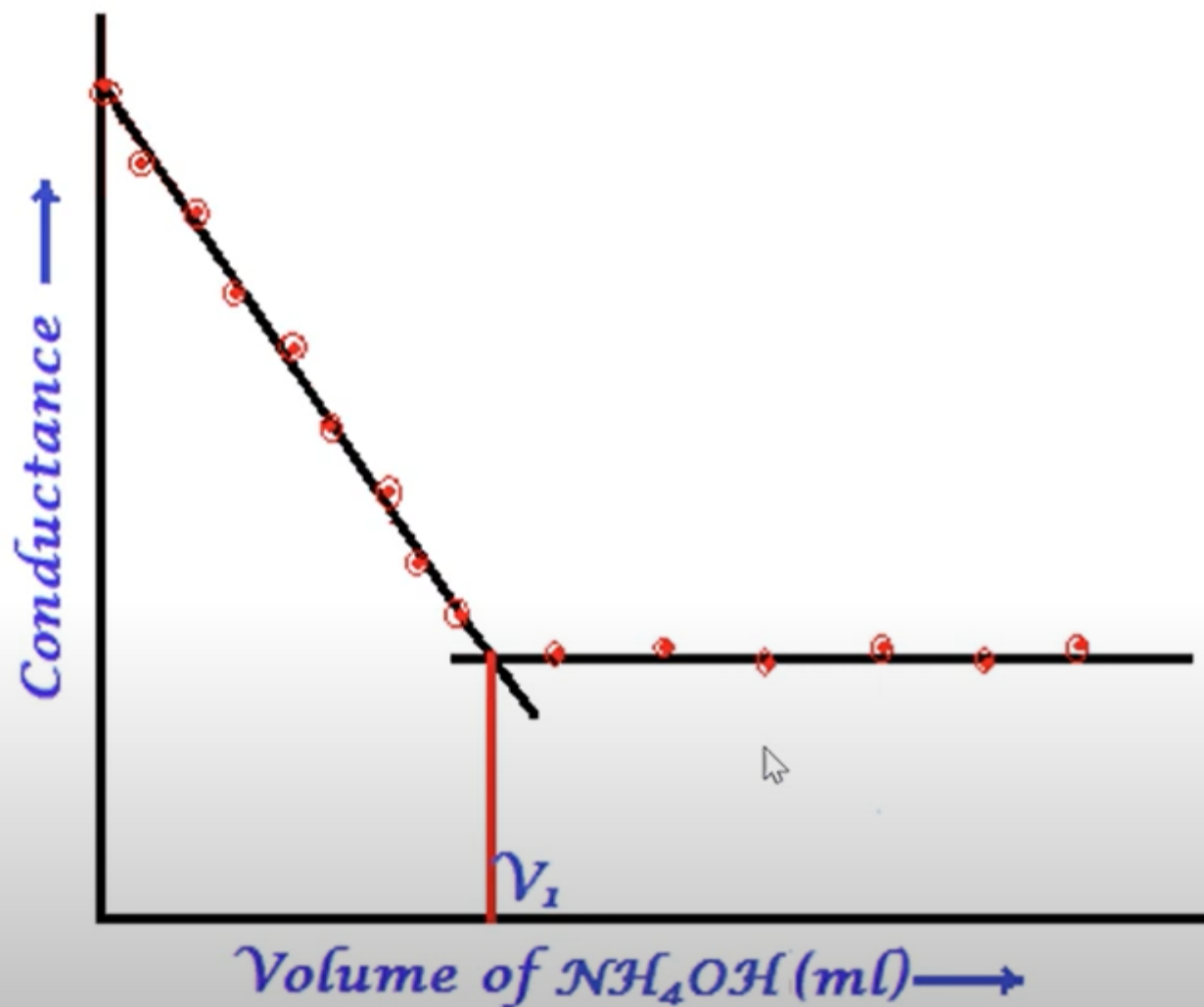
(HCl Vs NH₄OH)



High ionic conductivity – H⁺

*Low ionic conductivity – { NH₄⁺
Cl⁻*

TITRATION CURVE

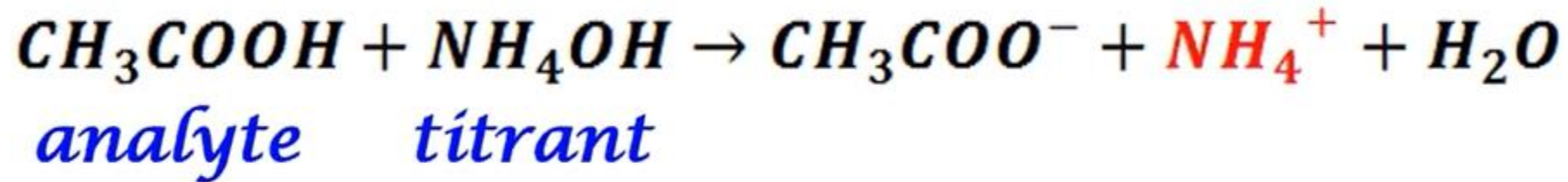


❖ *equivalence
point/neutralisation
point is determined
graphically*

*Conductometric titration
(Weak acid vs Weak base)*



(CH₃COOH Vs NH₄OH)



CH₃COOH & NH₄OH- does not dissociate easily

CH₃COONH₄ - dissociates better than CH₃COOH

NH₄⁺ - has low ionic conductivity

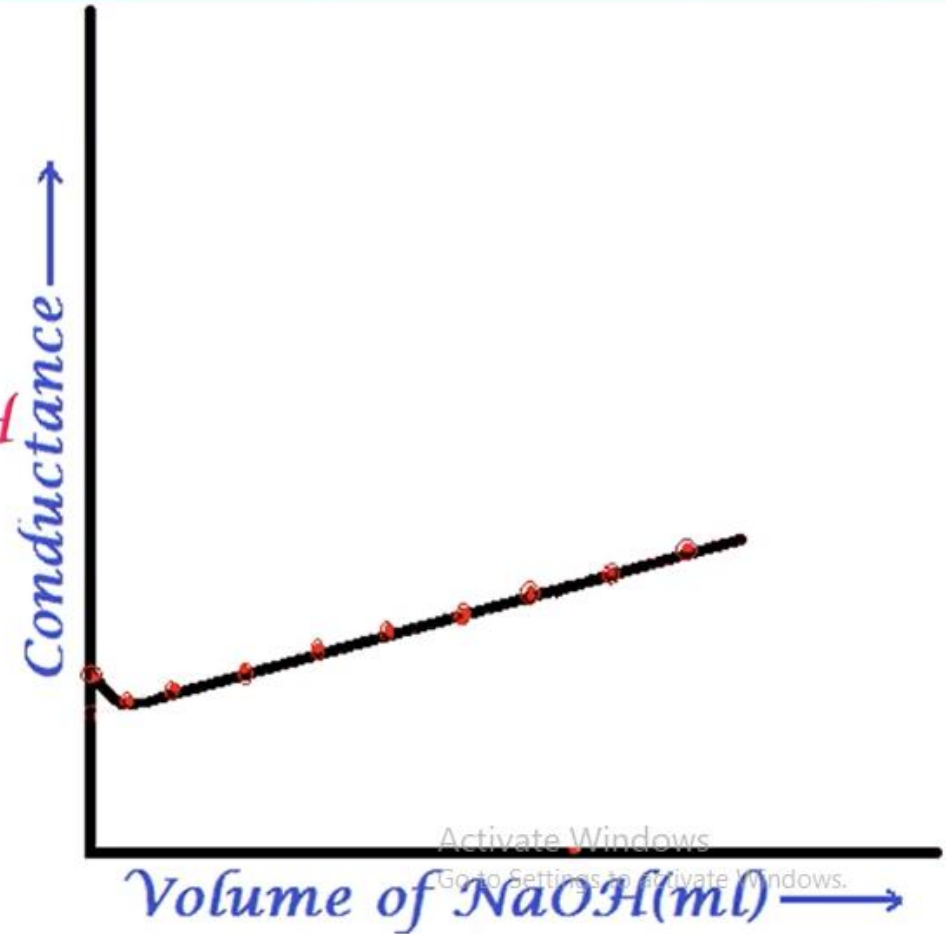


❖ Before titration - only CH_3COOH present

➤ CH_3COOH does not dissociate easily - low conductance

❖ Initial addition of NH_4OH - CH_3COOH and small amount of $\text{CH}_3\text{COO}^- \text{NH}_4^+$

➤ CH_3COOH does not dissociate easily due to common ion effect of CH_3COO^- - slight decrease in conductance



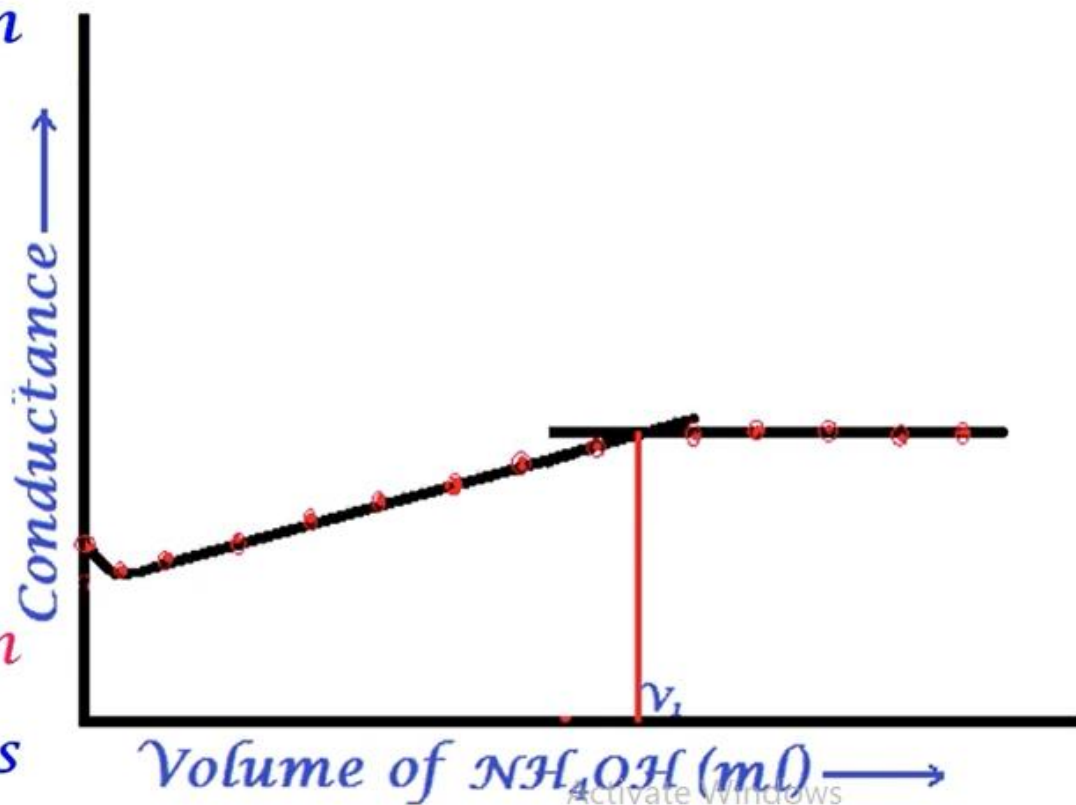


❖ At equivalence point/neutralisation point - CH_3COO^- and NH_4^+ are present

➤ Conductance increases

❖ After equivalence point - excess NH_4OH is added

➤ does not dissociate due to common ion effect - conductance remains constant



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DEBYE-HUCKEL THEORY

Debye-Huckel theory is the modern theory of strong electrolytes which explains their behaviour in solutions. According to this theory, strong electrolytes are completely ionized at all dilutions. Still equivalent conductance is less in concentrated solutions. This is due to fall in mobilities of ions as a result of inter-ionic attractions. The decrease in mobilities is accounted for by the following reasons.

- i) Asymmetric effect
- ii) Electrophoretic effect

1. ASYMMETRIC EFFECT

RELAXATION EFFECTS OR ASYMMETRY EFFECTS

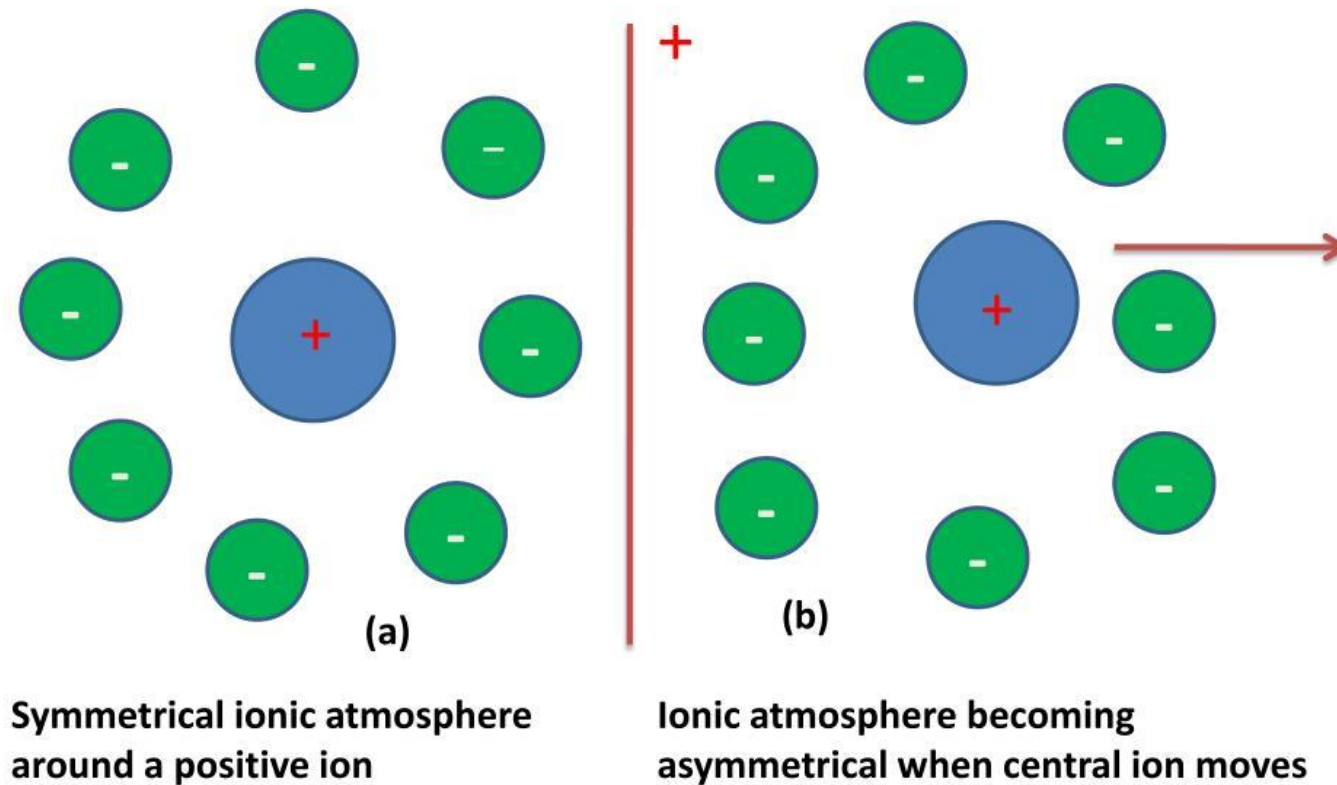


FIG:1

- In a solution, each ion is surrounded by ions of opposite charge, forming an **ionic atmosphere**.
- Without an electric field, this atmosphere is **symmetrical**, and the forces on the central ion are balanced.
- When an **electric field** is applied:
 - The positive ion moves toward the cathode.
 - The surrounding negative ions (ionic atmosphere) lag behind toward the anode.
- This **disturbs the symmetry**, creating more negative ions on one side.
- The positive ion now feels a **backward pull**, which **slows it down**.
- This slowing down due to the shifted ionic atmosphere is the **asymmetric effect**.

2. RELAXATION EFFECT

- As the positive ion moves, it leaves its old ionic atmosphere behind and tries to form a **new, balanced atmosphere** around it.
- **Formation of the new atmosphere takes time**, slower than the decay of the old one.
- This **time lag** is called **relaxation time**.
- The slowing down of the ion due to this delayed reorganization is called the **relaxation effect**.

- Each ion in a solution is surrounded by water molecules (hydrated).
- When a **positive ion moves to the cathode**, the **negative ions and their water molecules** move in the **opposite direction** (toward the anode).
- Similarly, **negative ions** moving to the anode face **positive ions and water molecules** moving toward the cathode.
- As a result, each ion **swims against the moving solvent**, which **slows it down**.
- This slowing down is called the **electrophoretic effect**.

Important questions

1. How can the principle of *conductometric titration* be applied to determine the end point in the titration of an acid mixture with sodium hydroxide?
2. Explain how *conductometric titration* can be used to study the neutralization reaction between *ammonium hydroxide* and *acetic acid*.
3. Describe the conductometric titration curve of strong acid vs. strong base and explain the change in conductivity
4. How can conductometric titration be used to find the end point in the titration of acetic acid with sodium hydroxide?

Important questions

- Write a note on the following
 - i) Pitting Corrosion
 - ii) Galvanic corrosion
 - iii) Caustic Embrittlement
 - iv) Corrosion inhibitors