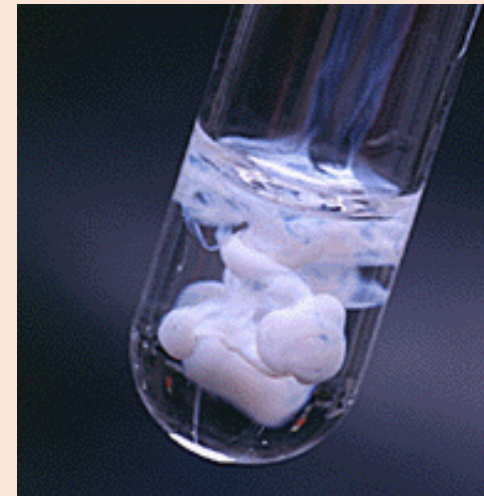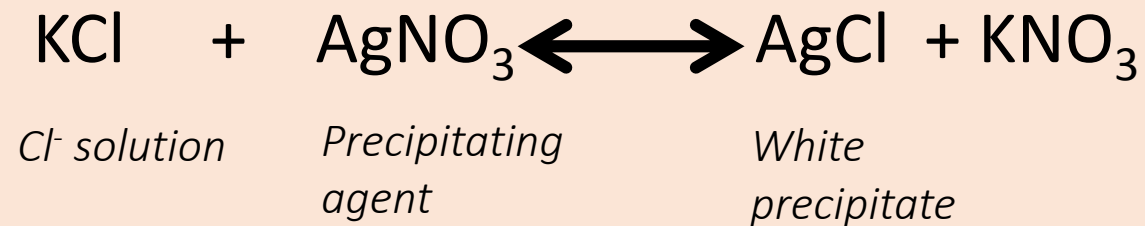# Precipitation Titration

Precipitation Reactions

❖ **Precipitation** is the formation of a <u>solid</u> in a <u>solution</u>

❖ 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.

$$KCl \ + \ AgNO_3 \longleftrightarrow AgCl \ + KNO_3$$

Cl⁻ solution   *Precipitating agent*   *White precipitate*

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

Precipitation Titrations

- *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.*

3

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^-)

- Pseudohalides (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:

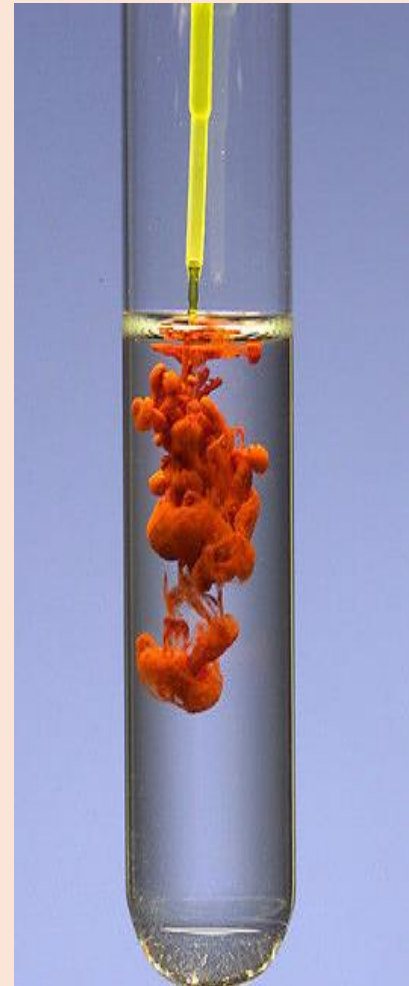- *Mohr's Method*

- *Fajan's Method*

- *Volhard'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 **silver chromate precipitate**,

- which signals the end point (1). The reactions are:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s) \qquad K_{sp} = 1.8 \times 10^{-10}$$
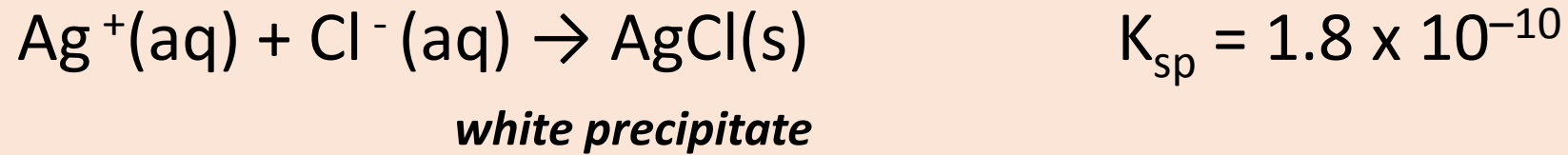
white precipitate

- **End point determination by brick red color precipitate, Ag₂CrO₄(s):**

$$2\,Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s) \qquad K_{sp} = 1.2 \times 10^{-12}$$
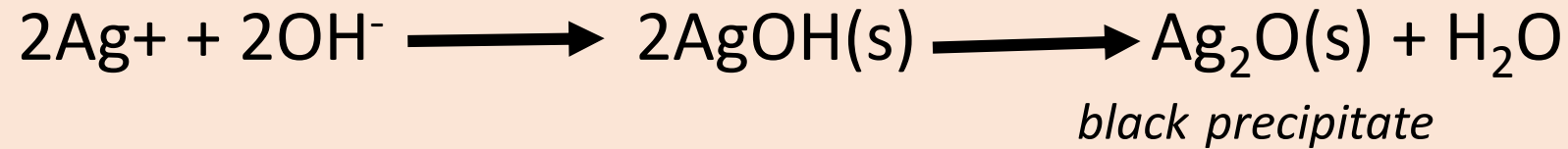
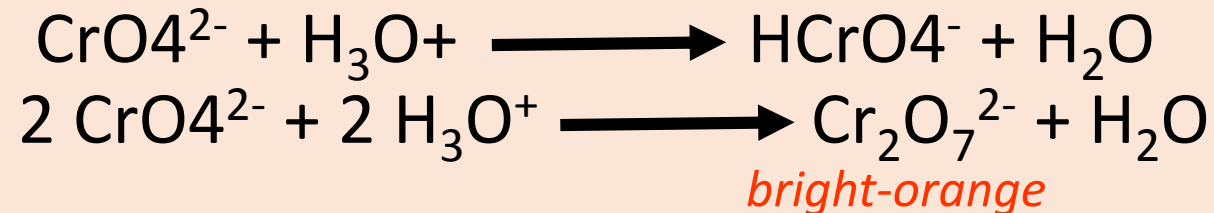- AgCl is less soluble than Ag_2CrO_4 so it will precipitate first

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 precipitate

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

$$CrO4^{2-} + H_3O+ \longrightarrow HCrO4^- + H_2O$$
$$2\ CrO4^{2-} + 2\ H_3O^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$

bright-orange

- Reducing [CrO4^{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 chlorides, bromides and iodides 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 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** <u>silver salt precipitate</u> 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⁻).**

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

The mechanism of indicators action:

- The best–known adsorption indicator is *fluorescein*, which is used to indicate the **equivalence point** in the titration of Cl^- with Ag^+. Fluorescein is a weak acid, which partially dissociates in water to form fluoresceinate anion.

HO ⌬⌬ OH   ⇌   HO ⌬O⌬ O⁻ + H +

Fluorescein   Fluoresceinate anion(Yellow green)
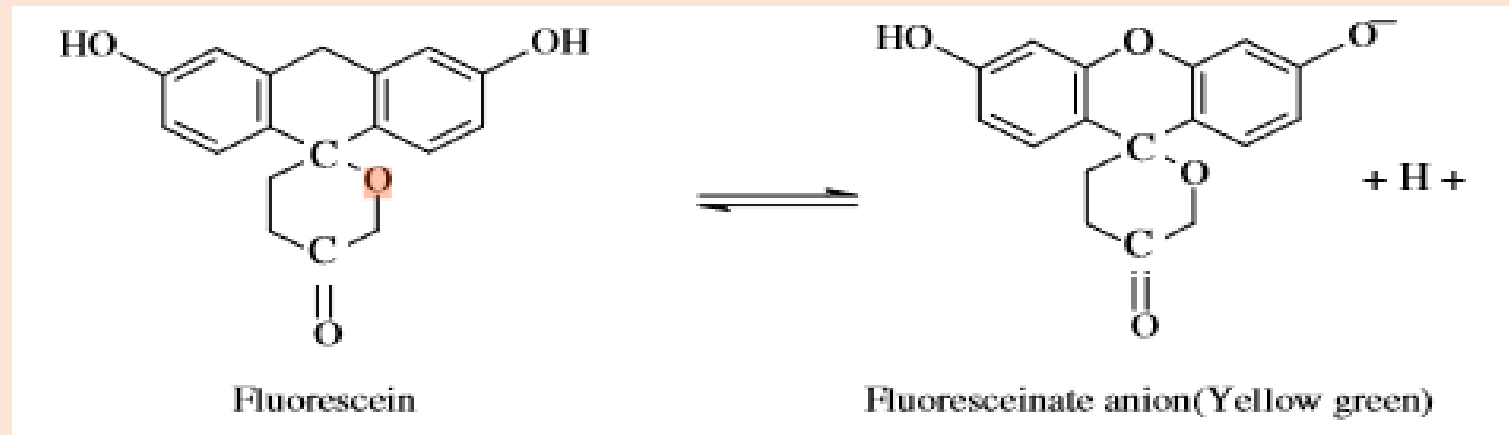
- The fluoresceinate anion has a *yellow–green colour* in solution.
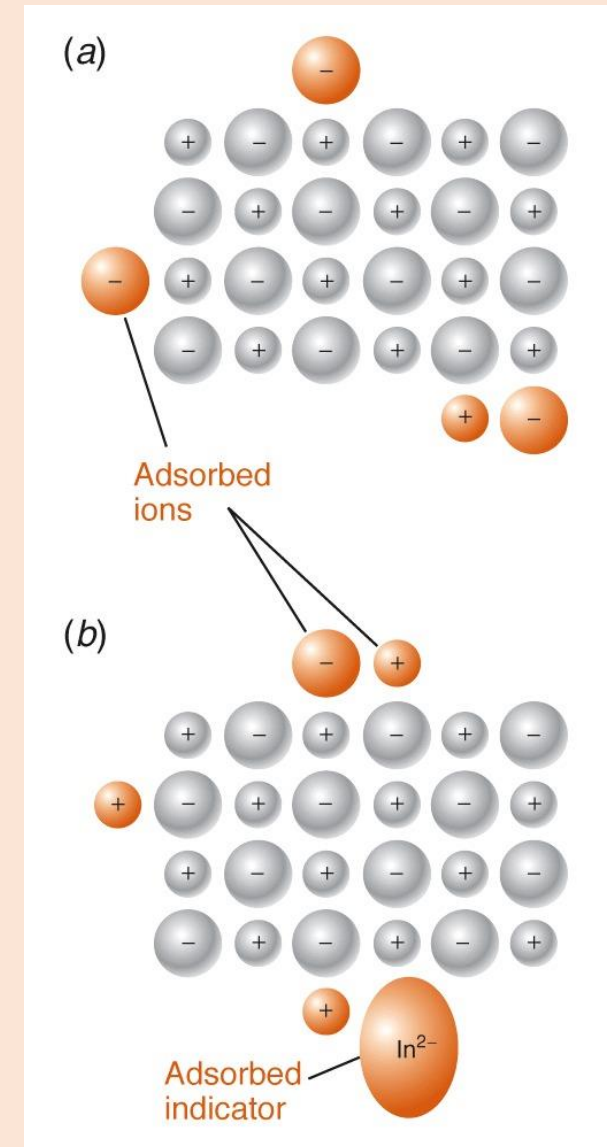
- When Cl⁻ is titrated with Ag⁺ in the presence of fluorescein, the **negatively charged fluoresceinate anions** are **initially repelled** by the **negatively charged AgCl colloidal** particles, with their primary **adsorption layer of Cl⁻ ions**.

- Thus the **fluorescein** remains in a *yellow–green colour* prior to the equivalence point.

- *At the equivalence point*, the colloidal AgCl particles undergo an abrupt change from a **negative charge** to a **positive charge** by **virtue of Ag⁺ ions adsorbed in the primary adsorption layer**.

- The **fluoresceinate ions** are strongly **adsorbed** in the counter–ion layer of the AgCl colloids, giving these particles a **red colour** and providing an **end point colour change** from **yellow–green** to **red** or **pink**.

- 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

Plots of titration curves are normally sigmoidal curves consisting of pAg (or pAnalyte) versus volume of $AgNO_3$ solution added.

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,

$$K_{sp} = [Ag^+][Cl^-]$$
$$logK_{sp} = -\log([Ag^+][Cl^-])$$
$$logK_{sp} = -\log[Ag^+] - log[Cl^-]$$
$$pK_{sp} = pAg^+ + pCl^-$$
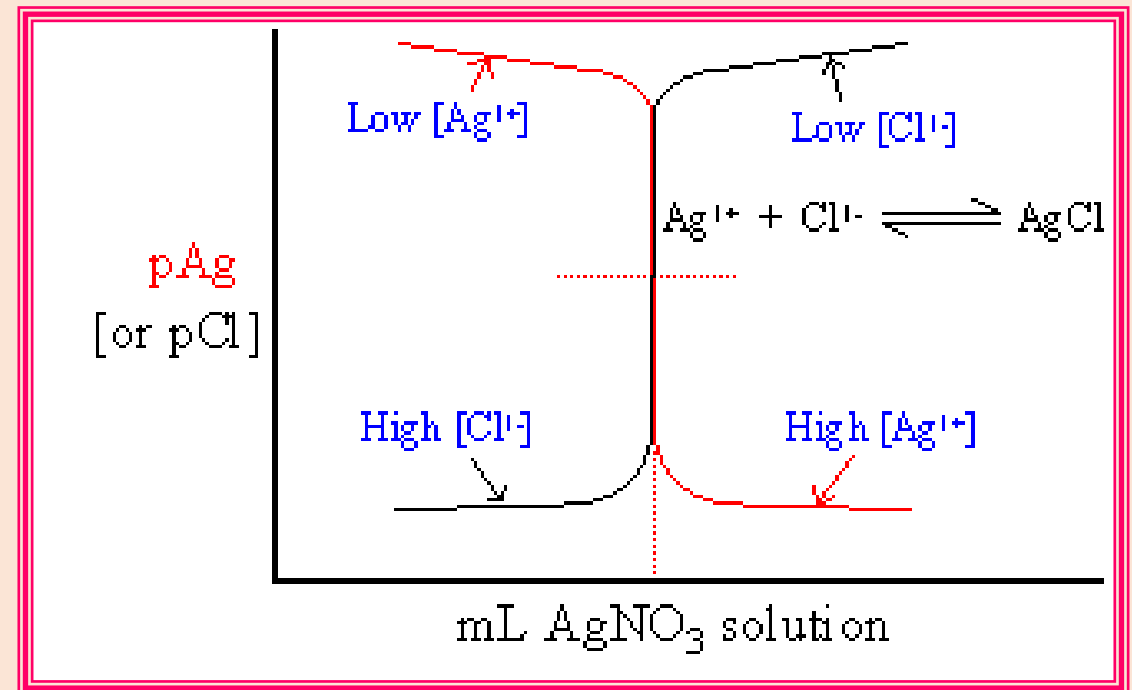
The points on the curve can be calculated, given the analyte concentration, $AgNO_3$ concentration and the appropriate K_{sp}.

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.

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

- 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, 99.5, 100.0 and 110.0 ml $AgNO_3$. K_{sp} AgCl is 1.0×10^{-10}

Solution

a) Addition of 0.0 ml Ag^+

$$[Cl^-] = 0.100 \text{ M}$$

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

$$= -\log 0.100$$

$$= 1$$

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

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

$$pCl = -\log [Cl^-]$$
$$= -\log 0.0667$$
$$= 1.18$$

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

$[Cl^-]$ left = $\dfrac{0.1}{(100+99)ml}$ = 5.01 x10^{-4} M

pCl = -log $[Cl^-]$

= -log 5.01 x10^{-4}

= 3.3

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 x10^{-10}

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

= 1.0 x 10^{-5}

pCl = -log 1.0 x10^{-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

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

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

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

     = 6.4