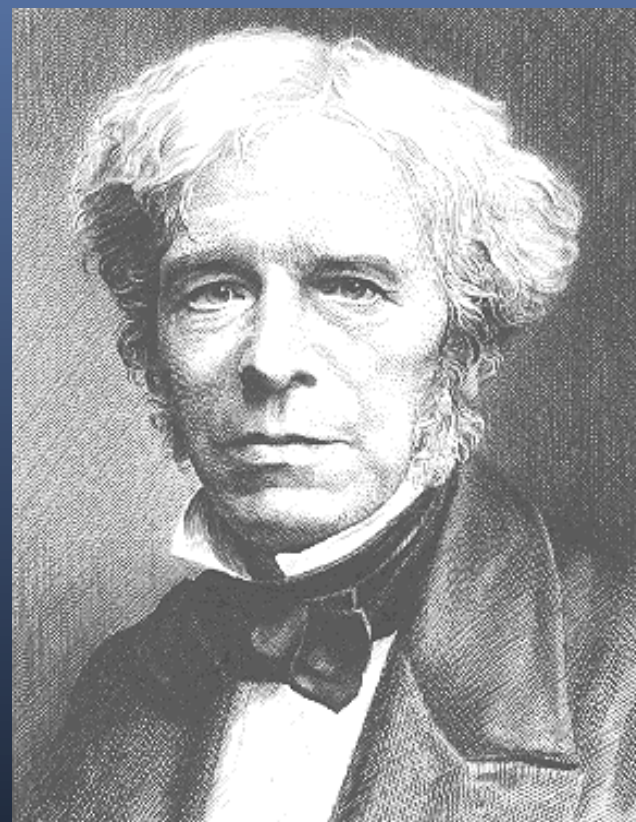# CONDUCTOMETRY

S. Y. B. Pharmacy
Pharmaceutical Analysis-II
SEM-IV

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Deaprtment of Pharmaceutical Chemitry

Michael Faraday (1791 - 1867)

Contents:

❖ Conductometry means measuring the conductivity of ionic solutions caused by mobility of ions towards respective electrodes in presence of an electric field.

❖ Conductivity is measured by using conductometer. Units of conductivity is mhos(Ω^{-1}).

❖ Conductivity is generally measured by using a Wheatstone bridge circuit and a conductivity cell made of platinum.

Electrical current, I
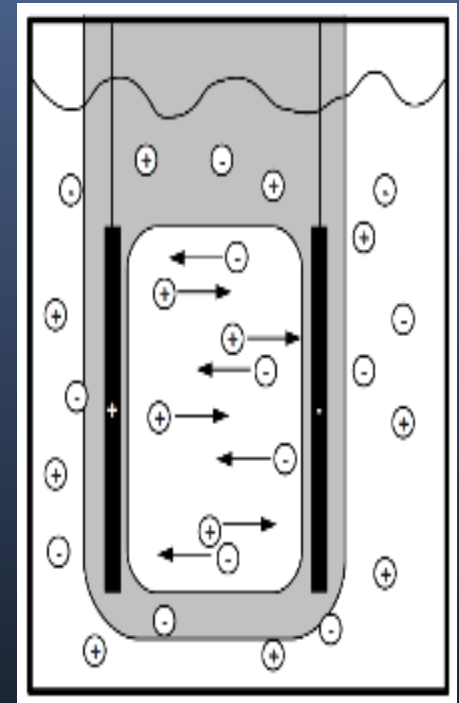
Voltage, V

Migration of ions in solution
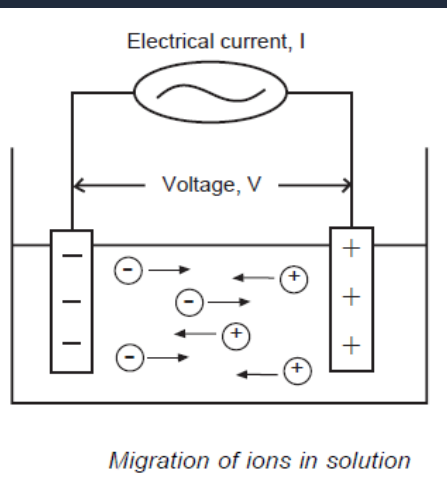
$$R = V/i$$

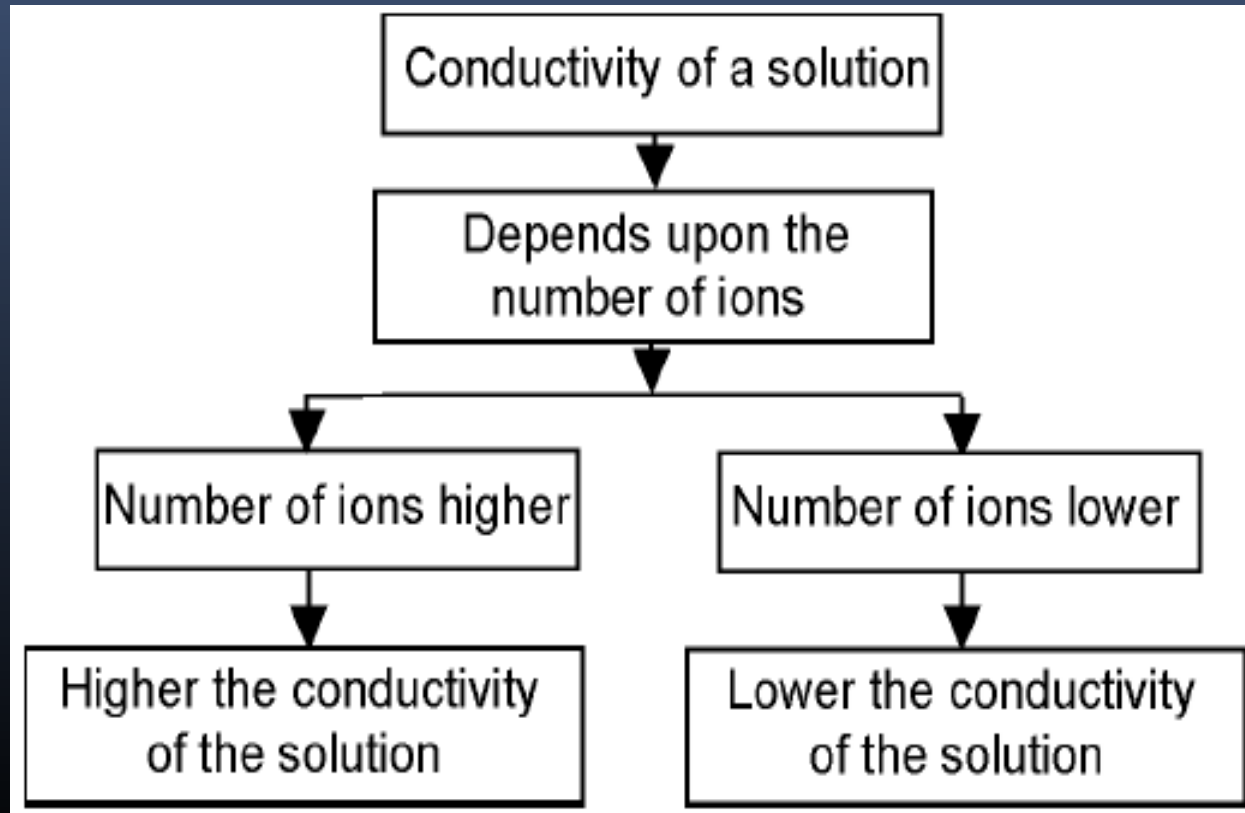V-potential difference in volts
i-current in amperes

$$C = 1/R$$

3

Total conductance of the solution is directly proportional to the sum of the n individual ion contributions .

$$G = \sum c_i \Lambda_{m,i}$$

Ohm's law-

The magnitude of conductometric titration is based on ohm's law.

$$i = e/R$$

where

Flow of Charge
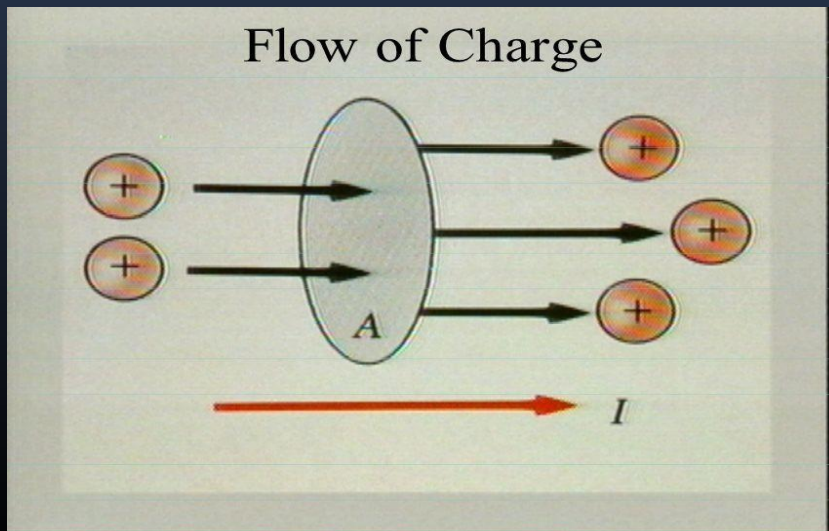
i = current in amperes
e = potential difference
R = resistance in ohm's

1. Electrodes

Two parallel platinized Pt. foil electrodes or Pt. black with electrodeposited a porous Pt. film which increases the surface area of the electrodes and further reduces faradaic polarization.

2. Primary standard solutions

Primary standard KCl solution ,at 25℃, 7.419g of KCl in 1000g o
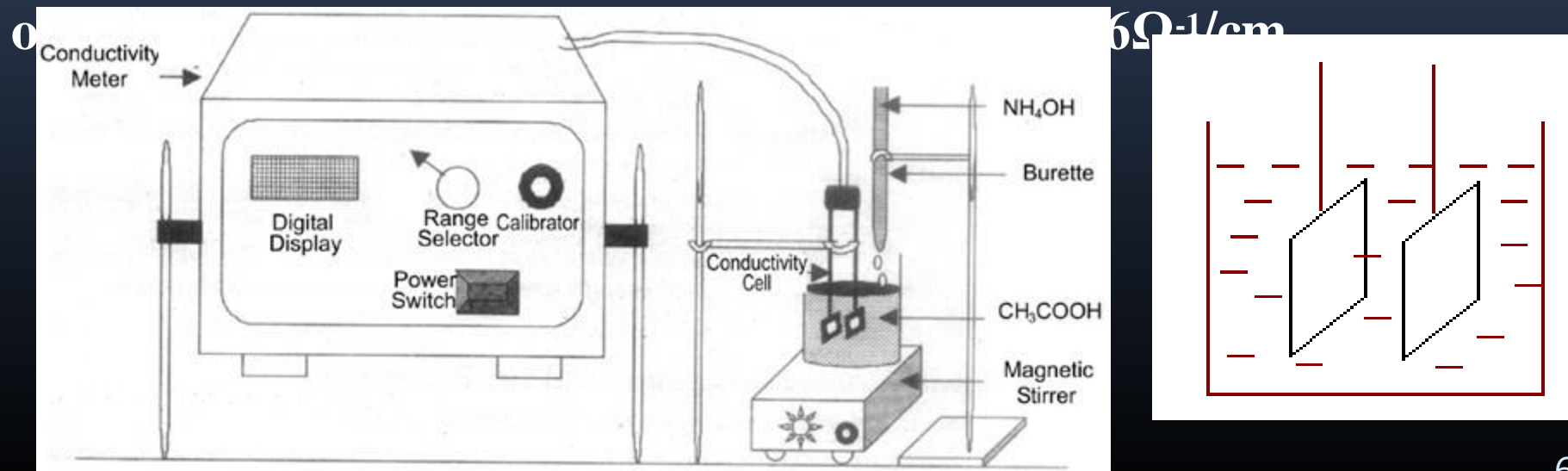
3. Conductivity Cell :

Avoid the change of temperature during determination

4. Wheat stone bridge :
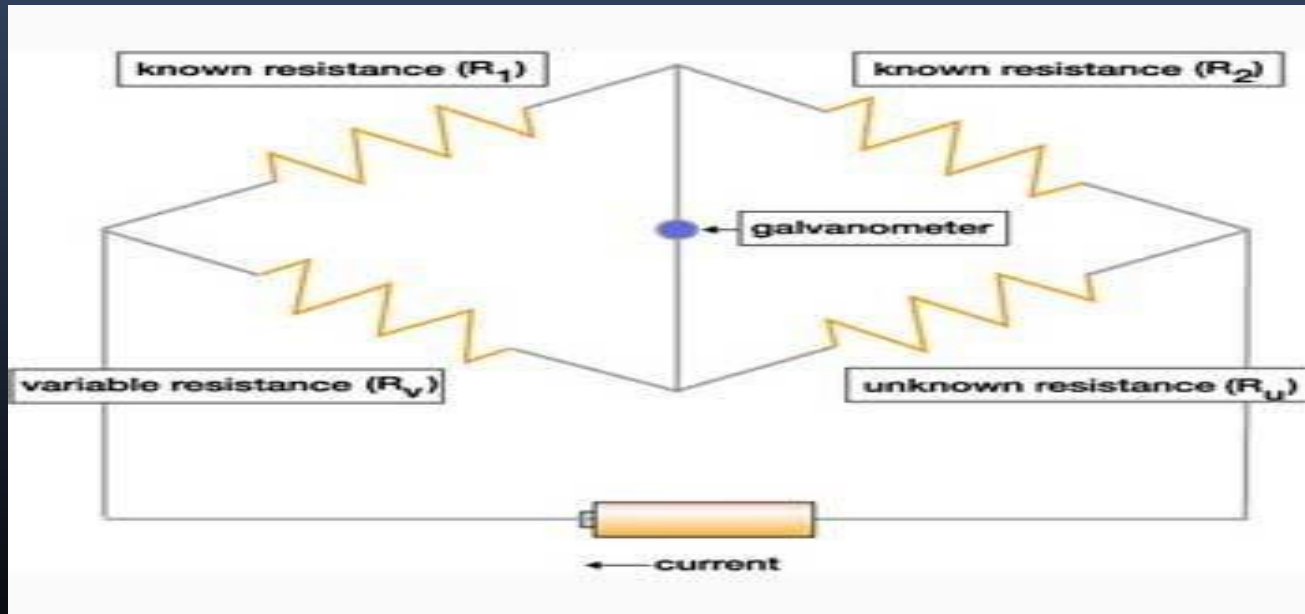
Factors affecting conductivity:
❖ Size of ions
❖ Temperature
❖ Number of ions
❖ Charge of ions

✓ Specific conductivity:-It is conductivity offered by a substance of 1cm length and 1sq.cm surface area. units are mhos/cm.
✓ Equivalent conductivity:-it is conductivity offered by a solution containing equivalent weight of solute in it.

Molar conductance of various ions at infinite dilution at 25℃

ions	molar conductance
K^+	73.52
Na^+	50.11
Li^+	38.69
H^+	349.82
Ag^+	61.92
Cl^-	76.34
Br^-	78.4
OH^-	198

❖Cell Constant:

- It is a constant characteristic of the cell in which the electrolyte is taken and its value depends on the distance between the electrodes and the area of cross-section of the electrodes.

$$\text{Cell constant} = \frac{\text{Distance between the electrodes}}{\text{Area of cross-section of each electrode}}$$

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

and specific conductance $K = \dfrac{l}{Ra}$.

Therefore, $\qquad$ specific conductance $= \dfrac{\text{Cell constant}}{R}$

or $\qquad$ cell constant = specific conductance $\times R$

- If the area of cross-section is in cm^2 and distance between the electrodes is in cm, the unit of cell constant is cm^{-1}.

The determination of specific conductance of an electrolytic solution, thus, consists of two steps:
• Determination of cell constant by using a standard KCl solution of known concentration in the conductivity cell.
• Determination of resistance of he given solution using the same cell. The reciprocal of this gives the value of conductance. Multiplication of conductance and cell constant gives the value of specific conductance of the solution.

In conductance measurements, the solutions are always prepared in conductivity water which has no conductance due to dissolved impurities.
It is prepared by distilling a number of times the distilled water to which a little $KMnO_4$ and KOH have been added in a hard glass distillation assembly.
Such water has very low conductance of the order of 4.3×10^{-8} ohm^{-1}. For ordinary purposes, double distilled water may be used.
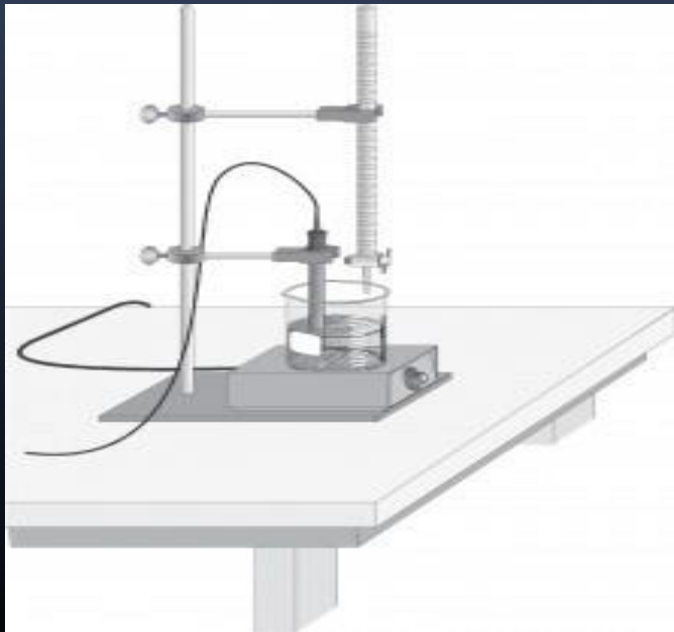
APPLICATIONS OF CONDUCTOMETRY

It can be used for the determination of:-
➢ Solubility of sparingly soluble salts
➢ Ionic product of water
➢ Basicity of organic acids
➢ Salinity of sea water (oceanographic work)
➢ Chemical equilibrium in ionic reactions
➢ Conductometric titration

CONDUCTOMETRIC TITRATIONS:

➢ The determination of end point of a titration by means of conductivity measurements are known as conductometric titrations.

Types of conductometric titrations:

➢ Acid-base titration
➢ Precipitation titration
➢ Replacement titration
➢ Redox (oxidation-reduction) titration
➢ Complexometric titration
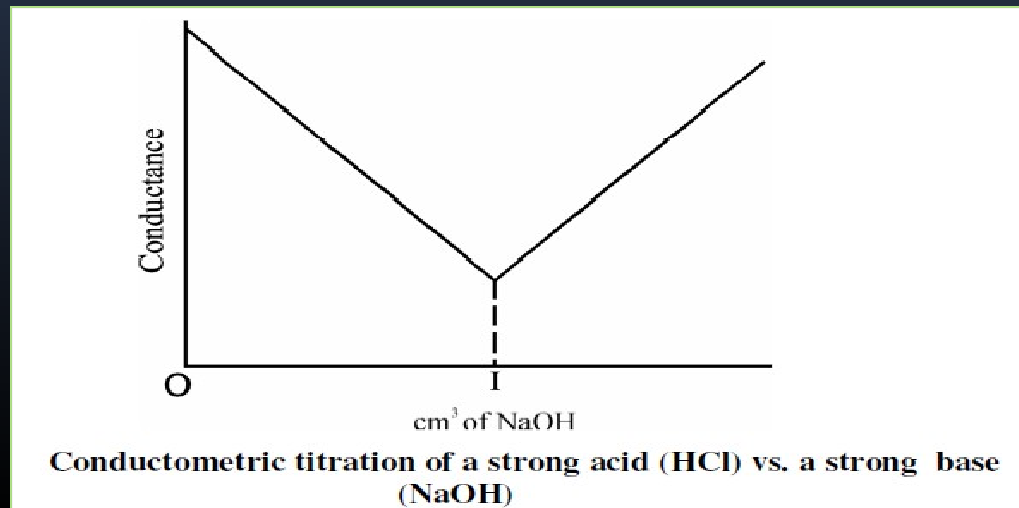
Strong Acid with a Strong Base.

e.g. HCl with NaOH:

Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions.

When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cations as H+ ions react with OH− ions to form undissociated water.

This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl.

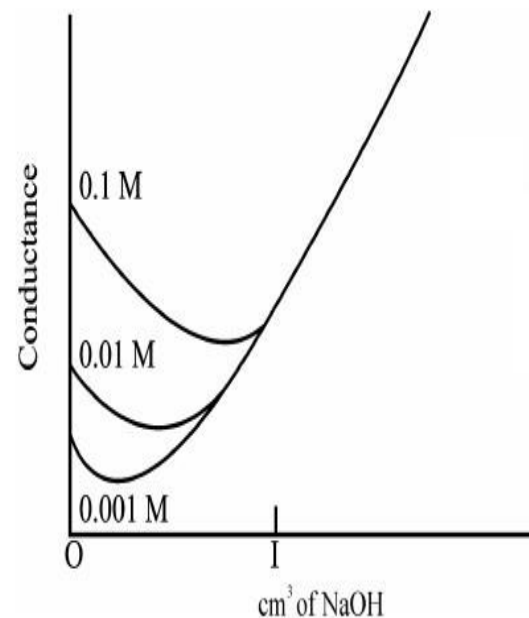After the equivalence point, the conductance increases due to the large conductivity of OH- ions

Conductometric titration of a strong acid (HCl) vs. a strong base (NaOH)

Weak Acid with a Strong Base,
e.g. acetic acid with NaOH:

Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of H+ by Na+ but also suppresses the dissociation of acetic acid due to common ion acetate.

But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated CH3COOH to CH3COONa which is the strong electrolyte.
This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt CH3COONa.

Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting OH– ions


Conductometric titration of a weak acid (acetic acid) vs. a strong base (NaOH)

Weak Acid with a Weak Base:

The nature of curve before the equivalence point is similar to the curve obtained by titrating weak acid against strong base.

After the equivalence point, conductance virtually remains same as the weak base which is being added is feebly ionized and, therefore, is not much conducting


cm³ of NH₃
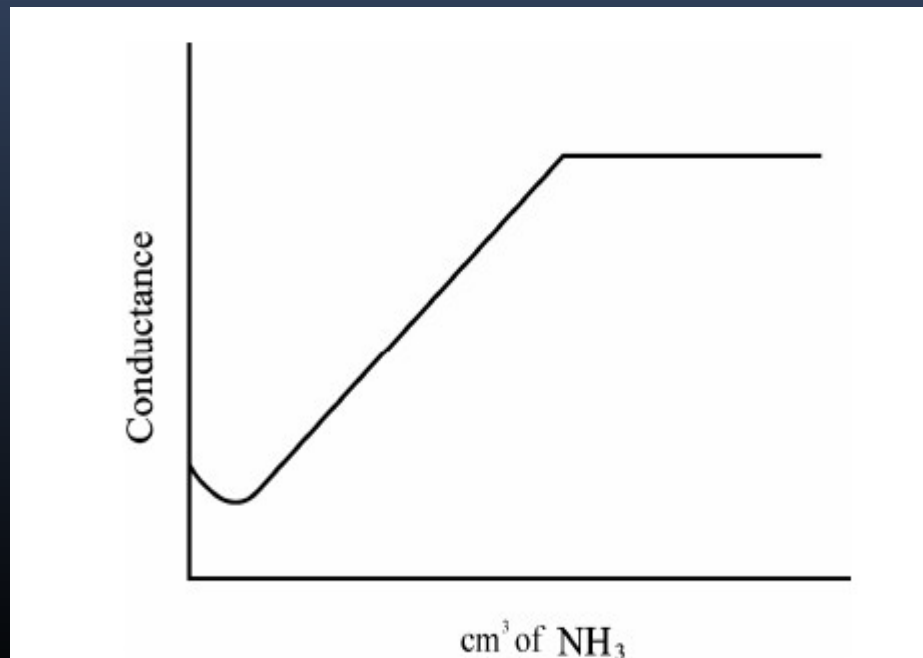
Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base:

In this curve there are two break points. The first break point corresponds to the neutralization of strong acid.

When the strong acid has been completely neutralized only then the weak acid starts neutralizing.

The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of OH^- ions in case of a strong base as the titrant.

However, when the titrant is a weak base, it remains almost constant after the end point similar to previous titration
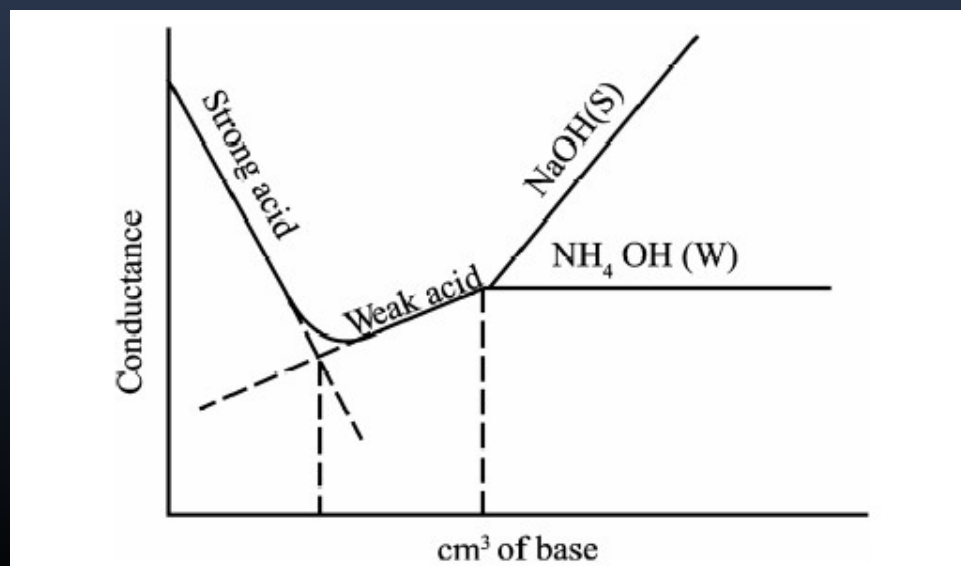
PRECIPITATION TITRATIONS:-
## $[K^+ + Cl^-] + [Ag^+ + No_3-]$

A reaction may be made the basis of a conductometric precipitation titration provided the reaction product is sparingly soluble or is a stable complex. The solubility of the precipitate (or the dissociation of the complex) should be less than 5%. The addition of ethanol is sometimes recommended to reduce the solubility in the precipitations.
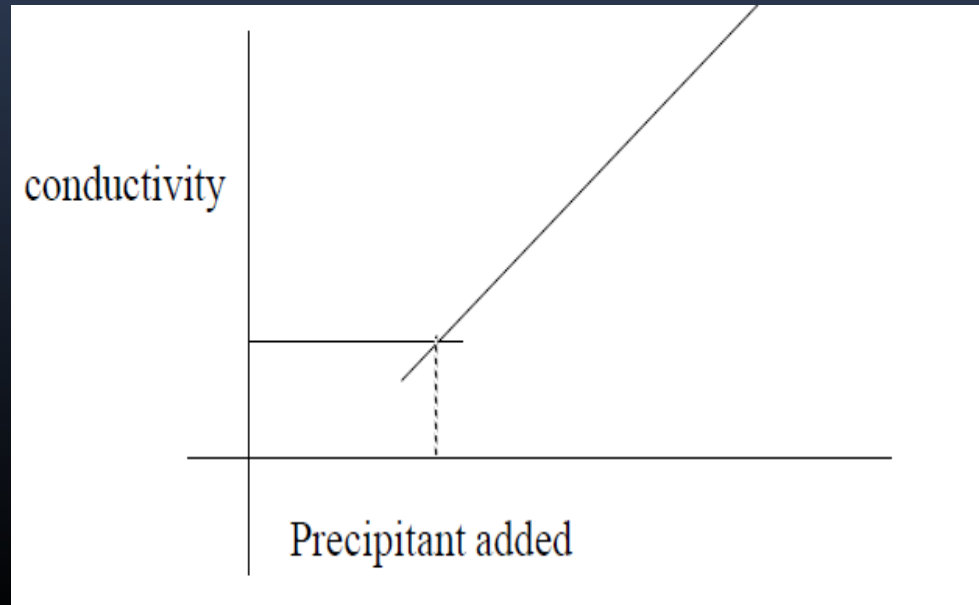
REPLACEMENT TITRATIONS

➢Salt of strong acid and weak base vs. strong base
Ex: ammonium chloride vs. sodium hydroxide

➢Salt of strong base and weak acid vs. strong acid
Eg: sodium acetate vs. hydrochloric acid
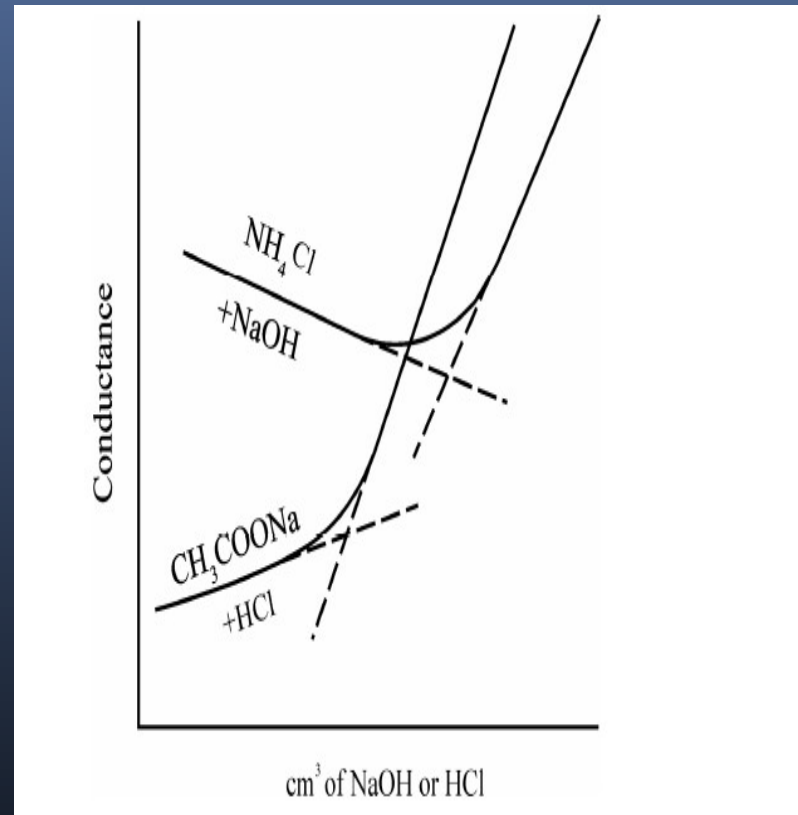
COMPLEXOMETRIC TITRATION
Ex.:-KCl vs. $Hg(ClO_4)_2$

➢Non-aqueous titrations can also be measured using conductometry.
Ex:-
a)titration of weak bases vs. perchloric acid in dioxan-formic acid.
b)Titration of weak organic acids in methanol vs. tetra methyl ammonium hydroxide in methanol-benzene.

ADVANTAGES OF CONDUCTOMETRIC TITRATIONS

➢No need of indicator

➢Colored or dilute solutions or turbid suspensions can be used for titrations.

➢Temperature is maintained constant throughout the titration.

➢End point can be determined accurately and errors are minimized as the end point is being determined graphically.

RECENT DEVLOPEMNTS

➢ In refinary industries.
➢ Estimation of polyelectrolytic solution.
➢ Biotechnology.
➢ Microbiosensors for enviromental monitoring.

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THANK YOU