Precipitation TITRATIONS

From Mountains
to
Mole Hills
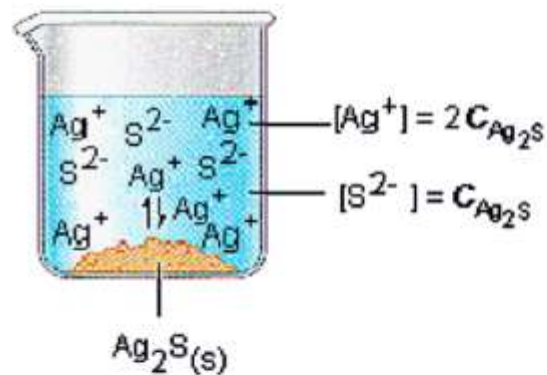it takes
KSP

$[Ag^+] = 2 C_{Ag_2S}$

$[S^{2-}] = C_{Ag_2S}$

$Ag_2S_{(s)}$

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FLOW

INTRODUCTION

THEORY of pptn titration

FACTORS AFFECTING to pptn tn

END pt DETECTION

INTRODUCTION

Defination:

- Titration involving reaction btwn titrant and titrate results in the formation of ppts or slightly soluble ionogen

[sum15]

Ideal requirement of pptn tn

- Ppt must be insoluble
- Rapid titration reaction
- Reaction should proceed with stoichiometric relationship
  E.g.

$$AgNO_3 + KSCN \longrightarrow AgSCN + KNO_3$$

  Analyte   reagent   ppt

- Absence of co-pptn and post-pptn
- Suitable method (indicator) to detect end point.

THEORY of pptn titration

SOLUBILITY PRODUCT (Ksp)

- Ppt (insolublility) and solublitiy of the product may explained as an reaction with equilibrium constant..

E.g.
- Aq. soln of slightly soluble AB compound,

$$BA_{(ppt)} \rightleftharpoons B^+ + A^-$$

- Equilibrium $k = \dfrac{[B^+]\ [A^-]}{[BA]}$

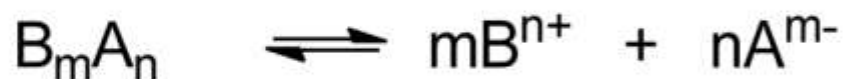- Now, in dilute solutions there is essentially activity of ppt BA will be constant, so…

$$K_{sp} = [B^+]\ [A^-]$$

THEORY of pptn tn

- Solubility product constant Ksp

$$K_{sp} = [B^+] \ [A^-]$$

- Ksp for general pptn rxn,

$$B_m A_n \ \rightleftharpoons \ mB^{n+} \ + \ nA^{m-}$$

$$K_{sp} = [B^{n+}]^m \ [A^{m-}]^n$$

Conclusion,

- a pdct ppted out when the ionic [ ] exceeds the Ksp value of pdct at particular solvent and temperature.
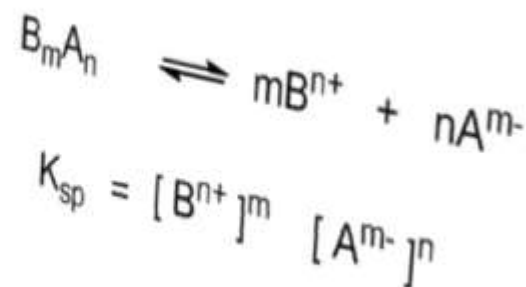
THEORY of pptn tn

Applications of Ksp

1. Calculation of solbility,

- e.g finding solubility of Ag_2CrO_4 , Ksp = 1.7×10^{-11} (mol/ L)^3

- Ionization reaction,

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

$$B_mA_n \rightleftharpoons mB^{n+} + nA^{m-}$$

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

$$K_{sp} = [\,B^{n+}\,]^m\ [\,A^{m-}\,]^n$$

- Here both ions produced at same proportions [ ], let us assume solubility Ag_2CrO_4 = S

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

  S   2S   S   S = concentration

THEORY of pptn tn

- Applications of Ksp

$$K_{sp} = (2S)^2 \; S$$

$$= 4S^3$$

$$1.7 \times 10^{-11} = 4S^3$$

$$\therefore \quad S = 1.5 \times 10^{-4} \text{ mol/ L}$$

Solubility as gram = 1.5×10^{-4} mol / L X 332 g/mol

$$= 0.049 \text{ g / L}$$

- The solubility of Ag_2CrO_4 is 0.049 g / L

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THEORY of pptn tn

2. Predicting the pptn of pdct

- If ionization [ ] of pdct (molar [ ] of ions = MIC) is less than its solubility pdct (Ksp), the soln is said to be unsaturated (no pptn).

- If ionization [ ] of pdct is more than its solubility pdct (Ksp), the soln is said to be saturated (pptn appears).

MIC < Ksp	Unsat. soln
MIC = Ksp	sat. soln
MIC > Ksp	Super sat. soln

THEORY of pptn tn

3. Inorganic qualitative analysis

- Cations of group II (Cu^{+2}, Sn^{+2}) are ppted as their sulphides by passing H2S gas in acidic media.

- Cations of group III are ppted as their hydrides by treating amm. Hydroxide + amm. chloride.

- Cations of group V are ppted as their carbonates by treating amm. Carbonate in acidic media.

THEORY of pptn tn

4. Fractional pptn

⌐9⟩ is the pptn of one compound in a condition that will not allow pptn of other substances.

- Cations ppted as sulphides, halides, hydroxides or carbonates.
- Pptn for particular compound can be controlled by pH of solution.

- Applied in limit test of impurities
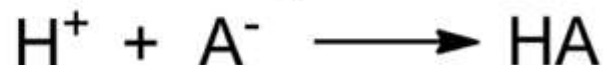
FACTORS AFFECTING to pptn tn

a. **Effect of temperature:**

- As the temp. ↑   solubility ↑   Ksp ↑

- E.g. solubility of AgCl   at 10^oC 1.72 mg / L
  at 100^oC 21.1 mg / L

b. **Effect of pH:**

- Solubility of any compound is affected by addition of strong acid or base.

- E.g. $MA \rightleftharpoons M^+ + A^-$

- If pH is ↓ by adding strong acid, proton removes A- ions . Hence increases the solubility of MA

$$H^+ + A^- \longrightarrow HA$$

FACTORS AFFECTING to pptn tn

c. **Effect of Chelating agents**
- Forms complex with cation (soluble fraction of compound) so it increase the solubility of ppts

d. **Effect of dilution**
- Increase the solubility
- Ksp remains constant

e. **Common Ion Effect**
- decrease the solubility
- E.g. Addition of NaCl ↓ solubility of AgCl

FACTORS AFFECTING to pptn tn

f. Diverse ion or Activity Effect
- increase the solubility
- Addition of inert electrolytes, the inert ion just shields the dissociated ion species and prevent their ppt forming reaction.
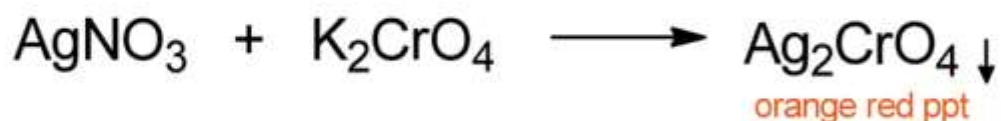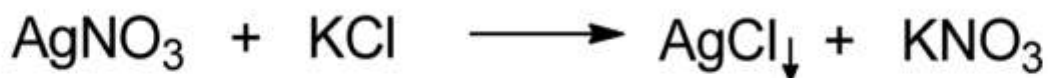
END pt DETECTION

1. Mohr's method (1856)

- Estimation of chlorides and bromides ions
- titrant is $AgNO_3$
- Indicator pot. Chromate

$$AgNO_3 + KCl \longrightarrow AgCl\downarrow + KNO_3$$

$$AgNO_3 + K_2CrO_4 \longrightarrow Ag_2CrO_4 \downarrow$$

orange red ppt

During titration…

- As $AgNO_3$ is added AgCl ppt first before the equivalence pt. Cl^- is in excess
- after the equivalence pt. Ag^+ (as there will be no more Cl^-) reacts with chromate ion and give orange-red ppt.

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END pt DETECTION

1. Mohr's method

- The [ ] of indicator is imp. for just start of ppt formation ($Ag_2CrO_{4\ ppt}$) at the equivalence pt.

- Need to find the right [ ] of indicator to generate the true end pt.

$$K_{sp^{AgCl}} = [Ag^+][Cl^-] \qquad \& \qquad K_{sp^{Ag_2CrO_4}} = [Ag^+]^2[CrO_4^-]$$

- At the pt (of end pt) of first appearance of red Ag_2CrO_4 ppt, both salts in equilibrium state with the soln.

$$\therefore \qquad \frac{K_{sp^{AgCl}}}{[Cl^-]} = [Ag^+] \qquad \& \qquad \frac{\sqrt{K_{sp^{Ag_2CrO_4}}}}{\sqrt{[CrO_4^-]}} = [Ag^+]$$

$$\therefore \qquad \frac{\sqrt{K_{sp^{Ag_2CrO_4}}}}{\sqrt{[CrO_4^-]}} = \frac{K_{sp^{AgCl}}}{[Cl^-]}$$

END pt DETECTION

1. Mohr's method

$$\therefore \quad \frac{[Cl^-]}{\sqrt{[CrO_4^-]}} = \frac{K_{sp}^{AgCl}}{K_{sp}^{Ag_2CrO_4}}$$

$$\therefore \quad \frac{[Cl^-]}{\sqrt{[CrO_4^-]}} = \frac{1.2 \times 10^{-10}}{\sqrt{1.7 \times 10^{-12}}}$$

$$\therefore \quad \frac{[Cl^-]}{\sqrt{[CrO_4^-]}} = 9.2 \times 10^{-5} \qquad \text{... Eq. 1}$$

END pt DETECTION

1. Mohr's method

- Now, at the equivalence pt. $[Ag^+] = [Cl^-]$

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

$$\therefore \quad = [Cl^-]^2$$

$$\therefore \quad [Cl^-] = \sqrt{K_{sp^{AgCl}}}$$

$$\therefore \quad [Cl^-] = \sqrt{1.2 \times 10^{-10}}$$

$$\therefore \quad [Cl^-] = 1.1 \times 10^{-5}$$

- Adding this value to ... Eq. 1

$$\therefore \quad \frac{1.1 \times 10^{-5}}{\sqrt{[CrO_4^-]}} = 9.2 \times 10^{-5}$$

END pt DETECTION

1. Mohr's method
- Thus..

$$\therefore \quad \frac{1.1 \times 10^{-5}}{9.2 \times 10^{-5}} = \sqrt{[CrO_4^-]}$$

$$\boxed{[CrO_4^-] = 1.4 \times 10^{-2}}$$

- If [ ] of indicator is > 0.014 Ag_2CrO_4 ppt before equivalence pt
- If [ ] of indicator is < 0.014 Ag_2CrO_4 ppt far after equivalence pt

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END pt DETECTION

1. Mohr's method
LIMITATIONS

- Mohr method should be applied in neutral or slightly alkaline pH (6.5 - 9)
    - In acidic media cromate ion degrades to dicromate ion
    - In alkaline media Ag gives side pdct of $Ag(OH)_2$ and Ag_2O
- Limited application,
    - Not applicable to iodide, SCN- bc AgI and AgSCN will adsorb chromate ion and generate false end pt.
- Performed at (only) r.t.
    - As temp. vary , solubility of ppt also vary

END pt DETECTION

2. Volhard's method (1856)

- Estimation of chlorides , bromides, iodide, + pseudo halides (OCN-,) ions
- titrant is $AgNO_3$

- Principle: indirect (back) titration
- sample (e.g. Cl^-) is reacted with excess $AgNO_3$
- Unreacted $AgNO_3$ back titrated with amm. thiocyanate
- Indicator: ferric amm. sulphate   to red

$$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + KNO_3 + AgNO_3$$
excess

$$AgNO_3 + NH_4SCN \longrightarrow AgSCN + NH_4NO_3$$

$$Fe^{+3} + NH_4SCN \longrightarrow Fe(SCN)^{+2}$$
Red color

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END pt DETECTION

2. Volhard's method (1856)

Conditions,

Must be acidic condition (HNO_3 is added)
- bc. in basic cond.n ferric ppt as hydrate and oxides

Use of nitrobenzene
- side rxn of AgCl

$$AgCl_\downarrow + SCN^- \longrightarrow AgSCN_\downarrow + Cl^-$$

- AgCl ppt may be filtered off before back titration,
- or, heavy organic liquid (immiscible with water, like CCl_4, chloroform, nitrob.) is added.
- These liq. form a coat over AgCl ppt and prevent their side reactions.
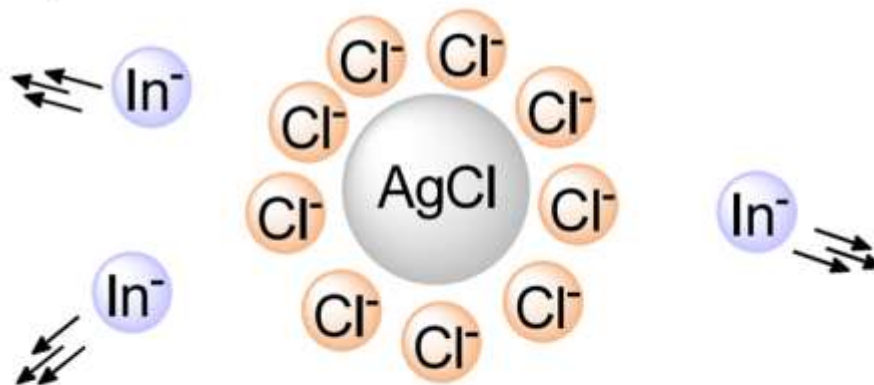
END pt DETECTION

3. Fajan's method   (1856)

- Adsorption Indicator (e.g. fluorecein)
- are organic dyes (wa-) , adsorbed to +ve charge of solid ppt formed during particles

E.g. of Cl^- titration with Ag^+ and fluorecein as indicator

- Before equivalence pt, sol.n excerts free indicator

$$AgNO_3 + NaCl \longrightarrow AgCl\downarrow + Cl^-$$
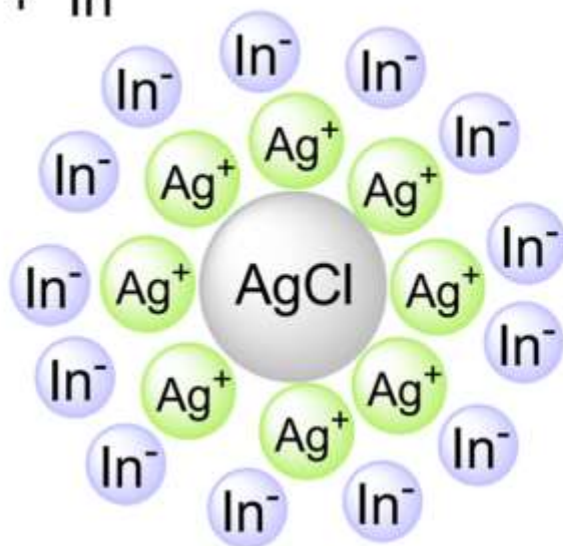$$\text{excess}$$

Diagarmatic representation of ion iteractions

(yellow-green colour)

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END pt DETECTION

3. Fajan's method

- After equivalence pt, sol.n excerts adsorbed indicator

$$AgCl \quad + \quad Ag^+ \quad + \quad In^-$$

Diagarmatic representation of ion iteractions
(red colour)

- The color of the adsorbed indicator is diff. from that of the unadsorbed indicator. That signals the end pt. of titation.

END pt DETECTION

3. Fajan's method

Common adsorption indicators:

Indicators	Color Change	Applicable
Fluorescein	Yellow-green to pink	Halides, pH 7-10
Eosin	Pink to red-violate	In absence of Cl- , pH > 1
Diiododimethylfluorescein	Orange to blue	I- , pH 4-7

END pt DETECTION

3. Fajan's method

Factors for consideration:

- Adsorption of indicator should happen near the equivalence point.
- Proper pH adjustment
- choose ionic form of indicator with opposite ionic charge in opposite of titrant ion.

Adv.

- rapid, accurate and reliable

Limitations:

- Not applicable for low reacting ions, low [ ] of ions (as not enough ppt to allow colour change)
- Method is pH dependent (for ionization of the indicator)

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4. **Non-precipitation method:**

- Used for the estimation of silver ion, titrant is std. NaCl soln.

- During titration AgCl ppt is formed , and are <u>allow to settle</u> at the bottom
- After that next drop of titrant is added
- The process is continued till the is no ppt formation observed, which indicates the end pt.

Factors for consideration:
- In acidic condition
- Use of coagulating agent (barium nitrate) to assist coagulation.

End of topic

Reference:

Ph'cal Analysis-I – Dr. Dimal Shah

Ph'cal Analysis – Dr. A.V. Kasture