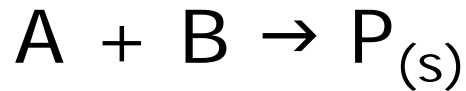


Chapter 5



Gravimetric Analysis

- Gravimetric analysis:
for macroquantitative analysis



- Procedure:
 - 1) Preparing the solution in proper form for precipitation.
 - 2) The precipitation process and how to obtain the precipitate in pure and filterable form.

- 3) The filtration and washing of the precipitate to prevent losses and impurities.
- 4) Heating of the precipitate to convert it to a weighable form.
- 5) Calculating the quantity of analyte from the weight of precipitate.

5.1 Unit Operations in Gravimetric Analysis

- Requirements for a gravimetric analysis:
 1. The separation process should be sufficiently complete.
 2. The substance weight should have a definite composition and should be pure.

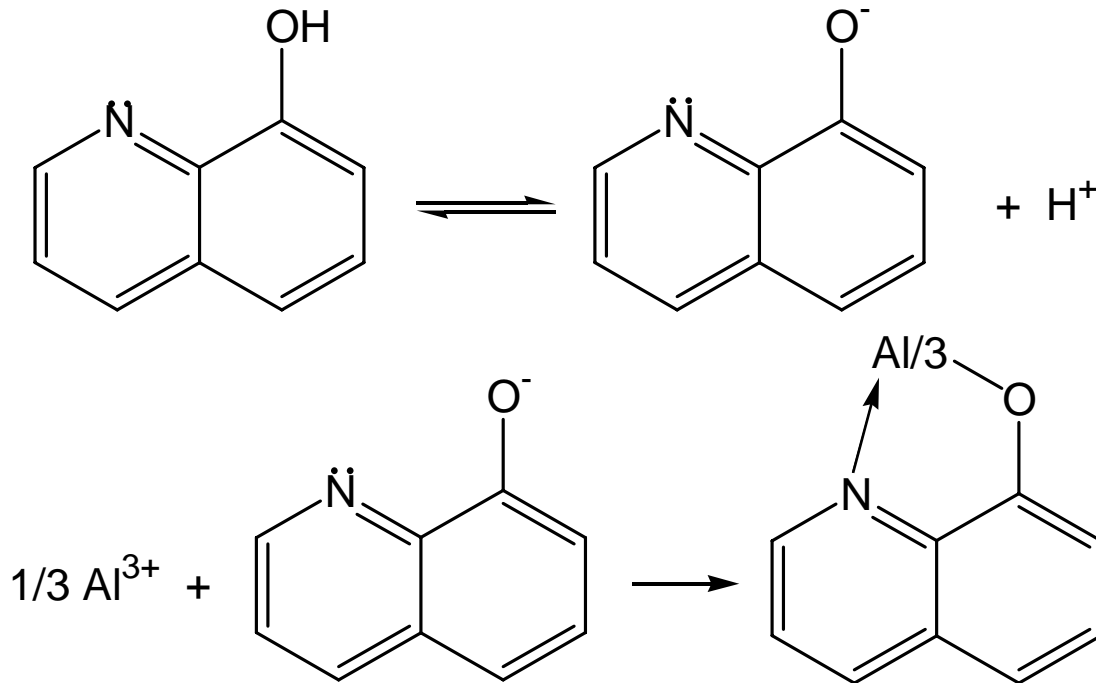
- Steps of a gravimetric analysis:
 1. Preparation of the solution
 2. Precipitation
 3. Digestion
 4. Filtration
 5. Washing
 6. Drying or igniting
 7. Weighing
 8. calculation

- Preparation of the solution:
 - 1) Separate or eliminate interfering materials.
 - 2) Adjust conditions to obtain precipitate in a form suitable for filtration.

- Factors that must be considered:
 - 1) the volume of the solution during precipitation
 - 2) the concentration range of the test substance
 - 3) the presence and concentrations of other constituents
 - 4) the temperature
 - 5) the pH

Ex: Calcium oxalate (CaC_2O_4) is insoluble in basic medium, but soluble in acidic medium.

Ex: 8-hydroxyquinoline (oxine)



at pH4 \Rightarrow Aluminum can be precipitated
but magnesium not

-
- Condition for analytical precipitation



precipitation process and particle size

- 1) nucleation: the formation of nuclei
- 2) the growth of these nuclei to form particles

supersaturation occurs

metastable condition

The higher the degree of supersaturation, the greater the rate of nucleation.

The formation of a greater number of nuclei per unit time will ultimately result in more total crystals of smaller size.

⇒ The total crystal surface area will be larger, with increased danger of adsorption of impurities.

The greater the supersaturation, the more rapid the crystal growth rate, with increased growth rate, there is increased chance of imperfections in the crystal and trapping of impurities.

□ Von Weimarn's Theory:

The initial rate of precipitation is proportional to the relative supersaturation.

⇒ The particle size of precipitates is inversely proportional to the relative supersaturation of the solution.

$$\text{relative supersaturation} = \frac{Q - S}{S}$$

Q: the concentration of the mixed reagents before precipitation occurs.

S: the solubility of the precipitate at equilibrium.

high relative supersaturation

→ many small crystals (high surface area)

low relative supersaturation

→ fewer, larger crystals (low surface area)

We want to keep Q low and S high during precipitation.

How to minimize supersaturation and obtain large crystals.

1. Precipitate from dilute solution, this keeps Q low.
2. Add dilute precipitating reagents slowly, with effective stirring.
3. Precipitate from hot solution. This increases S .
4. Precipitate at as low a pH as is possible to still maintain quantitative precipitation.

The concentration of impurities is kept lower, and the slower rate of precipitation decreases their chance of being trapped.

The larger crystals have a smaller specific surface area and so have less chance of adsorbing impurities.

□ Digestion of the precipitate:

When a precipitate is allowed to stand in the presence of the mother liquor, the large crystals grow at the expense of the small ones.

Fig 5.1

Digestion improves the purity and crystallinity of the precipitate, and is usually done at elevated temperatures.

Fig 5.2

The agglomerated particles results in an appreciable decrease in surface area.

Fig 5.2

colloidal particles: 1 to 100 μm

have a very large surface-to-mass ratio

primary layer:

counterlayer or secondary layer:

The counterlayer is close to primary layer

\Rightarrow form larger size particles \Rightarrow coagulation

The counterlayer is loosely bound

\Rightarrow form colloidal particles

- Peptization: a process of dispersing an insoluble material into a liquid as a colloid. An added electrolyte will result in a closer secondary layer and will promote coagulation.

□ There are two types of colloids:

hydrophilic: Lyophilic or emulsoid

⇒ solution is viscous

hydrophobic: Lyophobic or suspensoid

⇒ solution is called a sol.

Ex: $\text{Al}(\text{OH})_3$; $\text{Fe}(\text{OH})_3$

⇒ gelatinous precipitates

Ex: AgCl

⇒ curdy precipitate

□ Reprecipitation:

⇒ reduce the concentration of impurities

⇒ decrease the adsorption of impurities

□ Coprecipitation:

Ex: add H_2SO_4 to BaCl_2 in NO_3^-

BaSO_4 ↓ contain BaNO_3

1) Occlusion and inclusion:

Material is trapped within a crystal.

Ex: H_2O

Ions are trapped within the crystal lattice

Ex: K^+ in NH_4MgPO_4 precipitation.

<sol>

Digestion may help some
reprecipitation

2) Surface adsorption:

Paneth-Fajans-Hahn rule:

Ion in solution which is most strongly adsorbed is the one common to the lattice.

If no common ion is present, the ion in solution that forms the least soluble compound with one of the lattice ions is the most strongly adsorbed.

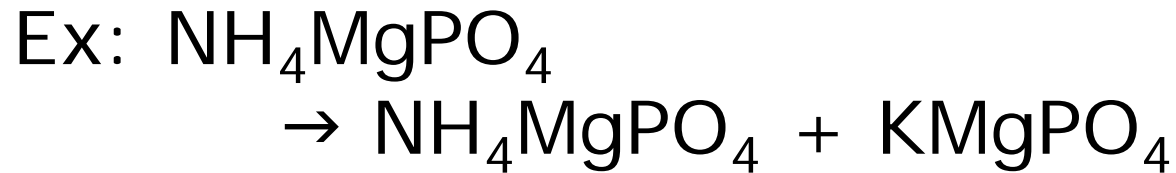
<sol> Washing

3) Postprecipitation:

Ex: CaC_2O_4 in Mg^{2+} ; CuS in Zn^{2+}

Isomorphous replacement:

the process result in a mixed crystal.



- Washing and filtering the precipitates:
adding an electrolyte to the wash liquid
Ex: HNO_3 or NH_4NO_3 for AgCl
- Drying or igniting the precipitate
Ex: $\text{AgCl} \Rightarrow 110$ for 2hrs
 $\text{MgNH}_4\text{PO}_4 \rightarrow$ pyrophosphate
 $\text{Mg}_2\text{P}_2\text{O}_7$ at 900
 $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3$

□ Precipitation from homogeneous solution:

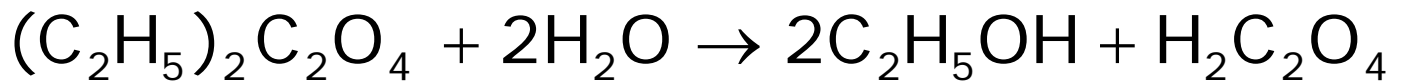
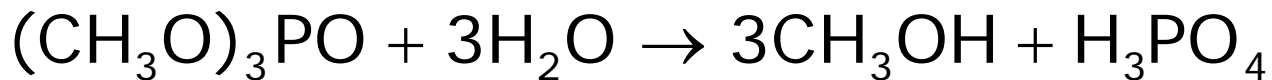
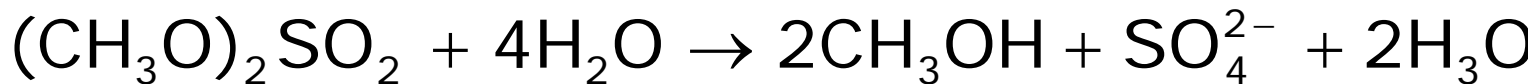
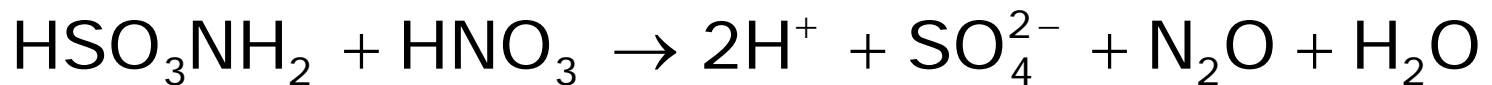
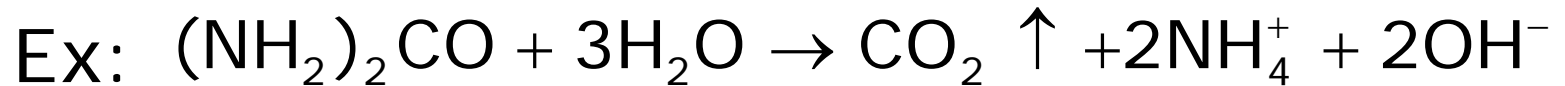


Fig 5.3 ; Fig 5.4

⇒ lead to both large and pure particles of a precipitate.

Fig 5.3 ; Fig 5.4

5.2 Gravimetric Calculations

$$\begin{aligned} \text{G.F.} &= \frac{\text{f.wt. analyte (g/mol)}}{\text{f.wt. precipitate (g/mol)}} \times \frac{a}{b} \left(\frac{\text{mol analyte}}{\text{mol precipitate}} \right) \\ &= \frac{\text{g analyte}}{\text{g precipitate}} \end{aligned}$$

$$\% \text{ sought} = \frac{\text{wt of precipitate} \times \text{GF}}{\text{wt of sample}} \times 100\%$$

5.3 Examples of Gravimetric Analysis

Table 5.1

5.4 Organic Precipitates

Obtain precipitates with very low solubility in water.

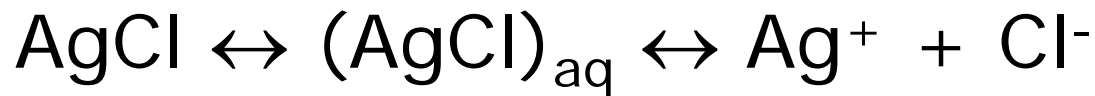
Chelating agent:

Chelate



see [Table 5.2](#)

5.5 Precipitation Equilibria: The Solubility Product



Solubility: g/L or mol/L

solubility product: $K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$

Common ion effect:

Fig 5.5

5.6 The Diverse Ion Effect on Solubility: K_{sp}°

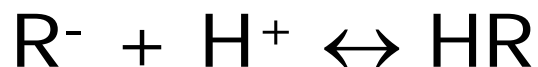
$$K_{sp}^{\circ} = a_{\text{Ag}^+} a_{\text{Cl}^-} = [\text{Ag}^+] f_{\text{Ag}^+} [\text{Cl}^-] f_{\text{Cl}^-}$$

$$K_{sp}^{\circ} = K_{sp} f_{\text{Ag}^+} f_{\text{Cl}^-}$$

The presence of diverse salts will increase the solubility of precipitates.

Fig 5.6

Acids frequently affect the solubility of a precipitate.



A complexing agent that reacts with the metal ion of the precipitate will increase the solubility.

