Chapter Five :

Precipitation titration :

Volumetric methods based upon the formation of slightly soluble precipitate are called " *precipitation titration* " .

Because of the precipitating titration based upon utilizing silver nitrate ($AgNO_3$) as a precipitating agent, then it called " *argentimetric processes* " .

Precipitation titration is a very important , because it is a perfect method for determine halogens and some metal ions .

Titration curves for precipitation titrations :

Titration curves are represents :

1) The change in conc. of reactants throughout titration .

2) Titration error that is likely occur when using the indicators .

3) The conditions at equivalent point .

EX. Derive a titration curve for the titration of 50ml of 0.1M NaCl with 0.1M $AgNO_3$, $KSP_{AgCl} = 1.82 \times 10^{-10}$?

Notes :

1) In precipitation titration we are using molar and formal conc. and we are not using normal conc.

2) Precipitation titration methods are used to determine halogin ions.

3) Precipitation titration curves are plotte as :

4) Precipitation titration curve is influenced by the conc. of Ag^+ and Cl^-

5) Precipitation titration curve is influenced by KSP value (completeness of reaction) . when KSP value is small the titration curve is perfect .

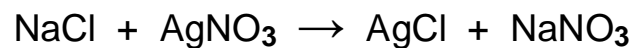Answewer of example :

a) before adding $AgNO_3$:

$$NaCl \rightarrow Na^+ + Cl^-$$
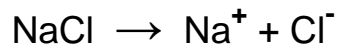
   0.1   0.1   0.1

pCl = - log $[Cl^-]$ = - log 0.1 = 1

pAg = zero

b) after adding 10ml of AgNO3 :

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$

(50x0.1)   (10x0.1)   0

   5   1   0

   4   0   1

$[Cl^-] = \dfrac{4}{60} = 6.7 \times 10^{-2}$

pCl = - log 6.7×10^{-2} = 1.17

$[Ag^+] = \dfrac{KSP}{[Cl-]} = \dfrac{1.82 \times 10 - 10}{6.7 \times 10 - 2} = 2.7 \times 10^{-9}$

pAg = - log 2.7×10^{-9} = 8.57

c) when adding 49.95ml of $AgNO_3$:

$$NaCl \ + \ AgNO_3 \ \rightarrow \ AgCl \ + \ NaNO_3$$
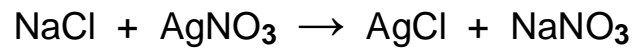
(50x0.1) (49.95x0.1)   0

  5   4.95   0

  0.05   0   0.05

$$[Cl^-] = \frac{0.05}{99.95} = 5 \times 10^{-5}$$
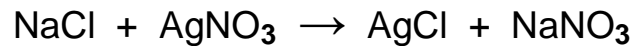
$pCl = - \log 5 \times 10^{-5} = 4.3$

$$[Ag^+] = \frac{1.82 \times 10^{-10}}{5 \times 10^{-5}} = 0.36 \times 10^{-5}$$

$pAg = - \log 0.36 \times 10^{-5}$

$pAg = 5.44$

d) at equivalent point , when adding 50ml of $AgNO_3$:

$$NaCl \ + \ AgNO_3 \ \rightarrow \ AgCl \ + \ NaNO_3$$

(50x0.1)   (50x0.1)   0

  5   5   0

  0   0   5

$[Ag^+] = [Cl^-] = 1.82 \times 10^{-10}$

$[Cl^-]^2 = 1.82 \times 10^{-10}$

$[Ag^+] = [Cl^-] = 1.35 \times 10^{-5}$

$pCl = pAg = 4.87$

e) after adding 52.5ml of AgNO$_3$:

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$
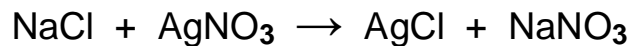
(50x0.1)   **(52.5x0.1)**   **0**

  5   5.25   0

  0   0.25   0.25

$$[Ag^+] = \frac{0.25}{102.5} = 2.4 \times 10^{-3}$$

$$[Cl^-] = \frac{1.82 \times 10 - 10}{2.4 \times 10 - 3} =$$

pAg = 2.62

pCl = 7.12

**End point detection precipitation titration :**

1) formation of a second colored precipitate (Mohr method):

This method depends on formation of second highly colored precipitate for detect end point.

This method has been widely applied to the titration of chloride ion and bromide ion with silver nitrate , and the indicator is chromate ion (CrO_4^{-2}) . the end point being signaled by the appearance of red silver chromate(Ag_2CrO_4) .

$$AgCl_{(s)} \rightarrow Ag^+ + Cl^-$$
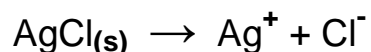
$KSP_{(AgCl)} = 1.35 \times 10^{-5}$ (from previous example)

$$Ag_2CrO_4 \rightarrow 2Ag^+ + CrO_4^{-2}$$
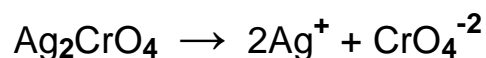
$KSP(Ag_2CrO_4) = 1.2 \times 10^{-12}$

$$KSP = [Ag^+]^2[CrO_4^{-2}]$$

$$[CrO_4^{-2}] = \frac{KSP}{[Ag+]2} = \frac{1.2 \times 10-12}{(1.35 \times 10-5)2}$$

$$[CrO_4^{-2}] = 6\times10^{-3}M$$

The titration is performed in neutral or slightly basic medium pH = (7-10) to prevent silver hydroxide formation at pH > 10 or formation of chromic acid at pH < 7 .

$$2CrO_4^{-2} + 2H^+ \rightleftharpoons 2HCrO_4^{-2} \rightleftharpoons Cr_2O_7^{-2} + H_2O$$

$$2Ag^+ + 2OH^- \rightleftharpoons 2AgOH \rightleftharpoons Ag_2O_{(s)} + H_2O$$

The presence of an excess of either sodium hydrogen carbonate or borax in the sol. tends to maintain the hydrogen ion conc. within suitable limits .

2) formation of colored complex (Volhard method) :

Volhard method can be use as a directly method to detect Ag^+ and an indirectly method to detect halides .

To detect silver ion : a standard sol. of thiocyanate is use as a titrant for silver ion . Iron ion (III) is use as an indicator imparting a red coloration to sol. with first slightly excess of thiocyanate.

$$Ag^+ + SCN^- \rightleftharpoons AgSCN_{(s)}$$

$$Fe^{+3} + SCN^- \rightleftharpoons Fe(SCN)^{+2}$$

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 , that the red $Fe(SCN)^{+2}$ complex color can detect at $6.4 \times 10^{-6}M$.

To detect halides ions : 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 thiocyanate sol.

$$Ag^+ + Cl^- \rightleftharpoons AgCl + Ag_{excess}$$

$$Ag_{excess} + SCN^- \rightleftharpoons AgSCN$$

Complex formation titration :

Complex ions (coordination compounds) are produce from reaction of many metal ions (electrons accepter) with electron pair donors .

The donor species (or called ligands) must have at least one pair of unshared electrons for bond formation .
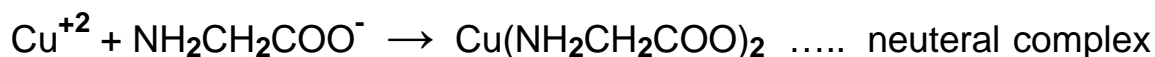
Metal ions are forms coordination complexes with anions or molecules :

a) anionic ligands : like , SCN^- , CN^- , OH^- ,…….ect.

b) molecular ligands : like , H_2O , NH_3 , RNH_2 , …..ect.

$[Ag(CN^-)_2]$, $[Cu(NH_3)_4]^{+2}$, $[Zn(H_2O)_4]^{+2}$
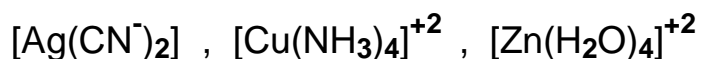
Species formed as a result of coordination can be classified as positive or   neutral or negative :

$$Cu^{+2} + 4NH_3^+ \rightarrow [Cu(NH_3)_4]^{+2} \quad …………………….. \quad \text{cationic complex}$$

$$Cu^{+2} + NH_2CH_2COO^- \rightarrow Cu(NH_2CH_2COO)_2 \quad ….. \quad \text{neuteral complex}$$

$$Cu^{+2} + 4Cl^- \rightarrow CuCl_4^{-2} \quad …………………………….. \quad \text{anionic complex}$$

Chelates : are produced when a metal ion coordinates with two or more donor groups of a single ligand , and forming a cyclic structure .

Chelates can be classified into :

a) Chelating agent (ligand) whose share only one electron pair is

called " mono dentate "

$$Cu^{+2} + 4NH_3^+ \rightarrow [Cu(NH_3)_4]^{+2}$$
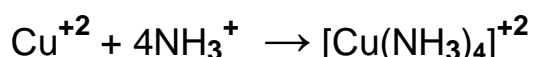
b) ligand whose share two electron pairs is called " Bidentate "

$$Cu^{+2} + NH_2CH_2COO^- \rightarrow Cu(NH_2CH_2COO)_2$$
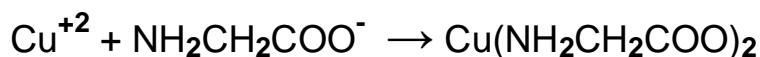
c) ligand whose share three electron pairs is called " Tridentate " , and four is called " Tetradentate " , " pentadentate " , " Hexadentate ".. ect.

Titration curve for complexation titration :

When a metal ion M with a coordination number of four is react with tetradentate ligand D :

$$M + D \rightleftharpoons MD$$

$$K_f = \frac{[MD]}{[M][D]}$$ K_f = formation constant

Similarly , the equilibrium between M and bidentate ligand B is :

$$M + 2B \rightleftharpoons MB_2$$

This equation can be write as :

$$M + B \rightleftharpoons MB \quad \ldots\ldots\ldots \quad K_{f1} = \frac{[MB]}{[M][B]} = 10^{12}$$

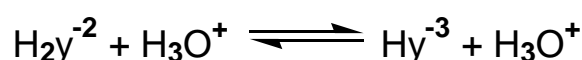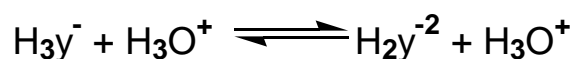$$MB + B \rightleftharpoons MB_2 \quad \cdots\cdots \quad K_{f2} = \frac{[MB2]}{[MB][B]} = 10^8$$

$$K_{f1} \times K_{f2} = \frac{[MB]}{[M][B]} \times \frac{[MB2]}{[MB][B]} = \frac{[MB2]}{[M][B]2} = 10^{20}$$

From the curve , the ligand that combines with a metal ion in 1:1 ratio is better from others , because the change in pM value at equivalent point region is largest . that means , combine in lower ratios with metal ions are ordinarily superior reagents for complex formation titration .

Composition of EDTA solution as a function of pH :

The most commonly chelon (or titrant) used in complexation titration is

EDTA (ethylenediamintetraaceticacid) .

EDTA is a weak acid dissociate in four steps :

$$H_4y + H_2O \rightleftharpoons H_3y^- + H_3O^+$$

$$H_3y^- + H_3O^+ \rightleftharpoons H_2y^{-2} + H_3O^+$$

$$H_2y^{-2} + H_3O^+ \rightleftharpoons Hy^{-3} + H_3O^+$$

$$Hy^{-3} + H_3O^+ \rightleftharpoons y^{-4} + H_3O^+$$

These values refers to that the first two protons are lost much more readily than the remaining two .

$$C_T = [H_4y] + [H_3y^-] + [H_2y^{-2}] + [Hy^{-3}] + [y^{-4}]$$

It found that EDTA values depends upon pH of solution , where is :

a) when pH (3 - 6) , H_2y^{-2} is predominate .

b) when pH (6 -10) , Hy^{-3} is predominate .

c) at pH > 10 , y^{-4} is predominate .

EDTA is a hexadentate because each nitrogen atom has an unshared paire of electrons in addition to four acidic hydrogens , thus , the molecule has six potential sites for bonding with a metal ion .

Note : because of limited solubility of EDTA (as acid) , and Na4y is completely dissociated in water , therefore, the standard solution of EDTA are usually prepared by dissolving the $Na_2H_2y.H_2O$ in a volumetric flask .

Note : most $Na_2H_2y.H_2O$ contain 0.3% moisture under normal atmospheric conditions . the excess of water must be taken into account when preparing standard solution .

$$\alpha_0 = \frac{[H4y]}{CT}$$

$$\alpha 1 = \frac{[H3y-]}{CT}$$

$$\alpha 2 = \frac{[H2y-2]}{CT}$$

$$\alpha 3 = \frac{[Hy-3]}{CT}$$

$$\alpha 4 = \frac{[y-4]}{CT}$$

$$\alpha_0 + \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 = 1$$

Complexes of EDTA and metal ions :

EDTA as a titrant is combines with metal ion in 1:1 ratio regardless of the charge of the cation. These reaction can be express by :
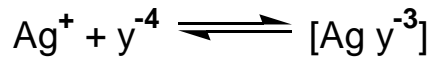
$$M^{+2} + H_2y^{-2} \rightleftharpoons My^{-2} + 2H^+$$

$$M^{+3} + H_2y^{-2} \rightleftharpoons My^{-1} + 2H^+$$

$$M^{+4} + H_2y^{-2} \rightleftharpoons My + 2H^+$$

$$M^{+n} + y^{-4} \rightleftharpoons My^{(n-4)+}$$
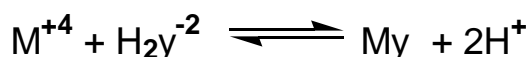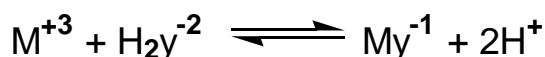
$$K_{My} = \frac{[My(n-4)+]}{[M+n][y-4]}$$

EDTA forms chelates with all cations in 1:1 ratio and these chelates are very stable . this great stability is come from the several complexing sites within the molecule .

Formation constant for EDTA complexes :

Cation	K_{My}	log K_{My}
Ag^+	2.1×10^7	7.32
Mg^{+2}	4.9×10^8	8.69
Ca^{+2}	5×10^{10}	10.7
Fe^{+2}	2.1×10^{14}	14.33
Sr^{+2}	4.3×10^8	8.63

$$Ag^+ + y^{-4} \rightleftharpoons [Ag\,y^{-3}]$$

$$K_{My} = \frac{[[Ag\,y-3]}{[Ag+][y-4]}$$

$$2.1 \times 10^7 = \frac{[[Ag\,y-3]]}{[Ag+][y-4]}$$

$$\propto 4 = \frac{[y-4]}{CT}$$

$$K\square_{My} = K_{My} \times \propto 4$$

$$K\square_{My} = \frac{[My(n-4)+]}{[Mn]CT}$$

Derivation of titration curves for EDTA titration :

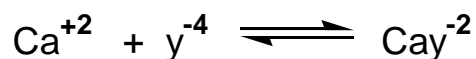Derive the titration curve for 50ml of 0.01F Ca^{+2} with 0.01F of EDTA in a solution has pH = 10 ?

a) $K\square_{Cay} = K_{Cay} \times \propto 4$

$K_{Cay} = 5 \times 10^{10}$ (from tables)

$K\square_{Cay} = 5 \times 10^{10} \times 3.5 \times 10^{-1}$

$K\square_{Cay} = 1.75 \times 10^{10}$

b) calculation of pCa befor end point :

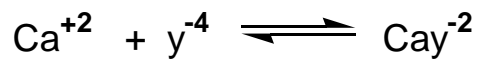$$Ca^{+2} + y^{-4} \rightleftharpoons Cay^{-2}$$

(50x0.01)	(25x0.01)	0
0.5	0.25	0
0.25	0	0.25

$$[Ca^{+2}] = \frac{0.25}{75} = 3.33 \times 10^{-3}$$

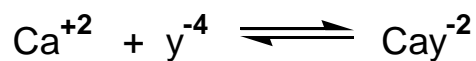$$pCa = -\log 3.33 \times 10^{-3} = 2.48$$

c) at end point :

$$Ca^{+2} + y^{-4} \rightleftharpoons Cay^{-2}$$

(50x0.01) (50x0.01)   0

  0.5   0.5   0

   0   0   5

$$[Ca^{+2}] = \frac{0.5}{100} = 0.005 \ F$$

$$Ca^{+2} + y^{-4} \rightleftharpoons Cay^{-2}$$

$$Ca^{+2} = C_T$$

$$K\square_{My} = \frac{[Cay-2]}{[Ca+2]C_T}$$

$$Ca = C_T$$

$$K\square_{Cay} = \frac{[Cay-2]}{[Ca]2}$$

$$1.75 \times 10^{10} = \frac{0.005}{[Ca]2}$$

$$[Ca^{+2}] = 5.35 \times 10^{-7}$$

$$pCa = -\log 5.35 \times 10^{-7} = 6.27$$

d) when adding 60ml of EDTA :

$$Ca^{+2} + y^{-4} \rightleftharpoons Cay^{-2}$$

(50x0.01) (60x0.01)   0

  0.5   0.6   0.1

   0   0.1   0.1

$$[Cay^{-2}] = \frac{50 \times 0.01}{110} = 4.5 \times 10^{-3}$$

$$[C_T] = \frac{10 \times 0.01}{110} = 9.1 \times 10^{-4}$$

$$K_{My} = \frac{[Cay-2]}{[Ca+2]C_T}$$

$$1.75 \times 10^{10} = \frac{4.5 \times 10-3}{[Ca+2] \times 9.1 \times 10-4}$$

$[Cay^{-2}] = x$

pCa = -log x

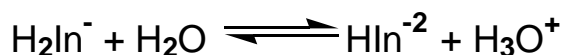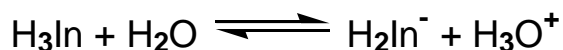## Indicators for EDTA titration :

Many indicators are used for metal ion titration with EDTA .

These indicators are organic dyes which form colored chelates with metal ions in range that is unique to the cation and dye .

The colored complexes being visible to eye in range of 10^{-6}M to 10^{-7}M .

Erochrome black T (EBT) , is one of the best indicators use in EDTA titration , it contain an aromatic azo dye . its structure as follow :

From the structure , the proton associated with sulphonic acid group is completely dissociated in an aqueous medium ,and , the phenolic protons are only partially dissociated :

$$H_3In + H_2O \rightleftharpoons H_2In^- + H_3O^+$$

$$H_2In^- + H_2O \rightleftharpoons HIn^{-2} + H_3O^+$$

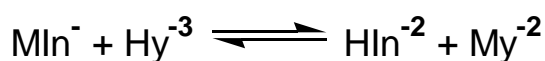$$HIn^{-2} + H_2O \rightleftharpoons In^{-3} + H_3O^+$$

EBT behaves also an acid-base indicator , because that the acids and there conjugate bases are differ in color .

Method complexes of EBT are red , then to indicate the color change with EBT the pH must be 7 or more ,so that the blue form of the species HIn^{-2} .

Predominates in the absence of metal ion .

The end point reaction is then :

$$MIn^- + Hy^{-3} \rightleftharpoons HIn^{-2} + My^{-2}$$

 red   blue
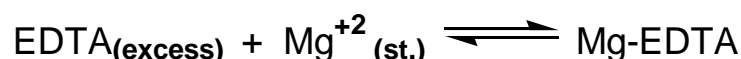
Titration method employing EDTA :

1) **Direct titration :** there are 25 metals or more can be determined by direct   titration with EDTA using metal ions indicators for end point detection .

Direct titration method are limited to metal ions that react rapidly with EDTA and that can be detect the end point of these reactions .

If direct method is fail , the analysis can be done by back-titration or displacement titration .

2) **Back – titration :** back- titration is useful analysis for cations that will form   very stable EDTA complexes and when a suitable indicator is not available   or it react slowly with EDTA .

In this method , excess from EDTA is added and the excess of EDTA is determine by back-titration with a standard Mg^{+2} solution using EBT as indicator .

$$M + EDTA_{(excess)} \;\rightleftharpoons\; M\text{-}EDTA + EDTA_{(excess)}$$

$$EDTA_{(excess)} + Mg^{+2}{}_{(st.)} \;\rightleftharpoons\; Mg\text{-}EDTA$$

3) **Displacement titration :** in this method :

Excess of solution containing Mg^{+2} or Zn^{+2} complex of EDTA (Mgy^{-2} or Zny^{-2}) is added to analyte (unknown metal ion) .

The analyte (unknown metal ion) is displace Mg^{+2} or Zn^{+2} and form a complex with EDTA .

If the analyte complex is more stable then of Mg^{+2} or Zn^{+2} , then the reaction is :

$$Mgy^{-2} + M^{+2} \;\rightleftharpoons\; My^{-2} + Mg^{+2}$$

$$Zny^{-2} + M^{+2} \;\rightleftharpoons\; My^{-2} + Zn^{+2}$$
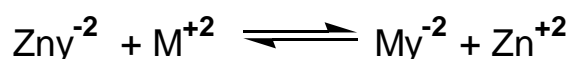
The liberated Mg^{+2} is titrated with a standard EDTA sol.

This technique is useful when a suitable indicator is not available for metal ion .

Solubility of precipitates

Solubility of precipitate is defined as disappeare 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 of inorganic compounds in water :

a) all ammonium , sodium , potassium salts are soluble in water.

b) all nitrates , acetates are soluble in water.

c) all chlorides are soluble in water except chlorides of silver , mercury and lead.

d) all sulphate are soluble in water except sulphate of barium and lead , while sulphate of calcium and strontium are moderately soluble.

e) all hydroxides are insoluble in water except hydroxide of ammonium , sodium and potassium.

Solubility product constant (K.S.P) :

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 .

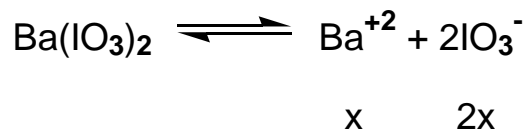It is calculate from multiplying of anion and cation concentrations :

$$AB \rightleftharpoons A^+ + B^-$$

$$K.S.P = [A^+][B^-]$$

$$A_m B_n \rightleftharpoons mA^{+n} + nB^{-m}$$
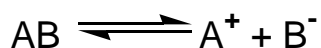
$$K.S.P = [A^{+n}]^m [B^{-m}]^n$$

EX. Calculate no. of grams of $Ba(IO_3)_2$ can be dissolved in 150ml of water in $25C^o$, $K.S.P = 1.75 \times 10^{-9}$?

$Ba(IO_3)_2 \rightleftharpoons Ba^{+2} + 2IO_3^-$

$\quad\quad\quad\quad\quad\quad\quad x \quad\quad 2x$

$K.S.P = [Ba^+][IO_3^-]^2$

$1.57 \times 10^{-9} = (x)(2x)^2$

$1.57 \times 10^{-9} = 4x^3$

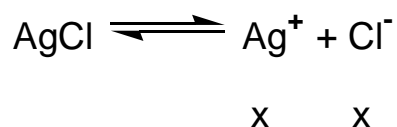$$X = \sqrt[3]{\frac{1.57 \times 10^{-9}}{4}}$$

$X = 7.3 \times 10^{-4}$ mole/L

mg of $Ba(IO_3)^2$ = solubility x M.wt x volume

$$= 7.3 \times 10^{-4} \frac{mole}{L} \times 487 \frac{gm}{mole} \times \frac{150}{1000} L$$

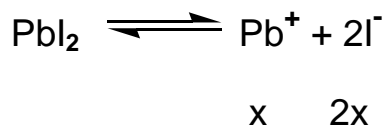$$= 0.0533 \text{ gm} \times 1000 = 53.3 \text{ mg}$$

We can express salts by :

a) AB : the ratio of cation to anion is 1:1 , like: Ag^+Cl^- , Pb^+S^-

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

$\quad\quad\quad\quad\quad x \quad\quad x$

$K.S.P = (x)(x) = x^2$

$X = \sqrt{KSP}$

b) AB_2 or A_2B : the ratio is 1:2 or 2:1, like: PbI_2 , HBr_2 , Ag_2CrO_4
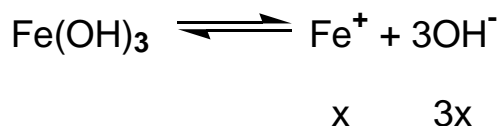
$PbI_2 \rightleftharpoons Pb^+ + 2I^-$

$$x \qquad 2x$$

$K.S.P = (x)(2x)^2$

$K.S.P = (x)(4x)^2 = 4x^3$

$$X = \sqrt[3]{\dfrac{ksp}{4}}$$

c) AB_3 : the ratio is 1:3 , like: $Fe(OH)_3$
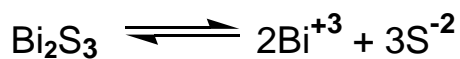
$Fe(OH)_3 \rightleftharpoons Fe^+ + 3OH^-$

$$x \qquad 3x$$

$K.S.P = (X)(3X)^3$

$K.S.P = (X)(27X)^3 = 27X^4$

$$X = \sqrt[4]{\dfrac{ksp}{27}}$$
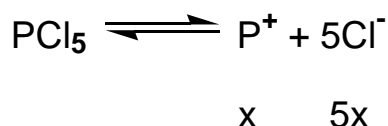
d) A_2B_3 : the ratio is 2:3 , like : Bi_2S_3

$Bi_2S_3 \rightleftharpoons 2Bi^{+3} + 3S^{-2}$

$K.S.P = (2x)^2 (3x)^3$

$K.S.P = (4x^2)(27x^3) = 108\, x^5$

$$X = \sqrt[5]{\dfrac{ksp}{108}}$$

e) AB_5 : the ratio is 1:5 , like : PCl_5

$$PCl_5 \rightleftharpoons P^+ + 5Cl^-$$

$$ x \quad\quad 5x$$

$$K.S.P = (x)(5x)^5 = 3125\, x^6$$

$$X = \sqrt[6]{\frac{ksp}{3125}}$$

EX. Calculate the solubility in mole/L for AgCl , KSP= 1.8×10^{-10} ?

$$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$$
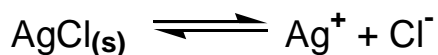
$$KSP = [Ag^+][Cl^-]$$

$$1.8 \times 10^{-10} = (x)(x)$$

$$1.8 \times 10^{-10} = x^2$$

$$x = \sqrt{1.8 \times 10 - 10} =$$

EX. The solubility of $BaSO_4$ is equal to 1.14×10^{-5} M , calculate KSP ?

$$KSP = [Ba^{+2}][SO_4^-]$$

$$KSP = [1.4 \times 10^{-5}]\,[1.4 \times 10^{-5}]$$

$$KSP = 1.3 \times 10^{-10}$$

EX. Calculate the solubility in mole/ L for Ag_2CrO_4 , KSP = 1.1×10^{-12} ?

$$Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{-2}$$

$$KSP = (2x)^2(x) = 4x^3$$

$$X = \sqrt[3]{\frac{1.1 \times 10 - 12}{4}} =$$

Application of KSP in precipitation :

1) **Completments of precipitation :**

<u>Q:</u> How can you predict weather a precipitate is formed or doesn't formed when a solution of positive ion is mixed with other solution of negative ion ?

The predict that a precipitate formed or not is depends upon the value of KSP and IP .

In a solution contain Ag^+ ion and Cl^- ion , therefore :

$IP = [Ag^+][Cl^-]$

Then , If IP< KSP   no precipitate occur because the solution is unsaturated with AgCl .

If IP > KSP   the solution is just saturated and not ppt. occur.

If IP = KSP   the solution is super saturated and ppt. take place

(or form).

<u>EX.</u> 10ml of 10^{-5}M $AgNO_3$ solution mixed with 10ml of 10^{-5}M HCl solution is the ppt. formed , KSP =

في حالة مزج المحلولين فانه سوف يتخفف المحلول ‘ وعند التخفيف يقل التركيز ويزداد الحجم.

$[Ag^+] = 10^{-5}/2$

$[Cl^-] = 10^{-5}/2$

$IP = 10^{-5}/2 \times 10^{-5}/2 =$

Because of IP < KSP , therefore there is no precipitate .

2) **Dissolution of precipitate:**

When it is a precipitate in the solution , then it is heterogeneous system and the solution is saturated.

<u>Q:</u> How we can dissolve more than of precipitate ?

We must make the solution unsaturated to dissolve a precipitate or we must make IP < KSP .

EX. AgCl is in equilibrium with its ions ,

$AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$
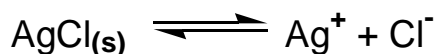
How we can dissolve more of AgCl ?

It done by reducing or lowering the concentration of Ag or Cl or make IP<KSP.

If we added aqueous solution of NH_3 to the solution , Ag^+ ion react with NH_3 and formed complex ion , by this way we can reduce the concentration of Ag^+ .

$Ag^+ + 2NH_3 \rightleftharpoons Ag(NH_3)_2$ ………. (complex ion)
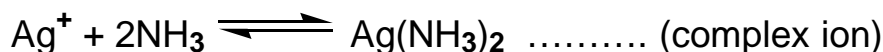
3) **Prevention of precipitation :**

$Ag^+ + Cl^- \rightleftharpoons AgCl$ IP<KSP

We added NH_3 to prevent precipitation and to make IP< KSP , the addition of ammonia chloride to $AgNO_3$ will not give any precipitate .

$Zn^{+2} + 2OH^- \rightleftharpoons Zn(OH)_2$

To prevent formation of $Zn(OH)_2$, we can make it by acidic solution.

Factors effecting the solubility of precipitates :

1) 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 .
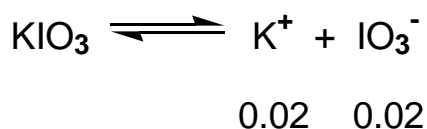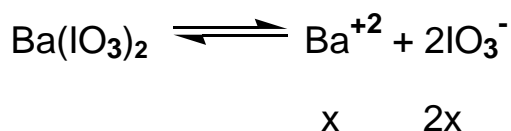
$AgCl \rightleftharpoons Ag^+ + Cl^-$

$X = [Ag^+] = [Cl^-] = \sqrt{KSP}$

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

$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$

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

Note : it is nessecery exist a little excess from precipitate solution to prevent losses of same precipitate through dissolving.

EX.   Calculate the solubility in mole/L for $Ba(IO_3)_2$ in a solution of 0.02M KIO_3 , $KSP(BaIO_3)_2 = 1.57 \times 10^{-9}$?

$Ba(IO_3)_2 \rightleftharpoons Ba^{+2} + 2IO_3^-$

$\qquad\qquad\qquad\quad x \qquad 2x$

$KIO_3 \rightleftharpoons K^+ + IO_3^-$

$\qquad\qquad 0.02 \quad 0.02$

$KSP = [Ba^+] [IO_3^-]^2$

$KSP = (x) (\underline{2x} + 0.02)^2$ ………..($\underline{2x}$ is ignored because it is very small)

$1.57 \times 10^{-9} = (x)(0.02)^2$

$1.57 \times 10^{-9} = 0.04x$

$X = 3.9 \times 10^{-6}$ mole/L

The example show, that the solubility of $Ba(IO_3)_2$ is 3.9×10^{-6} mole/L in presence of common ion , from another example , it found that the solubility of $Ba(IO_3)_2$ in water (absence of common ion) is 200 folds grater than the first value. That means , the presence of common ion cause a decreasing in solubility value of the precipitate.

2) 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 .

$$Mg(OH)_2 \rightleftharpoons Mg^{+2} + 2OH^-$$
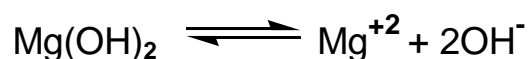
Solubility of precipitate will decreasing with increase of $[OH^-]$ concentration.

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 .

$$CaF_2 \rightleftharpoons Ca^{+2} + 2F^-$$

$$\downarrow 2H_3O^+$$

$$2HF + 2H_2O$$
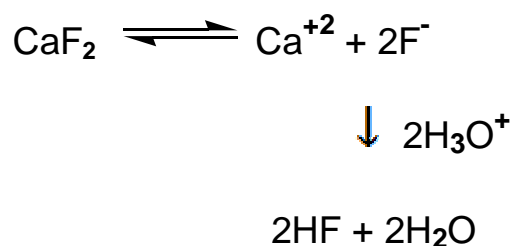
CaF_2 is a salt of a weak acid (HF) , according to **Le Chatelier principle** , increasing in $[H_3O^+]$ concentration causes an increasing in HF concentration and decreasing in F^- concentration. then , solubility of precipitate will be increase.

3) **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.

$$Al(OH)_3 \rightleftharpoons Al^{+3} + 3OH^-$$

$$\downarrow + 6F^-$$

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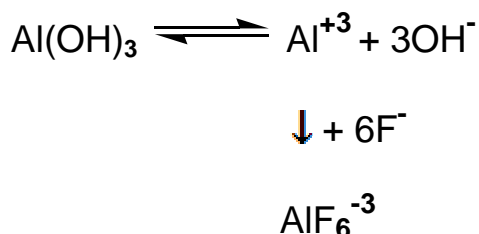
The precipitate of (Al^{+3}) with base is never complete in the presence of F^- ion even thought $Al(OH)_3$ has low solubility , therefore, the compete is extremely between F^- and OH^- for Al^{+3}. when F^- concentration is increased, more of $Al(OH)_3$ is dissolved and converted to AlF_6^{-3} ions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

4) **Temperature :** increasing of temperature will causes an increasing in solubility of precipitate , and that leading to an increase in KSP value for precipitates with slightly soluble.

Effect of electrolyte concentration on solubility :

It is found experimentally that the precipitates tend to be more soluble in an electrolyte solution than in water. provided that the electrolytes contains no ions in common with the precipitate.

The effect of an electrolyte upon solubility stems from the electrostatic attraction between the foreign ions of opposite charge in the precipitate. Such the interactions shift to the position of the equilibrium.

The figure demonstrate the magnitude of this effect for three precipitates . a two fold increase in the solubility of $BaSO_4$ is observed when the

KNO_3 concentration is increased from (0-0.02M) . the same change in electrolyte concentration increases the solubility of $Ba(IO_3)_2$ by a factor of only 1.25 and AgCl by 1.20

The data of table shows that the degree of dissociation of acetic acid is increase in the presence of sodium chloride, and the shift in equilibrium can be attributed to the attraction between the ions of the electrolyte and the charged hydronium and acetate ions.

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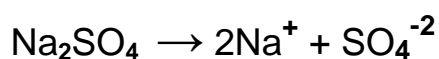
Ionic strength $(\mu) = \frac{1}{2} \Sigma c_i z_i^2$ where : c_i = conc. of ions .

z_i = charge of ions .

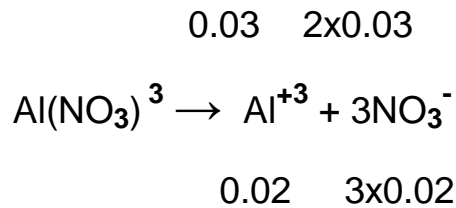**EX.** Calculate ionic strength of 0.1M sol. of KNO_3 and for 0.1M sol. Na_2SO_4 ?

$KNO_3 \rightarrow K^+ + NO_3^-$

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

$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{-2}$
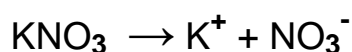
$\mu = \frac{1}{2} (0.2 \times 1^2 + 0.1 \times 2^2) = 0.3$

EX. Calculate ionic strength of a sol. contains 0.03M of $ZnCl_2$ and 0.02M   of $Al(NO_3)^3$?

$ZnCl_2 \rightarrow Zn^{+2} + 2Cl^-$

$$0.03 \quad 2\times0.03$$

$$Al(NO_3)^3 \rightarrow Al^{+3} + 3NO_3^-$$

$$0.02 \quad 3\times0.02$$

$$\mu = \tfrac{1}{2}\,(0.03 \times 2^2 + 0.06 \times 1^2 + 0.02 \times 3^2 + 0.06 \times 1^2) =$$

Coefficient of activity :

The calculation that related with solubility by using molar concentration are true in case of diluted sol. $\approx$ (10^4 M) , but in case of sol. with 10^2 M , there is a difference between theoretical and practical results . and the difference is more than in concentrated sol. (up to 10^2 M) because of interionic attraction formation of complex ion or both.

Therefore , the active concentration for ions that called (activity) will be various from actual concentration. and the relation between activity and actual concentration can be expressed as :

$a = cf$ where : a = activity or active concentration.

c = actual concentration.

f = coefficient of activity.

f can be calculate from Debye-Huckel limiting low as:

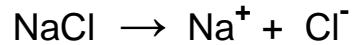$\log f = - 0.5\, z^2 \sqrt{\mu}$ where :   f = coefficient of activity.

0.5 = constant for water as a solvent at 25C^o .

z = charge of ion.

μ = Ionic strength.

EX. If $Ba(SO_4)^{-2}$ is precipitated from a sol. contains 0.012M NaCl and 0.002M BaCl$_2$, what is the concentration of SO_4^{-2} that is enough to saturate the sol. with $BaSO_4$?
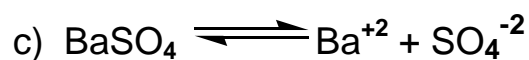
a) ionic strength:

$$NaCl \rightarrow Na^+ + Cl^-$$

$$0.012 \quad 0.012$$

$$BaCl_2 \rightarrow Ba^{+2} + 2Cl^-$$

$$0.002 \quad 2\times0.002$$

$\mu = \frac{1}{2}\ (0.012\times1^2 + 0.012\times1^2 + 0.002\times2^2 + (2\times0.002)\times1^2)$

$= 0.018$

b) $\log f = -0.5\ (2\times2)\ \sqrt{0.018} = 0.6$

c) $BaSO_4 \rightleftharpoons Ba^{+2} + SO_4^{-2}$

$KSP = [Ba][SO_4]$

$1.1\times 10^{-10} = (0.002)(SO_4)$

$[SO_4^-] = 5\times10^{-8}$ mole/L

This result (5×10^{-8} mole/L) was calculated in absence of μ and f .

While , in presence of both, then :

$KSP = f\ [Ba]\ f\ [SO_4]$

$1.1\times10^{-10} = 0.6(0.002) \times 0.6\ [SO_4]$

$[SO_4^-] = 1.39\times10^{-7}$ mole/L

$\dfrac{1.39\times10^{-7}}{5\times10^{-8}} = 2.8$ folds (the difference)