

Analytical Chemistry

1st stage students

Gravimetric analysis

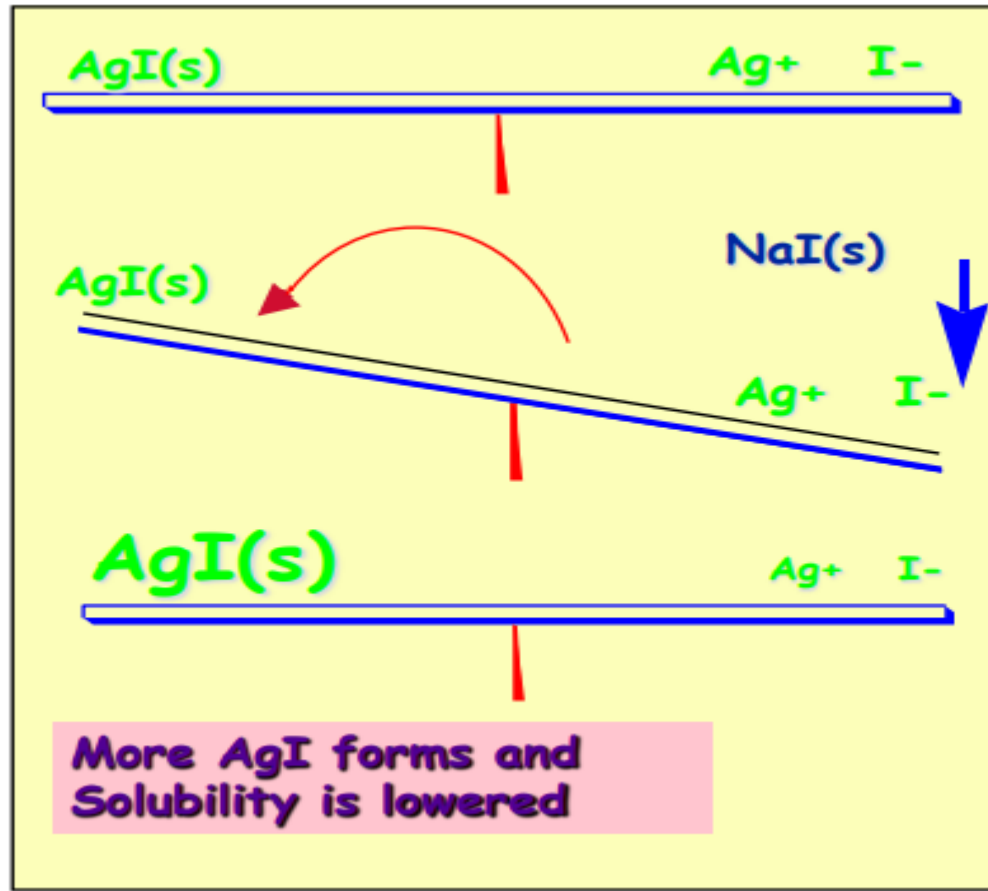
Lecture I

by/ Dr. khawla salman

Solubility

- Solubility is defined as the upper limit of solute that can be dissolved in a given amount of solvent at equilibrium.
- In such an equilibrium, Le Chatelier's principle can be used to explain most of the main factors that affect solubility.
- Le Châtelier's principle dictates that the effect of a stress upon a system in chemical equilibrium can be predicted in that the system tends to shift in such a way as to alleviate that stress.

according to LeChatelier



Solubility

Solubility of precipitate is defined as disappearance of atoms or molecules or ions of solute through atoms or molecules of solvent. Or it refers to the amount of solute capable to dissolve in a volume of solvent. Therefore, the chemical substances can be classified depends upon its solubility to: soluble, or partially soluble, or insoluble.

solubility product constant K_{sp}

K.S.P is an important constant which is applied to saturated solution of slightly soluble but completely ionized such as salts or metal hydroxide.

It is calculate from multiplying of anion and cation concentrations:



solubility product constant K_{sp}



$$K_{sp} = [A^+][B^-]$$



$$K_{sp} = [A^{+n}]^m [B^{-m}]^n$$

Solubility

EX9: What is the solubility of PbI_2 , in g/L, if the solubility product is 7.1×10^{-9} ?

Solution

The equilibrium is $\text{PbI}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{I}^-$, and $K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^-]^2 = 7.1 \times 10^{-9}$. Let s represent the molar solubility of PbI_2 . Then

$$[\text{Pb}^{2+}] = s \quad \text{and} \quad [\text{I}^-] = 2s$$

$$(s)(2s)^2 = 7.1 \times 10^{-9}$$

$$s = \sqrt[3]{\frac{7.1 \times 10^{-9}}{4}} = 1.2 \times 10^{-3} \text{ M}$$

Therefore, the solubility, in g/L, is

$$1.2 \times 10^{-3} \text{ mol/L} \times 461.0 \text{ g/mol} = 0.55 \text{ g/L}$$

Solubility

EX6: The K_{sp} of AgCl at 25°C is 1.0×10^{-10} . Calculate the concentrations of Ag^+ and Cl^- in a saturated solution of AgCl, and the molar solubility of AgCl?

Solution

When AgCl ionizes, equal amounts of Ag^+ and Cl^- are formed; $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$ and $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$. Let s represent the molar solubility of AgCl. Since each mole of AgCl that dissolves gives one mole of either Ag^+ or Cl^- , then

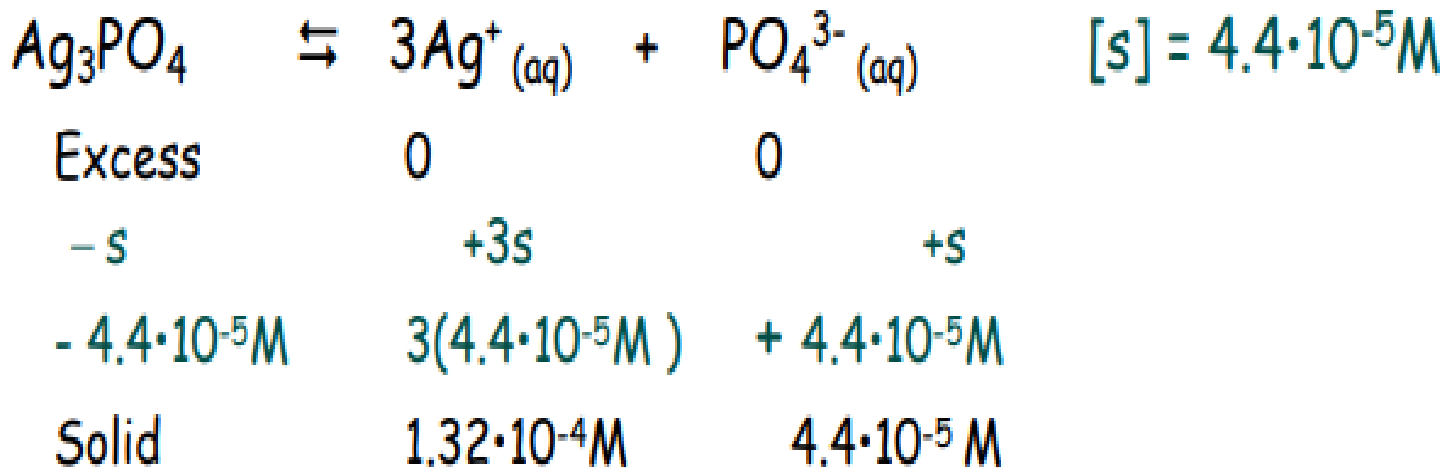
$$[\text{Ag}^+] = [\text{Cl}^-] = s$$

$$s^2 = 1.0 \times 10^{-10}$$

$$s = 1.0 \times 10^{-5} \text{ M}$$

The solubility of AgCl is $1.0 \times 10^{-5} \text{ M}$. 

Example :What is the solubility product K_{sp} , for the following reactions:



Solubility: $K_{sp} = [1.32 \cdot 10^{-4}]^3 \cdot [4.4 \cdot 10^{-5}] = 1.01 \cdot 10^{-16}$

Factors Affecting Solubility (s).

- Polarity(Nature of Solute)
- In most cases solutes dissolve in solvents that have a similar polarity. "Like dissolves like". Non-polar solutes do not dissolve in polar solvents and the other way round.
- Temperature Factor
- Solids/Liquids- Solubility increases with Temperature (mostly) Increase increases motion and collision between solute / solvent.
- gas - Solubility decreases with Temperature Increase. result in gas escaping to atmosphere.

Factors Affecting Solubility (s).

- **Pressure Factor**
- Solid and liquid solutes, pressure does not affect solubility.
- Gas solutes, Solubility increases with Pressure.
- **Common ion effect :**
- in chemical equilibrium , Le Chatelier principle predicted that the solubility of ionized substances or electrolyte is reduce with extent of excess amount of ions that formed the substance in a solution .

Factors effecting the solubility of precipitates

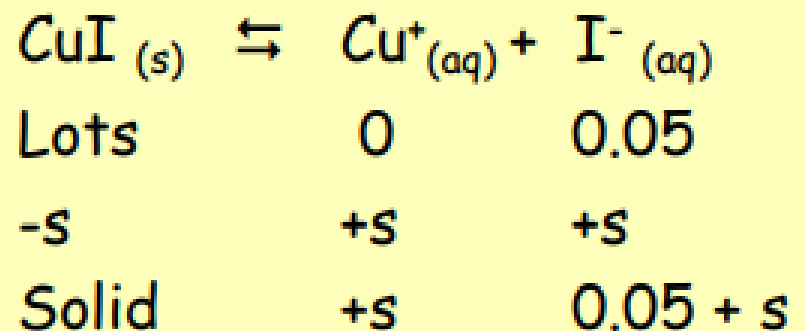
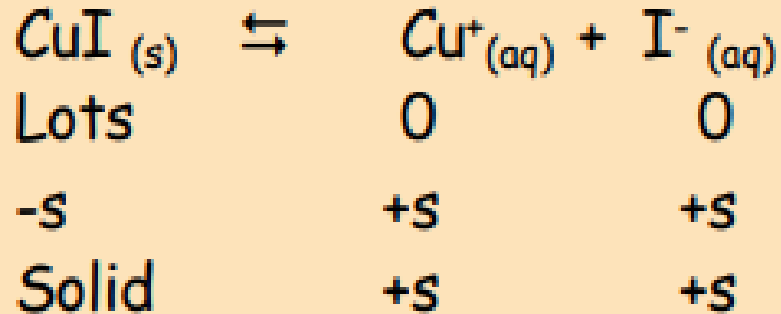


$$X = [\text{Ag}^+] = [\text{Cl}^-] = \sqrt{K_{\text{SP}}}$$



The common ion effect is reduce the solubility of the precipitate.

Calculate the solubility of copper(I) iodide, CuI ($K_{sp} = 1.1 \cdot 10^{-12}$)
 a) water b) 0.05 M sodium iodide



a) $K_{sp} = 1.1 \cdot 10^{-12} = [\text{Cu}^+][\text{I}^-] = s^2$
 $1.05 \cdot 10^{-6} = s$

b) $K_{sp} = 1.1 \cdot 10^{-12} = [\text{Cu}^+][\text{I}^-]$
 $= s * (0.05\text{M} + s)$
 $= s * (0.05\text{M})$
 $2.0 * 10^{-11} = s$

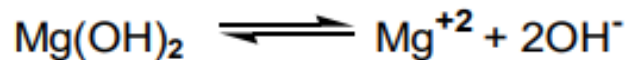
Without common ion, solubility is, $s = 1.05 \cdot 10^{-6} \text{ M}$
 but with common ion, solubility is, $s = 2.0 \cdot 10^{-11} \text{ M}$

Factors effecting the solubility of precipitates

Effect of hydronium ion concentration (pH) :

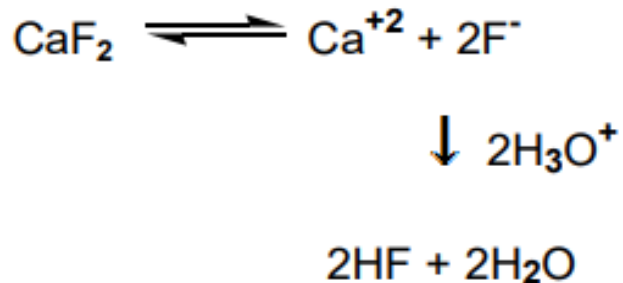
Precipitates are effected by hydronium or hydroxyl ion concentration of solvent . There are two types of these effects :

a) when $[H_3O^+]$ or $[OH^-]$ is a part of precipitating compound .



Solubility of precipitate will decreasing with increase of $[OH^-]$ concentration.

b) second type is more complicated from the first , when anion or cation of precipitate is capable to react with $[H_3O^+]$ or $[OH^-]$ of solvent .

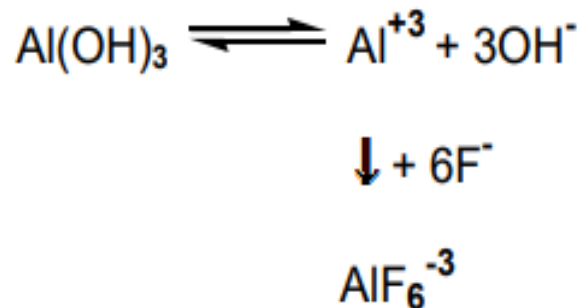


Factors effecting the solubility of precipitates

- CaF_2 is a salt of a weak acid (HF) , according to Le Chatelier principle , increasing in $[\text{H}_3\text{O}^+]$ concentration causes an increasing in HF concentration and decreasing in F^- concentration. then , solubility of precipitate will be increase.

Formation of complex ion :

The solubility of precipitate may be greatly altered with presence of some species that forms a soluble complex with anion or cation of the precipitate.



Factors effecting the solubility of precipitates

The precipitate of (Al^{+3}) with base is never complete in the presence of F^- ion even though $Al(OH)_3$ has low solubility, therefore, the compete is extremely between F^- and OH^- for Al^{+3} . when F^- concentration is increased, more of $Al(OH)_3$ is dissolved and converted to AlF_6^{-3} ions that will be more stable than $Al(OH)_3$.

Even though $AgCl$ is insoluble in water, it does dissolve in aqueous ammonia to form the complex ion $[Ag(NH_3)_2]^+$

But if the concentration of NH_3 is made high enough ...

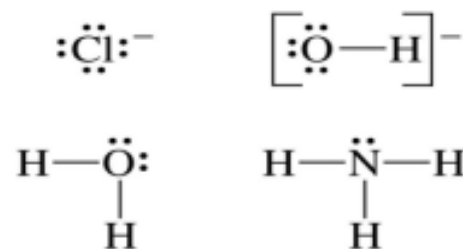
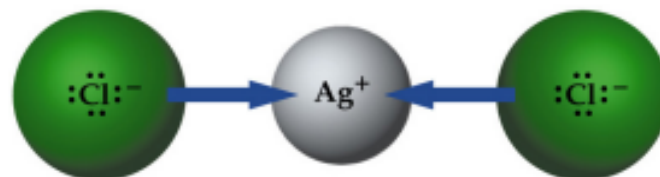
AgCl is insoluble in water.

... the $AgCl$ forms the soluble $[Ag(NH_3)_2]^+$ ion.

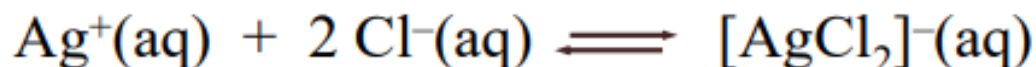
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Factors effecting the solubility of precipitates

- A **complex ion** consists of a central metal atom or ion, with other groups called **ligands** bonded to it.
- The metal ion acts as a Lewis acid (accepts electron pairs).
- Ligands act as Lewis bases (donate electron pairs).
- The equilibrium involving a complex ion, the metal ion, and the ligands may be described through a **formation constant, K_f** :



Common ligands



$$K_f = \frac{[\text{AgCl}_2]^{-}}{[\text{Ag}^+][\text{Cl}^-]^2} = 1.2 \times 10^8$$

Effect of electrolyte concentration on solubility

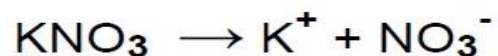
- Note: There are two important generalization to explain the influence of electrolyte concentration on solubility :
 - a) The magnitude of the effect is highly dependent upon the **charges of the species involved in the equilibrium**.
 - b) The effect are essentially independent of the kind of electrolyte and dependent only upon concentration parameter of the solution called **ionic strength** .

Ionic strength (μ) = $\frac{1}{2} \sum c_i z_i^2$ where : c_i = conc. of ions .

z_i = charge of ions .

Factors effecting the solubility of precipitates

EX. Calculate ionic strength of 0.1M sol. of KNO_3 and for 0.1M sol. Na_2SO_4 ?



$$\mu = \frac{1}{2} (0.1 \times 1^2 + 0.1 \times 1^2) = 0.1$$



$$\mu = \frac{1}{2} (0.2 \times 1^2 + 0.1 \times 2^2) = 0.3$$

Argentometric Titrations

Titrations with Ag^+ are called argentometric titrations.

For argentometric titrations, three classical methods based on color indicators can be used for endpoint detection:

- **Mohr titration**

Formation of colored precipitate at the end point.

- **Volhards titration**

Formation of a soluble, colored complex at the end point.

- **Fajans titration**

Adsorption of a colored indicator on the precipitate at the endpoint

MOHR METHOD

- The Mohr method was first published for chloride analysis.

1-) Direct method for determination halides

2-) In the precipitation of chloride by silver ion, chromate ion CrO_4 is used as an indicator.

3-) At end point formation Ag_2CrO_4 , a reddish-brown precipitate formed .

-At first titration.



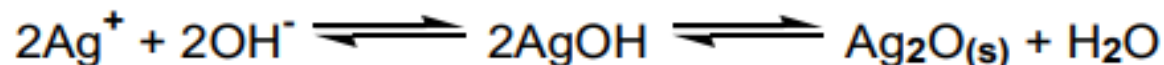
- Mohr indicator reaction (end point),



MOHR METHOD

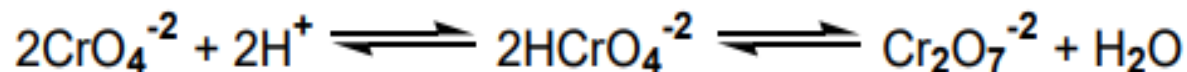
4-)The titrations are performed only in neutral or slightly basic medium(PH 7-10) to prevent silver hydroxide formation

*at pH > 10.



↓
black precipitate

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



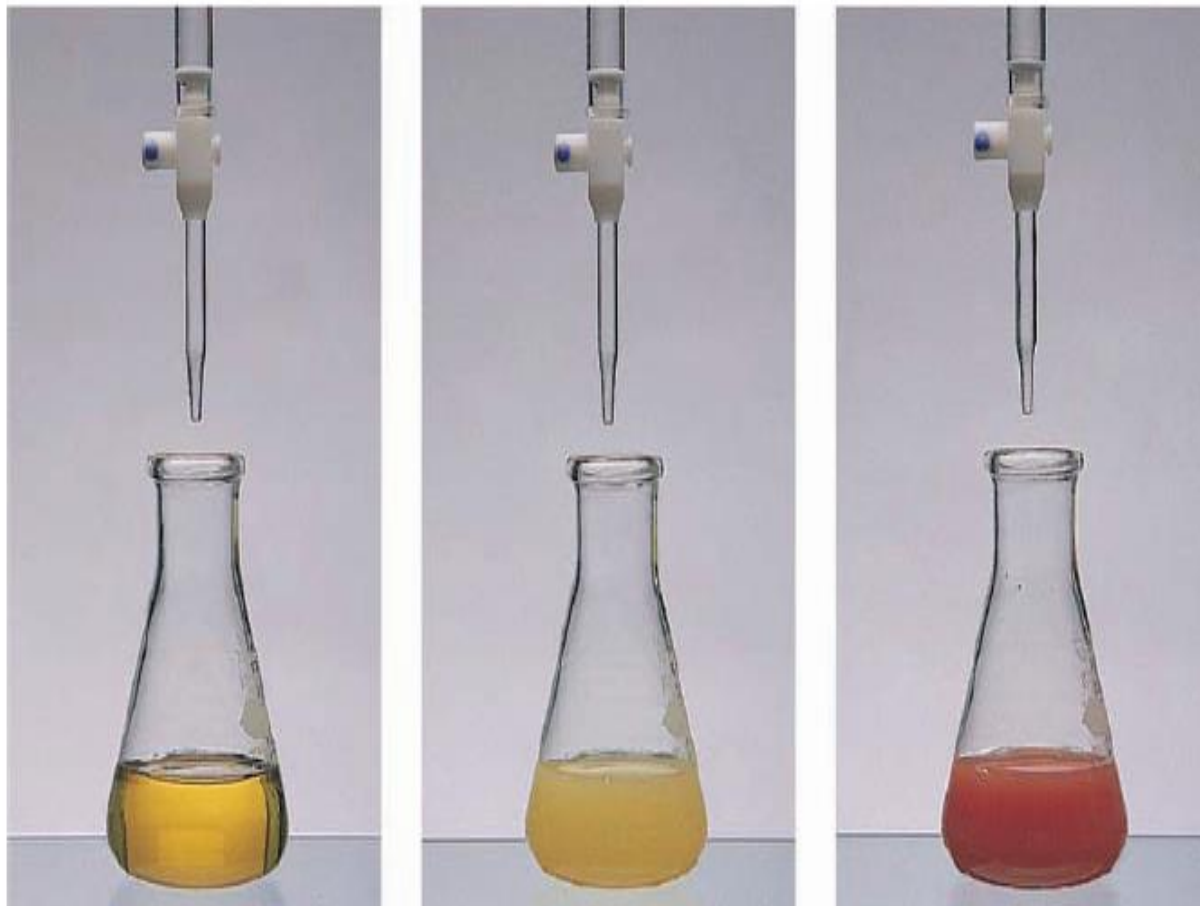
[CrO₄]become lower , more Ag⁺ to be added to reach endpoint, which cause error.

MOHR METHOD

FIGURE 17.5 ▶

Titration of chloride ion by silver nitrate using potassium chromate as an indicator

Left: A small amount of K_2CrO_4 (yellow) has been added to a solution containing an unknown amount of Cl^- ion. *Center:* The solution is titrated by $AgNO_3$ solution, giving a white precipitate of $AgCl$. *Right:* When nearly all of the Cl^- ion has precipitated as $AgCl$, silver chromate begins to precipitate. Silver chromate, Ag_2CrO_4 , has a red-brown color, and the appearance of this color signals the end of the titration. An excess of Ag^+ was added to show the color of Ag_2CrO_4 more clearly.



VOLHARD METHOD

- Indirect method for determination of halides
- Determination of Cl⁻ For titration of silver ion with thiocyanate (SCN⁻)
- Used back titration for standard solution (KSCN)
- At end point red solution appears from Fe(SCN)²⁺ complex.
- Iron(III) used as an indicator.
- The titration is usually done in acidic medium (HNO₃) to prevent precipitation of iron hydroxides, Fe(OH)₃.

- Reactions:

- titrant -1-



- titrant -2-



VOLHARD METHOD

- The endpoint is routinely used for halide determinations where a known excess of silver ion is added to precipitate the halide ion, and the excess silver ion is back titrated using the thiocyanate /iron(III) as the indicator.
- The silver chloride precipitate is filtered, and the excess silver ion is titrated with thiocyanate producing a white precipitate of AgSCN .
- •Once the silver is consumed, the excess thiocyanate reacts with the iron(III) ion producing a red FeSCN^{2+} complex. Thus, the appearance of the red color at the endpoint.

VOLHARD METHOD

- The titration must be done in acidic medium to prevent the precipitate of Iron(III) as hydrated oxide (iron hydroxide) . also , most of ions in neutral or weak acid medium are gives a precipitate with Ag^+ . It found from the experimental ,
- volhared method can be applicated for the indirect determination of halides by measured the excess of standard silver nitrate sol. that added to the sample (halides) , and the excess of silver ion determine by back-titration with a standard thiocvanate sol.



VOLHARD METHOD

- To find the weight of Cl ion in sample
- 1-find the ml of AgNO₃ equivalent volume SCN⁻(back titration)
- $N_{\text{SCN}} \times V_{\text{SCN}} = N_{\text{AgNO}_3} \times (V \text{ ml AgNO}_3 ?)$
- 2-find the volume of AgNO₃ reacted with Cl
- $V_{\text{AgNO}_3 \text{ reacted with Cl}} = 20\text{ml} - V_{\text{AgNO}_3 ?}$
- Not. 20 ml the excess volume of AgNO₃ was added at beginning
- $N_{\text{AgNO}_3} \times V_{\text{AgNO}_3} = \text{Wt of Cl}^- / \text{eq.wt Cl}^- \times 100$
- $\text{Wt of Cl}^- = (\text{----})\text{gm}$

Fajans Method (Adsorption Indicators)

- **Adsorption indicators** are organic compounds that tend to be adsorbed on to the surface of the solid precipitate in a precipitation titration.

Fluoresceinate adsorbs to silver ions on the surface of a precipitate when excess silver ion is present, producing a reddish-colored surface

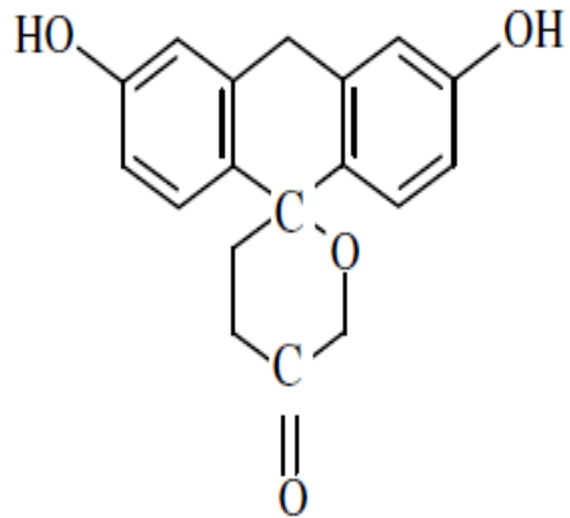
Fajans Method

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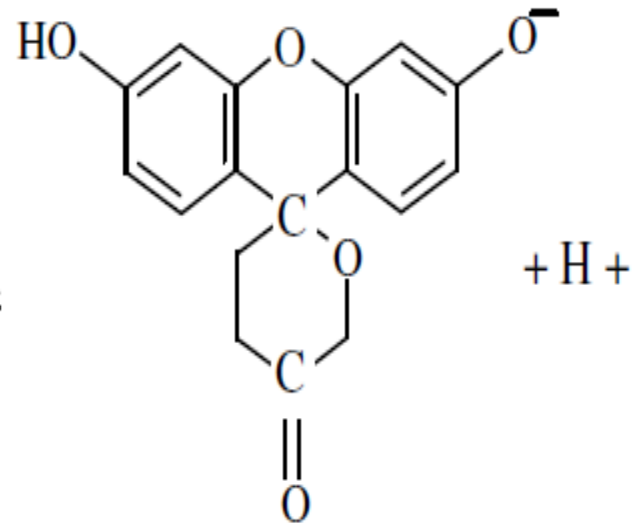
Titration of NaCl with AgNO₃

- $\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl(s)}$
- titrant analyte white precipitate
- During the titration, colloids are formed.
- Before the equivalence point, the surface of the precipitant particles will be negatively charged due to the adsorption of excess Cl⁻ on the surface of the particles. A diffuse positive counter-ion layer will surround the particles.
- The primary adsorption layer is negatively charged and the anionic indicator is repelled

Fajans Method



Fluorescein



Fluoresceinate anion (Yellow green) + H⁺