Precipitation Titrations!

Titrations which results in the formation of precipitate or sparingly soluble salt.

* Requirements for a precipitation reaction to be included in precipitation titration :-

① Precipitation reactions reaches equilibrium rapidly after each addition of titrant.

② No interferring reaction be present (eg. co-precipitation, adsorption)

③ Indicator capable of locating the equivalence point with fair accuracy should be readily available.

$$A^+ + B^- \rightleftharpoons \underset{\text{(sparingly soluble)}}{AB}.$$

→ most of the times, reactions involving silver ions are included in precapitation reactions.

* ARGENTIMETRIC TITRATIONS :-

→ most common and frequently used precipitation titrations involves titration of halides (chloride, bromide, iodide) by silver. They are called as Argentimetric titrations.

$$Ag^+ + X^- \rightleftharpoons AgX_{(s)} \qquad (X = Cl^-, Br^-, I^-) \quad — ①$$

For a sparingly soluble salt, solubility product is given by,

$$K_{sp} = [Ag^+][X^-]$$

For Rxn 1, equilibrium constant $K = \dfrac{1}{[Ag^+][X^-]}$

$$K = \frac{1}{K_{sp}}.$$

Greater the Ksp ; Smaller the K.

	Ksp	K
AgCl	1.2×10^{-10}	8.33×10^{9}
AgBr	5.2×10^{-13}	1.92×10^{12}
AgI	1.7×10^{-16}	5.88×10^{15}

eg. During a precipitation titration of $AgNO_3$ v/s NaCl.

$$Cl^- + Ag^+ \rightleftharpoons AgCl_{(s)}.$$

titrand - NaCl
titrant - $AgNO_3$

- Initially only Cl^- ions are present.
- As the titration proceeds, the conc. of chloride ions changes.
- The change in Cl^- ions will be significant in the vicinity of equivalence point.
- Greater the K value, greater will be the change in the concentration.
- Chemical indicator which produces a visually detectable change in colour or turbidity in the solution is used to select the end point of titration.

① Mohr's method ⟶ formation of second coloured precipitate / complex.

② Vohlard's method ⟶ formation of coloured complex / precipitate.

③ Fajan's method ⟶ adsorption Indicator.

* Construction of Titration Curve :-

- Titration curve for precipitation titration are similar to those for acid-base titration.
- Equilibrium calculations are based upon the solubility product constant.
- Titration curves are useful for deducing the properties of the indicator for the titration as well as titration error that is likely to be encountered.

eg. 10 cm^3 0.1 M NaCl v/s 0.1 M $AgNO_3$.

$$NaCl + AgNO_3 \longrightarrow AgCl \downarrow + NaNO_3.$$

$$Cl^- + Ag^+ \longrightarrow AgCl \downarrow.$$

$$K_{sp} = [Ag^+][Cl^-]$$
$$= 1.2 \times 10^{-10}$$

ⓐ At the beginning :-

→ no $AgNO_3$ has been added.
→ only Cl^- ions are present.

$$[Cl^-] = 0.1$$

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

ⓑ 2.0 cm^3 of $AgNO_3$ is added.

volume of NaCl reacted = 2 cm^3
volume of NaCl unreacted = 8 cm^3
Total volume of solution = 12 cm^3

$$[Cl^-] \times 12\,cm^3 = 0.1 \times 8\,cm^3$$

$$[Cl^-] = \frac{0.1 \times 8}{12}$$

$$[Cl^-] = 6.66 \times 10^{-2}$$

$$\therefore pCl = -\log[Cl^-]$$
$$= -\log[6.66 \times 10^{-2}]$$
$$pCl = 1.18$$

ⓒ 5 cm^3 of $AgNO_3$ is added :-

volume of NaCl reacted = 5 cm^3
volume of NaCl unreacted = 5 cm^3
Total volume of solution = 15 cm^3

$$[Cl^-] \times 15\,cm^3 = 0.1 \times 5\,cm^3$$

$$[Cl^-] = \frac{0.1 \times 5}{15}$$

$$[Cl^-] = 3.33 \times 10^{-2}$$

$$\therefore \quad pCl^- = -\log[Cl^-]$$

$$= -\log[3.33 \times 10^{-2}]$$

$$pCl^- = 1.48.$$

ⓓ Vicinity of equivalence point :- (9.9 cm^3)

volume of NaCl reacted = 9.9
volume of NaCl unreacted = 0.1
Total volume of solution = 19.9

$$[Cl^-] \times 19.9 = 0.1 \times 0.1$$

$$[Cl^-] = \frac{0.1 \times 0.1}{19.9}$$

$$[Cl^-] = 5.025 \times 10^{-4}$$

$$\therefore pCl^- = -\log[Cl^-]$$

$$= -\log[5.025 \times 10^{-4}]$$

$$pCl^- = 3.30$$

ⓓ At equivalence point :- (10.0 cm^3 $AgNO_3$)

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

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

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

$$K_{sp} = [Ag^+]^2 = [Cl^-]^2$$

$$\therefore [Ag^+] = [Cl^-] = \sqrt{K_{sp}}$$

$$= \sqrt{1.2 \times 10^{-10}}$$

$$[Ag^+] = [Cl^-] = 1.095 \times 10^{-5}$$

$$pAg^+ = pCl^- = -\log[Cl^-]$$

$$= -\log[1.095 \times 10^{-5}]$$

$pCl^- = 4.96$

f. 10.1 cm^3 $AgNO_3$ is added.

volume of $AgNO_3$ in excess = 0.1 cm^3

Total volume of soln = 20.1 cm^3.

$$[Ag^+] \times 20.1 = 0.1 \times 0.1$$

$$[Ag^+] = \frac{0.1 \times 0.1}{20.1}$$

$$[Ag^+] = 4.975 \times 10^{-3}$$

$$p[Ag^+] = -\log [Ag^+]$$

$$= -\log [4.975 \times 10^{-3}]$$

$$p[Ag^+] = 3.303$$

$$pAg^+ + pCl^- = pAgCl.$$

$$3.303 + pCl^- = 9.92$$

$$pCl^- = 9.92 - 3.303$$

$$pCl^- = 6.517$$

g) 11.0 cm^3 of $AgNO_3$ is added :-

vol. of $AgNO_3$ in excess = 1 cm^3

Total volume of soln = 21 cm^3.

$$[Ag^+] \times 21 = 0.1 \times 1$$

$$[Ag^+] = 4.76 \times 10^{-3}$$

$$p[Ag^+] = -\log [Ag^+]$$

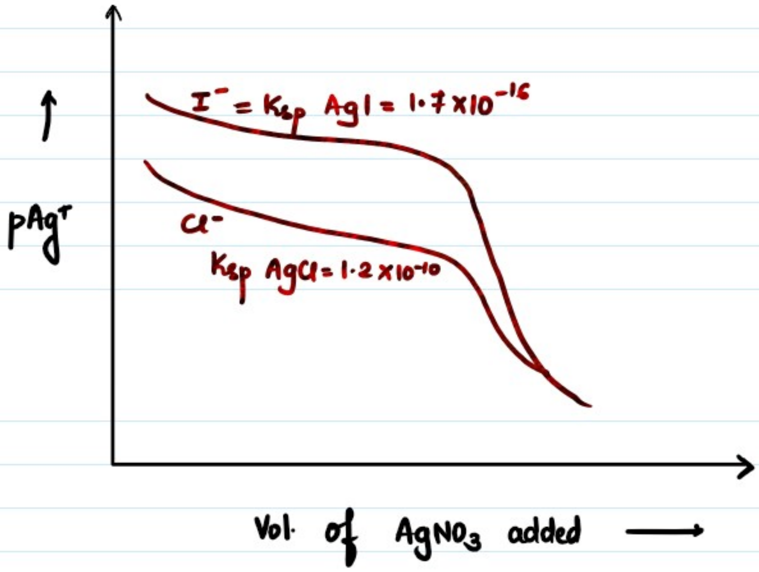
$$= -\log [4.76 \times 10^{-3}]$$

$$p[Ag^+] = 2.322$$

$$pAg^+ + pCl^- = pAgCl$$

$$pCl^- = 9.92 - 2.322$$

$$pCl^- = 7.60$$



① Vohlards method :-

- → based on formation of soluble coloured complex.
- → used to determine the end-point in argentimetric titration.
- → Titration of silver in acid solution with standard potassium thiocyanate using ferric nitrate or ferric alum solution.

$$Ag^+ + SCN^- \rightleftharpoons Ag(SCN) \quad —①$$

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

Reddish brown in colour.

After Rxn 1, slight excess reacts with Fe^{3+} ions

→ determination of halides (Cl^-, Br^-, I^-) in acid solⁿ = indirect method.

→ measured excess amount of $AgNO_3$ is added to acid solⁿ of halide.
excess $AgNO_3$ is back titrated with KSCN with ferric nitrate / ferric alum as indicator.

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

✓ $\underset{(excess)}{Ag^+} + \underline{\underline{SCN^-}} \rightleftharpoons AgSCN.$

} sparingly soluble salt.

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

$K_{sp}\ (AgCl) = [Ag^+][Cl^-]$ $\qquad$ $[Ag^+] = \dfrac{K_{sp}\ (AgCl)}{[Cl^-]}$

$K_{sp}\ (AgSCN) = [Ag^+][SCN^-]$ $\qquad$ $[Ag^+] = \frac{K_{sp}\ (AgSCN)}{[Cl^-]}$

$$\frac{K_{sp}\ (AgCl)}{[Cl^-]} = \frac{K_{sp}\ (AgSCN)}{[SCN^-]}$$

$$\frac{[Cl^-]}{[SCN^-]} = \frac{K_{sp}\ (AgCl)}{K_{sp}\ (AgSCN)} = \frac{1.2 \times 10^{-10}}{7.1 \times 10^{-3}} \simeq 170$$

$$AgCl + SCN^- \rightleftharpoons Ag(SCN) + \underline{\underline{Cl^-}}$$

This reaction takes place before indicator ferric ions react with SCN^-.
Thus, it is important to prevent this reaction.

① Filtration of precipitated AgCl and then titration with KSCN.
Ppt is usually contaminated with silver ions, hence suspension is boiled for few minutes to remove the adsorbed silver ions

② A coagulant like potassium nitrate is added immediately after addition of silver nitrate. Boil, cool and then titrate immediately.
KNO_3 prevents readsorption of Ag^+ ions.

③ Immiscible organic solvent is added to reduce the reaction b/w AgCl & KSCN.
eg. Benzene
Nitrobenzene ⇒ Cl^- estimation (1 mL for 50 mg Cl^-).

coagulation of AgCl happens and coating of solvent to the coagulated AgCl prevents its from reacting with the aqueous layer.

AgBr ($K_{sp} = 3.5 \times 10^{-13}$) } less soluble than Ag (SCN) = $K_{sp} = 7.1 \times 10^{-13}$
AgI ($K_{sp} = 1.7 \times 10^{-16}$) } practically no rxn takes place.

However AgI, indicator is not added unless excess $AgNO_3$ is present, otherwise I^- will react with the indicator

$$2I^- + 2Fe^{3+} \rightleftharpoons 2Fe^{2+} + I_2$$

2) Mohr's method :-

→ determination of end-point in argentimetric titration.

→ based on formation of secondary soluble coloured complex with distinct colour.

Titration of NaCl / NaBr v/s $AgNO_3$ K_2CrO_4 = indicator.

$$\left.\begin{array}{l} Cl^- + Ag^+ \rightleftharpoons AgCl. \\ Ag^+ + CrO_4^{2-} \rightleftharpoons \underset{\text{(brick red ppt)}}{Ag_2CrO_4} \end{array}\right\} \text{sparingly soluble.}$$

→ secondary ppt is distinct brick red.

→ Usually buff colour is considered as end-point of the titration

$$AgCl \rightarrow K_{sp} = 1.2 \times 10^{-10} \longrightarrow s = 1.1 \times 10^{-5} \text{ moles/L}$$

$$Ag_2CrO_4 \rightarrow K_{sp} = 1.7 \times 10^{-12} \longrightarrow s = 8.4 \times 10^{-5} \text{ moles/L.}$$

→ Ag^+ is added to large vol. of Cl^- & less vol. of CrO_4^{2-}.

Ag^+ reacts with Cl^- to form AgCl and it will not react with CrO_4^{2-} unless the concentration exceeds solubility product of Ag_2CrO_4.

eg. 0.1 M NaCl v/s 0.1 M $AgNO_3$.

At equilibrium, AgCl and Ag_2CrO_4 concentration are in equilibrium.

$$K_{sp} = [Ag^+][Cl^-] \qquad\qquad K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} \qquad\qquad [Ag^+] = \sqrt{\frac{K_{sp}}{[CrO_4^{2-}]}}$$

$$\frac{K_{sp}\,(AgCl)}{[Cl^-]} = \sqrt{\frac{K_{sp}\,(Ag_2CrO_4)}{[CrO_4]^{2-}}}$$

$$\frac{[Cl^-]}{\sqrt{[CrO_4^{2-}]}} = \frac{K_{sp}\,(AgCl)}{\sqrt{K_{sp}\,(Ag_2CrO_4)}} = \frac{1.2 \times 10^{-10}}{\sqrt{1.7 \times 10^{-12}}} = 9.2 \times 10^{-5}$$

$\longrightarrow [Ag^+] = [Cl^-] = 1.1 \times 10^{-5}$ (equivalence pt)

$$[CrO_4^{2-}] = \left(\frac{[Cl^-]}{9.2 \times 10^{-5}}\right)^2$$

$$= \left(\frac{1.1 \times 10^{-5}}{9.2 \times 10^{-5}}\right)^2$$

$$= 1.4 \times 10^{-2}$$

$$[CrO_4^{2-}] = 0.014$$

conc. of 0.014 is avoided. As deep orange colour of chromate ion makes it difficult to detect brick red colour of silver chromate.

Usually sol^n of 0.003 - 0.005 M is used.

$$\left.\begin{array}{l} [Ag^+] = \sqrt{\frac{K_{sp}}{CrO_4^{2-}}} = \sqrt{\frac{1.7 \times 10^{-12}}{0.003}} = 2.4 \times 10^{-5} \\ [Ag^+] = 1.1 \times 10^{-5} \end{array}\right\} \text{difference} = 1.3 \times 10^{-5} \text{ per } 1000 \text{ mL}$$

- This titration is neglected.

- blank indicator titration determination i.e. measuring vol. of std $AgNO_3$ required to give perceptible colouration in DW. This volume is subtracted from titre value of argentimetric titration.

→ Titration should be carried out in neutral / faintly alkaline pH.
pH value range of 6.5 to 9.2.

$$\left.\begin{array}{l} \text{In acidic medium,} \\ 2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^{2-} \rightleftharpoons Cr_2O_7^{2-} + H_2O \\ \text{In alkaline medium,} \\ 2Ag^+ + 2OH^- \rightleftharpoons 2AgOH \rightleftharpoons Ag_2O + H_2O \end{array}\right\} \text{avoided}$$

- At high temperature, solubility of Ag_2CrO_4 increases.

→ I^- & SCN^- = this technique can't be used as they both strongly adsorb chromate ion and end point can't be detected.

3) Adsorption Indicator :-

→ use of adsorption indicator was developed by Fajan

→ used weak organic acid, fluorescein for titration of Cl^- with std. $AgNO_3$

→ In 1st stage, AgCl in colloidal state tends to adsorb the Cl^- ion in sol^n. Thus -ve charged colloidal state repels the fluorescein indicator.

↓

As equivalence point is approached, the adsorbed Cl^- ions are removed by Ag^+ ions.

↓

first excess of Ag^+ is adsorbed by the AgCl colloidal state sol^n. Now the -vely charged fluorescein indicator is attracted to the positively charge surface imparting pink to reddish colour.

→ Because of adsorption and not precipitation.

→ Dextrin is added as protective colloid to keep the ppt highly dispersed.

→ low conc. ; less exposure to light ⟹ to prevent photo-decomposition of $AgNO_3$

Thank-You