

# Gravimetry

gravimetric methods are quantitative methods that are based on determining the mass of a pure compound to which the analyte is chemically related.

It is based on precipitating the component of substance under test from solution as an insoluble compound of known chemical composition.

Sample  $\longrightarrow$  dissolved components  $\xrightarrow{\text{ppting agent}}$



## Impurities In precipitates (Purity of precipitates)

$\rightarrow$  when a precipitate separates from a solution, it is not always perfectly pure even after extensive washing, depends on the nature of the precipitate and condition of precipitation. It may contain varying amount of impurities due to :-

① Co precipitation

② Post precipitation

Types of co-precipitation

- $\rightarrow$  (a) Surface adsorption
- $\rightarrow$  (b) Mixed Crystal formation
- $\rightarrow$  (c) Occlusion
- $\rightarrow$  (d) Mechanical entrapment

Co-precipitation - If a precipitates is contaminated by substances which are normally soluble in the solution under the condition of precipitation, then co-precipitation is said to have taken place.

9) To a mixture of  $\text{BaCl}_2$  and  $\text{KMnO}_4$  solution, 65  
 excess of  $\text{H}_2\text{SO}_4$  is added slowly in small portion  
 and then  $\text{KMnO}_4$  is reduced by addition of some reducing  
 agent. After reaction solution becomes colourless but  
 precipitate appears to be violet colour. This indicates  
 that some of  $\text{KMnO}_4$  is coprecipitated together with  
 $\text{BaSO}_4$ .

Types of co-precipitation

(a) Surface Adsorption - Adsorption is a absorption on  
 the surface.

Adsorption is a common source of co-precipitation  
 and is likely to cause significant contamination of



precipitates with large specific surface area.  
 → Adsorption is reversible process which can overcome by  
 desorption.

eg →  $\text{AgCl}$  ppt adsorbs ion preferentially  $\text{Ag}^+$  and  $\text{Cl}^-$  ions.

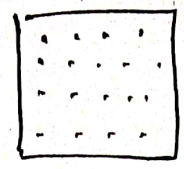
Factors affecting surface adsorption:

- ① Effect of conc.
- ② Effect of temp.
- ③ Effect of the nature of adsorbed ion.
- ④ Effect of precipitation.
- ⑤ Effect of adsorbent area.

(b) Mixed Crystal formation - Mixed crystal formation  
 is a troublesome phenomenon,  
 in which one of the ions in the crystal lattice of a solid  
 is replaced by an ion of another element.

for this exchange to occur, it is necessary that the 2 ions have the same charge and that their sizes differ by not more than about 5%.

This problem occurs with both colloidal suspensions and crystalline precipitates.

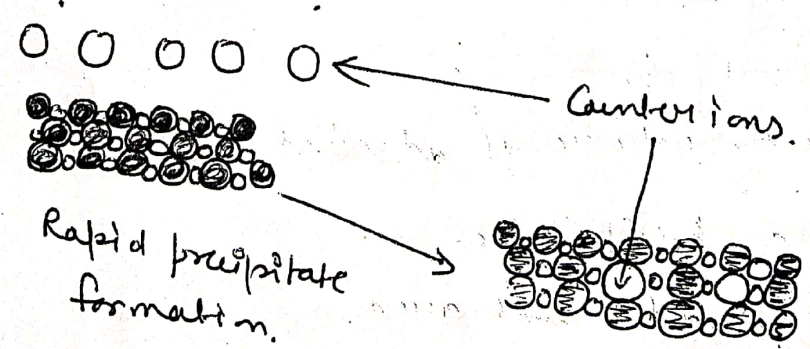


eg - lead ion replaces some of the barium ion.

© Occlusion: - Occlusion is a type of co-precipitation in which a compound is trapped within a pocket formed during rapid crystal growth, material that is not a part of the crystal structure is trapped within a crystal. If crystal growth is so rapid some counterions do not have time to escape from the structure.

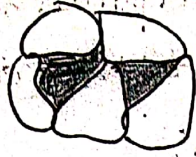


ex: - water may be trapped in pockets when  $AgNO_3$  crystals are formed.



Occluded impurities are very difficult to remove. Digestion may help some but is not completely effective. The impurities cannot be removed by washing.

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Mechanical entrapment: - Mechanical entrapment occurs when crystals lie close together during growth. Here several crystals grow together and in so doing trap a portion of the solution in a tiny pocket.



Mechanical entrapment can be minimized when the rate of precipitate formation is low i.e. under conditions of low super saturation. In addition, digestion is often remarkably helpful in reducing this type of co-ppn.

Q. what is post precipitation

Ans → Some time when the precipitate is allowed to stand in presence of mother liquor the second substance will form the precipitate with precipitating agent.

The process by which an impurity is deposited after precipitation of the desired substance is termed as post-precipitation. when there is a possibility that post-precipitation may occur, directions call for filtration to be made shortly after the desired precipitate is formed.

\* Longer the precipitate remain in the solution greater will be the error due to post-precipitation.

eg → Calcium oxalate is precipitated in presence of  $Mg^{+}$ , magnesium oxalate does not precipitate immediately because it tends to form supersaturated solution, but if this precipitate is allowed to stand for longer time, before filtration magnesium oxalate separates out as precipitate of calcium oxalate.

Q. What is co-precipitation -

A.  $\rightarrow$  If a precipitate is contaminated by substances which are normally soluble in the solution under the conditions of precipitation, then co-precipitation is said to have taken place. Co-precipitation occurs by the adsorption or Occlusion.

Ex  $\rightarrow$  To a mixture of  $\text{BaCl}_2$  and  $\text{KMnO}_4$  solution, excess of  $\text{H}_2\text{SO}_4$  is added slowly in small portions and then  $\text{KMnO}_4$  is reduced by addition of some reducing agent. After reaction solution becomes colorless but precipitate appears to be violet colour.

This indicates that some of the  $\text{KMnO}_4$  is co-precipitated together with  $\text{BaSO}_4$ .

Q → Step Explain the steps involved in the gravimetry.

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- Ans:-
- ① Sampling
  - ② Dissolution of sample
  - ③ Precipitation.
  - ④ Testing of completeness of precipitation ~~reaction~~ <sup>reaction</sup>
  - ⑤ Digestion or Ageing.
  - ⑥ Filtration
  - ⑦ Washing of precipitate.
  - ⑧ Drying or Igniting of precipitate.
  - ⑨ Weighing and calculation.

① Sampling → Sample should be identical in all properties with the bulk of the material from it is taken.  
→ Sample should be homogeneous and in the form of powder.  
→ Cost of test, value of product, end use of product, accuracy of test method and nature of material used are considered.

② Dissolution of sample :- To dissolve the sample analyte, taken a clean beaker and transfer the weighed sample completely to the beaker. Add sufficient water or acid or alkali to the sample to get a clear solution.

③ Precipitation :- Selection of precipitant is based on the specificity and selectivity of reagent.  
→ Ideal precipitant should be react with analyte to form the ppt which can be easily filtered, washed, low solubility, stable.

④ Testing of completeness of precipitation reaction -

- For the testing of this, the precipitating agent is added in slight excess.
- During the formation of precipitate, it is allowed to settle down and then few drops of precipitating agents are added slowly through to the upper supernatant liquid.
- If ppt<sup>n</sup> occurs at this stage, the precipitation is not complete and more reagents should be added to the solution.
- But if no precipitation occurs at this stage, precipitation is complete and there is no need of adding more ppting agent reagent.

⑤ Digestion or ageing - The primary precipitate to remain

in contact with the solution from which it is formed normally at highest temp. This is called digestion or ageing.

The smaller particles exhibit higher solubility and dissolve. As a result the solution becomes supersaturated with respect to the larger particles. The result is the deposition of the dissolved particles on the larger particles and ↑ in the average particle size.

This is known as digestion, ageing or Ostwald ripening of the precipitate.

⑥ Filtration! - precipitate is separated from mother liquor.

various types of filter media are used for this purpose.

⑦ Filter paper! - should have low ash content.  
→ lower value of ash content are usually achieved by washing with HCl and HF during its manufacture.

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Filter paper made is generally of 3 degrees of possibility :-  
one of gelatinous coarse particles.

Second for medium size particles

third for very fine part precipitates.

(i) filter pulp - for gelatinous precipitates.

→ Quantitative filter papers cannot be used as the pores tend to be clogged by the precipitate.

→ For filtration pulp is used instead of filter paper.

→ filter pulp can be prepared by macerating the filter paper torn into pieces with hot distilled water.

(ii) filter mats - are following types -

(a) Crucible - It is a filter mat of purified asbestos, supported just inside the platinum crucible.

→ The bottom of crucible is perforated with numerous small holes.

→ Porcelain and silica crucible also used for this purpose.

→ The crucible can be dried to constant weight.

for temp upto 250°C electric oven can be used.

(b) Munroe Crucibles - Because of high cost of platinum

Munroe crucible are not generally used for routine gravimetric analysis. The main advantages of this crucible are resistance to chemicals, filtration of finest particles, rapidity of filtration and heating to a very high temp.

(c) Glass fibre disc - In expensive glass fibre discs are available for use instead of asbestos mat. A circle of glass fibre filter paper may be placed in a coarse porosity filter crucible for rapid filtration.



→ Glass fibers are made from fine borosilicates glass fiber fibres.  
→ unaffected by chemical reagents and by heating up to 500°C.

(d) Permanent porous filter discs: - following type: -

(i) Sintered glass crucible - These crucibles are made up of resistant glass (Pyrex glass) and have porous disc of sintered ground glass fused in the body of the crucible.  
→ These filter discs are of various porosities. They are of G<sub>1</sub>, G<sub>2</sub>, G<sub>3</sub> and G<sub>4</sub> types.  
→ Their pore sizes are 100-120 μ, 40-50 μ, 20-30 μ and 5-10 μ respectively.  
→ The crucible G<sub>1</sub> type is used for coarse particles while G<sub>4</sub> type used for very fine particles.  
→ These crucibles can be heated to 200°C. If heated above 430°C, permanent stains are produced and they soften above 610°C.

(ii) Silica crucible - If drying of precipitate is to be done above 200°C, silica crucibles can be used.

They are similar to sintered glass crucible but are made up of pure fused silica.  
→ They are available in G<sub>1</sub>, G<sub>2</sub>, G<sub>3</sub> and G<sub>4</sub> type.  
→ These crucibles can be used for drying of ppt up to 1000°C. These crucibles are resistant to chemical agents but are affected by phosphate, strong alkalis and hydrofluoric acid.

(iii) Porcelain crucible - Porcelain crucible is glazed inside and outside.

→ Bottom of porcelain crucible consists of a plate of porous porcelain.

for washing of precipitate - surface of the ppt can be removed by washing of ppt. (73)

→ Mother liquor which is entrapped in ppt is also removed by washing.

→ various types of washing solutions are:-

- (a) washing with the solution of ppt.
- (b) washing in solution of electrolyte.
- (c) washing in substances which suppress the hydrolysis of the ppt.
- (d) washing with water.

(8) Drying or Ignition of precipitate -

→ for removal of water and the adsorbed electrolyte from washing solution.

→ It is depend on the nature of ppt, and the filtering media used for this purpose.

Drying → temp  $< 250^{\circ}\text{C}$

Ignition → temp  $250^{\circ}\text{C} - 1200^{\circ}\text{C}$ .

(9) weighing and Calculation:-

$$\text{G.F. (gravimetric factor)} = \frac{\text{formula wt (F.W.) (substance sought)}}{\text{formula weight (F.W.) (substance weighed)}}$$

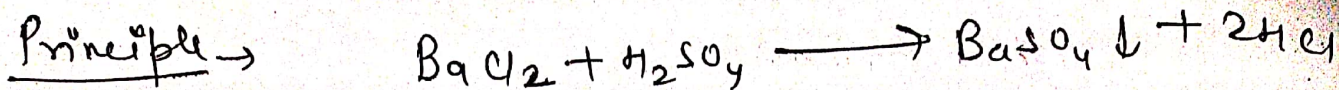
$$\% A = \frac{\text{weight precipitate (g)} \times \text{G.F.} \times 100}{\text{weight of sample (g)}}$$

Sought  
 $\text{SO}_3$   
 $\text{MgO}$

weight  
 $\text{BaSO}_4$   
 $\text{Mg}_2\text{P}_2\text{O}_7$

## Estimation of Barium Sulphate

(1) Barium as  $(BaSO_4)$  Barium sulphate



A white gelatinous precipitate is obtained is filtered, washed, dried, ignited and weighed as barium sulphate  $(BaSO_4)$ .

Reagent - Barium chloride solution.

Precipitating agent.

wash solution. (Hot distilled water)

### Procedure

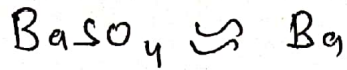
- (1) Pipette out 25 ml of given solution of barium chloride  $BaCl_2$  in 500 ml beaker.
- (2) Add 0.5 ml of conc.  $H_2SO_4$  and 100 ml of distilled water.
- (3) Heat the resulting solution to boiling.
- (4) In this hot solution, add dil.  $H_2SO_4$  solution drop wise with constant stirring until the ppt is not complete.
- (5) Allow the ppt to settle down and test the supernatant liquid for complete pptation.
- (6) Now filter the ppt by decanting method through Whatman filter paper No 42.
- (7) Wash the precipitate 3-4 times with hot water and dry it by placing the funnel in an oven.
- (8) After drying transfer the filter paper containing ppt to the pre constantly weighed crucible and ignite it till all the carbonaceous matter is not burnt off.
- (9) Now cool the crucible and add one drop of each of conc.  $HCl$  and conc.  $H_2SO_4$ .

Cool the crucible by placing in a desiccator and weigh it. (7)

(ii) Repeat the process of heating, igniting, cooling, and weighing till the constant weight is obtained.

Calculation :-

constant weight of barium sulphate ( $\text{BaSO}_4$ )  
ppt be X W grams.



$$233.42 \rightleftharpoons 137.36$$

233.42 g of  $\text{BaSO}_4$  contains = 137.36 g of  $\text{Ba}^{2+}$  ions.

Therefore Wg of  $\text{BaSO}_4$  contains =  $\frac{137.36}{233.42} \times \text{Wg of Ba}^{2+}$  ions.

# Conductometry

## Introduction -

→ It is an electrochemical method of analysis or measurement of the electrical conductance of electrolyte solution by means measure the electric conductance by conductometer.

## Electrical Conductivity depends on:-

- ① Types of ion (cation, Anion, + or - etc)
- ② Cons. of Ion.
- ③ Temp.
- ④ mobility of ions.
- ⑤ changes of conductivity due to the changes in ion

→ means ions will transfer from one place to another place and change in ion will also occur.

So due to change in transfer of ion then the conductivity of solution will be changed and that change will be measured by conductometer.

⑥ Replacement of ion will also occur.  
ex  $H^+$  ion replaced by  $Na^+$  ion  
 $H^+$  ion have higher conductance than  $Na^+$  ion.  
So the conductivity will decrease.

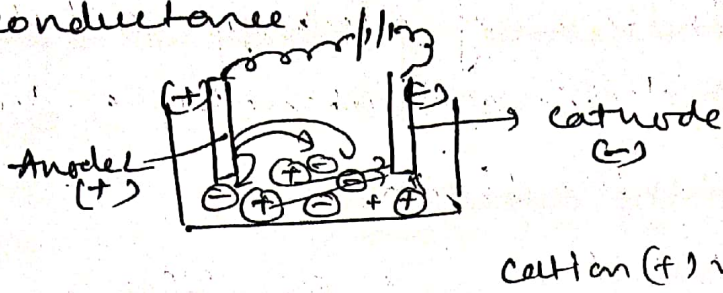
★ Principle:- The conductance of the electric current through electrolyte solution is similar to metallic conductance.

→ The electrical conductance according to ohm's law which states that the strength of current (i) passing through conductor is directly proportional to potential difference (V) and inversely proportional to resistance

$$i = \frac{V}{R}$$

conductance depends upon Area and length

Conductance - It is the flow of electricity through an electrolytic solution is called electric conductance.



Due to this movement of ions conductivity will take place so this is called conductance and it is denoted by  $G$ .

$$G = \frac{1}{R}$$

unit is  $\text{ohm}^{-1}$  or mho.

Resistance - It is directly proportional to its length ( $l$ ) and inversely proportional to the cross section area ( $a$ ). Resistance is denoted by  $R$ .

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

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

$$\text{if } l = 1 \text{ c.m.}, \quad a = 1 \text{ c.m}^2$$

then Resistance is called as Specific resistance which is denoted by  $\rho$ .

$$\text{So } \boxed{\rho = R}$$

Specific conductance! - The specific conductance of any conductor is the reciprocal of specific resistance and is denoted by  $K$  (Kappa)

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

$$R = \rho \frac{l}{A}$$

$$\rho = R \frac{A}{l}$$

$$k = \frac{l \times A}{R \times A}$$

$$k = \frac{l}{R} \times \frac{1}{A} \text{ ohm}^{-1} \text{ cm}^{-1}$$

if  $l = 1$  and  $A = 1$

$$k = \frac{1}{R} = \frac{1}{\rho}$$

$$\text{unit of } k = \frac{\cancel{\text{m}}}{\cancel{\text{m}^2}} \times \text{Siemen} = \text{Siemen} \cdot \text{m}^{-1}$$

### Principle of conductometry -

- \* Conductometry is based on the principle of determination of changes in conductivity.
- \* changes in the conductance is due to the replacement of ions with each other.
- \* It is known that at infinite dilution or in very dilute solution, ions act independent of each other and they contribute to the conductance of the solution.
- \* Both cation and anion have varying degree of ionic mobilities (or conductance value). Thus when a solution of '1 electrolyte' is added to the solution of another electrolyte, the overall conductance (after addition) will depend on the

check whether a reaction occurs or not.

\* If no chemical reaction occurs between the electrolyte solution and another added to it, the overall conductance of the solution will ↑.

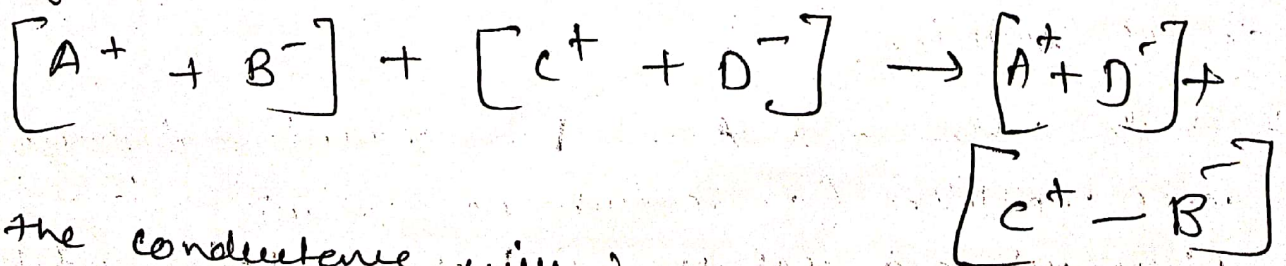
\* All ions will contribute to the conductance of the solution.

eg - ① Addition of sod. nitrate solution to the sod. chloride solution.

When a chemical reaction ~~is~~ occurs, replacement or substitution of ions takes place and depending upon the ionic conductance of replaced and replacing ions conductance will either increase or decrease.

eg - ② when NaOH solution is added to HCl solution, there is replacement of  $H^+$  ion of high mobility with that of the  $Na^+$  ions of low mobility takes place and conductance is found to ↓.

The principle of conductance is based on the substitution of ions of mobility by the less mobile ions of mobility.



\* The conductance will increase or decrease depending upon whether the mobility of  $C^+$  ion is greater or less than that of ion  $A^+$ .



# Instrumentation of Conductivity meter

① Current source: - used to produce current or alternating current, we have to use high frequency current generator because of this high potential difference and ultimately current conduction takes place.

② Conductivity meter 3 parts ..

(a) Digital Display.

(b) Calibrate (cell is calibrated by key)

(c) Power switch for power supply.

③ Conductivity cell (electrodes)

→ cell is made up of 2 electrodes i.e. ⚡

Cathode -  $\ominus$ ve attract  $\oplus$ ve ion cations

Anode -  $\oplus$ ve attract  $\ominus$ ve ion Anion.

→ electrodes are made up of Pt [area of Pt electrode is  $1\text{cm}^2$ ]  $A = 1\text{cm}^2$

→ and distance b/w electrode =  $1\text{cm}$ .

→ Electrodes are coated with Pt Pt Black to avoid the

(i) polarized effect

(ii) To ↑ the surface area for absorption of cations & Anions.

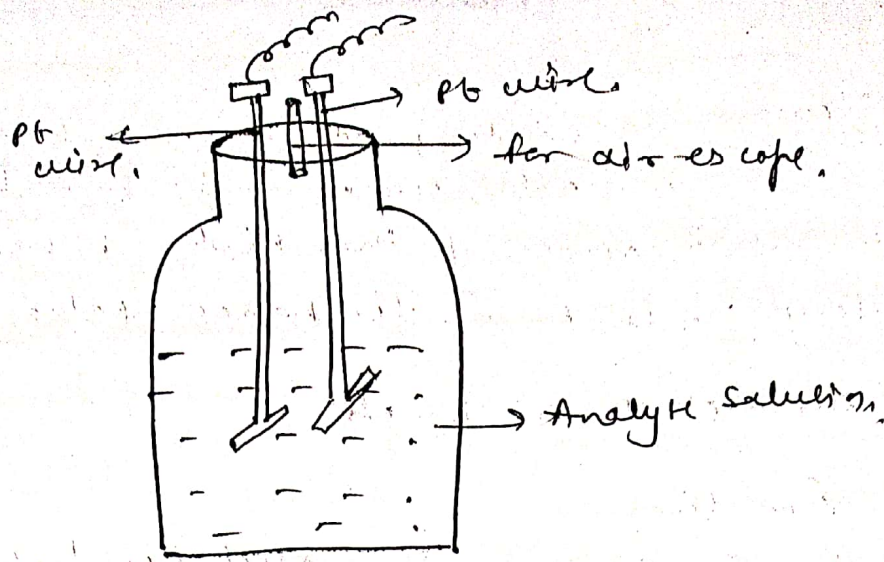
(iii) Coating is done with 5% chloroplatinic acid and 0.02 - 0.03 g of lead acetate.

Conductivity cell are 3 types: -

① Low conductance measurement cell. - It is usually wide mouth borosilicate glass bottle duly fitted with leak stop & is provided with 3 holes in it.

→ 1st hole for enabling the Pt wires ( $1\text{sq. cm}$ ) to pass through them.

→ and 3rd one for allowing the gases to escape from the cell and both.



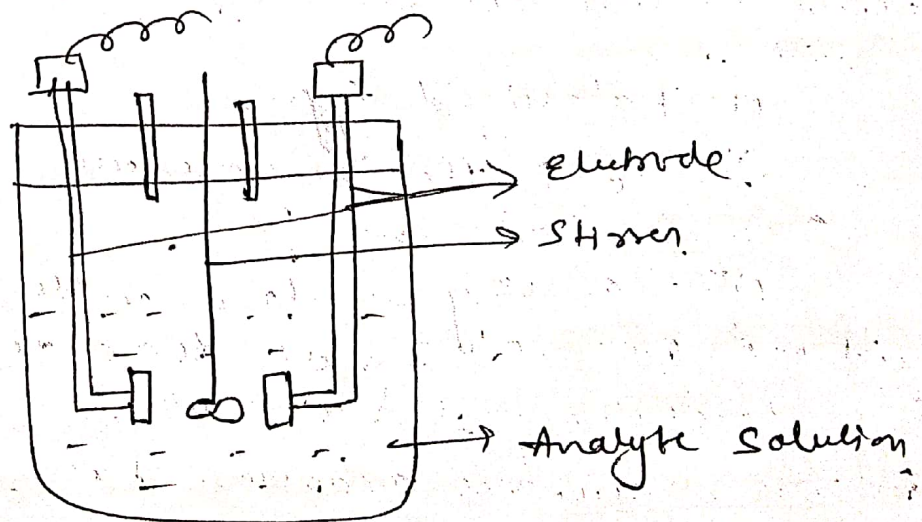
Low conductance measurement cell.

⑤ Conductivity cell for precipitation type of reaction -

→ It is used for the reaction product is sparingly soluble or having a stable complex.

→ 2 electrodes are fixed in pyrex lid which is duly provided with adequate passage for the mechanical stirrer and also the tip of burette for introducing the titrant into the reaction cell.

→ here electrode plates are both vertical and parallel.

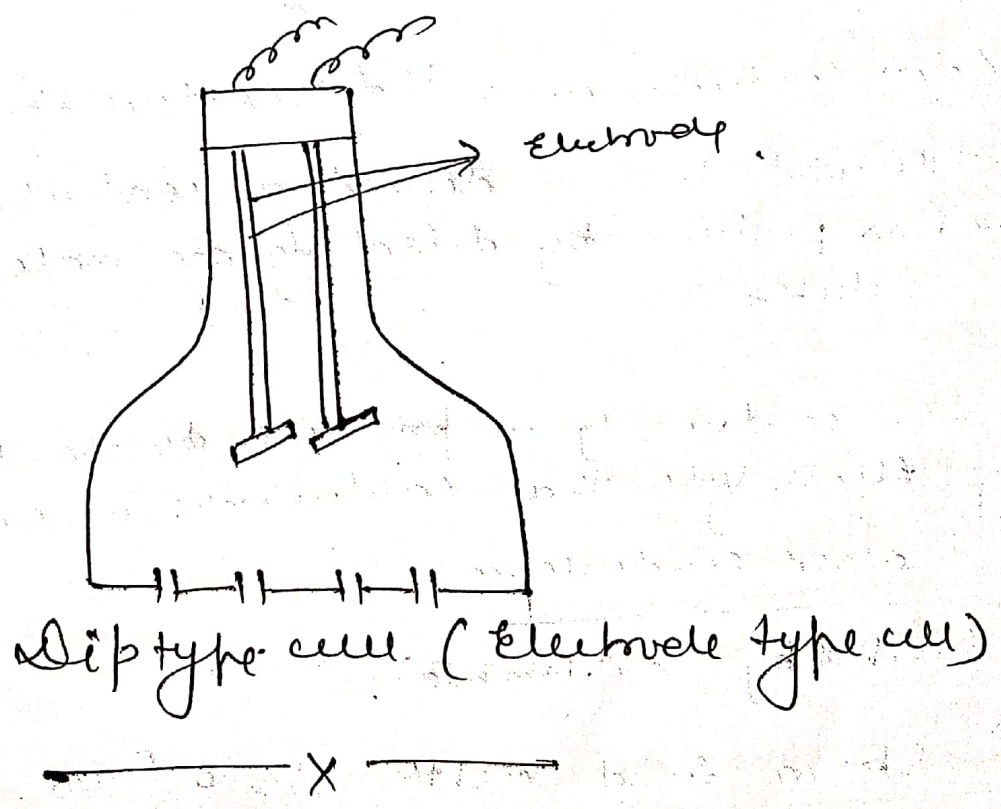


③ Dip type - (Electrode type cell) - (Most widely used)

→ It consists of wide mouth glass tube of borosilicate glass duly fixed to 2 copper wires, the tip of which is adequately provided to 2 Pt plates.

of 1 sq. C.M. each in dimension fixed apart at 1 C.M.

- 2 Cu terminals are taken out for necessary corrections.
- Exact position of the wires are fixed adequately in glass tube with the help of rosin (Natural gum)
- 2 inside faces of the Pt electrode plates are carefully coated with Pt Black which helps to minimize the resulting polarization effect, and thus,
- Permit the due adsorption of ion on the surface to promote conductance



## Conductometric Titration

Various types of acid-base titration, replacement titration, ppt titration, Redox titration and complex formation titration are done by conductometry.

- ① Acid Base Titration -
- (a)  $SA \bar{c} SB$
  - (b)  $\omega A \bar{c} SB$
  - (c)  $SA \bar{c} \omega B$
  - (d)  $\omega A \bar{c} \omega B$
- ② Displacement or Replacement titration -
- ③ precipitation titration.
- ④ complexometric titration.

★ Imp →

Molar Conductance or Molar Conductivity -

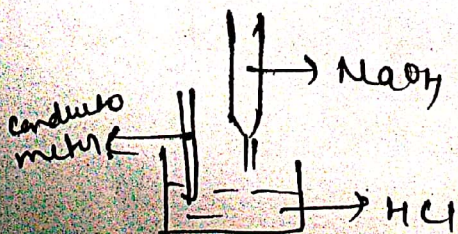
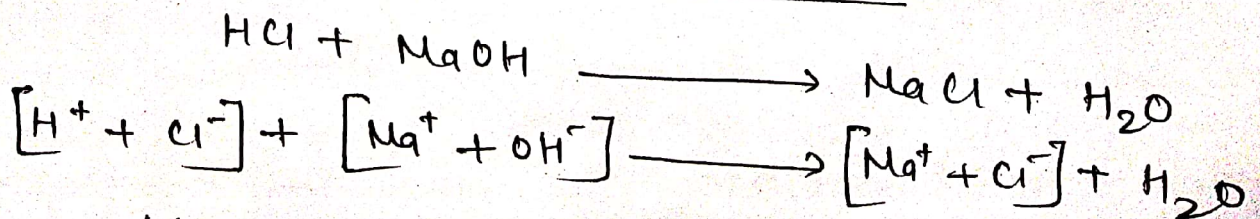
Molar conductivity is defined as conducting power to all the ions produced by dissolving one mole of an electrolyte in solution.

or

when conductivity is produced by the 1 Molar solution of electrolyte that conductivity is called as Molar conductance.

denoted by  $\lambda$  (lambda).

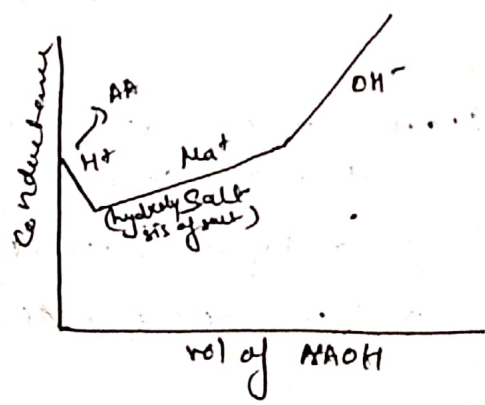
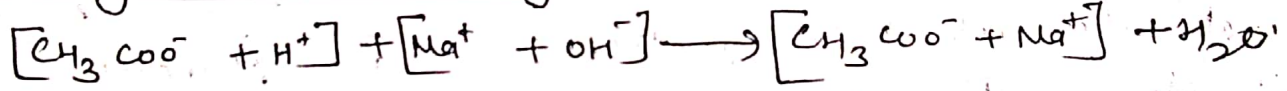
① Strong Acid with strong Base -



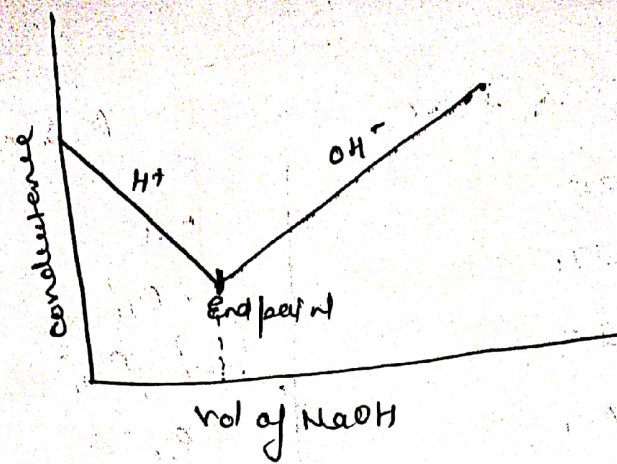
## Molar Conductivity of various ions :-

<u>Cations (+ve)</u>		<u>Anions (-ve)</u>	
H <sup>+</sup>	350	OH <sup>-</sup>	198
Na <sup>+</sup>	74	CO <sub>3</sub> <sup>2-</sup>	82
NH <sub>4</sub> <sup>+</sup>	73	SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup>	80
Ba <sup>2+</sup>	64	Br <sup>-</sup>	78
Ag <sup>+</sup>	62	Cl <sup>-</sup>	76
Ca <sup>2+</sup>	60	I <sup>-</sup>	77
⋮	⋮	CO <sub>3</sub>	69
Li	34	CH <sub>3</sub> COO <sup>-</sup>	41

② Weak acid with strong Base



- Some conductance is obtained due to H<sup>+</sup> ion of AA at the before titration.
- when small amount of NaOH is added to AA than conductance is low due to weak ionization of AA.
- On the further addition of NaOH, there is decrease in conductance due to —



→ At 0 ml addn of NaOH - than the conductance is high due to presence of highly mobile

$H^+$  ions.

→ Addn of NaOH - when the NaOH is added to HCl than the highly mobile  $H^+$  ions is replaced by less mobile  $Na^+$ . So we observe the decrease in the conductivity.

→  $H^+$  cations are replaced by another cations  $Na^+$ .

→  $H^+$  ions react with  $OH^-$  ions to form  $H_2O$  molecule which is undissociate form of molecule.

→ ~~so~~ → So continuous decrease in the conductance is observed.

→ At the End point - Now when all HCl is finished and solution now only contains only  $Na^+$  &  $Cl^-$  and  $H_2O$  molecule. that time conductivity is very low (lowest) this the ~~end~~ End point.

→ After the End point - If we add more NaOH than, conductance is  $\uparrow$  due to NaOH ( $\because$  NaOH is strong Base) so it will react in fully dissociate form and  $Na^+$  &  $OH^-$  so now conductivity is  $\uparrow$  due to  $OH^-$  ions that have higher conductance than the remaining ions.

Initially conductance of HCl is higher when the 0 ml addition of  $\text{NH}_4\text{OH}$ .

- $\text{H}^+$  had the conductance in the solution.
- when  $\text{NH}_4\text{OH}$  is added to HCl, conductance is less due to the replacement of fast moving  $\text{H}^+$  by slow moving  $\text{NH}_4^+$  ions.

$\text{H}^+$  replaced by  $\text{NH}_4^+$  ion.

Here formation of  $\text{NH}_4\text{OH}$   $\text{NH}_4\text{Cl}$  in the solution, which provide  $\text{NH}_4^+$  ion <sup>max</sup> as compare to  $\text{NH}_4\text{OH}$ .

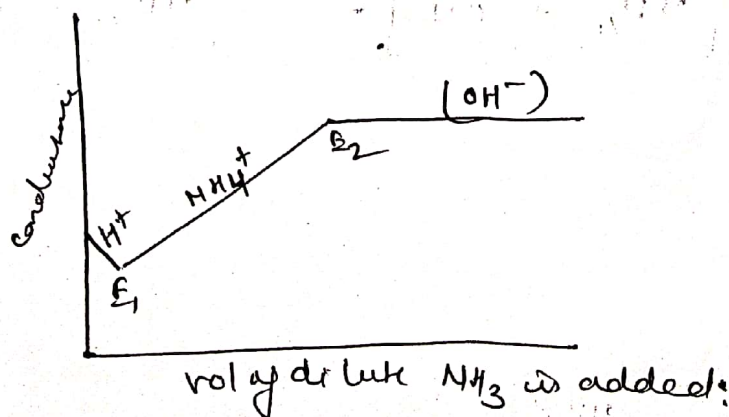
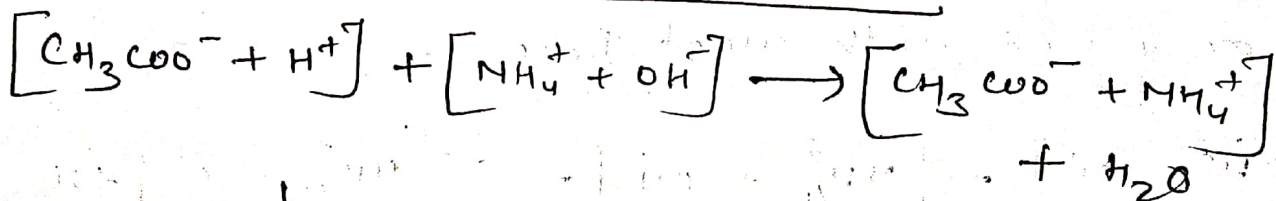
- After the End point - there is no change in conductance almost horizontal is obtained.

b/c Now the solution contains excess

$\text{NH}_4\text{OH}$  which is not fully ionized and.

Same constant reading is obtained due to  $\text{NH}_4^+$  ion of  $\text{NH}_4\text{Cl}$ .

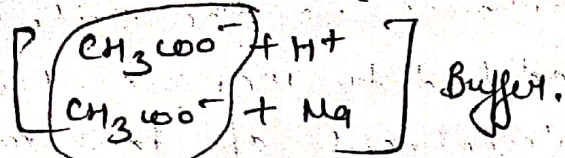
#### ④ weak acid with weak Base



- 2 End point is obtained  $E_1$  &  $E_2$ ..
- this Before  $E_1$  → Conductance is found

(a) Replacement of  $H^+$  ion by  $Na^+$  ion.

(b) here dissociation of  $CH_3COOH$  is suppressed due to common ion Acetate in the solution.



After the End point 1  $\rightarrow$  common ion.

$\rightarrow$  After that now the addition of NaOH after the falling in conductance, the conductance will  $\uparrow$  due to the NaOH neutralizes undissociated  $CH_3COOH$  molecule and form  $CH_3COONa$  and it is salt,  $\therefore$  is a strong Electrolyte.

Strong Electrolyte  $\uparrow$  the conductance

$\rightarrow$  This  $\uparrow$  is rise upto the End point.

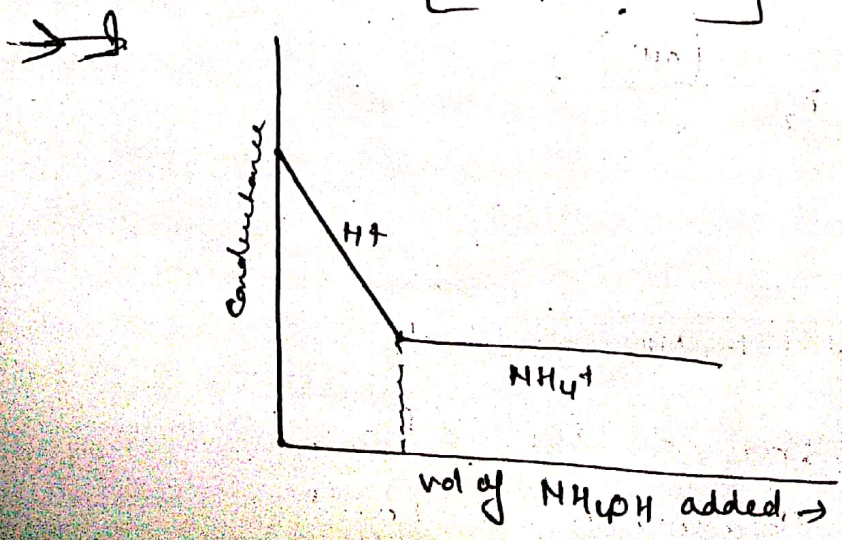
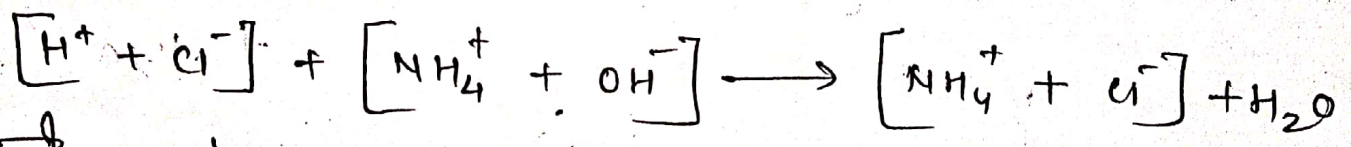
$\rightarrow$  ~~After this point~~

After the End point 2  $E_2$  — After the  $E_2$  point conductance is  $\uparrow$  more rapidly

with the addition of NaOH.

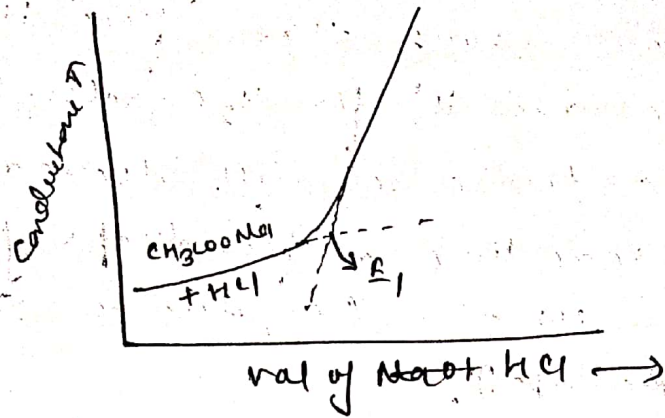
Now here solution contains more NaOH and NaOH is strong Base, fully dissociate and conductance is found  $\uparrow$  in due to the  $OH^-$ .

(3) Strong acid with weak Base. —





when Anion ( $\text{CH}_3\text{COO}^-$ ) of weak acid (AA) is replaced by that of strong acid (HCl) and weak acid (AA) liberated in undissociated form.



→ only slight  $\uparrow$  in conductance is observed up to the end point, due to the  $\text{Cl}^-$  ion b/c solution contains  $\text{CH}_3\text{COO}^-$ ,  $\text{Na}^+$ ,  $\text{H}^+$  =  $\text{CH}_3\text{COOH}$  molecule, &  $\text{Cl}^-$  ion.

So,  $\text{Cl}^-$  ion conductance is  $\uparrow$  as compare to other.

→ when replacement of  $\text{CH}_3\text{COO}^-$  is completed by HCl

→ then after that point the solution contains only  $\text{H}^+$  &  $\text{Cl}^-$ , &  $\text{Na}^+$  and molecule of AA

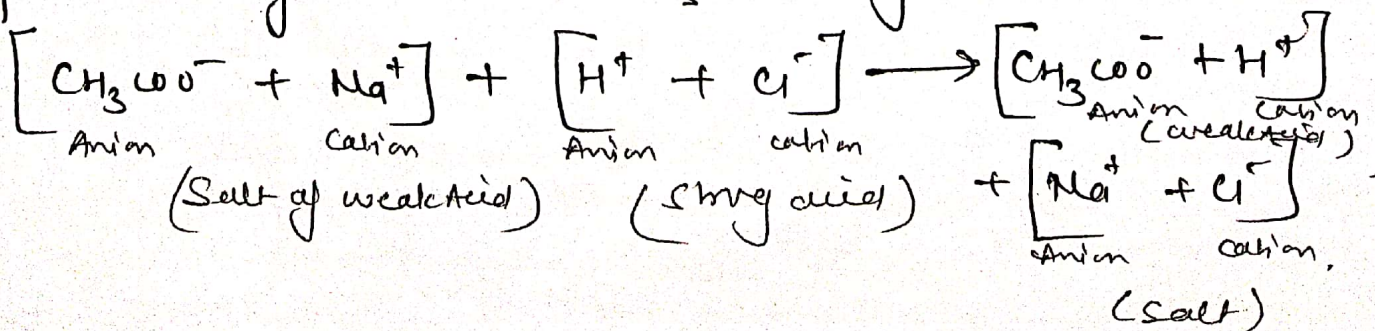
molecule of AA will not more dissociate so only limited  $\text{CH}_3\text{COO}^-$  ion is present.

So due excess of HCl,  $\text{H}^+$   $\uparrow$  es the conductance and the end point is obtained by intersection of 2 lines.

- at the 0ml addition of  $\text{NH}_4\text{OH}$ , <sup>some</sup> conductance is observed due to free of  $\text{H}^+$  ion of Acetic Acid ( $\because$  AA is weak acid & very less  $\text{H}^+$  ion is found in the solution).
- $\rightarrow$  when titration is start, than free  $\text{H}^+$  is replaced by  $\text{NH}_4^+$  ion and  $\text{H}^+$  from  $\text{H}_2\text{O}$  molecule
  - $\rightarrow$  So Now conductance will decreased.
  - $\rightarrow$  But after some time or few drops of addition of  $\text{NH}_4\text{OH}$  conductance will also  $\uparrow$ es, due to Salt formation. (Ammonium Acetate).
  - $\rightarrow$  molecule of AA is (undissociate) reacted with  $\text{NH}_4\text{OH}$  molecule and form the  $\text{CH}_3\text{COO}^- \text{NH}_4^+$ .
  - $\rightarrow$  So solution contains Now molecule of AA and molecule  $\text{H}_2\text{O}$  and ion of  $\text{CH}_3\text{COO}^-$  & ion of  $\text{NH}_4^+$
  - So conductance will  $\uparrow$ es due to  $\text{NH}_4^+$  ions.
  - $\rightarrow$  But when all  $\text{CH}_3\text{COOH}$  is neutralized with  $\text{NH}_4\text{OH}$  and that point is  $E_2$ .
  - $\rightarrow$  after the  $E_2$  or addition of more  $\text{NH}_4\text{OH}$  than  $\text{NH}_4\text{OH}$  is a very weak Base so it is partial dissociates, fixed quantity of  $\text{NH}_4^+$  or  $\text{OH}^-$  is found and so straight line is obtained due to  $\text{OH}^-$  ion of weak Base.

### ⑤ Displacement or Replacement Titration.

eg  $\rightarrow$  Salt of weak acid vs strong acid



## Application of Conductometric Titrations

(90)

- 1) Determination of solubility of sparingly soluble materials
- 2) Kinetic studies - Rate of reaction
- 3) Degree of dissociation of weaker electrolyte
- 4) Basicity of organic acids
- 5) Determination of concentrations
- 6) Determination of ions.

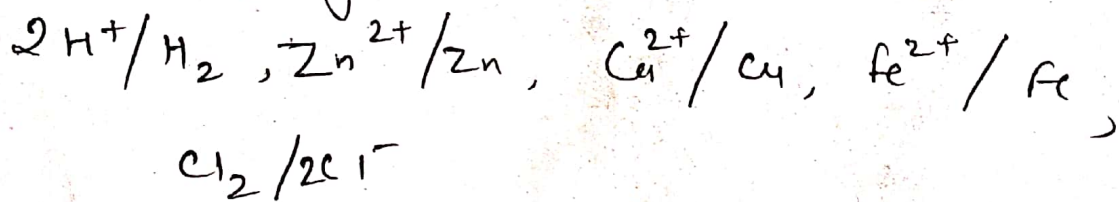
# Potentiometry

(31)

- Potentiometry is one type of electrochemical analysis method
- Electrochemistry is a part of chemistry, which determines electrochemical properties of substance.
- A electrical circuit is required for measuring current 'A' ampere & potential V (volt) (voltage) created by movement of charged particles.  
ex:- Galvanic cell, Electrochemical cell.
- Cell is a device which converts physical process or chemical process/energy into electrical energy

$$\text{cell} = \text{half cell} + \text{half cell}$$

various half cells are there:-



★ Electrode potential → It is potential difference between 2 half cells.

ex → If hydrogen electrode is taken as standard and zinc electrode is taken as sample electrode the difference b/w potential of their electrode is known as electrode potential.

Potential on an electrode depends on the ions present in the solution & their concentration.

By this way electrochemical cells can be used to determine ions & their conc. when a metal rod (electrode) is immersed in the solution of its own ions eg → zinc rod dipped in zinc sulphate.