Chapter-7

Conductometry

By Ermias H.

Introduction

What are the advantages of electrochemical methods?

1- Shorten the time required for analysis.

2- Used when classical methods of analysis can not be applied,

e.g. In case of colored, turbid, very dilute solutions

Or when there is no suitable indicator.

Classification of electrochemical methods

1- **Conductometry** and electrophoresis: these methods depend on the **movement of ions** in an electric field leading to conductance of electricity without occurrence of redox reaction at the electrode (inert) surface (i.e. no electron transfer).

2- **Potentiometry** and polarography: these methods depend on measuring of voltage or current between two electrodes electron transfer occurs. where redox reactions take place at the electrodes surfaces.

3- **Electrogravimetry**: in this method the electrolytes are converted to weighable form by means of an electric current.

Electrical Units

1- Coulomb (Q): It is the unit of charge or quantity of electricity. It is quantity of electricity or the charge required to convert 0.001118 g of silver ions to silver metal, **one coulomb represents 6.24 x 10^{18} electrons (charge).**

2- Faraday (F): It is the unit of quantity of electricity but much bigger than Q.

$F = 10^5$ Q (96490 Q).

If it passes in the solution it will precipitate all the equivalent weight of the substance.

It is the charge required to cause one equivalent chemical change.

It corresponds to 6.02 x 10^{23} charged particles.

3- Ampere (i) : It is the unit of current strength. It is a measure of the number of charges flowing through a conductor / second. It corresponds to the rate of one coulomb, i.e. the current, which upon flowing for a second causes the change of 0.001118 g of silver ion to silver metal.

4- Volt (V) : It is the unit of potential between two points. It is the potential required to produce a current flow of one ampere through resistance of one ohm.

5- Ohm : It is the unit of electrical resistance R. It is that resistance through which a difference in potential of one volt will produce a current of one ampere.

CONDUCTOMETRY

This is a method of analysis based on measuring electrolytic conductance.

➤ **Conductance:** is the ability of the medium to carry the electric current.

❑ Electric current passes through metallic conductor, e.g. wires of iron or copper in the form of electron flow.

❑ But conduction of electricity through an electrolyte solution involves migration of positively charged cations towards the cathode and negatively charged anions towards the anode.

❑ i.e. current is carried by all ions present in solution.

➢ When two electrodes are immersed in a solution and a potential is applied across them, a current will be produced in the external circuit that connects the two electrodes. The mechanism of electrical communication between the two electrodes in solution is the movement of ions in the solution.

➢ The conductance of a solution is a reciprocal of its resistance:

$$G = 1/R, \quad (G = \text{conductance and } R = \text{resistance})$$
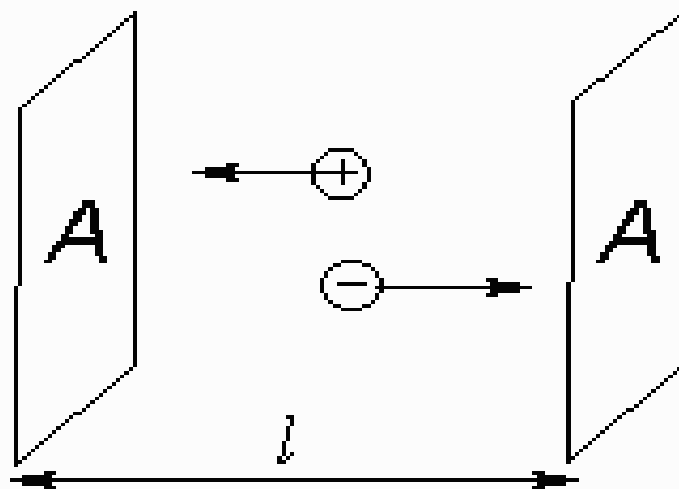
From Ohm's law:

$$R = E/I$$

(E is the potential difference, I is the current intensity)

✓ Unit of resistance = ohm

✓ Unit of conductance = ohm^{-1} or seimen or mho

➢ **conductance cell**, which consists of two parallel sheets of platinum (pt.) as inert electrodes.

The conductance of electrolytic solutions depends on:

1- Nature of ions:

➢ The velocity by which ions move towards the electrodes carrying the electric current varies according to their nature

   (i.e. size, molecular weight, number of charge the ion carries).

(Thus a di-positive ion contributes twice as much to the conductance as a mono-positive cation)

2- Temperature:

❑ Conductance is increased by increase of temperature as:
                    Energy of ions is increased &
             viscosity and hydration are decreased.

➢ An increase of temperature by 1^0C is accompanied by 2% increase in conductance.

➢ for this reason the measurement must be carried out at constant temperature using thermostatically controlled conditions.

3- Concentration of ions:

➢ The electrical conductance of a solution is a summation of contribution from all ions present.

❑ It depends on the number of ions/unit volume of solution and their nature

   i.e. each ion represents itself independently.

➢ As the number of ions increases the conductance of the solution increases.

❑ The linear relationship between conductance and **c** is valid only for diluted solutions. In highly conc solu, there is interionic attraction forces which decreases conductance.

❑ But at infinite dilution, interionic attraction is negligible and <u>each ion represents itself independently.</u>

❑ At infinite dilution <u>activity (a) equals concentration (c)</u> and activity coefficient a/c = 1, outside the infinite dilution a/c < 1

❖ <u>So conductometric determination must be carried out on dilute solution</u>

4- The size of the electrodes:

❑ Conductometric measurements are usually carried out in a **conductance cell**, which consists of two parallel sheets of platinum (pt.) as inert electrodes.

❑ The pt. electrodes must be platinized, i.e. Covered by pt.black this will give large surface area which will absorb tiny quantities of electrode reaction products produced during passage of current.

➢ The conductance (G) is directly proportional to the surface area (A) and inversely proportional to the distance between the two electrodes (L).

$$G \alpha A, \quad G \alpha 1/L, \quad G \alpha A/L$$

G= K A/L

➢ **K** is known as specific conductance or conductivity

it is the conductance

when L is unity (1cm) and

A is unity (1cm^2).

OR it is the conductance of a one cubic cm of liquid (1cm^3).

➢ **K = G L/A**

(where L/A is known as cell constant)

➢ The dimension of **K** is 1 / ohm.cm or $ohm^{-1}cm^{-1}$ or seimen/cm.

➢ K, is a constant value for a specific solution. But it changes with (is affected by) concentration, temperature and change in cell constant.

➢ N.B. For solution with high conductance(G) we use cells with low A/L or high cell constant (L/A) and vice versa.

➢ For solutions of very high G we cannot measure it by Instrument so we have to decrease it by changing in cell constant

Equivalent Conductance:

➤ It is the conductance of one gram equivalent of solute contained between two electrodes spaced one centimetre apart.

➤ Equivalent conductance

$$\lambda = \frac{K}{C} \text{ x}1000$$

C = concentration in gram equivalent / liter, N.

➤ So as: the equivalent wt of the substances ↑ their equivalent conductances **(λ)** ↓

e.g. The λ of HCl (eq.wt. 36.5) is higher than NaCl (eq.wt. 58.5)

➤ **Equivalent conductance** is used to express the ability of individual substance to conduct electric current.

5- Viscosity of the solvent,

➢ by increasing viscosity decreasing the rate of migration, decreasing the conductance

Types of electrolytes

Electrolytes may be divided into two classes:

(1) Strong electrolytes

(2) Weak electrolytes

1. Strong electrolytes

Definition: A substance that gives a solution in which almost all the molecules are ionized.

- The solution itself is called a strong electrolytic solution. Such solutions are good conductors of electricity and have a high value of equivalent conductance even at low concentrations.

Example:

(1) The strong acids e.g., HCl, H_2SO_4, HNO_3, HBr and HI.

(2) The strong bases e.g., NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$

(3) The salts: Practically all salts (NaCl, KCl, etc) are strong electrolytes.

2. Weak electrolytes

Definition: A substance that gives a solution in which only a small proportion of the solute molecules are ionized.

- Such a solution is called a weak electrolytic solution, that almost has low value of equivalent conductance.

Example:

(1) The weak acids: All organic acids such as acetic acid

(2) The weak bases: Most organic bases e.g., alkyl amines

(3) Salts: A few salts such as mercury (II) chloride and lead (II) acetate.

a- For strong electrolytes

a linear relationship exists

between λ & $\sqrt{c}$

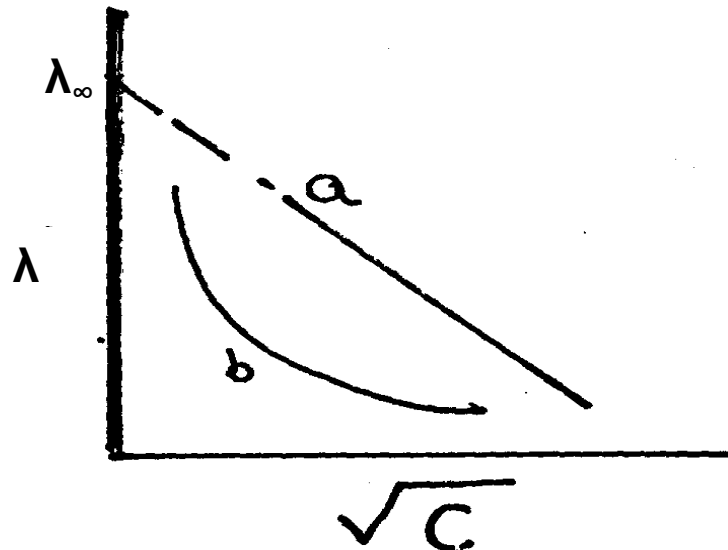$$\lambda = \lambda_\infty - a\sqrt{c}$$

a = constant

Extrapolation of this straight-line relationship to zero concentration yields a value for the mobility

b- For weak electrolytes

non linear relationship exists

between λ & $\sqrt{c}$

their motilities' are determined

by knowledge of the equivalent

ionic conductance of their ions.

❑ From the previous equation it is clear that the equivalent conductance increases as the concentration decreases until it reaches a constant value at infinite dilution which is known as:

Equivalent conductance at infinite dilution

or

Limiting equivalent conductance,

or

Mobility(λ_∞).

Which is the conductance of the equivalent weight of the substance at infinite dilution.

It is characteristic for the solutes.

Equivalent ionic conductance:

➤ At infinite dilution, interionic attractions become nil; the overall conductance of the solution consists of the sum of the individual equivalent ionic conductance.

➤ Overall conductance = $\lambda_\infty^+ + \lambda_\infty^-$

λ_∞^+ is the equivalent ionic conductance of the cation at infinite dilution.

λ_∞^- is the equivalent ionic conductance of the anion at infinite dilution.

➤ Equivalent ionic conductance differ according to the nature of ions (i.e. Charge, size, hydration).

What is λ_∞ affected by?

> ➢ **It is not affected by concentration**

> ➢ **It is not affected by dilution**

> ➢ <u>**It is affected by the nature of ions**</u>

Cations	λ_∞	anions	λ_∞
H^+	350	OH^-	198
Na^+	42.6	Cl^-	76
K^+	74	NO_3^-	71
NH_4^+	73	CH_3COO^-	41
Ag^+	62	propionate	36
½ Ba^{2+}	64	½ SO_4^{2-}	80

EQUIVALENT IONIC CONDUCTANCES AT 25°C

Cation	λ^0_+	Anion	λ^0_-
H_3O^+	349.8	OH^-	199.0
Li^+	38.7	Cl^-	76.3
Na^+	50.1	Br^-	78.1
K^+	73.5	I^-	76.8
NH_4^+	73.4	NO_3^-	71.4
Ag^+	61.9	ClO_4^-	67.3
$\frac{1}{2}Mg^{2+}$	53.1	$C_2H_3O_2^-$	40.9
$\frac{1}{2}Ca^{2+}$	59.5	$\frac{1}{2}SO_4^{2-}$	80.0
$\frac{1}{2}Ba^{2+}$	63.6	$\frac{1}{2}CO_3^{2-}$	69.3
$\frac{1}{2}Pb^{2+}$	69.5	$\frac{1}{2}C_2O_4^{2-}$	74.2
$\frac{1}{3}Fe^{3+}$	68.0	$\frac{1}{4}Fe(CN)_6^{4-}$	110.5
$\frac{1}{3}La^{3+}$	69.6	—	—

Cations	(Λ_o)	Anions	(Λ_o)
H^+	350	OH^-	198
Na^+	50.1	Cl^-	76
K^+	74	NO_2^-	71
NH_4^+	73	CH_3COO^-	41
Ag^+	62	$CH_3CH_2COO^-$	36
$\frac{1}{2}Ba^{2+}$	64	$\frac{1}{2}SO_4^{2-}$	80
Li^+	38.7	Br^-	78.1
Pb^{2+}	73	I^-	76.8
Ca^{2+}	59.5	NO_3^-	71.44
Sr^{2+}	59.46	ClO_4^-	67.32
Cu^{2+}	54	ClO_3^-	64.58
Fe^{2+}	54	BrO_3^-	55.78
Mg^{2+}	35.06	IO_4^-	54.4
Zn^{2+}	52.8	CH_3COO^-	40.9

Problem:

❖ The measured conductance of 0.1 N solu. of a drug is 0.0563 ohm^{-1} at 25^0c. The cell constant is 0.52 cm^{-1}, what is the specific conductance? And what is the equivalent conductance at that concentration?

So/n:

➢ K = G L/A (where L/A is known as cell constant)

$\quad$ = 0.0563 ohm^{-1} x 0.52 cm^{-1}

$\quad$ = 0.0293 ohm^{-1}cm^{-1}

➢ $\lambda = \dfrac{K}{C} \text{x}1000$, C= 0.1N = 0.1eq/cm^3

$\quad$ = $\dfrac{0.0293 \text{ ohm}^{-1}\text{cm}^{-1} \text{ x } 1000}{0.1\text{eq/cm}^3}$

$\quad$ = 293 ohm^{-1} cm^2 /eq

Problem

❖ A certain cell was filled with 0.01M KCl, (K= 0.001409 ohm^{-1}cm^{-1}), it had a resistance of 161.8 ohm at 25°C, and when filled with 0.005M NaOH it had a resistance of 190 ohm. What is the equivalent conductance of the NaOH solution?

So/n: K = G L/A → L/A = K/G = 0.001409/ (1/161.8)

$$= 0.22797 \text{ cm}^{-1}$$

K (for NaOH) = G L/A = (1/190) x 0.22797

$$= 0.0011998 \text{ ohm}^{-1}\text{cm}^{-1}$$

$$\lambda = \frac{K}{C} \times 1000 \quad = \frac{0.0011998 \text{ ohm}^{-1}\text{cm}^{-1} \times 1000}{0.005 \text{ eq/cm}^3}$$

$$= 240 \text{ ohm}^{-1}\text{cm}^2/ \text{ eq.}$$

N.B.

➢ On dilution Sp. Cond., K, decreases, as the No. of ions per unit volume is decreased.

➢ Conversely, eq. cond., of strong electrolyte increases on dilution, because on dilution, the interionic effect decreases, so the ionic move faster(quantity of ions remain constant)

➢ The cell constant should be first determined using an electrolyte of known K, e.g. KCl (measure its conductance)

INSTRUMENT USED IN CONDUCTOMETRIC DETERMINATION

➢ To carry out a conductometric measurement it is necessary to measure the resistance (R) of the solution and the conductance (G= l/R)

The instrument consists of two parts:

1- Conductance cell:

It is the cell in which the solution to be Measured will be filled.
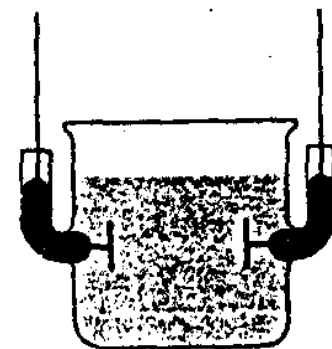
2- Conductivity bridge (Kohlrausch bridge):

A mean to measure the resistance and then converts it to conductivity unit and it is formed of:

a- Wheatstone bridge.

b- An oscillator (to produce A.C. From D.C.).

Application of Conductometry

1- Direct or Absolute Measurements:

1. This is used in industry for checking the purity of distilled water or other chemicals.

2. Determination of physical constant such as ionization constant.

3. Determination of unknown concentration of pure substance:

where, a series of standard solutions of exact known concentrations is prepared from pure grade of the substance to be determined.

❑ The conductance of the solutions is measured and a **calibration curve** is plotted representing the conductance against the concentration. A solution of exact known concentration of the substance to be determined is prepared and checked from the curve.
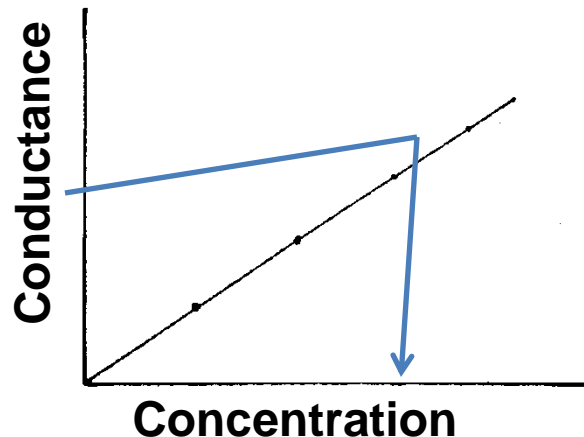
2- Indirect Conductometry (Conductometric Titrations):

➤ A conductometric titration involves measurements of the conductance after successive addition of the titrant.

➤ The end point is obtained from a plot of the conductance against ml of titrant.

➤ The most important advantages of this method are that it can be used for determination of:

1-Turbid and highly colored solutions.

2-very dilute solutions

3-Reactions which are not complete and where is no suitable indicator e.g. reaction between weak acid and weak base.

Precautions to be Considered in Conductomertic Titrations

1- Upon carrying out the titration; the titrant used must be at least **10** times concentrated as the solution to be determined.

  e.g. on determination of solution 0.01 N HCl, the titrant NaOH should be at least 0.1 N.

➢ By this way, we can minimize decrease in conductance due to dilution.

❑ However a correction factor must be used to compensate for this dilution.

$$\text{Correction factor} = V_i + V_t \: / \: V_i$$

V_i = initial volume of the solution.

V_t = titrant volume added.

2- Avoid the presence of external ions which will not enter the reaction (such as the presence of buffer or concentrated acids).

➢ These ions will change the initial conductance during the titration and can not be accurately observed.

3- The method is suitable for detection of end point in neutralization and precipitation reactions but not for redox reactions as there is no electron transfer at the electrode surface.
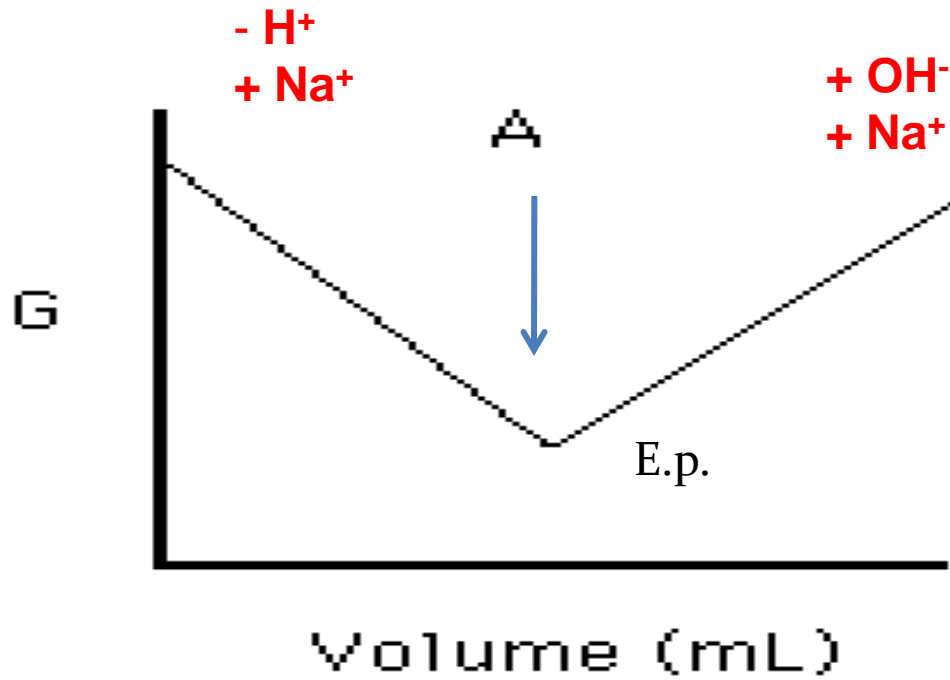
I- Titration of Strong Acid with Strong Base:

e.g. HCl ≠ NaOH

$$HCl + NaOH \rightarrow NaCl + H_2O$$

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$
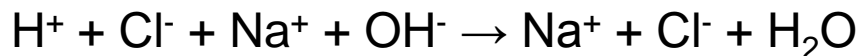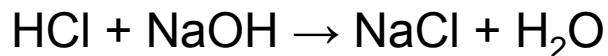
➤ Before titration the conductance is high which is due to

HCl → H$^+$ + Cl$^-$ mobility of **H$^+$** is 350 and that of **Cl$^-$** ion is 73.

➤ Upon addition of **NaOH** the **H$^+$** ion reacts with **OH$^-$** ion to form the very weakly ionized water molecule.

✓ This means that the **H$^+$** ion is removed from the medium and replaced by **Na$^+$** ion which has a mobility of 43; thus a continuous abrupt decrease in conductance occurs during the titration till the end point.

➤ Beyond the end point there is **excess Na$^+$** and **OH$^-$** ions with 43 and 198 mobility due to continuous addition of **NaOH**

✓ So there is continuous increase in conductance and the curve will have a V shape , the end point is the minimum of the curve.

$\downarrow$ Amount of H⁺ &
inc. Na⁺

- H⁺
+ Na⁺

+ OH⁻
+ Na⁺

A

G

E.p.

Volume (mL)

2- Titration of weak acid with strong base
e.g. CH3COOH ≠ NaOH

$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2O$
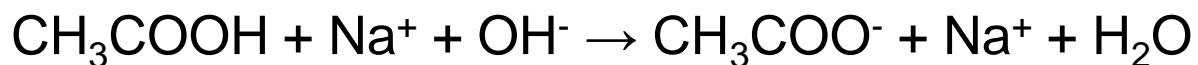
➤ Before titration low initial conductance is observed due to low H^+ obtained during dissociation of **weak CH_3COOH**.

➤ During titration we can observe slight decrease of conductance due to consumption of H^+. During progress of titration we can observe slight increase in conductance due to the presence of **CH_3COO^- (41) & Na^+ (43)** and nearly constant H^+ due to the buffer action of the produced **CH_3COONa** and the remaining **CH_3COOH**.

❖ After end point excess **NaOH** will lead to increase in conductance due to increasing of **Na^+ (43)** and **OH^- (198)**

G

+ OH⁻
+ Na⁺

+ CH₃COO⁻
+ Na⁺

E.p.

Volume (mL)
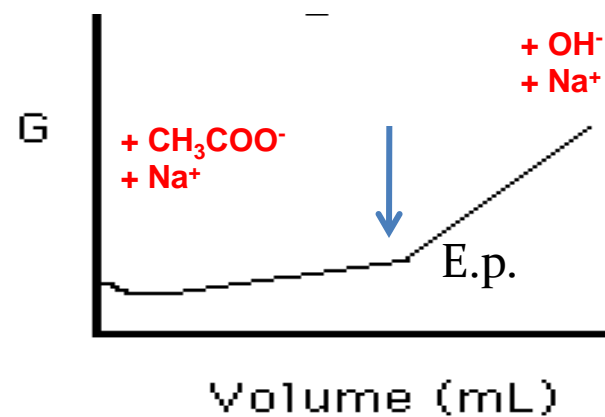
3. Strong Acid with a Weak Base,

e.g. sulphuric acid with dilute ammonia:

➤ Initially the conductance is high and then it decreases due to the replacement of H⁺.

➤ But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate (Fig.).

Fig : Conductometric titration of a strong acid (H_2SO_4) vs. a weak base (NH_4OH)
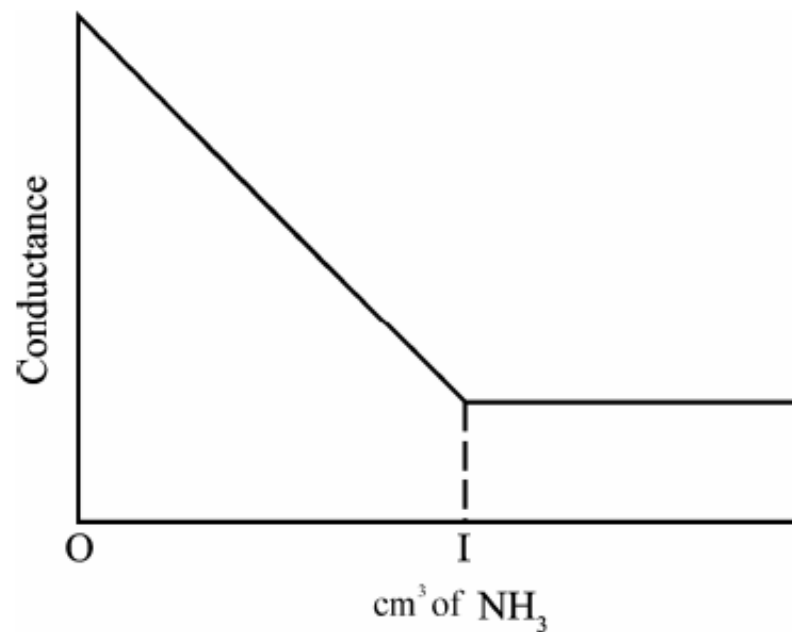
4- Mixture of strong acid and weak acid aganist strong base.

e.g. HCl/ CH3COOH mix ≠ NaOH

➤ The initial conductivity is high it is due to **HCl** which by common ion effect suppress the ionization of **CH_3COOH**.

❖ Upon titration; decrease in conductivity occurs due to replacement of **H^+** ion with mobility 350 by **Na^+** ion with mobility 43 , till all the **H^+** ions from **HCl** are neutralized.

❑ **CH_3COOH** will thus ionize and react with **NaOH**.

❑ The change in conductivity will take place in similar way as described above. for acetic acid.
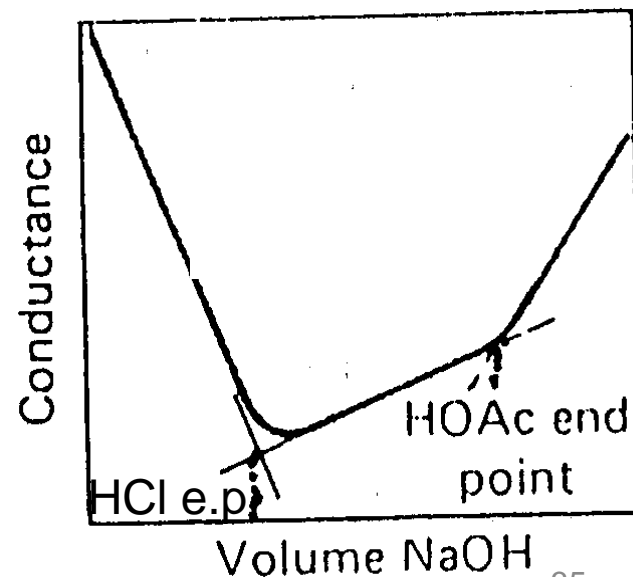
5. Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak Base:

➢ In this curve there are two break points.

i. 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.

ii. 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.
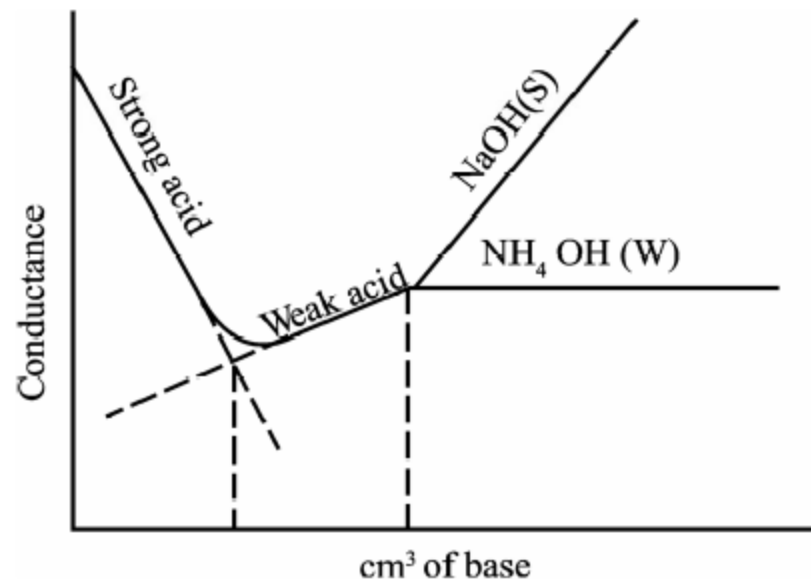

Fig.: Conductometric titration of a mixture of a strong acid (HCl) and a weak acid (CH3COOH) vs. a strong base (NaOH) or a weak base (NH4OH)
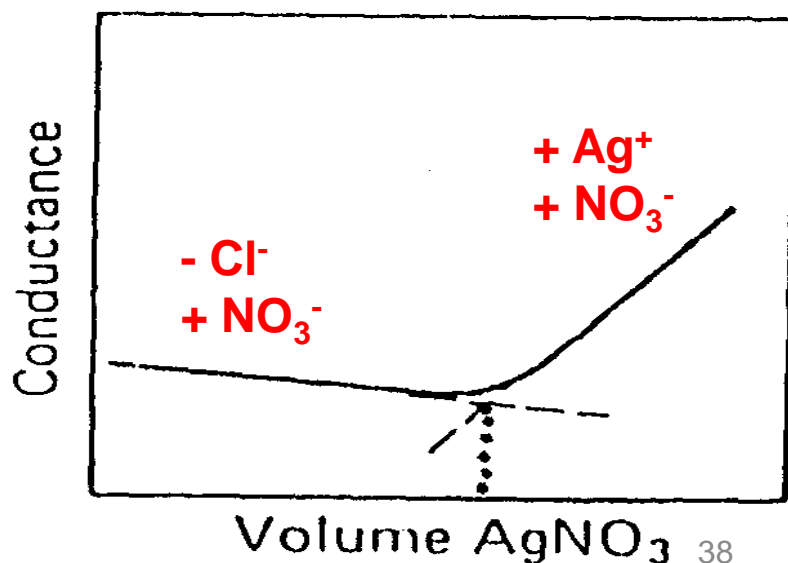
6- Precepitation Titrations

➤ It is important to choose the suitable titrant which gives sharp change at the equivalence point.

❑ Titrant must have mobility that varies greatly from the sample **because the products are weakly ionizable** leading to decrease in conductance during titration till the endpoint.

e.g. Titration of NaCl ≠ AgNO₃

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$

$$Na^+ + Cl^- + Ag^+ + NO_3^- \rightarrow AgCl + NO_3^- + Na^+$$
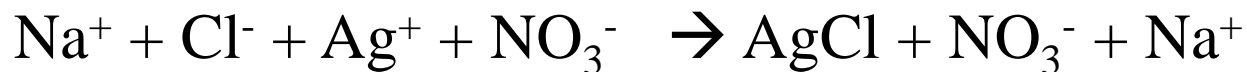
➢ During titration of NaCl against AgNO₃, Ag⁺ precipitate Cl⁻ as AgCl and NO₃⁻ replace Cl⁻ in the medium.

➢ As mobility of NO₃⁻ (71.5) is nearly equal that of Cl⁻ (76.3) we observe nearly no change in conductance during titration.

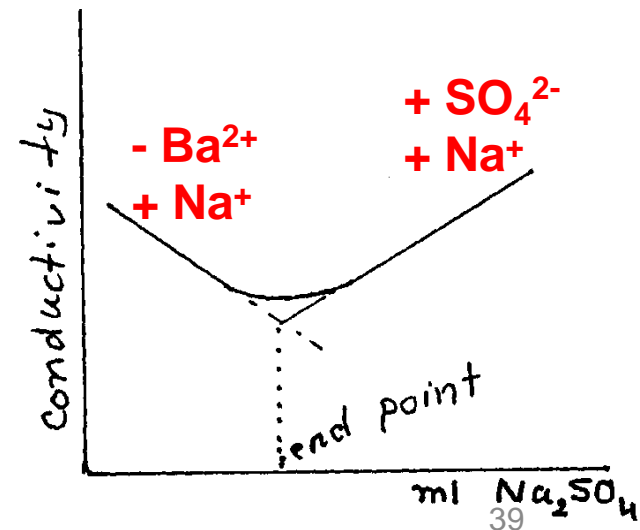➢ After complete precipitation of Cl⁻ , excess Ag⁺ (61.9) and NO₃⁻ (71.5) will increase conductance of solution.

e.g. Titration of $BaCl_2 \neq Na_2SO_4$

$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2\ NaCl$$

$$Ba^{2+} + 2Cl^- + 2Na^+ + SO_4^{2-} \rightarrow BaSO_4 + 2Cl^- + 2Na^+$$
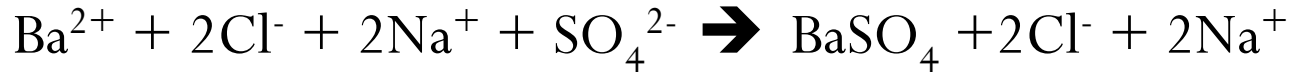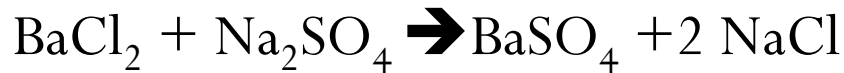
☐ During titration of $BaCl_2$ against Na_2SO_4 , SO_4^{2-} precipitate Ba^{2+} as $BaSO_4$ i.e 1/2 Ba^{2+} (mobility 63.6) is replaced by Na^+ (mobility 43), therefore conductance is decreased during titration.

☐ After complete reaction conductance is increased due to addition of excess Na^+ (43) and SO_4^{2-} (mobility of ½ SO_4^{2-} 80) after the end point.

☐ The curve is V shape its minimum is the end point . It is obtained by extrapolation of the two arms of the curve.

THANK YOU