



Ministry of Higher Education
and Scientific Research
Alrasheed college university
Pharmacy department

Lecture (4)

- **Acid – Base Indicators**
- **Titration one Base or Mixture of two Bases with Strong Acid**
- **Precipitation titrations**
- **Determination of End point for precipitation**



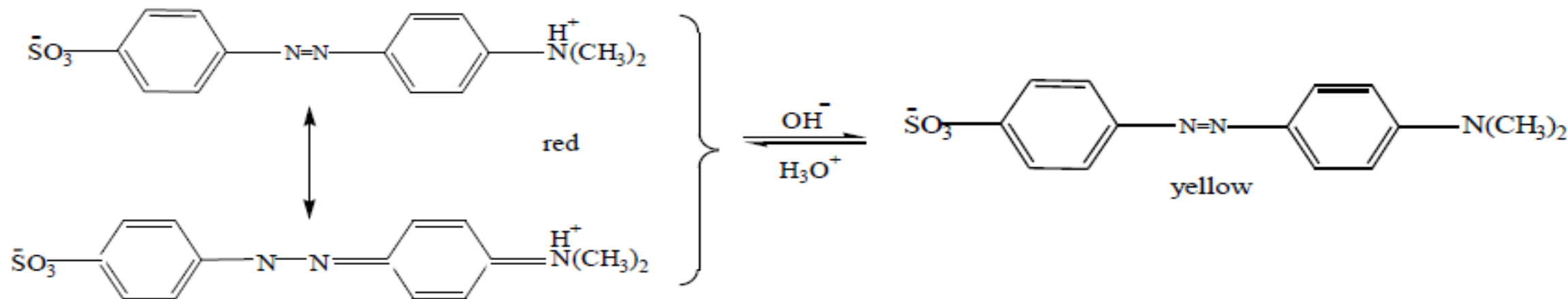
Acid – Base Indicators

The acid – base indicator is a weak organic acid or base whose undissociation form differs in color from its conjugate form.

Examples of acid-base indicators.

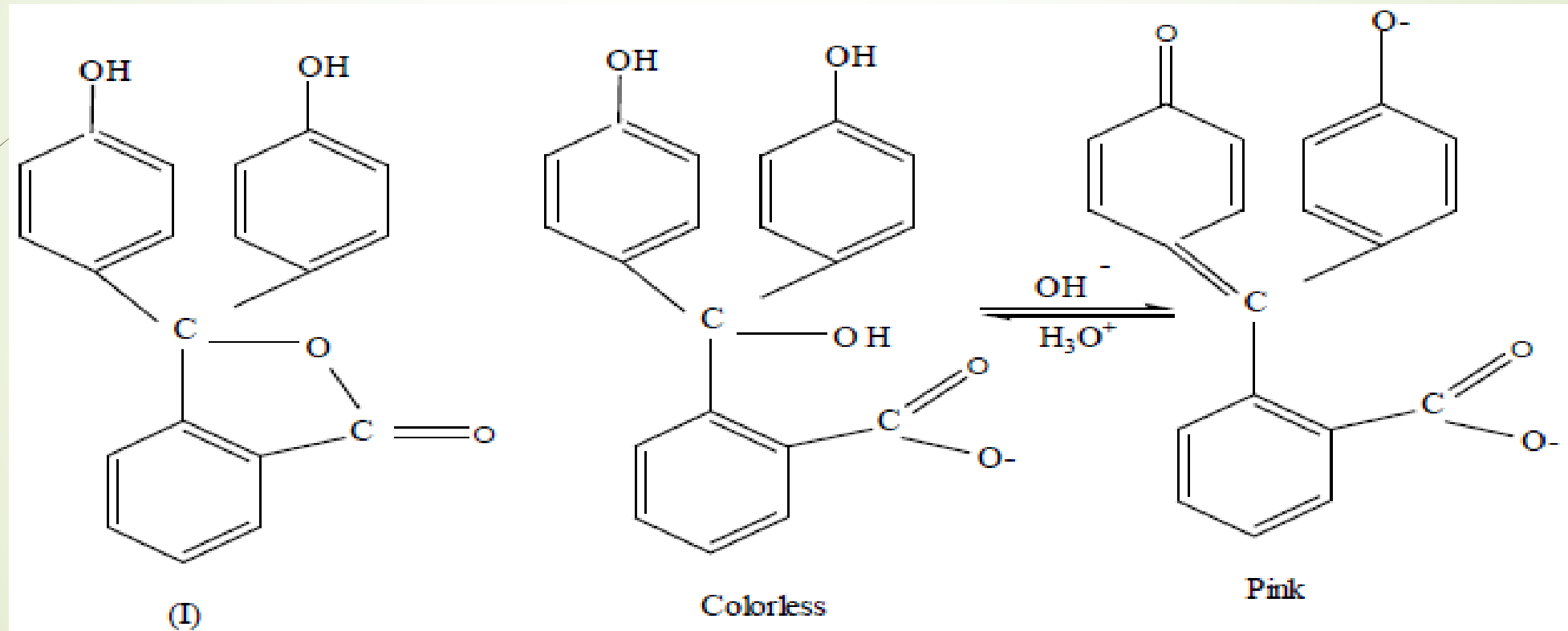
✓ Methyl Orange

It is benzenesulphonic acid, 4-[[4-(dimethylamino)phenyl]azo]-, whereas its chemical structure .



✓ Phenolphthalein

It is 1(3H)-isobenzofuranone, 3,3-bis(4-hydroxyphenyl) its chemical structure(I) is :





Titration one Base or Mixture of two Bases with Strong Acid

- The analysis of such mixtures (containing Na_2CO_3 , NaHCO_3 and NaOH , either alone or admixed) requires two titrations: one with an alkaline range indicator, such as phenolphthalein, and the other with an acid-range indicator, such as methyl Orange.
- The composition of the solution can then be deduced from the relative volumes of acid needed to titrate the sample.

Sample	Indicator		Volume of HCl, mL
	ph.ph (change solution from pink to colorless)	M.O (change solution from yellow to red)	
NaOH	$V_1 = \text{NaOH}$	----	V_1
NaHCO_3	----	$V_2 = \text{NaHCO}_3$	V_2
Na_2CO_3	$V_1 = 1/2 \text{Na}_2\text{CO}_3$	$V_2 = 1/2 \text{Na}_2\text{CO}_3$	$V_1 = V_2$
$\text{NaOH} + \text{Na}_2\text{CO}_3$	$V_1 = \text{NaOH} + 1/2 \text{Na}_2\text{CO}_3$	$V_2 = 1/2 \text{Na}_2\text{CO}_3$	$V_1 > V_2$
$\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$	$V_1 = 1/2 \text{Na}_2\text{CO}_3$	$V_2 = \text{NaHCO}_3 + 1/2 \text{Na}_2\text{CO}_3$	$V_1 < V_2$

Example 1:-

A 30mL of mixture of two bases is titrated with 0.1 N HCl. If the mixture requires 25 mL of acid for reach to end point of phenolphthalein indicator and 5mL of HCl for reach to end point of methyl orange indicator. Identify the bases and calculate the normality of each base.

Solution:

$$V_1 = 25 \text{ mL} \quad , \quad V_2 = 5 \text{ mL} \quad \Rightarrow \quad V_1 > V_2$$

The mixture is NaOH and Na_2CO_3

$$V_1 = \text{NaOH} + 1/2 \text{Na}_2\text{CO}_3 \quad , \quad V_2 = 1/2 \text{Na}_2\text{CO}_3$$

$$V_{\text{HCl}} = \text{Na}_2\text{CO}_3 = V_2 \times 2 = 5 \times 2 = 10 \text{ mL}$$

$$V_{\text{HCl}} = \text{NaOH} = V_1 - V_2 = 25 - 5 = 20 \text{ mL}$$

no. meq of HCl = no. meq of Na_2CO_3

$$N_{\text{HCl}} \times V_{\text{HCl}} = N_{\text{Na}_2\text{CO}_3} \times V_{\text{Na}_2\text{CO}_3}$$

$$0.1 \times 10 = ? \times 30 \quad \Rightarrow \quad N_{\text{Na}_2\text{CO}_3} = 0.033$$

no. meq of HCl = no. meq of NaOH

$$N_{\text{HCl}} \times V_{\text{HCl}} = N_{\text{NaOH}} \times V_{\text{NaOH}}$$

$$0.1 \times 20 = ? \times 30 \quad \Rightarrow \quad N_{\text{NaOH}} = 0.067$$

Example 2:-

A 10mL of mixture of two bases is titrated with 0.1 N HCl. If the mixture requires 15 mL of acid for reach to end point of phenolphthalein indicator and 40 mL of HCl for reach to end point of methyl orange indicator. Identify the bases and calculate the normality of each base.

Solution:

$$V_1 = 15 \text{ mL} \quad , \quad V_2 = 40 \text{ mL} \quad \Rightarrow V_1 < V_2$$

The mixture is Na_2CO_3 and NaHCO_3

$$V_1 = 1/2 \text{ Na}_2\text{CO}_3 \quad , \quad V_2 = \text{NaHCO}_3 + 1/2 \text{ Na}_2\text{CO}_3$$

$$V_{\text{HCl}} = \text{Na}_2\text{CO}_3 = V_1 \times 2 = 15 \times 2 = 30 \text{ mL}$$

$$V_{\text{HCl}} = \text{NaHCO}_3 = V_2 - V_1 = 40 - 15 = 25 \text{ mL}$$

no. meq of HCl = no. meq of Na_2CO_3

$$N_{\text{HCl}} \times V_{\text{HCl}} = N_{\text{Na}_2\text{CO}_3} \times V_{\text{Na}_2\text{CO}_3}$$

$$0.1 \times 30 = ? \times 10 \quad \Rightarrow N_{\text{Na}_2\text{CO}_3} = 0.3$$

no. meq of HCl = no. meq of NaHCO_3

$$N_{\text{HCl}} \times V_{\text{HCl}} = N_{\text{NaHCO}_3} \times V_{\text{NaHCO}_3}$$

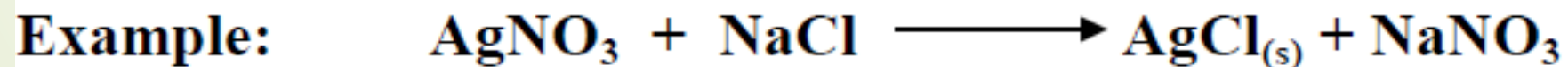
$$0.1 \times 25 = ? \times 10 \quad \Rightarrow N_{\text{NaHCO}_3} = 0.25$$

Precipitation titrations

Precipitation titration is a titration in which the reaction between the analyte and titrant involves a precipitate.

Conditions for Precipitation Titrations

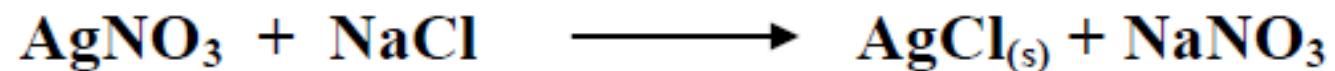
- ✓ The formed precipitate is insoluble in water.
- ✓ The precipitation process is rapidly occurred.
- ✓ The distinguishing of end point is readily by using visual indicator.



Example 4:-

Calculate the pAg and pCl of the solution during the titration 50 mL of 0.05 M NaCl with 0.1 M AgNO₃ after the addition the following volumes of reagent: 0 , 5 ,10 , 15 , 20 , 25 , 30 , 35 , 40 , 45 , 50 mL. If K_{sp} of AgCl=1.8×10⁻¹⁰.

Solution:



- **Initial point**

Before any AgNO₃ is added, [Ag⁺] = 0 and pAg is indeterminate.

[NaCl] = 0.05 M = [Cl⁻] and pCl = -log[Cl⁻] = -log 0.05 \implies pCl= 1.30

• **After Addition of 10 mL of AgNO₃**

Initial mmol Cl⁻ = 50 mL × 0.05 mmol/mL = 2.5 mmol

mmol Ag⁺ added = 10 mL × 0.1 mmol/mL = 1 mmol

	Ag ⁺	+	Cl ⁻	↔	AgCl
Initial (mmol)	1		2.5		0
Equilibrium (mmol)	0		1.5		1

$$[\text{Cl}^-] = \frac{\text{Initial no. mmol NaCl} - \text{no. mmol AgNO}_3 \text{ added}}{\text{Total volume of solution}}$$

$$[\text{Cl}^-] = \frac{(0.05 \times 50) - (0.1 \times 10)}{50 + 10} = \frac{2.5 - 1}{60} = \frac{1.5}{60} = 0.025\text{M} = [\text{Cl}^-]$$

$$\text{pCl} = -\log[\text{Cl}^-] = -\log 0.025 \implies \text{pCl} = \mathbf{1.60}$$

$$K_{\text{sp}} = [\text{Ag}^+] \times [\text{Cl}^-] \implies [\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Cl}^-]} = \frac{1.8 \times 10^{-10}}{0.025} = 7.2 \times 10^{-9} \text{ M}$$

$$\text{pAg}^+ = -\log[\text{Ag}^+] = -\log 7.2 \times 10^{-9} \implies \text{pAg} = \mathbf{8.14}$$

- **After Addition of 15 mL of AgNO₃**

Initial mmol Cl⁻ = 50 mL × 0.05 mmol/mL = 2.5 mmol

mmol Ag⁺ added = 15 mL × 0.1 mmol/mL = 1.5 mmol

	Ag ⁺	+	Cl ⁻	↔	AgCl
Initial (mmol)	1.5		2.5		0
Equilibrium (mmol)	0		1		1.5

$$[\text{Cl}^-] = \frac{(0.05 \times 50) - (0.1 \times 15)}{50 + 15} = \frac{2.5 - 1.5}{65} = \frac{1}{65} = 0.0154 \text{ M} = [\text{Cl}^-]$$

$$\text{pCl} = -\log[\text{Cl}^-] = -\log 0.0154 \quad \Rightarrow \quad \text{pCl} = 1.81$$

$$K_{\text{sp}} = [\text{Ag}^+] \times [\text{Cl}^-] \quad \Rightarrow \quad [\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Cl}^-]} = \frac{1.8 \times 10^{-10}}{0.0154} = 1.17 \times 10^{-8} \text{ M}$$

$$\text{pAg}^+ = -\log[\text{Ag}^+] = -\log 1.17 \times 10^{-8} \quad \Rightarrow \quad \text{pAg} = 7.93$$

Additional points defining the curve in the region before the equivalence point are obtained in the same way.

✓ Equivalence point

$$\text{Initial mmol Cl}^- = 50 \text{ mL} \times 0.05 \text{ mmol/mL} = 2.5 \text{ mmol}$$

$$\text{mmol Ag}^+ \text{ added} = 25 \text{ mL} \times 0.1 \text{ mmol/mL} = 2.5 \text{ mmol}$$

	Ag^+	+	Cl^-	\leftrightarrow	AgCl
Initial (mmol)	2.5		2.5		0
Equilibrium (mmol)	0		0		2.5

At the equivalence point neither NaCl nor AgNO₃ is in excess and $[\text{Ag}^+] = [\text{Cl}^-]$,

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

$$K_{sp} = [\text{Cl}^-]^2 \implies [\text{Cl}^-] = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5} \text{ M}$$

$$\text{pCl} = -\log[\text{Cl}^-] = -\log 1.3 \times 10^{-5} \implies \text{pCl} = 4.89 = \text{pAg}$$

- **After Addition of 35 mL of AgNO₃**

The solution now contains an excess of AgNO₃ .

$$\text{Initial mmol Cl}^- = 50 \text{ mL} \times 0.05 \text{ mmol/mL} = 2.5 \text{ mmol}$$

$$\text{mmol Ag}^+ \text{ added} = 35 \text{ mL} \times 0.1 \text{ mmol/mL} = 3.5 \text{ mmol}$$

	Ag^+	+	Cl^-	\leftrightarrow	AgCl
Initial (mmol)	3.5		2.5		0
Equilibrium (mmol)	1		0		2.5

$$[\text{Ag}^+] = \frac{\text{no. mmol AgNO}_3 - \text{Initial no. mmol NaCl}}{\text{Total volume of solution}}$$

$$[\text{Ag}^+] = \frac{(0.1 \times 35) - (0.05 \times 50)}{35 + 50} = \frac{3.5 - 2.5}{85} = \frac{1}{85} = 0.0118 \text{ M} = [\text{Ag}^+]$$

$$\text{pAg}^+ = -\log[\text{Ag}^+] = -\log 0.0118 \quad \Rightarrow \quad \text{pAg} = 1.93$$

$$K_{\text{sp}} = [\text{Ag}^+] \times [\text{Cl}^-] \quad \Rightarrow \quad [\text{Cl}^-] = \frac{K_{\text{sp}}}{[\text{Ag}^+]} = \frac{1.8 \times 10^{-10}}{0.0118} = 1.53 \times 10^{-8} \text{ M}$$

$$\text{pCl} = -\log[\text{Cl}^-] = -\log 1.53 \times 10^{-8} \quad \Rightarrow \quad \text{pCl} = 7.82$$

- **After Addition of 50 mL of AgNO₃**

Initial mmol Cl⁻ = 50 mL × 0.05 mmol/mL = 2.5 mmol

mmol Ag⁺ added = 50 mL × 0.1 mmol/mL = 5 mmol

	Ag ⁺	+	Cl ⁻	↔	AgCl
Initial (mmol)	5		2.5		0
Equilibrium (mmol)	2.5		0		2.5

$$[\text{Ag}^+] = \frac{(0.1 \times 50) - (0.05 \times 50)}{50 + 50} = \frac{5 - 2.5}{100} = \frac{2.5}{100} = 0.025 \text{ M} = [\text{Ag}^+]$$

$$\text{pAg}^+ = -\log[\text{Ag}^+] = -\log 0.025 \quad \Rightarrow \quad \text{pAg} = 1.60$$

$$K_{\text{sp}} = [\text{Ag}^+] \times [\text{Cl}^-] \quad \Rightarrow \quad [\text{Cl}^-] = \frac{K_{\text{sp}}}{[\text{Ag}^+]} = \frac{1.8 \times 10^{-10}}{0.025} = 7.2 \times 10^{-9} \text{ M}$$

$$\text{pCl} = -\log[\text{Cl}^-] = -\log 7.2 \times 10^{-9} \quad \Rightarrow \quad \text{pCl} = 8.14$$

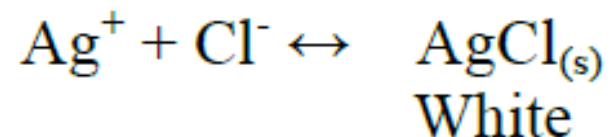
✚ Determination of End point for precipitation titrations: Indicator

There are three indicators used in precipitation titration, example argentometric titration, that is titration involving Ag^+ .

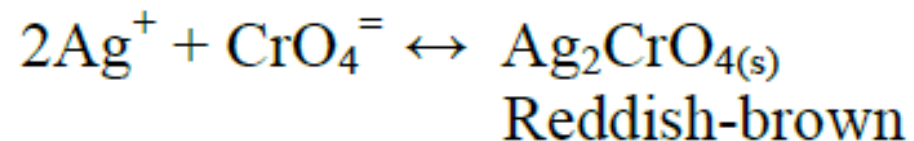
✓ **Mohr Method (formation of a colored precipitate)**

In Mohr titration, Ag^+ is titrated with Cl^- in the presence of $\text{CrO}_4^{=}$. When Cl^- has titrated completely with Ag^+ , the excess of small amount of Ag^+ will react with indicator ($\text{CrO}_4^{=}$) and form reddish-brown precipitate (Ag_2CrO_4) at the equivalent point.

Titration reaction:



Indicator reaction:



❖ Mohr method is dependent on:

1- The amount of indicator (K_2CrO_4)

The amount of K_2CrO_4 added is small enough that the end point is always later than the equivalence point. A free reagent blank is analyzed to determine the volume of $AgNO_3$ needed to change the indicator's color. The volume for the reagent blank is subtracted from the experimental end point to give the true end point.

2- The pH of solution

The Mohr method must be carried out at a pH of **7 to 10**. If the pH is too acidic, CrO_4^{2-} is present as $HCrO_4^-$, and the end point will be in significant error, because the CrO_4^{2-} concentration is too low to produce the reddish-brown precipitate at the end point.



If the pH > 10, the Ag^+ is precipitating as silver hydroxide.



3- Temperature

Mohr method is carried out at room temperature.

Example 4:-

A sample weighing 0.490 g is dissolved and titrated using Mohr method requiring 36.5 mL standard solution of 0.1 M AgNO₃. Calculate the percentage of chloride in the sample. (A.wt_{Cl}=35.43)

Solution:

no. mmol of Cl⁻ = no. mmol of AgNO₃

$$(M \times V)_{\text{Cl}^-} = (M \times V)_{\text{AgNO}_3}$$

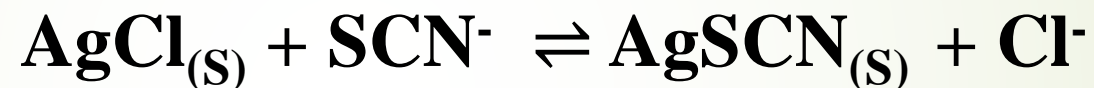
$$\frac{\text{wt}_{\text{Cl}^-}}{\text{A.mass}_{\text{Cl}^-}} \times \frac{1000}{V_{\text{Cl}^-}(\text{mL})} \times V_{\text{Cl}^-}(\text{mL}) = (M \times V)_{\text{AgNO}_3}$$

$$\frac{\text{wt}_{\text{Cl}^-}}{35.43} \times 1000 = 36.5 \times 0.1 \Rightarrow \text{wt}_{\text{Cl}^-} = 0.1293 \text{ g}$$

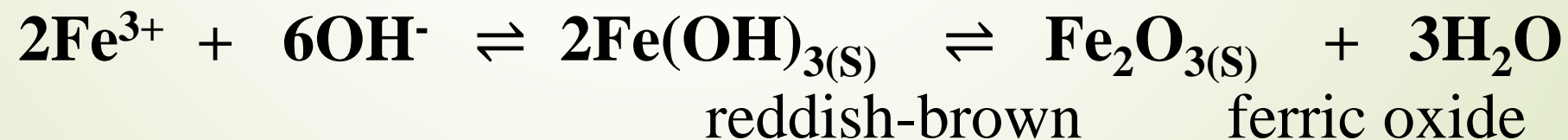
$$\% (\text{w/w})_{\text{Cl}^-} = \frac{0.1293}{0.490} \times 100 = 26.39$$

✓ Important notes:

In case of determination of Cl^- , the AgCl precipitate must be filtrated to avoid this reaction:



This reaction will happen because AgCl is more soluble than AgSCN . The Volhard method must be carried out in acidic solution to prevent precipitation of iron (III) as the hydrate oxide.



✓ Fajan Method (adsorption indicators)

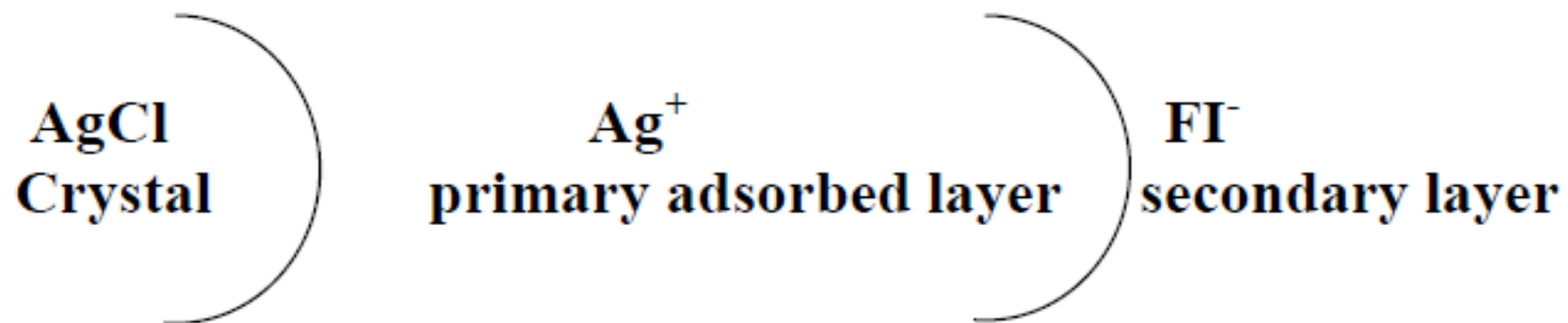
- Fajan method uses indicators that can adsorb onto the precipitate at the end point of titration.
- When the indicator is adsorbed onto the surface of the precipitate, the compound structure will change and the color will be different, hence the end point of titration can be detected.
- Indicator, such as fluorescein (written as HFI), which can exist as an ionized form (anion form), example FI^- . In the titration between Ag^+ with Cl^- , before the equivalence point, Cl^- is in excess, hence the primary adsorbed layer is Cl^- and will repulse anion from the indicator.

Before equivalence point:



- At the equivalent point, Cl^- had reacted completely with Ag^+ . When Ag^+ is added in excess, the primary layer consists of Ag^+ .

After equivalence point:



- The indicator (FI^-) will adsorb onto the surface of the precipitate. The color of the adsorbed indicator will change, and that will mark the end point in titration.



Thank you



Thank you