GROUP-1

Monday, 6 January 2025 1:37 AM

CATIONS

Grp-1: Pb^{2+} & Ag^{+}

Reagent ⇒ HCl

Form insoluble salts $\underbrace{PbCl_2 \text{ \& } AgCl}_{\text{white ppt.}}$

↳ $PbCl_2$, however is slightly soluble in water & therefore lead is never completely precipitated by adding dil. HCl to a sample.

↳ Lead readily dissolves in moderately conc. HNO_3

$$Pb + HNO_3 \longrightarrow Pb^{2+} + NO_3^{-1} + NO\uparrow + H_2O$$

The colourless NO gas, when mixed with air, is oxidized to reddish brown NO_2.

$$\underset{\text{Colourless}}{NO} + O_2 \longrightarrow \underset{\text{reddish brown.}}{NO_2}$$

↳ With conc. HNO_3 a protective film of $Pb(NO_3)_2$ is formed on the surface of the metal & prevents further dissolution

Rx^n of Pb^{2+} ions: Salt ⇒ $Pb(NO_3)_2$ or $Pb(CH_3COO)_2$

1. Dilute HCl or soluble Chloride like NaCl or KCl

$$Pb^{2+} + 2Cl^- \rightleftharpoons PbCl_2\downarrow \{\text{white ppt}\}.$$

The ppt. is soluble in hot water but separates again in long, needle-like crystals when cooling

It is also soluble in conc. HCl or conc. KCl.

$$PbCl_2 \downarrow + 2Cl^- \longrightarrow \underset{\text{Tetra Chlorido Plumbate (II)}}{[PbCl_4]^{2-}}$$

If the ppt. is washed by decantation & dil NH_3 is added, no visible change {difference from Ag^+} though, a ppt. exchange rx^n takes place & $Pb(OH)_2$ is formed.

$$\underset{\text{white}}{PbCl_2 \downarrow} + NH_3 + H_2O \longrightarrow \underset{\text{white}}{Pb(OH)_2 \downarrow} + NH_4^+ + Cl^-$$

2. H_2S {gas or saturated aq. sol^n} in neutral or dilute acidic medium

$$Pb^{2+} + H_2S \longrightarrow \underset{\text{black}}{PbS \downarrow} + 2H^+$$

↳ PPt. is incomplete if strong mineral acids are present in more than 2M conc.

↳ When H_2S gas is introduced into a mixture which contains a ppt. of $PbCl_2$

$$\underset{\text{white}}{PbCl_2 \downarrow} + H_2S \longrightarrow \underset{\text{Black}}{PbS \downarrow} + H^+ + Cl^-$$

↳ If the test is carried out in the presence of larger amounts of Chloride {saturated KCl} initially a red ppt.

↳ If the test is carried out in the presence of larger amounts of Chloride {saturated KCl} initially a red ppt. of lead sulphochloride is formed when introducing H_2S gas.

$$Pb^{2+} + H_2S + Cl^- \longrightarrow \underset{\text{red}}{Pb_2SCl_2\downarrow} + H^+$$

This however decomposes on dilution or on further addition of H_2S & a black ppt of PbS is formed.

$$Pb_2SCl_2\downarrow \longrightarrow PbS\downarrow + PbCl_2\downarrow$$

$$Pb_2SCl_2\downarrow + H_2S \longrightarrow PbS\downarrow + Cl^- + H^+$$

↳ Lead sulphide decomposes when conc. HNO_3 is added & white finely divided elemental S is ppt.

$$PbS\downarrow + HNO_3 \longrightarrow Pb^{2+} + NO_3^{-1} + S\downarrow + NO\uparrow + H_2O$$

If the mixture is boiled, sulphur is oxidized by nitric acid to sulphate which immediately forms white $PbSO_4$.

$$S\downarrow + HNO_3 \longrightarrow SO_4^{2-} + H^+ + NO\uparrow$$

$$Pb^{2+} + SO_4^{2-} \longrightarrow \underset{\text{white}}{PbSO_4\downarrow}$$

↳ On boiling PbS with H_2O_2, the black ppt turns white

$$\underset{\text{Black}}{PbS\downarrow} + H_2O_2 \longrightarrow PbSO_4\downarrow + H_2O$$

3. Ammonia sol^n

$$Pb^{2+} + NH_3 + H_2O \longrightarrow \underset{\text{white}}{Pb(OH)_2} \downarrow + NH_4^+$$

4. Sodium Hydroxide

$$Pb^{2+} + 2\bar{OH} \longrightarrow \underset{\text{white}}{Pb(OH)_2} \downarrow$$

The ppt. dissolves in excess reagent,

$$Pb(OH)_2 \downarrow + \bar{OH} \longrightarrow \underset{\text{Tetrahydroxido Plumbate (II)}}{[Pb(OH)_4]^{2-}}$$

↳ Hydrogen peroxide or ammonium peroxodisulphate, when added to a Sol^n of $[Pb(OH)_4]^{2-}$, forms a black ppt. of PbO_2

$$[Pb(OH)_4]^{2-} + H_2O_2 \longrightarrow \underset{\text{black}}{PbO_2} \downarrow + \bar{OH} + H_2O$$

$$[Pb(OH)_4]^{2-} + S_2O_8^{2-} \longrightarrow \underset{\text{black}}{PbO_2} \downarrow + \bar{OH} + SO_4^{2-}$$

5. Dilute H_2SO_4 (or soluble sulphates)

$$Pb^{2+} + SO_4^{2-} \longrightarrow \underset{\text{white}}{PbSO_4} \downarrow$$

↳ The ppt. is insoluble in excess reagent. Hot, conc. sulphuric acid dissolves the ppt. owing to formation of $Pb(HSO_4)_2$

$$PbSO_4 \downarrow + H_2SO_4 \longrightarrow \underbrace{Pb^{2+} + HSO_4^{-1}}$$

Solubility is much lower in the presence of ethanol.

↳ $PbSO_4$ is soluble in more conc. Sol^n of NH_4CH_3COO or ammonium tartarate in the presence of NH_3, where tetraaceto plumbate (II)

↳ $PbSO_4$ is soluble in more conc. solⁿ of NH_4CH_3COO or ammonium tartarate in the presence of NH_3, where tetraacetoplumbate (II) & ditartratoplumbate (II) ions are formed.

$$PbSO_4\downarrow + CH_3COO^- \longrightarrow [Pb(CH_3COO)_4]^{2-} + SO_4^{2-}$$

$$PbSO_4\downarrow + C_4H_4O_6^{2-} \longrightarrow [Pb(C_4H_4O_6)_2]^{2-} + SO_4^{2-}$$

The stabilities of these complexes are not very great; chromate ions, for ex. can ppt. $PbCrO_4$ (yellow) from their solⁿ.

↳ When boiled with Na_2CO_3, the $PbSO_4$ is transformed into $PbCO_3$ in a ppt. exchange rxⁿ.

$$\underset{\text{white}}{PbSO_4\downarrow} + CO_3^{2-} \longrightarrow \underset{\text{white}}{PbCO_3\downarrow} + SO_4^{2-}$$

On washing the ppt. by decantation with hot water, sulphate ions can be removed & the ppt. will dissolve in HNO_3.

$$PbCO_3\downarrow + H^+ \longrightarrow Pb^{2+} + H_2O + CO_2\uparrow$$

6. K_2CrO_4 in neutral, acetic acid or ammonium solⁿ

$$Pb^{2+} + CrO_4^{2-} \longrightarrow \underset{\text{yellow ppt.}}{PbCrO_4\downarrow}$$

Nitric acid or NaOH dissolve the ppt.

$$PbCrO_4\downarrow + H^+ \rightleftharpoons Pb^{2+} + Cr_2O_7^{2-} + H_2O$$

$$PbCrO_4\downarrow + OH^- \rightleftharpoons [Pb(OH)_4]^{2-} + CrO_4^{2-}$$

7. Potassium iodide

$$Pb^{2+} + 2I^- \longrightarrow \underset{\text{yellow}}{PbI_2\downarrow}$$

An excess of a more conc. sol^n of the reagent dissolves the ppt.

$$PbI_2\downarrow + 2I^- \rightleftharpoons [PbI_4]^{2-}$$

8. Sodium sulphite in neutral sol^n

$$Pb^{2+} + SO_3^{2-} \longrightarrow PbSO_3\downarrow$$

The ppt. is less soluble than $PbSO_4$, though it can be dissolved by both HNO_3 & $NaOH$.

$$PbSO_3\downarrow + H^+ \longrightarrow Pb^{2+} + H_2O + SO_2\uparrow$$

$$PbSO_3\downarrow + OH^- \longrightarrow [Pb(OH)_4]^{2-} + SO_3^{2-}$$

9. Sodium Carbonate

$$Pb^{2+} + CO_3^{2-} + H_2O \longrightarrow \underbrace{Pb(OH)_2\downarrow + PbCO_3\downarrow}_{\text{white ppt.}} + CO_2\uparrow$$

The ppt. dissolves in dilute HNO_3 & CO_2 liberate

$$Pb(OH)_2\downarrow + PbCO_3\downarrow + H^+ \rightarrow Pb^{2+} + CO_2\uparrow + H_2O$$

10. Disodium hydrogen phosphate

$$Pb^{2+} + HPO_4^{2-} \rightleftharpoons \underset{\text{white}}{Pb_3(PO_4)_2\downarrow} + H^+$$

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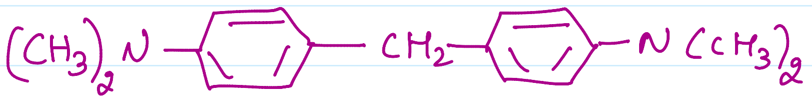
The rx^n is reversible, strong acids (HNO_3) dissolve the ppt.
The ppt. is also soluble in NaOH.

11. **Potassium cyanide**

$$Pb^{2+} + CN^- \longrightarrow \underset{\text{white}}{Pb(CN)_2\downarrow}$$

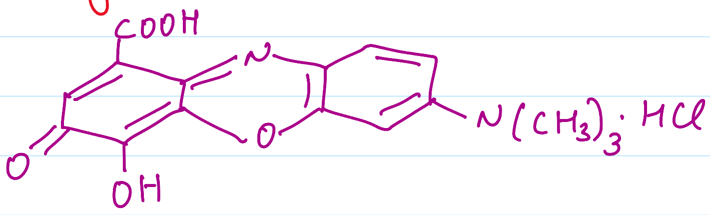
This ppt. is insoluble in the excess of reagent.

12. **Di-(4-dimethylaminodiphenyl) methane or tetrabase**



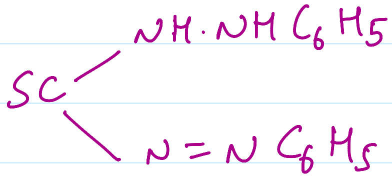
a blue oxidation product is formed

13. **Gallocyanine**



deep-violet ppt. of unknown composition is formed.

14. **Diphenylthiocarbazone (or Dithizone)**



$$SC\begin{cases} NH\cdot NH\,C_6H_5 \\ N=N\,C_6H_5 \end{cases}$$

Brick-red complex salt in neutral, ammonical, alkaline

Brick-red complex salt in neutral, ammonical, alkaline or alkalicyanide solⁿ.

SILVER:

↳ Silver is insoluble in HCl, dil HNO_3 or dil HNO_3 solⁿ.
↳ Silver dissolves in more conc. HNO_3 or in hot conc. H_2SO_4.

$$Ag + HNO_3 \longrightarrow Ag^+ + NO\uparrow + NO_3^{-1} + H_2O$$
$$Ag + H_2SO_4 \longrightarrow Ag^+ + SO_2\uparrow + SO_4^{2-} + H_2O$$

Rxⁿ's of Ag^+ ⇒ $AgNO_3$ salt

1. Adding thiosulphate ion

$$S_2O_3^{2-} + 2Ag^+ \longrightarrow \underset{\text{white}}{Ag_2SO_3\downarrow} \Big\} \text{ excess } Ag^+$$

The ppt. get dissolve in excess of Ag^+ salt

$$S_2O_3^{2-} + Ag^+ \longrightarrow [Ag(S_2O_3)_2]^{3-} \Big\} \text{ excess } S_2O_3^{2-}$$

The ppt. is unstable, turning dark on standing

$$Ag_2S_2O_3\downarrow + H_2O \rightarrow \underset{\text{Black}}{Ag_2S\downarrow} + H^+ + SO_4^{2-}$$

2. Dilute HCl (or soluble chlorides)

$$Ag^+ + Cl^- \longrightarrow \underset{\text{white}}{AgCl\downarrow}$$

↳ With conc. HCl ppt. does not occur.

white

↳ With conc. HCl ppt. does not occur.

↳ AgCl ppt can be dissolved in conc. HCl.

$$AgCl_{(s)} + Cl^{-1} \rightleftharpoons [AgCl_2]^{-1}$$

↳ Dilute ammonia solⁿ dissolves the ppt. to form the diammine argentate complex ion.

$$AgCl\downarrow + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$$

↳ Dilute HNO_3 or HCl neutralizes the excess ammonia & the ppt reappears.

↳ KCN dissolves the ppt. with formation of complex.

$$AgCl + CN^- \longrightarrow [Ag(CN)_2]^{-1} + Cl^-$$

↳ Sodium thiosulphate dissolves the ppt. with the formation of a dithiosulphatoargentate complex.

$$AgCl\downarrow + S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-} + Cl^{-1}$$

This rxⁿ takes place when fixing photographic -ve or +ve prints after development.

Sunlight or UV irradiation decomposes the AgCl ppt., which turns to greyish or black owing to formation of silver metal.

$$AgCl\downarrow \xrightarrow{h\nu} Ag\downarrow + Cl_2\uparrow$$

3. H_2S {gas or saturated aq. solⁿ}

$$Ag^+ + H_2S \longrightarrow \underset{\text{Black}}{Ag_2S\downarrow} + H^+$$

Hot conc. HNO_3 decomposes the Ag_2S

$$Ag_2S + HNO_3 \longrightarrow \underset{\text{white}}{S\downarrow} + NO\uparrow + Ag^+ + NO_3^{-1} + H_2O$$

If the mixture is heated with conc. HNO_3 for a considerable time, S is oxidized to SO_4^{2-} & ppt. disappears

$$S\downarrow + HNO_3 \longrightarrow SO_4^{2-} + NO\uparrow + H^+$$

Ag_2S can be ppt. from sol^n containing diammine, dicyanato or dithiosulphato argentate complexes with H_2S.

4. Ammonia sol^n

$$Ag^+ + NH_3 + H_2O \longrightarrow \underset{\text{Brown}}{Ag_2O\downarrow} + NH_4^+$$

The rx^n reaches an eq^l & therefore ppt. is incomplete at any stage. {if NH_4NO_3 is present in the original sol^n or the sol^n is strongly acidic no ppt. occurs}

The ppt. dissolves in excess of the reagent.

$$Ag_2O\downarrow + NH_3 + H_2O \longrightarrow [Ag(NH_3)_2]^+ + \bar{O}H$$

5. NaOH

$$Ag^+ + \bar{O}H \longrightarrow \underset{\text{Brown}}{Ag_2O\downarrow} + H_2O$$

A well washed suspension of the ppt. shows a slight alkaline rx^n owing to the hydrolysis eql.

$$Ag_2O\downarrow + H_2O \rightleftharpoons Ag(OH)_2 \rightleftharpoons Ag^+ + \bar{O}H$$

The ppt. is insoluble in excess reagent
The ppt. dissolves in NH_3 & HNO_3.

$$Ag_2O + NH_3 + H_2O \longrightarrow [Ag(NH_3)_2]^+ + O\bar{H}$$

$$Ag_2O\downarrow + H^+ \longrightarrow Ag^+ + H_2O$$

6. KI

$$Ag^+ + \bar{I} \longrightarrow \underset{\text{yellow}}{AgI\downarrow}$$

The ppt. is insoluble in dilute or conc. NH_3, but dissolves readily in KCN & in $Na_3[Ag(S_2O_3)_2]$

$$AgI\downarrow + C\bar{N} \longrightarrow [Ag(CN)_2]^{-1}$$

$$AgI\downarrow + S_2O_3^{2-} \longrightarrow [Ag(S_2O_3)_2]^{3-}$$

7. K_2CrO_4 in neutral sol^n

$$Ag^+ + CrO_4^{2-} \longrightarrow \underset{\text{red}}{Ag_2CrO_4\downarrow}$$

The ppt. is soluble in dilute HNO_3 & NH_3 sol^n

$$Ag_2CrO_4\downarrow + H^+ \longrightarrow Ag^+ + \underset{\text{orange}}{Cr_2O_7^{2-}} + H_2O$$

$$Ag_2CrO_4\downarrow + NH_3 \longrightarrow [Ag(NH_3)_2]^+ + CrO_4^{2-}$$

$$Ag_2CrO_4\downarrow + NH_3 \longrightarrow [\overset{\vee}{Ag}(NH_3)_2]^+ + CrO_4^{2-}$$

The acidified solⁿ turns to orange because of $Cr_2O_7^{2-}$.

8. KCN

$$Ag^+ + CN^- \longrightarrow \underset{\text{white}}{AgCN\downarrow}$$

When KCN is added in excess, the ppt. disappears/dissolves.

$$AgCN\downarrow + CN^- \longrightarrow [Ag(CN)_2]^-$$

9. Na_2CO_3

$$Ag^+ + CO_3^{2-} \longrightarrow \underset{\text{white}}{Ag_2CO_3\downarrow}$$

When heating, the ppt. decomposes & brown Ag_2O formed.

$$Ag_2CO_3\downarrow \xrightarrow{\Delta} Ag_2O\downarrow + CO_2\uparrow$$

HNO_3 & NH_3 dissolves the ppt.

10. Disodium hydrogen phosphate in neutral solⁿ

$$Ag^+ + HPO_4^{2-} \longrightarrow \underset{\text{yellow}}{Ag_3PO_4\downarrow} + H^+$$

11. Hydrazine sulphate (Saturated)

↳ $H_2N\text{-}NH_2\cdot H_2SO_4$ when added to a solⁿ of $[Ag(NH_3)_2]^+$ ions forms finely divided silver mirror, while gaseous N_2 is evolved.

$[Ag(NH_3)_2]^+ + H_2N-NH_2 \cdot H_2SO_4 \rightarrow Ag\downarrow + N_2\uparrow$

Silver mirror test.

Q.3 A colorless aqueous solution contains nitrates of two metals, **X** and **Y**. When it was added to an aqueous solution of NaCl, a white precipitate was formed. This precipitate was found to be partly soluble in hot water to give a residue **P** and a solution **Q**. The residue **P** was soluble in aq. NH_3 and also in excess sodium thiosulfate. The hot solution **Q** gave a yellow precipitate with KI. The metals **X** and **Y**, respectively, are

(A) Ag and Pb
(B) Ag and Cd
(C) Cd and Pb
(D) Cd and Zn

Q.10 Choose the correct statement(s) among the following.

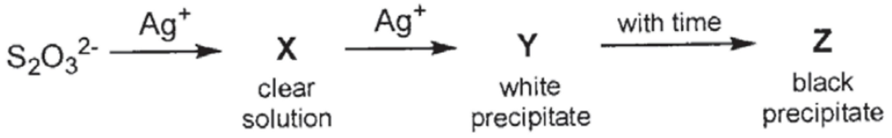
(A) $SnCl_2 \cdot 2H_2O$ is a reducing agent.
(B) SnO_2 reacts with KOH to form $K_2[Sn(OH)_6]$.
(C) A solution of $PbCl_2$ in HCl contains Pb^{2+} and Cl^- ions.
(D) The reaction of Pb_3O_4 with hot dilute nitric acid to give PbO_2 is a redox reaction.

Do this question only for this option

Q.17 The reaction of $Pb(NO_3)_2$ and NaCl in water produces a precipitate that dissolves upon the addition of HCl of appropriate concentration. The dissolution of the precipitate is due to the formation of

(A) $PbCl_2$
(B) $PbCl_4$
(C) $[PbCl_4]^{2-}$
(D) $[PbCl_6]^{2-}$

Q.21 In the following reaction sequence in aqueous solution, the species **X**, **Y** and **Z**, respectively, are



(A) $[Ag(S_2O_3)_2]^{3-}, Ag_2S_2O_3, Ag_2S$
(B) $[Ag(S_2O_3)_3]^{5-}, Ag_2SO_3, Ag_2S$
(C) $[Ag(SO_3)_2]^{3-}, Ag_2S_2O_3, Ag$
(D) $[Ag(SO_3)_3]^{3-}, Ag_2SO_4, Ag$

9. An aqueous solution of a substance gives a white precipitate on treatment with dilute hydrochloric acid, which dissolves on heating. When hydrogen sulfide is passed through the hot acidic solution, a black precipitate is obtained. The substance is a

(a) $Hg^{2+}{}_2$ salt
(b) Cu^{2+} salt
(c) Ag^+ salt
(d) Pb^{2+} salt
(2002)