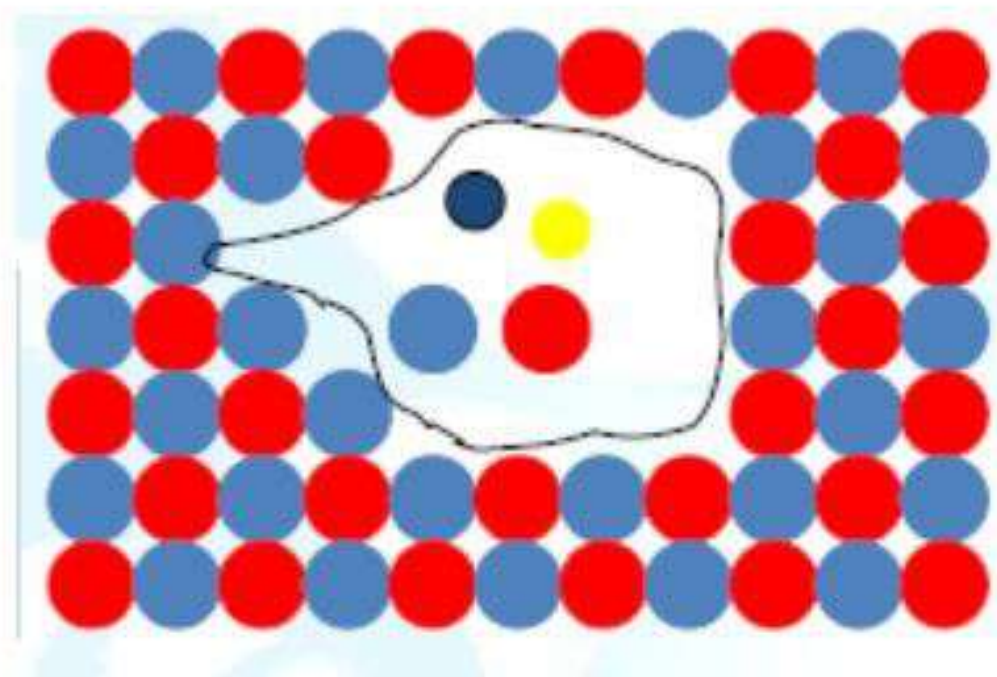


Mechanical Entrapment:

A type of co-precipitation in which coprecipitated physically trap a *pocket of solution* within a precipitate during rapid precipitate formation.

● Problem solving: Digestion

Mixed-crystal formation may occur in both colloidal and crystalline precipitates, but occlusion and mechanical entrapment are confined to crystalline precipitates

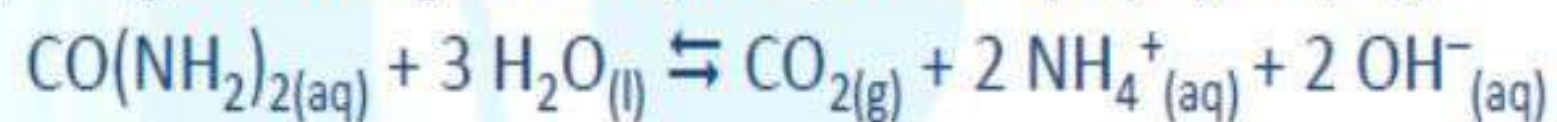


Precipitation from Homogeneous Solution

Homogeneous precipitation

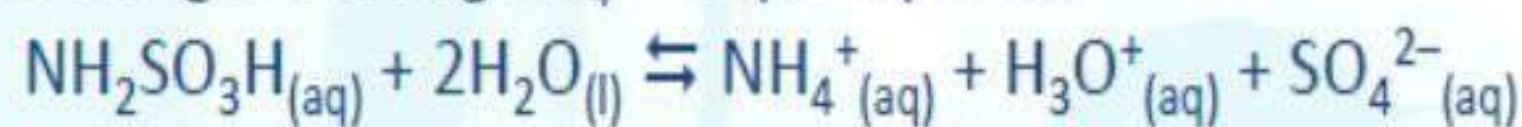
is a process in which a precipitate is formed by slow generation of a precipitating reagent homogeneously throughout a solution. Solids formed by homogeneous precipitation are generally purer and larger in size

Example 1: Urea, for generating OH^- as precipitant (Al(III), Fe(III))



* Generation rate can be controlled by temperature

Example 2: For generating SO_4^{2-} as precipitant



* Generation rate can be controlled by pH

Drying and Ignition of Precipitates

A gravimetric precipitate is heated until its mass becomes constant.

- ✓ Heating removes the solvent and any volatile species carried down with the ppt.
- ✓ Some precipitates are also ignited to decompose the solid and form a compound of known composition. This new compound is often called the *weighing form*.

- The temperature required to dehydrate a precipitate completely may be as low as 100C or as high as 1000C
- Moisture is completely removed from silver chloride at temperatures higher than 110C, but dehydration of aluminum oxide is not complete until a temperature greater than 1000C is achieved.
- The thermal curve for calcium oxalate is considerably more complex than the others
- Recording thermal decomposition curves is called **thermogravimetric analysis**, and the mass versus temperature curves are termed **thermograms**.

Types of Precipitating agents

1- Inorganic Precipitating Agents: this reagents typically forms lightly soluble saltes or hydrous oxide with the analyte.

TABLE 12-2

Some Inorganic Precipitating Agents	
Precipitating Agent	Element Precipitated*
NH ₃ (aq)	Be (BeO), Al (Al ₂ O ₃), Sc (Sc ₂ O ₃), Cr (Cr ₂ O ₃) [†] , Fe (Fe ₂ O ₃), Ga (Ga ₂ O ₃), Zr (ZrO ₂), In (In ₂ O ₃), Sn (SnO ₂), U (U ₃ O ₈)
H ₂ S	Cu (CuO) [†] , Zn (ZnO or ZnSO ₄), Ge (GeO ₂), As (As ₂ O ₃ or As ₂ O ₅), Mo (MoO ₃), Sn (SnO ₂) [†] , Sb (Sb ₂ O ₃), or Sb ₂ O ₅ , Bi (Bi ₂ S ₃)
(NH ₄) ₂ S	Hg (HgS), Co (Co ₃ O ₄)
(NH ₄) ₂ HPO ₄	Mg (Mg ₂ P ₂ O ₇), Al (AlPO ₄), Mn (Mn ₂ P ₂ O ₇), Zn (Zn ₂ P ₂ O ₇), Zr (Zr ₂ P ₂ O ₇), Cd (Cd ₂ P ₂ O ₇), Bi (BiPO ₄)
H ₂ SO ₄	Li , Mn , Sr , Cd , Pb , Ba (all as sulfates)
H ₂ PtCl ₆	K (K ₂ PtCl ₆ or Pt), Rb (Rb ₂ PtCl ₆), Cs (Cs ₂ PtCl ₆)
H ₂ C ₂ O ₄	Ca (CaO), Sr (SrO), Th (ThO ₂)
(NH ₄) ₂ MoO ₄	Cd (CdMoO ₄) [†] , Pb (PbMoO ₄)

2- Reducing Agents

convert an analyte to its elemental form form for weighing

TABLE 12-3

Some Reducing Agents Used in Gravimetric Methods

Reducing Agent	Analyte
SO ₂	Se, Au
SO ₂ + H ₂ NOH	Te
H ₂ NOH	Se
H ₂ C ₂ O ₄	Au
H ₂	Re, Ir
HCOOH	Pt
NaNO ₂	Au
SnCl ₂	Hg
Electrolytic reduction	Co, Ni, Cu, Zn Ag, In, Sn, Sb, Cd, Re, Bi

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3-Organic Precipitating Agents

Some organic reagents react with metal ions then produce insoluble coordination cmpds.

✓ Reagents that form coordination compounds of this type are called **chelating agents**, and their products are called **chelates**.

✓ Those metal chelates are relatively nonpolar and have **low solubilities in water**.

✓ Usually, these compounds possess low densities and are often intensely colored. Because they are not wetted by water, coordination compounds are easily freed of moisture at low temperatures.

Common organic precipitating agents

Name	Structure	Ions precipitated
Dimethylglyoxime		Ni ²⁺ , Pd ²⁺ , Pt ²⁺
Cupferron		Fe ³⁺ , VO ₂ ⁺ , Ti ⁴⁺ , Zr ⁴⁺ , Ce ⁴⁺ , Ga ³⁺ , Sn ⁴⁺
8-Hydroxyquinoline (oxine)		Mg ²⁺ , Zn ²⁺ , Cu ²⁺ , Cd ²⁺ , Pb ²⁺ , Al ³⁺ , Fe ³⁺ , Bi ³⁺ , Ga ³⁺ , Th ⁴⁺ , Zr ⁴⁺ , UO ₂ ²⁺ , TiO ₂ ²⁺
Salicylaldoxime		Cu ²⁺ , Pb ²⁺ , Bi ³⁺ , Zn ²⁺ , Ni ²⁺ , Pd ²⁺
1-Nitroso-2-naphthol		Co ²⁺ , Fe ³⁺ , Pd ²⁺ , Zr ⁴⁺
Nitron		NO ₃ ⁻ , ClO ₄ ⁻ , BF ₄ ⁻ , WO ₄ ²⁻
Sodium tetraphenylborate	Na ⁺ B(C ₆ H ₅) ₄ ⁻	K ⁺ , Rb ⁺ , Cs ⁺ , NH ₄ ⁺ , Ag ⁺ , organic ammonium ions
Tetraphenylarsonium chloride	(C ₆ H ₅) ₄ As ⁺ Cl ⁻	Cr ₂ O ₇ ²⁻ , MnO ₄ ⁻ , ReO ₄ ⁻ , MoO ₄ ²⁻ , WO ₄ ²⁻ , ClO ₄ ⁻ , I ₃ ⁻

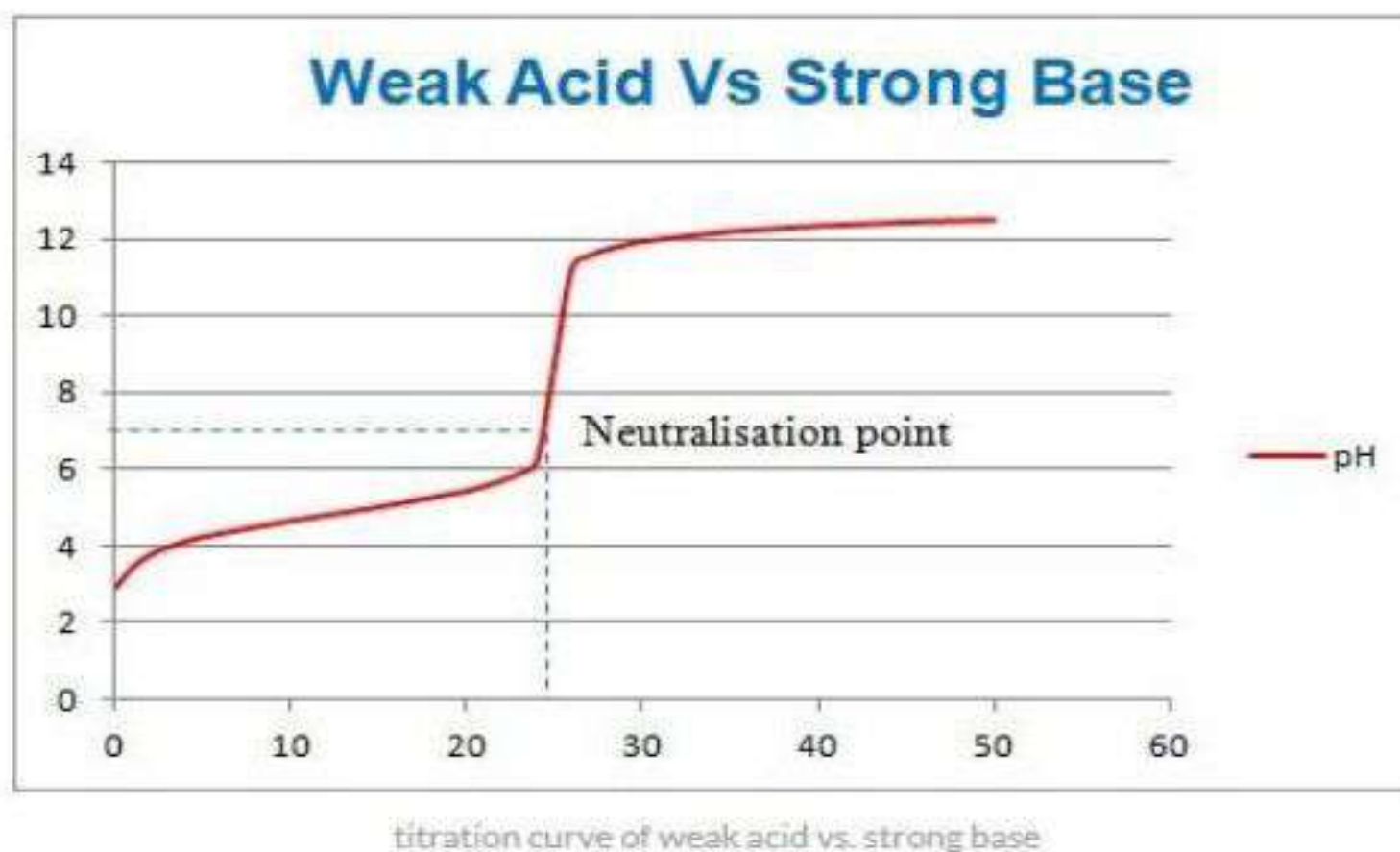
Organic ppting agents have the advantages

- 1- Som of organic ppting agents are very selctive and very broad in the number of elements they will ppt.
- 2- Giving pptes with very low solubility in water
- 3- Give a favorable gravimetric factor

Types of titration curves:

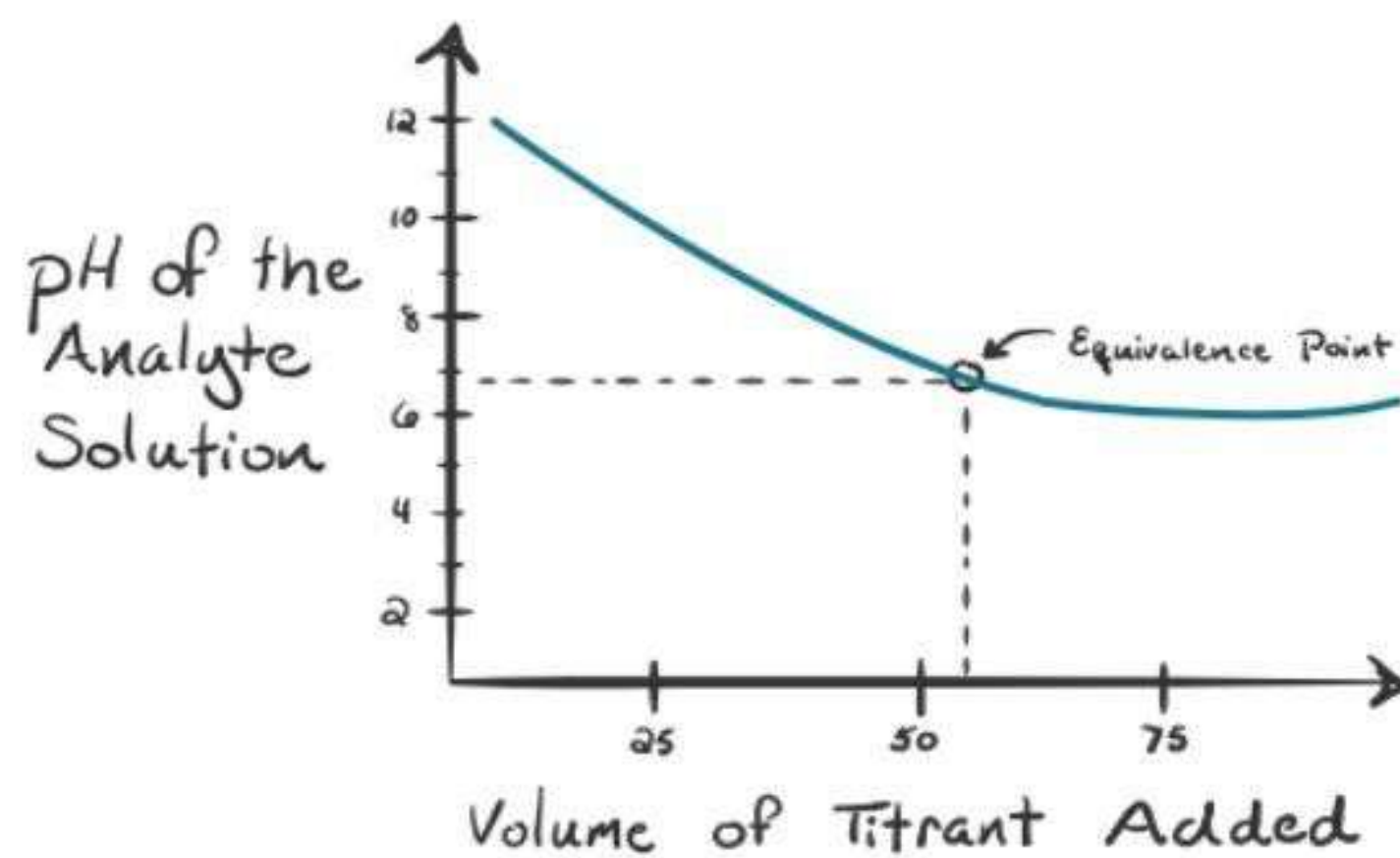
A **titration curve** is a graph of the pH as a function of the amount of titrant (acid or base) added.

- 1- First type called a sigmoidal curve important observation are confined to a small region surrounding the equivalence point the p – function of analyte as function of reagent volumes.



2- A liner segment curve

Measurements are made on both sides of but well away from the equivalence point the vertical axis represents an instruments is directly proportional to the conc. Of the analyte.



The solubility of precipitation

Solubility is a chemical property referring to the ability for a given substance, the solute, to dissolve in a solvent. It is measured in terms of the maximum amount of solute dissolved in a solvent at equilibrium. The resulting solution is called a saturated solution

Ex AgCl slightly dissolve in water giving Cl^- and Ag^+ where



Ex :

What weight of $\text{Ba}(\text{IO}_3)_2$ M.WT (487) can be dissolved in to 500ml of water ?

$$K_{sp} = [\text{Ba}].[\text{IO}_3]^2$$

$$1.57 \cdot 10^{-9} = S \cdot (2S)^2$$

$$S = 3.72 \cdot 10^{-4} \text{ M}$$

$$\text{Wt Ba}(\text{IO}_3)_2 = 3.72 \cdot 10^{-4} \cdot 500/1000 \cdot 487$$