Lecture 11 - 12

PRECIPITATION TITRATION

- Precipitation titrations are based upon reactions that yield ionic compounds of limited solubility (insoluble).
- The most important precipitating reagent is silver nitrate. Titrimetric methods based upon silver nitrate are sometimes termed Argentometric methods.
- In a precipitation titration, the stoichiometric reaction is a reaction which produces in solution a slightly soluble salt that precipitates out.
- To determine the concentration of chloride ion in a particular solution, one could titrate this solution with a solution of a silver salt, say silver nitrate, whose concentration is known.
- The chemical reaction occurring is

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

Solubility product : $AgCl \leftrightarrows Ag^+ + Cl^-$

$$Ksp = [Ag^+].[Cl^-] / [AgCl]$$
$$= [Ag^+].[Cl^-]$$

This constant is called the **"solubility product "** or "Ksp".

$$Ksp\ AgCl = [Ag^+].[Cl^-].$$

Generally

$$Ksp.\ AxBy = [A^+]^x.[B^-]^y$$

- It is possible to calculate the solubility product from the solubility ,

  eg. If the solubility of AgCl in water is 0.0015g/L
- Molar Conc. = solubitiy /MW = 0.0015/143.5 = 1.05×10^{-5} .
- Since salts freely ionise , the conc. of salt = conc. of its ions
- $[AgCl] = [Ag^+] = [Cl^-] = 1.05 \times 10^{-5}$.
- $Ksp = [Ag^+].[Cl^-] = 1.05 \times 10^{-5} \times 1.05 \times 10^{-5} = 1.1 \times 10^{-10}$

  .

- We can **calculate the solubility** of slightly soluble compound from the solubility product ,

  eg. the solubility product of Ag_2CrO_4 = 2.4 x 10^{-12} ·

  Ksp of Ag_2CrO_4 = $[Ag^+]^2.[CrO_4^{2-}]$

- If conc.is represent by “A”

  then conc. of Ag_2CrO_4 will be “A” , that of Ag^+ “2A” , CrO_4^{2-} will be “A”

- Ksp = $(2A)^2$ x A = $2A^3$ = 2.4 x 10^{-12} ·
- A = 8.4 x 10^{-5} ·
- Since the molecular weight of the salt is 331.8
- The solubility = Molecular Conc x MW

  = 8.4 x10^{-5} **x** 331.8 = 0.0279 g/L

When a precipitate is formed ؟

- **A precipitate is formed in solution of spairingly soluble salts when the conc.of its ions in solution increase to an extent that the product of multiplication of their conc. exceeds the solubility product .**
- $[A^+].[B^-] > Ksp$
- **The formed ppt is affected by ions in common with it , which lowers the solubility .**
- **Salt like AM , $[A^+].[M^-] > Ksp$,**
- **Since the conc. of the ionised salt = the conc. of the ions , then the conc. of any ion such as $[A] = Ksp/[M]$**
- **When [M] is increase, the product of Ksp/[M] become smaller, and hence the conc. of A or AM is decreased i.e the conc. of the ionised part of salt should decrease by forming a ppt.**

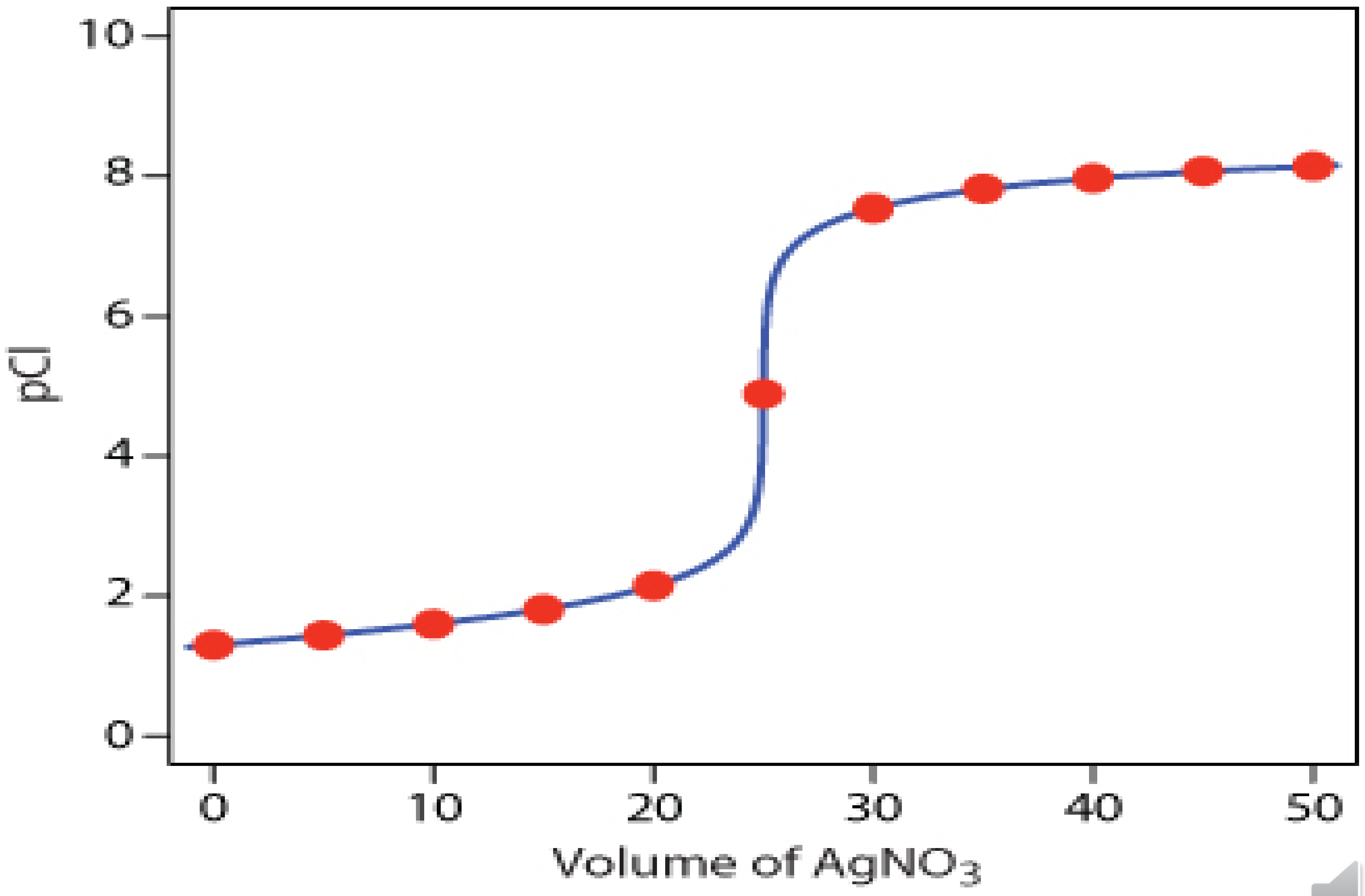
Fractional precipitation

- The solubility product can be used as index of insolubility , the smaller the solubility product the more springlly solule is the compound i.e. the compound with the smaller “S” is first precipitate when a precipitant is added to a mixture of precipitable ions . The more insoluble is precipitated first .
- **Ksp.AgCl =$[Ag^+].[Cl^-]$ = 1.05 x 10^{-10}**
- **KspAgBr =$[Ag^+].[Br^-]$ = 1.05 x 10^{-12}**
- **Ksp.AgI = $[Ag^+].[I^-]$ = 1.05 x 10^{-15}**
- **If $AgNO_3$ is added to to Cl^- ,Br^- and I^- solution , AgI is ppt first ,then AgBr , then AgCl .**

- Argentometric methods can be divided into two types :
- 1 - Direct determinations , in which a standard solution of silver nitrate is added to the sample solution until the end point is reached .
- 2 - Indirect determinations , in which an excess of silver nitrate is added to the sample solution and the excess silver nitrate is back titrated with another standard solution , usually ammonium or potassium thiocyanate .
- Direct titrations are to be preferred but it is not possible to apply the method in all cases .
- If the solubility of the precipitate formed during the titration is too great , the end point cannot be detected . In this case , it is better to add an excess of the reagent thereby repressing the solubility of the precipitate , and determine the excess by another method (Indirect Method).

Titration Curves

- In order to understand the theoretical basis of end points and the sources of titration errors , it is often helpful to derive *a titration curve* .
- titration curves consist of a plot of reagent volume as the abscissa and some function of the analyte or reagent concentration as the ordinate.


10
8
6
4
2
0
pCl
0
10
20
30
40
50
Volume of AgNO$_3$

- **Consider the titration of 100.0 ml of 0.1 M NaCl solution with a 0.1 M solution of $AgNO_3$. The solubility product constant for AgCl is 1.0×10^{-10} at 25 oC .**

1 - At the beginning of the titration :

- **The concentration of Cl- ions is 0.1 M (10^{-1}); pCl will thus be 1.0 , and 0.0M Ag+**

2 - During the titration but before the equivalence point :

a.After addition of 10.0 ml of $AgNO_3$ solution

$$CCl = \frac{90 \times 0.1}{110} = 6.7 \times 10^{-2}$$

pCl = 1.17

b. a.After addition of 50.0 ml of AgNO3 solution

$$CCl = \frac{50 \times 0.1}{150} = 3.3 \times 10^{-2}$$

pCl = 1.48

c.After addition of 90.0 ml of AgNO3 solution

$$CCl = \frac{10 \times 0.1}{190} = 5.3 \times 10^{-3}$$

pCl = 2.28

3 - At the equivalence point :

- This point is reached when 100.0 ml of AgNO3 solution have been added . The concentration of the two ions are therefore equal and readily calculated from the solubility product expression :
- $[Cl^-]$ = ⍰ KS = ⍰ $1.0 \times 10\text{-}^{10}$ = 1.0×10^{-5} mol/L
- pCl = 5.0

- The conc. of Ag+ in all the above calculation is easly calculated from the following equation :

$$[Ag^+].[Cl^-] = 1.05 \times 10^{-10}$$

$$p[Ag^+] + p[Cl^-] = 10$$

If pCl = 1.48 . pAg = 10 - 1.48 = 8.52

4 - After the equivalence point :

When 101 ml AgNO3 are added , 1 ml excess

$$CAg = \frac{1 \times 0.1}{201} = 5 \times 10^{-4}$$

pAg = 3.3

pCl = 10 - 3.3 = 6.76

FACTORS INFLUENCING THE SHARPNESS OF END POINTS

- A sharp and easily located end point is observed in titrations whose curves show sharp breaks in the region of the end point
- 1 - Reagent concentrations:

The break in the titration curve become more pronounced (Sharp EP) with increasing reagent concentration

2 - Solubility of the precipitate :

- Figure 3 demonstrate the effect of solubility on the sharpness of end points .
- Clearly , the greatest change in pAg occurs in the titration of iodide ion , which forms the least soluble silver salt and hence reacts most completely with silver ion . So the break (sharpness) at the end point decreases as Ksp increases (i.e. as the solubility of the precipitate increases).

- Argentometric methods may classified into three main methods depending on the indicator used and whether the titration is direct or indirect . The three methods are :

Endpoint Detection Methods

Mohr method (Formation of colored ppt.)(Direct)

The Mohr method is a titration scheme for analysis of anions that react with Ag^+ to form a precipitate(Cl^-, Br^- and CN^-). Ag^+ ($AgNO_3$) is added as the titrant. Potassium chromate can serve as an end point indicator by reacting with silver ions to form a brick-red silver chromate precipitate in the equivalence point region.

After the equivalence point, the excess Ag^+ reacts with chromate ion by the following reaction:

$Ag^+ + X^-$ (analyte) → $AgX(s)$

$2Ag^+$ (after eq. pt.) + CrO_4^{-2} → $Ag_2CrO_4(s)$

The $Ag_2CrO_4(s)$ is a orange-yellow precipitate. When the color change is observed, the titration is ceased.

- ## Limitation of Mohr's Method

1 - The titration should be carried out in neutral solution or in very faintly alkaline solution . i.e. in the pH range 7 - 9 .

In acid solution :

$$2\,CrO_4^{2-} + 2\,H^+ \;====\; 2HCrO_4^{-} == Cr_2O_7^{2-} + H_2O$$

$2HCrO_4^{-}$ is a weak acid , consequently the chromate ion concentration is reduced and the solubility product of silver chromate may not be exceeded (soluble dichromate , no clear E.P) .

- In markedly alkaline solution AgOH might be precipitated

$$2\,Ag^+ + 2\,OH^- \;----\; 2\,AgOH \;---\; Ag_2O \text{ (black ppt.)} + H_2O$$

- A convenience way of maintaining a suitable pH is to add an excess of solid sodium hydrogen carbonate or borax to the solution being titrated .
- In presence of Ammonium salts the pH must not exceed 7.2 because of the effect of ammonia upon the solubility of silver salts .

2 - Titration of iodide and thiocyanate is not successful because AgI and AgSCN absorb chromate ions so strongly that a false end point is obtained .

3 - The Mohr's method is not suitable to the determination of iodide because chromate ion oxidizes iodide ion to iodine .

Volhard method (formation of colored solution)Back titration

The Volhard method is used for titrating a solution containing Ag^+.

Other analytes(halides; Cl^-,Br^-,I-,CN^-.) are determined in coupled reaction schemes where the analyte reacts with excess Ag^+. The excess Ag^+ is then back-titrated with SCN^-. After the Ag^+/SCN^- equivalence point is reached, the excess SCN^- reacts with added Fe^{+3} (added in a small amount as an indicator) to form $FeSCN^{+2}$ which is a red complex.

Ag^+ (in excess) + X^- (analyte) → AgX(s)

Ag^+ (remaining excess) + SCN^- → AgSCN(s)

SCN^- (excess after equivalence point) + Fe^{+3} → $FeSCN^{+2}$

(red complex)

At the first observation of the red color, the titration is ended and the titrant volume is noted.

- **Interference and limitations**

1 - For chloride determination , we have the following two equilibrium during the titration of excess silver ion :

$$Ag^+ + Cl^- \ === \ AgCl$$

$$Ag^+ + SCN^- \ === \ AgSCN$$

- The two sparingly soluble salts will be in equilibrium with the solution , hence

$$\frac{[Cl^-]}{[SCN^-]} = \frac{Ks\ AgCl}{Ks\ AgSCN} = \frac{1.0 \times 10^{-10}}{7.1 \times 10^{-13}} = 140$$

- when the excess of silver ion has reacted , the thiocyanate may react with the AgCl , since AgSCN is the less soluble salt until the ratio [Cl-]/[SCN-] is 140 .
- This will take place_before reaction occurs with the ferric ions in the solution , and there will consequently be a considerable titration error .

- It is therefore necessary to prevent the reaction between the thiocyanate and silver chloride this may be affected by :
- a - The silver chloride is filtered off before back titration , the suspension should be boiled for a few minutes to coagulate the silver chloride and thus remove most of the adsorbed silver ions from its surface before titration , the cold filtrate is titrated with KSCN .
- b - An immiscible liquid is add to coat the silver chloride particles and thereby protect them from interaction with the thiocyanate . The most successful liquid is nitrobenzene (1.0 ml for each 50.0 ml of chloride) .

2 - With bromide and iodide determination there are no need for separation of the precipitated silver bromide or silver iodide as Ks AgBr = 3.5 x 10^{-13} ,

- KsAgI = 1.7 x 10^{-16} , i.e. thiocyanate ions would not react with AgBr or AgI .

3 - The titration is carried out **in acid medium(nitric acid** of concentration 0.2 to 1.6 M). Too high acid concentration will retard the formation of the colored Fe(SCN)$^{2+}$ complex . The nitric acid must also be free from nitrous acid as it gives a red color with tiocyanate which may be mistaken the end point . Too low acid concentration allow anions such as carbonate , phosphate , arsenate to interfere.

4 - The precipitated silver halide tends to adsorb silver ions from solution , therefore vigorous shaking near the end point is necessary .

5 - Titration should be done at $25^{o}C$ because above $25^{o}C$ nitric acid tends to bleach the colored $Fe(SCN)^{2+}$ complex , causing too low result .

6 - Ions which form stable complex with thiocyanate ion (e.g. Hg^{2+}) or with iron(III) (e.g. F^- , PO_4^{3-}) must be absent .

Fajans method (adsorption indicator method)Direct

During a precipitation titration, the precipitate that is formed has excess surface charge. If the ion in the titrand that is participating in the titration reaction has a negative charge, the precipitate will have an excess negative charge prior to the equivalence point. For example, if AgNO3 solution (titrant) is added through a buret to a solution containing Cl- (titrand), the titration reaction is:

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

Prior to the equivalence point, Cl- is in excess in the reaction solution and the AgCl thus formed will have a small negative surface charge. After the equivalence point Ag+ is in excess so the precipitate AgCl will have a positive surface charge.

- In the Fajans method, a small amount of a colored indicator is added to the titration solution. The indicator is an adsorption indicator that adsorbs to the surface of the precipitate particles from the titration reaction. The indicator changes color if the precipitate surface changes. Thus, the solution visibly changes color from before to after the equivalence point.
- The successful application of an adsorption indicator requires that the precipitate and the indicator should have the following properties :

1 - The particles of the precipitate must be of colloidal dimension in order to maximize the quantity of indicator adsorbed .

2 - The precipitate must strongly adsorb its own ion .

3 - The indicator dye must be strongly held in the counter ion layer by the primarily adsorbed ion . In general , this type of adsorption occurs when the solubility of the salt formed by the dye and the lattice ion is low . At the same time , this salt must be sufficiently soluble so that it does not precipitate .

4 - The pH of the solution must be such as to ensure that the ionic form of the indicator predominates . Because the active constituent of most adsorption indicators is an ion that is the conjugate acid or base of the dye molecule , the concentration of that ion is pH -dependent .

5 - High electrolyte concentrations must be avoided , because electrolytes tend to cause coagulation of the precipitate , a process that decreases the surface area on which adsorption occurs .

6 - Most adsorption indicators are weak acids . Their use is thus confined to basic , neutral , or slightly acidic solutions , where the indicator exists predominantly as the anion . A few cationic adsorption indicators suitable for titrations in strongly acidic solutions are known , however . For such indicators , adsorption of the dye and coloration of the precipitate occur in the presence of an excess of the precipitate anion (that is , when the precipitate particles possess a negative charge) .

Indicator	Use	Titrant	pH	Color change
Fluorescein	Cl^- , Br^- , I^- ,SCN^-	Ag^+	7.8	yellow-pink
Dichloro fluorescein	Cl^- , Br^- , I^- ,SCN^-	Ag^+	neutral	yellow-pink
Tetrabromo fluorescein (eosin)	Br^- , I^- ,SCN^-	Ag^+	2-8	pink-red
Diiodo fluorescein (erythrosin)	I^-	Ag^+	2-8	orange-violet
Dichloro-tetra iodo fluorescein (rose bengal)	I^-	Ag^+	neutral	carmine violet

Other precipitimetric Titrations

- 1 – Mercurous nitrate (HgNO3) or mercuric nitrate Hg(NO3)2 can be used for determination of Cl- and Br- .
- 2 – Potassium ferrocynide (K4Fe(CN)6 is used for detemination of Zn2-
- 3 – **Liebig-Deniges** method for determinatin of CN- using AgNO3 as titrant

Ag+ + CN- → AgCN

AgCN + excess CN- → Ag(CN2)- soluble complex

At end point Ag(CN2)- + Ag**+** → **2AgCN ppt (tubidity)**

Deniges _

improves the method by using KI /NH4OH as indicator

at the end point yellow ppt of AgI is formed .