Precipitation Titration

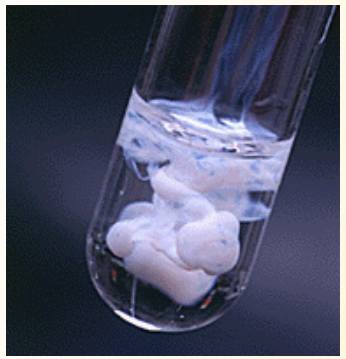
Lecture Three 2024-2025

Precipitation Reactions

- **Precipitation** is the formation of a solid in a solution
- solid formed is called the **precipitate**
- *A **precipitation reaction*** occurs when water solutions of two different ionic compounds are mixed and an **insoluble solid** separates out of solution.

$$KCl + AgNO_3 \leftrightarrow AgCl_{(s)} \downarrow + KNO_3$$

Cl^- solution — Precipitating agent



White precipitate

- The precipitate is itself ionic; the cation comes from one solution and the anion from another.

Precipitation Reactions

- **Precipitation titration** is a titration method based on the formation of precipitate, which is slightly soluble
- **The basic requirements are:**
- The reaction must be sufficiently rapid and complete,
- lead to a product of reproducible composition and of low solubility.
- And a method must exist to locate the end point.

- **Precipitation titrations are not so popular in present-day routine analysis. Why????**

Some difficulties in meeting these requirements must be noted. (Precipitation reactions are generally).

- Slow
- Involving periods of digestion, cooling, filtration etc.
- This tends to limit the reactions that are available for titration.

Argentometric titration:

- Titrations involving **silver** are termed argentometric, from the Latin name for silver, **argentum**.
- **The major precipitation reaction used is that of silver with a range of anions. These anions include:**

✓ Halides (Cl^-, Br^-, I^-)

✓ Pseudo halides (S^{2-}, HS^-, CN^-, SCN^-)

- The reaction rates for the silver salt precipitation is **rapid**.
- The reaction ratio is **1:1** and silver salts formed are generally quite **insoluble**.
- Argentometric methods involving precipitation **titrimetry**:

➢ Mohr's Method

➢ Volhard's Method

➢ Fajan's Method

Mohr's Method:

- This **direct method** uses potassium chromate (**chromate ions (CrO_4^{2-})** as **an indicator** in the titration of (**Cl^-, Br^-, and CN^-)ions (analyte)** with a **silver nitrate standard solution (titrant)**.
- After all the chloride has been precipitated as **white silver chloride**, the first excess of titrant results in the formation of a **red silver chromate precipitate**, which signals the end point . The reactions are:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s) \qquad K_{sp} = 1.82 \times 10^{-10}$$

White ppt

- End point determination by brick red color precipitate, $Ag_2CrO_{4(s)}$:

$$2\ Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s) \qquad K_{sp} = 1.2 \times 10^{-12}$$

red ppt

- AgCl is less soluble than Ag_2CrO_4 so it will precipitate first

Conditions for Mohr's method:

- The titrations are performed only in neutral or slightly basic medium to prevent silver hydroxide formation (at pH > 10).

$$2Ag^{+} + 2OH^{-} \longrightarrow 2AgOH(s) \longrightarrow Ag_2O(s) + H_2O$$

Black ppt

- Or the formation of chromic acid at pH < 7.

$$CrO4^{2-} + H_3O^{+} \longrightarrow HCrO_4^{-} + H_2O$$
$$2\ CrO_4^{2-} + 2\ H_3O^{+} \longrightarrow Cr_2O_7^{2-} + H_2O$$

bright-orange

- Reducing $[CrO_4^{2-}]$ will delay the formation of the precipitate although more Ag^{+} to be added to reach end point, which cause error.

Volhard method:

- This method uses a **back titration** with potassium thiocyanate and is suitable for the determination of (Cl^-, Br^-, and I^-) in ***acidic solutions***.
  - First, Cl^- is precipitated by excess $AgNO_3$

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$

  - Removing AgCl(s) by filtration / washing
  - Excess Ag^+ is titrated with KSCN in the presence of Fe^{3+}

$$Ag^+(aq) + SCN^-(aq) \rightarrow AgSCN(s)$$

  - When Ag^+ has been consumed, a red complex forms as a result of:

$$Fe^{3+}(aq) + SCN^-(aq) \rightarrow FeSCN^{2+}(aq)$$

Red complex

- The Volhard titration can be used for any anion that forms an insoluble salt with silver

Conditions for Volhard's method:

- The solution must be **acidic**, with a concentration of about 1 M in nitric acid to ensure the **complex formed is stable**, and to prevent the precipitation of Iron(III) as hydrated oxide.

- The **indicator concentration** should not be *more than 0.2M*.

- In case of I^-, indicator should not be added until all the I^- is precipitated with Ag^+, since it would be **oxidized by the Fe(III)**.

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

The AgX ↓precipitate **must be** filtered off, before titrating with SCN^- to prevent any error, for example in the case of chloride ion, AgCl will react with the titrant (SCN^-) and cause a diffuse end point.

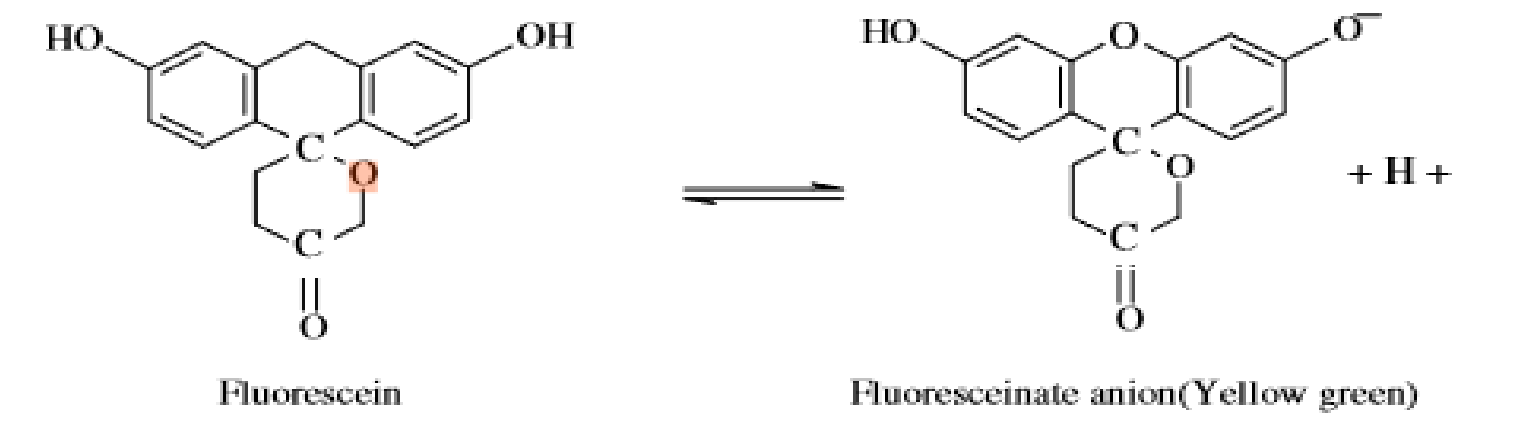
$$AgCl + SCN^- \longrightarrow AgSCN + Cl^-$$

OR

Use tartrazine (E.P bright lemon-yellow) as indicator instead of Iron(III) .

Fajan's Method

- This method uses an **adsorption indicator** such of Fluorescein (Dichlorofluorescein) and Eosin.
- The indicator **adsorb onto the surface of the silver salt precipitate** at the **endpoint**.
- The adsorption process causes a **change in the color** of the **indicator**.
- Common Fajans adsorption **indicators** are weakly acidic organic compounds and in **alkaline conditions** will exist as the conjugate base,(or Ind^-).



Fluorescein ⇌ Fluoresceinate anion(Yellow green)

- This form of the indicator which interacts with the precipitate.

- Adsorption indicator whose color when adsorbed to the precipitate is different from that when it is in solution

Indicator	Solution	Surface of precipitate	Ions
Fluoroscein	greenish yellow	pink	Cl^-
Eosine	**yellowish-red**	**redish - violet**	Br^-, I^-

Comparison of argentometric titration methods

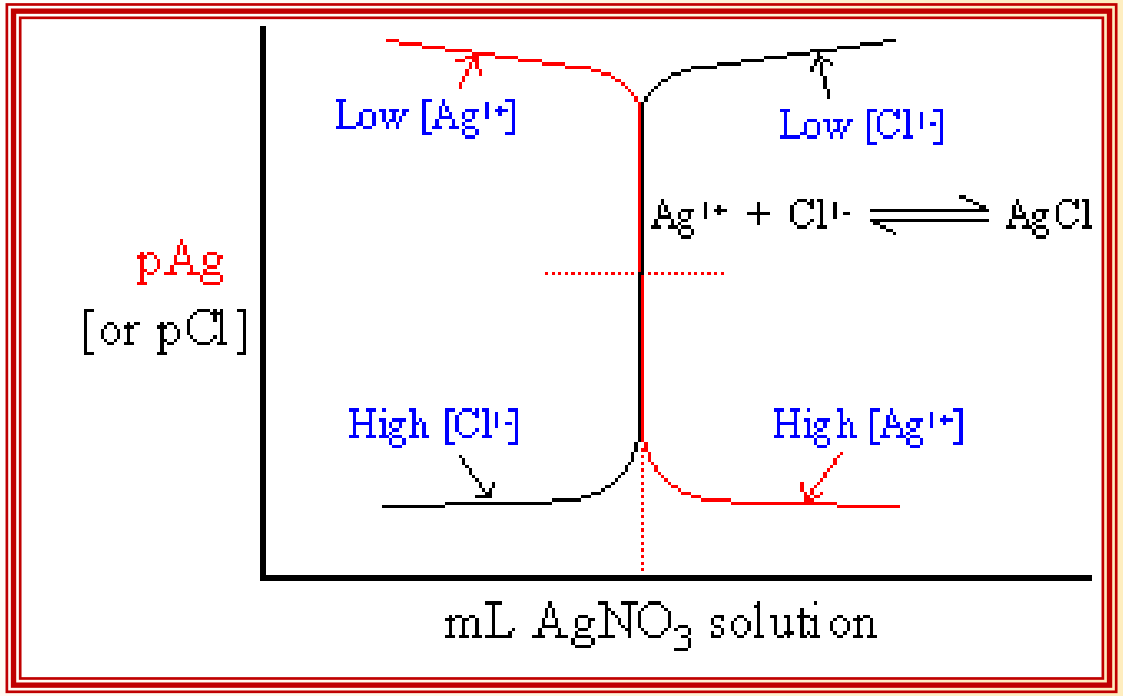
Method	Advantages	Disadvantages
Mohr	Simple	• Alkaline solution only • Not suitable for I^- • Requires a blank
Volhard	• Capable for direct Ag^+ and indirect halide analyses • Very clear colour change	• Must use 1M of nitric acid solution • Some problems with some ions
Fajans	• Capability for different pH ranges and selectivity with different indicators	• Difficult with dilute solutions • Should not be a high background ionic level

Titration Curves for Argentometric Methods

- A titration curve is the plot of the pAg (or pAnalyte) versus the volume of the titrant ($AgNO_3$) added as the titration progresses.
- **Example: Titration of chloride with silver.**

- A useful relationship can be derived by taking the negative logarithm of both sides of a solubility-product expression. Thus, for silver chloride,

$$K_{sp} = [Ag^+][Cl^-]$$
$$-logK_{sp} = -\log([Ag^+][Cl^-])$$
$$-logK_{sp} = -\log[Ag^+] - log[Cl^-]$$
$$pK_{sp} = pAg^+ + pCl^-$$



- The points on the curve can be calculated, given the analyte concentration, $AgNO_3$ concentration and the appropriate K_{sp}.

Plotting precipitation titration curves

- Consider titration of Cl^- with a standard solution of $AgNO_3$. Titration curve prepared by plotting pCl ($-\log[Cl^-]$) against the volume of $AgNO_3$ in a manner similar to acid-base titration.
- **Before titration started** – only have Cl^-.

$$pCl = -\log[Cl^-]$$

- **Titration proceed** – part of Cl^- is removed from solution by precipitation as $AgCl$.

$$pCl = -\log [\text{remaining } Cl^-]$$

- **At equivalence point** - we have solution a saturated solution of $AgCl$.

$$[Cl^-] = \sqrt{K_{sp}}$$

- **Excess $AgNO_3$ added** – excess Ag^+. $[Cl^-]$ is determine from the concentration of Ag^+ and K_{sp}.

$$[Cl^-] = K_{sp}/[Ag^+]$$

Example

Calculate pCl for the titration of 100.0 ml 0.100 M NaCl with 0.100 M $AgNO_3$ for the addition of 0.0, 20.0, 99.0, 100.0 and 100.5 ml $AgNO_3$. K_{sp} AgCl is 1.0×10^{-10}

Solution

a) Addition of 0.0 ml Ag^+

$[Cl^-] = 0.100$ M

$pCl = -\log [Cl^-]$

$= -\log 0.100$

$= 1$

b) Addition of 20.0 ml Ag^+

Initial mmol Cl^- = 100.0 ml x 0.100 M = 10.0 mmol

mmol added Ag^+ = 20.0 ml x 0.100 M = 2.0 mmol

mmol Cl^- left = **8.0** mmol

$$[Cl^-] \text{ left} = \frac{8.0}{(100+20)\text{ ml}} = 0.0667 \text{ M}$$

$pCl = -\log [Cl^-]$

$= -\log 0.0667$

$= 1.18$

Volume $AgNO_3$	PCl
0.0	1
20.0	1.18
99.0	
100.0	
100.5	

c) Addition of 99.0 ml Ag

Initial mmol Cl^- = 100.0 ml x 0.100 M = 10.0 mmol

mmol added Ag^+ = 99.0 ml x 0.100 M = 9.9 mmol

mmol Cl^- left = **0.1** mmol

$$[Cl^-] \text{ left} = \frac{0.1}{(100+99)\text{ml}} = 5.01 \times 10^{-4} \text{ M}$$

$pCl = -\log [Cl^-]$

$= -\log 5.01 \times 10^{-4}$

$= 3.3$

Volume $AgNO_3$	PCl
0.0	1
20.0	1.18
99.0	3.3
100.0	5
100.5	

d) Addition of 100.0 ml

Initial mmol Cl^- = 100.0 ml x 0.100 M = 10.0 mmol

mmol added Ag^+ = 100.0 ml x 0.100 M= 10.0 mmol

Equivalence point is reached. The solution contain saturated AgCl solution

$K_{sp} = [Ag^+][Cl^-] = 1.0 \times 10^{-10}$

$[Cl^-] = \sqrt{K_{sp}} = \sqrt{1.0 \times 10^{-10}}$

$= 1.0 \times 10^{-5}$

$pCl = -\log 1.0 \times 10^{-5}$

$= 5$

e) Addition of 100.5 ml Ag^+

Initial mmol Cl = 100.0 ml x 0.100 M = 10.0 mmol

mmol added Ag^+= 100.5 ml x 0.100 M =10.05 mmol

mmol Ag^+ excess = = **0.05** mmol

$[Ag^+]$ excess = **0.05**/200.5 ml = 2.5×10^{-4} M

$K_{sp} = [Ag^+][Cl^-] = 1.0 \times 10^{-10}$

$$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.0 \times 10^{-10}}{2.5 \times 10^{-4}\ M} = 4.0 \times 10^{-7}$$

$pCl = -\log 4.0 \times 10^{-7}$

$= 6.4$

Volume $AgNO_3$	PCl
0.0	1
20.0	1.18
99.0	3.3
100.0	5
100.5	6.4