Precipitation Titrations

Precipitation Titrations are the titrations that involves the formation of precipitate.

In the precipitation titration the titrant react with Analyte and forms an insoluble substance called precipitate. It continues till the last amount of analyte is consumed.

→ This type of titrations are not frequently used compared to the other titrimetric methods due to lack of suitable indicators & slow rate of reaction.

→ In this precipitate titrations silver nitrate is widely used as a precipitating agent. so that these titrations are also called as Argentimetric titrations.

→ precipitation titrations are mainly used on the principle of solubility product.

Solubility product (Ksp) :- & solubility.

Solubility: Concentration of saturated solution is known as solubility and it is temperature dependent.

Eg:- NaCl is taken dissolved in water then the reaction is

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

By applying law of mass of action

$$K = \frac{[Na^+][Cl^-]}{[NaCl]} \quad -①$$

$$K \times [NaCl] = [Na^+][Cl^-] \quad -②$$

$$\text{So } K \times [NaCl] = Ksp \quad -③$$

here K is constant

K_{sp} → solubility product

Conc of [NaCl] is always constant and it is present in solid form & no effect of temparature in solubility.

$\therefore K_{sp} = [Na^+][Cl^-]$ - (1)

Here

$K_{sp} > [Na^+][Cl^-]$ No precipitation is formed

$K_{sp} = [Na^+][Cl^-]$ saturation of solution takes place

$K_{sp} < [Na^+][Cl^-]$ precipitation is formed

Relation Ship between Solubility(S) & solubility product (K_{sp})

we take NaCl is an Example. NaCl is dissolved it can follows as

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

if solubility of NaCl = s mol/L (represents as)

Then it will produce s mole of Na^+ & s mole Cl^-

so, $K_{sp} = [Na^+][Cl^-]$

$K_{sp} = s \times s$

$K_{sp} = s^2$ (or) $s = \sqrt{K_{sp}}$

At equivalance point in the ppt titrations, the concentration of ions is given by the square root of solubility product. $S = \sqrt{K_{sp}}$

→ The sharpness of titration curve of the ppt titration is depends upon the concentrations of solutions & as well as solubility products

Some of the Ksp values are in below at temp 25°c (room temp).

→ Silver chloride — Ksp value is 1.2×10^{-10}

→ $Ba(No_2)_2$ — 4.64×10^{-3}

→ $PbSo_4$ — 2.53×10^{-8}

→ Hg_2Cl_2 — 1.43×10^{-18}

→ Ag_2CrO_4 — 1.2×10^{-12}

In Argentimetric titrations the determination of End point can be Expressed by ~~Differ~~ using different methods

They are (1) Direct method

(2) Indirect method.

factor's effecting solubility of precipitation:-

Acid effect :- solubility of salt will be increased by increasing acid.

Eg: when slightly soluble salt BA & a weak acid HA is taken, then the equilibrium equation we observes as

Salt BA $\rightleftharpoons$ $B^+ + A^-$

(weak acid) HA $\rightleftharpoons$ $H^+ + A^-$ Common ion effect

Anion of salt should be conjugate of the weak acid

Effect of Temparature :- most of inorganic salts are increased by increasing solubility Temparature

Eg: AgCl $\begin{cases} 10^\circ C - 1.72\ g/L \\ 100^\circ C - 21\ g/L \end{cases}$

$BaSO_4$ $\begin{cases} 10^\circ C - 2.2\ g/L \\ 100^\circ C - 3.9\ g/L \end{cases}$

3) Effect of solvent :- nitric acid

most of the inorganic solvents are more soluble in water.
here water shows dipole moment & attracts cations, & anions.

Eg: Addition of 20:1 ethanol into $PbSO_4$
$PbSO_4$ is not completely soluble & forms precipitate

Precipitation titrations :-

In this precipitation of titrations widely or mostly used the $AgNO_3$ (Silver Nitrate) as a precipitating reagent.
so that it is also called as Argentometric titrations.

By using the $AgNO_3$ (precipitating reagent) we can analyse the titrations of halides & pseudo halides.
(Cl^-, Br^-, I^-) ($SCN^-, SO_4^{2-}, CN^-, HS^-$).

Titration of NaCl by $AgNO_3$:-

Titration of 20 ml 0.1M NaCl with 0.1 M $AgNO_3$.

pre equivalance region

when 0.0 ml titrant ($AgNO_3$) is added

$[Cl^-] = 0.1M$

$pCl = -\log([Cl^-]) = -\log(0.1) \Rightarrow \log 1/0.1 = \log 10 = 1$

When 10 ml of 0.1 M $AgNO_3$ is added into 20 ml NaCl

total volume = 20 ml NaCl + 10 ml $AgNO_3$ = 30 ml

Remaining conc of Cl^- = $\frac{10}{30} \times 0.1 \Rightarrow \frac{1}{30}$

$pCl = -\log \frac{1}{30} = \log \frac{30}{1} = 1.4771$.

At equivalance point

When 20 ml of 0.1 M $AgNO_3$ is added into 20 ml 0.1 M NaCl.

$[Ag^+] = [Cl^-]$ - ① ; $K_{sp}[AgCl] = [Ag^+][Cl^-]$ - ②

$K_{sp}[AgCl] = 1.7 \times 10^{-10}$ - ③

$[Ag^+][Cl^-] = 1.7 \times 10^{-10}$ - ④

$[Cl^-][Cl^-] = 1.7 \times 10^{-10}$ (or) $[Cl^-]^2 = 1.7 \times 10^{-10}$ - ⑤

$[Cl^-] = \sqrt{1.7 \times 10^{-10}} \Rightarrow 1.33 \times 10^{-5}$

$pCl = -\log 1.33 \times 10^{-5} = 5 - \log 1.33 \Rightarrow 5 - 0.224$

$pCl \Rightarrow 4.876$

post equivalance point;

when 21 ml of 0.1 M $AgNO_3$ is added then final volume = 41 ml

$[Ag^+] = \frac{1}{41} \times 0.1 = \frac{0.1}{41} = \frac{1}{410}$

$pAg = -\log 1/410 = \log 410 \Rightarrow 2.613$.

Then final pCl = $4.876 + 2.613 = 7.489$