Volumetric Precipitation Titration

Precipitation titrations are volumetric methods based on the formation of a slightly soluble precipitate. They are in many ways simpler than gravimetric methods. The precipitate needs not be separated, and needs not be pure, as long as the impurity does not consume titrant. The substance is determined simply by converting it into an insoluble form of known composition by adding a standard solution of the titrant. The equivalence point is reached when an equivalent amount of the titrant has been added. From the volume of the latter, the amount of the substance is calculated. The precipitate must be sufficiently insoluble to ensure completion of the reaction and to ensure a marked change in the concentration of the ions of precipitate at the equivalence point of the titration.
Ionic reactions are actually complete when any change occurs that lowers the concentrations of ions to very small values. The factor governing the completeness of a precipitation reaction is the solubility of the precipitate formed. The more insoluble the precipitate, the more complete is the reaction at the equivalence point of the titration, and the larger is the change in concentration of the reacting ions. The equilibrium constant expressing the solubility of a precipitate is the familiar solubility product constant.

Let us consider what happens when the sparingly soluble salt AB comes in contact with water. Some of the salt dissolves in water and, assuming this compound to be an ionic solid, dissociates into its ions $A^+$ and $B^-$. This reaction can be represented in its simplest form (i.e. without considering hydration of the ions) by the equation:

$$AB \rightarrow A^+ + B^- \quad (1)$$

However, as the salt AB dissolves, more and more $A^+$ and $B^-$ are in solution, with the net result that the chance of their recombining to form AB increases; that is, the equilibrium
represented simply by equation (2) for the saturated solution is established.

\[
\text{AB (solid)} \rightarrow \text{A}^+ + \text{B}^- \text{ (solution)} \quad (2)
\]

The equilibrium constant for this reaction is:

\[
K = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]}
\]

Since the concentration of AB is constant as long as the temperature remains constant and there is some solid AB in contact with the solution, this equilibrium expression becomes.

\[
K_x \text{ const.} = [\text{A}^+] [\text{B}^-] = S_{ab} - \text{Solubility product constant.}
\]

Let us consider in the same way the saturated solution of the sparingly soluble salt \(X_m Y_n\) which dissociates into \(m\) cation, \(X^{n+}\) and \(n\) anions, \(Y^{m-}\). The equilibrium for this saturated solution can be represented by the equation:

\[
[X^{n+}]^m [Y^{m-}]^n = S_{XmYn}
\]
Calculation of the solubility product from solubility (Molar solubility):

Example (1):
If the solubility of AgCl is 0.0015 g/l what is the solubility product.

.: Molar concentration of saturated solution = 0.0015/143 = 1.05x10^{-5} g.mol/L (143 is Molecular weight)

\[ [AgCl] = [Ag^+] = [Cl^-] \]

\[ Sp_{AgCl} = [Ag^+] [Cl^-] = (1.05x10^{-5}) (1.05x10^{-5}) = 1.05x10^{-10} \]

\[ Sp_{AB} = S^2 \quad (S = \text{molar solubility}) \]

Example (2):
Calculate the solubility product of Pb₃(PO₄)₂ (solubility= 0.00014 g/l).

.: Molar concentration of saturated solution = 0.00014/811.7 = 1.4x10^{-7} g. mol/l (811.7 is M.W.)

If we consider we have A mol/l.

\[ \text{Pb}_3(\text{PO}_4)_2 \rightarrow 3\text{Pb}^{2+} + 2\text{PO}_4^{3-} \]

A mole \quad 3 A \quad 2A

\[ \text{Pb}_3(\text{PO}_4)_2 = [3A]^3 [2A]^2 \]

\[ = [3(1.7x10^{-7})]^3 [2(1.7x10^{-7})]^2 \]

\[ = 1.5x 10^{-32} \]
Calculation of solubility from solubility product.

Example (3): Calculate the solubility of silver sulphide in pure water.

\[ \text{Ag}_2S \rightleftharpoons 2 \text{Ag}^+ + \text{S}^{2-} \]
\[ \text{Ag}_2S = [\text{Ag}^+]^2[\text{S}^{2-}] = 6 \times 10^{-50} \]

1 mole of \( \text{Ag}_2S \rightleftharpoons 2 \text{Ag}^+ + \text{S}^{2-} \)

A mole \( \rightleftharpoons 2 A + A \)

\[ \text{SP}_{\text{Ag}_2S} = [2A]^2[A] \]
\[ 6 \times 10^{-50} = 4 A^3 \]

\[ A = \sqrt[3]{\frac{6}{4} \times 10^{-50}} \]

Factors Affecting Solubility of the Precipitate

1- Common ion effect on solubility (C.I.):

A common ion is one of the component ions of sparingly soluble salt but found in solution from ionization of other salts e.g. if \( \text{AgCl} \) is dissolved in \( \text{NaCl} \) or \( \text{KC1} \). The chloride ion obtained from ionization of these salts form a common ion with chloride ion produced from ionization of \( \text{AgCl} \), similarly if \( \text{AgCl} \) is dissolved in \( \text{AgN0}_3 \) solution. The common ion usually causes depression of the solubility. Thus, if we have a saturated solution
of sparingly soluble salt e.g. AgCl there is equilibrium between solid phase and soluble molecule i.e. with the ions in solution. To illustrate the C.I. effect we will discuss the case when Cl\(^-\) or Ag\(^+\) are added to saturated solution of AgCl. Thus, if AgCl\(_{(s)}\) is shaken with pure water \(Sp_{AgCl} = [Ag^+] [Cl^-]\), if Ag\(^+\) are added (from AgNO\(_3\)) excess Ag\(^+\) will disturb the equilibrium and this ions will combine with Cl\(^-\) to form precipitate AgCl till equilibrium is again reached where \([Ag^+] [Cl^-] = Sp_{AgCl}\) i.e. the solubility decreases. A similar effect occurs if excess Cl\(^-\) is added to the solution.

One can calculate the extent of the depression of the solubility if the concentration of common ion is known.

**Example:** Calculate the solubilities of AgCl in 0.001 M, 0.01M and 0.1MKCl.

In 0.001 MKCl \([Cl^-] = 10^{-3}\)

In a saturated solution of AgCl

\(Sp_{AgCl} = [Ag^+] [Cl^-]\)

\[1.1 \times 10^{-10} = [Ag^+][10^{-3}]\]

\[\therefore [Ag^+] \approx 10^{-7}\]

\[\therefore \text{molar solubility of AgCl} = 10^{-7}\]

This is explained by the fact that Ag\(^+\) is found in solution only from the ionization of soluble part of AgCl at saturation, and since each 1 mol AgCl furnishes one Ag\(^+\) \(\therefore\) molar Ag\(^+\) concentration = [AgCl]
soluble. Similarly

\[
\text{in 0.01 M KC1 solution } [\text{Cl}^-] = 10^{-2}
\]

\[
\therefore 1.1 \times 10^{-10} = [\text{Ag}^+][10^{-2}]
\]

\[
\therefore [\text{Ag}] \approx 10^{-8}
\]

\[
\therefore \text{molar solubility of } [\text{AgCl}] = 10^{-9}
\]

in 0.1 KC1 solution the solubility will be 10^{-9}

In pure water 1.05 \times 10^{-5}

\[
S = S_{\text{AgCl}}
\]

Depression of solubility by common ion effect is of great importance in gravimetric analysis, to ensure complete precipitation excess of precipitating agent is added which by common ion effect minimize the solubility.

However, in some cases the presence of common ion may increase solubility and this is due to complex formation and must be avoided.

2- **Increased solubility by complex formation:**

The solubility can be increased by including an ion which forms a complex with one of ion components of the precipitate, e.g. when potassium cyanide is added to silver nitrate a white precipitate of silver cyanide is first formed, because the solubility product of silver cyanide is exceeded. Addition of excess CN^- will dissolve the precipitate due to the formation of complex ion \([\text{Ag(CN)}_2^-]\).
Notice that AgCl, AgBr and AgI are soluble in alkaline cyanide solutions while Ag₂S is not \((\text{Sp}_{\text{Ag}_2\text{S}} = 10^{-51})\). Also silver ion forms complex with ammonia.

\[
\text{Ag}^+ + 2\text{NH}_3 \rightarrow [\text{Ag(NH}_3)_2]^+
\]

The concentration of silver ion produced from dissociation of the complex is insufficient in presence of chloride to exceed the solubility product of silver chloride but it approaches that of bromide and exceeds that of iodide in their presence. So silver chloride is soluble in ammonia while bromide is partially soluble and silver iodide is insoluble.

3- **Effect of temperature on solubility:**

Increase of temperature mostly increases the solubility of precipitate.

4- **Diverse ion effect:**

Diverse salts increase the solubility of precipitates and have more effect on precipitates with multiply charged ions.

The presence of diverse salts will generally increase the solubility of precipitates due to the shielding of the dissociated ionic species, for example \(\text{BaSO}_4\) in presence of \(\text{NaNO}_3\) (diverse ion).
5- Effect of solvent:

The solubility of most inorganic compounds is reduced by the addition of organic solvents such as methanol, ethanol, propan-1-ol and acetone. For example, the addition of about 20 vol% ethanol renders the solubility of lead sulphate practically negligible, thus permitting quantitative separation. Similarly, calcium sulphate separates quantitatively from 50 vol% ethanol.

**Fractional Precipitation**

We shall study the situation which arises when a precipitating agent such as Ag⁺ is added to a solution containing two anions e.g. chloride and iodide both of which form slightly soluble salt with the same cation. The questions which arise are:

1- Which salt will precipitate first?
2- How completely will the first salt be precipitated before the second ion begins to react with reagent?

The solubility product of AgCl and AgI is $1.1 \times 10^{-10}$ and $1.7 \times 10^{-16}$ respectively.

It is the initial concentration of iodide is 0.1 M, upon addition
of silver ion precipitation of silver iodide commences when the molar concentration of silver ion is.

\[
[Ag^+] = \frac{Sp_{AgI}}{[Cl^-]} = \frac{10^{-16}}{10^{-1}} = 10^{-15}
\]

And for chloride if the initial concentration is 0.1M silver chloride will begin to precipitate when the molar concentration of silver ion is:

\[
[Ag^+] = \frac{Sp_{AgI}}{[Cl^-]} = \frac{10^{-10}}{10^{-1}} = 10^{-9}
\]

So, when silver ion concentration reaches \(10^{-15}\) iodide will be precipitated while chloride will not until silver ion concentration is raised and by \(10^{-9}\). Such rise in silver ion concentration will only reach when practically all iodide is precipitated as silver iodide. In fact, both AgI and AgCl will be precipitated simultaneously when:

\[
\frac{[Ag^+]}{[Cl^-]} = \frac{Sp_{AgI}}{Sp_{AgCl}} = \frac{10^{-10}}{10^{-16}} = 10^6
\]

i.e. when the ratio of I\(^-\) : Cl\(^-\) = 1:10\(^6\)

This type of successive precipitation using the same precipitating agent is known by fractional precipitation.
Lecture 10 & 11 (4 hrs) ......../......../........ (Precipitometry)


Determination of end points in precipitation reaction

Many methods are utilised in determining end points in these reactions, but only the most important will be mentioned here.

A- Formation of a coloured precipitate (Mohr method):

An example of the use of formation of second highly coloured precipitate for detection of end point is the Mohr’s method for determination of chloride and bromide ions with silver nitrate.

Here, chromate ion is the indicator; the end point is detected by the appearance of brick red silver chromate (Ag$_2$CrO$_4$) in neutral medium,
The molar solubility of silver chromate is several times greater than that of silver chloride or bromide.

Thus silver chloride tends to form first in the titration mixture. By adjusting the chromate concentration to a suitable level, formation of silver chromate can be retarded until the silver ion concentration in the mixture is equal to the theoretical equivalence point for chloride. This can be easily determined as follows:

At equivalence point:

\[ [\text{Ag}^+] = [\text{Cl}^-] = \sqrt{\text{AgCl}} \]

\[ [\text{Ag}^+] = 1.05 \times 10^{-5} \]

The chromate concentration required to initiate precipitation of silver chromate under these condition can be also calculated from its solubility product:

\[ K_{\text{Sp}}_{\text{Ag}_2\text{CrO}_4} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] \]

\[ [\text{CrO}_4^{2-}] = K_{\text{Sp}} \cdot \frac{[\text{Ag}^+]^2}{[1.5 \times 10^{-5}]^2} = 10^{-2} \]

This means that the concentration of chromate necessary to give the brick red of silver chromate at equivalence point is 0.01 M in fact it is 0.015M exactly.
Interferences and limitations of Mohr method:

1-The Mohr titration is applicable only in neutral or faintly alkaline solution with pH values from about 6 to 10. In acid solution, the CrO$_4^{2-}$ concentration is greatly decreased according to the following equilibrium:

\[ 2H^+ + 2 \text{CrO}_4^{2-} \rightarrow 2 \text{HCrO}_4^- \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \]

and dichromate is formed whose silver salt is soluble. Therefore, no indicator precipitate forms.

If, on the other hand, the medium is alkaline, silver will precipitate as its oxide:

\[ 2 \text{Ag}^+ + 2 \text{OH}^- \rightarrow 2 \text{AgOH} \rightarrow \text{Ag}_2\text{O} + \text{H}_2\text{O} \]

This interferes with the titration, the silver oxide may even precipitate before silver chromate especially where the solubility product of Ag$_2$O is exceeded. If ammonium salts are present, the pH of the solution must not exceed pH 8 otherwise free ammonia will be produced and dissolve the silver chloride precipitate. Therefore, the halide solution should be neutralized before titration if necessary, by adding NaHCO$_3$ or dilute HNO$_3$, as the case may be.
2- Cations which give **insoluble chromate** e.g. barium ions: They must be absent or removed before the titration.

3- The **reverse titration of silver ion with chloride ion using chromate as indicator is not feasible**, the flocculated Ag$_2$CrO$_4$ formed initially, reacts slowly with chloride especially near the end point of the titration. However to determined silver by Mohr method, it is possible to add excess standard chloride solution and then back-titrate using the chromate indicator.

4- **Titration of iodide**: and of thiocyanate is not successful because silver iodide and silver thiocyanate adsorb chromate ions so strongly that a false and somewhat indistinct end point is obtained.

**B- Formation of a soluble coloured compound (Volhard method):**

This procedure is exemplified by the method of Volhard for the titration of silver in the presence of free nitric acid with standard potassium or ammonium thiocyanate solution. The indicator is a solution of ferric nitrate or of ferric ammonium alum. The addition of the thiocyanate solution produces first a precipitates of silver thiocyanate (S.P. $7.1 \times 10^{-13}$).
\[ \text{Ag}^+ + \text{SCN}^- \rightarrow \text{AgSCN} \]

When this reaction is complete, the slightest excess of thiocyanate produces a reddish-brown colouration, due to the formation of the complex ferrithiocyanate ion:

\[ \text{Fe}^{+++} + \text{SCN}^- \rightarrow [\text{FeSCN}]^{++} \]

This method may be applied to the determination of chlorides, bromides, and iodides in acid solution. Excess of standard silver nitrate solution is added, and the excess is back-titrated with standard thiocyanate solution. For the chloride estimation, we have the following two equilibria during the titration of excess of silver ions:

\[ \text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \]
\[ \text{Ag}^+ + \text{SCN}^- \rightarrow \text{AgSCN} \]

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

\[
\frac{[\text{Cl}^-]}{[\text{SCN}^-]} = \frac{S_{\text{AgCl}}}{S_{\text{AgSCN}}} = \frac{1.2 \times 10^{-10}}{7.1 \times 10^{-13}} = 170
\]

When the excess of silver has reacted, the thiocyanate may react with the silver chloride, since silver thiocyanate is the less soluble until the ratio \([\text{Cl}^-] / [\text{SCN}^-]\) in the solution is 170.

\[ \text{AgCl} + \text{SCN}^- \rightarrow \text{AgSCN} + \text{Cl}^- \]
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 absolutely necessary to prevent the reaction between the thiocyanate, and the silver chloride. This may be effected in several ways, of which the first is probably the most reliable:

a) The silver chloride is filtered off before back titration.
b) After the addition of the silver nitrate, the suspension is boiled for about 3 minutes, cooled and then titrated immediately,
c) An immiscible liquid is added to "coat" the silver chloride particles and thereby protect them from interaction with the thiocyanate. The most successful liquid is nitrobenzene.

With bromides, we have the equilibrium;

\[
\frac{[\text{Br}^-]}{[\text{SCN}^-]} = \frac{\text{AgBr}}{\text{AgSCN}} = \frac{3.5 \times 10^{-13}}{7.1 \times 10^{-13}} = 0.5
\]

The titration error is small, and no difficulties arise in the determination of the end point. Silver iodide (S.P. 1.7x10^{-16}) is less soluble than the bromide, the titration error is negligible but the ferric ion indicator should not be added until excess of silver is present, since the dissolved iodide reacts with the ferric iron.

\[2 \text{Fe}^{+++} + 2 \text{I}^- \rightarrow 2 \text{Fe}^{++} + \text{I}_2\]
C- Use of adsorption indications (Fajan method):

Fajan has introduced a useful type of indicator for precipitation reactions as a result of his studies on the nature of adsorption. The action of these indicators is due to the fact that at the equivalence point the indicator is adsorbed by the precipitate, and leads to a substance of different colour, they have therefore been termed adsorption indicators. The substances employed are either acid dyes, such as fluorescein, eosin, rose bengal, dichloro-fluorescein, and di-iodo-diemthyl-fluorescein; or basic dyes, such as rhodamine (6G), which are applied as the halogen salts.

The theory of the action of these indicators is based upon the properties of colloids. When a chloride solution is titrated with a solution of silver nitrate, the precipitated silver chloride adsorbs chloride ions (a precipitate has a tendency to adsorb its own ions); this is termed the primarily adsorbed layer, and it will hold by secondary adsorption oppositely charged ions present in solution (Fig. 2a). As soon as the stoichiometric point is reached silver ions are present in excess; these will now be primarily adsorbed, and nitrate ions will be held by secondary adsorption (Fig. 2b). If fluorescein is also present in the solution, the negative fluorescein ion, which is much more strongly adsorbed than the nitrate ion, is immediately adsorbed and will reveal, its presence on the precipitate, not by its colour, which is that of the
solution, but by the formation of a pink complex of silver and a modified fluoresceinate ion in the surface with the first trace of excess of silver ions (Fig. 2c).

An alternative view is that during the adsorption of the fluorescein ion a rearrangement of the structure of the ion occurs with the formation of a coloured substance. It is important to notice that the colour change takes place at the surface of the precipitate.

The following conditions will govern the choice of a suitable indicator:

i. The precipitate should separate as far as possible in colloidal conditions. The solution should not be too dilute as the amount of precipitate formed will be small and the colour change is not sharp with certain indicators.

ii. The indicator ion must be of opposite charge to the ion of the precipitating agent.

iii. The indicator ion should not be adsorbed before the particular compound has been completely precipitated, but is should be strongly adsorbed immediately after the

Fig. 2
equivalence point.

Some adsorption indicators and their applications:

1- **Fluorescein**: can be used during the titration of halides. This is a very weak acid (\(K_a = 1 \times 10^{-8}\)) hence even a small amount of other acids reduces the already minute ionisation, thus rendering the detection of the end point (which depends essentially upon the adsorption of the free anion) either impossible or difficult to observe. The optimum pH range is between 7 and 10.

2- **Dichlorofluorescein**: is a stronger acid and may be utilised in slightly acid solution of pH greater than 4.4. This indicator has the further advantage that it is applicable in very dilute solutions.

3- **Eosin (tetrabromofluorescein)**: is a stronger acid and can used down to a pH of 1.2. The colour change is sharpest in an acetic acid
**d- Turbidity method:**

The appearance of a turbidity sometimes utilized to mark the end point of a reaction, as Liebig's method for cyanides. When a solution of silver nitrate is added to a solution containing cyanide ions (e.g. alkali cyanide) a white precipitate is formed when the liquids first come into contact with one another, but on stirring it re-dissolves owing to the formation of stable complex cyanide, the alkali salt of which is soluble:

\[
\text{AgNO}_3 + 2 \text{KCN} \rightarrow \text{KAg(CN)}_2 + \text{KNO}_3
\]

or

\[
\text{Ag}^+ + 2 \text{CN}^- \rightarrow [\text{Ag(CN)}_2]^{-}
\]

When the above reaction is complete, further addition of silver nitrate solution yields the insoluble silver argento cyanide.

\[
\text{Ag}^+ + [\text{Ag(CN)}^2]^- \rightarrow \text{Ag[Ag(CN)}^2]
\]

The end point of the reaction is therefore indicated by the formation of permanent turbidity.

In Denige's modification of Liebig method, iodide ion is used as indicator and aqueous ammonia is introduced to solubilise the silver cyanide:
Ag[Ag(CN)₂] + 4NH₃ → 2[Ag(NH₃)₂]⁺ + 2CN⁻

The iodide ion and ammonia solution are added before the titration is commenced, the formation of silver iodide (as turbidity) will indicate the end point.

[Ag(NH₃)₂]⁺ + I⁻ → AgI + 2NH₃

During the titration any silver iodide which would be formed will be kept in solution by the excess of cyanide ion always present until the equivalence point is reached:

AgI + 2CN⁻ → [Ag(CN)₂]⁻ + I⁻

The method can also be utilized indirectly for the determination of several metals, notably nickel, cobalt, and zinc, which form stable stoichiometric complexes with cyanide ion. Thus if a Ni(II) salt in ammoniacal solution is heated with excess of cyanide ion, the Ni-cyano complex ion is formed quantitatively and since it is more stable than Ag[(CN)₂]⁻ ion, the excess of cyanide may be determined by the Liebig-Deniges method.

Limitations of Argentometric titrations:

1- Reducing agents, such as, sulphur dioxide interferes by
reducing the silver ions, and must be removed by previous oxidation.

2- Coloured compounds of any sort obscure the end point, which is taken as the faintest ting of colour detectable on the precipitated silver halide, or in solution, as the case may be.

3- Silver halides are sensitive to photodecomposition, and the titration should be carried out in diffused daylight, or artificial light.

4- Most cations except the alkalies and alkaline earths interfere in several ways,
   a) Some, such as Fe$^{3+}$ form insoluble coloured hydroxide in neutral or slightly acid medium;
   b) Some, such as Al$^{3+}$, hydrolyse to insoluble basic salts in neutral or slightly acid solution, showing a tendency to coprecipitate chloride;
   c) Hg$^{2+}$ form soluble complexes with halides of the type [Hgl$_4$]$^{2-}$.
1- **Determination of zinc ions by precipitation with potassium ferrocyanide:**

Zinc ions in neutral or acid medium react with potassium ferrocyanide solution to form a very sparingly soluble potassium zinc ferrocyanide:

$$3\text{Zn}^{++} + 2\text{K}_4\text{Fe(CN)}_6 \rightarrow \text{K}_2\text{Zn}_3[\text{Fe(CN)}_6]_2$$

The end point of the reaction is determined by means of external indicators, such as uranyl nitrate and ammonium molybdate. The acidified zinc solution is slowly titrated at 60°-80°C with ferrocyanide solution until a drop of the solution gives a light brown colour then tested, with a drop of uranyl nitrate on a white spot plate (due to the formation of uranyl ferrocyanide). The method must be repeated several times to obtain accurate results.

The external indicator method has been replaced by internal indicator method using diphenylamine. Diphenylamine is a redox indicator; it changes its colour according to the ratio of the concentration of the oxidised form to the reduced form of redox system. If it is oxidised by oxidising ion (ferricyanide) the colour of the oxidised form will appear and if it is reduced by
reducing ion (ferrocyanide) the colour of the reduced form will appear. So, titration of zinc ion is carried out by 0.05 M standard ferrocyanide solution to which 0.3 g of potassium ferricyanide per liter is added (0.01M). During the titration the ferrocyanide added reacts with zinc ions and its concentration is very small. The concentration of ferricyanide predominates over ferrocyanide indicator and the former oxidises the indicator and the colour of the oxidised form of indicator appears (blue violet).

As soon as zinc ions are quantitatively precipitated, the first excess of ferrocyanide causes a sudden increase in its concentration, so it predominates over ferricyanide and causes reduction of the indicator. The colour change will be from blue violet (oxidised form) to colourless (reduced form of indicator).

2- Determination of barium and of sulphates:

Weakly acidified barium solution (with HCl) give a red precipitate of barium rhodizonate with a freshly prepared solution of the sodium salt of rhodizonic acid.
The solubility of the red compound is much greater than that of barium sulphate, hence upon the addition of a sulphate solution to a solution of barium salt, the barium will be completely precipitated when the red colour changes to colourless (in weak acid solution) or yellow (in neutral solution).

2- Determination of mixtures:

a) Chloride-iodide mixture:

By direct titration using Fajan’s method fluorescein indicator for total halide then the iodide is determined using eosin.

b) Bromide-iodide mixture:

Similar to chloride iodide mixture. Total with eosin or fluorescein. For Y only use diiododimethyl fluorescein.

c) Chloride cyanide, bromide cyanide or iodide cyanide mixtures:

Such mixtures are analysed using a combination of Liebig's and Volhard's method. Liebig's procedure determines the cyanide only while the total is determined by Volhard's

\[ 2CN^- + Ag^+ \rightarrow [Ag(CN)_2]^- \text{ Liebig's} \]
\[ [\text{Ag(CN)}_2]^- + \text{Ag}^+ \rightarrow \text{Ag-Ag(CN)}_2 \text{ (Volhards)} \]

So the volume of standard silver nitrate equivalent to cyanide by the Liebig's method is \( \frac{1}{2} \) the volume of Volhards.

Titration curve for AgNO\(_3\) vs. I\(^-\) and Cl\(^-\). AgI precipitates first while Cl\(^-\) remains in solution. As [Ag\(^+\)] increases, than AgCl precipitates. The system used 0.0502 M KI and 0.050 M KCl with 0.0845M AgNO\(_3\) titrant.