JEE Advanced Revision Notes
Chemistry
Principles of Qualitative Analysis

Introduction

Qualitative Inorganic analysis deals with the identification of radicals present in salt.

- Cation derived from the base is termed as basic radical.
- Anion derived from acid is termed an acidic radical.

Example: $NaOH + HCl \rightarrow NaCl + H_2O$

Physical properties of salts:

Observation	Inference
The substance is coloured	
Light pink	Hydrated salt of Mn
Reddish pink	Hydrated salt of Co(II)
Red	HgO, HgI, Pb_3O_4
Orange-red	Sb_2S_3, some dichromats and ferricyanides
Redish brown	Ferric chloride, Fe_2O_3
Light yellow or brown	$As_2S, AsS_2, AgBr, AgI, PbI_2, CdS, SnS_2$, a few iodides and ferrocyanides.
Green	K_2MnO_4, Ni salts, hydrated ferrous salts, some Cu(II) compounds
Dark green	Salt of Cr(III)
Blue	Hydrated $CuSO_4$
Black	Sulphide of Cu(II) and Fe(II), $MnO_2, Fe_3O_4, FeO, CuO, Ni_2O_3$
Light yellow or brown	Ferric salts

Substance smells	
Ammoniacal smell	Ammonium carbonates and other Ammonium salts.
Bitter almond type	Cyanides
Vinegar or acetic acid type	Acetates
Chlorine gas smell	Hypochlorites.
Solution is colored	
Green or blue	$Ni^{2+} \cdot Fe^{2+}, [Fe(CN)_6]^{4-}$
Pink	Mn^{2+} and Co^{2+}
Yellow	CrO_4^{2-}, Fe^{3+},
Orange or purple	Dichromate (orange), Permanganates (Purples).
Substance is heavy	Salt of Pb and Hg
The substance is light	Carbonates of Mg, Al, Zn, Ca, Sr, Bi

Heating Effects on various salts

S.No	Observation	Inference
1	Substance decrepitates (Cracking noise)	$NaCl, KI, Pb(NO_3)_2, Ba(NO_3)_2$
2	Substance melts	Salts of alkali metals and salts having water of crystallization.
3	Substance swells (due to loss of water of crystallization)	Alums, borates and Phosphates.
4	The substance sublimes and the color of sublimate is:	
White		$HgCl_2, NH_4X, AlCl_3, HgCl_2, As_2O_3, Sb_2O_3$

Yellow	As_2S_3 and HgI_2 (turns red when rubbed with a glass rod) Iodides
Blue-black and violet vapor	
5	A residue (general oxides) is left and its color is
Yellow (hot) and White (cold)	ZnO
Reddish-brown (hot), Yellow	PbO
Black (hot); Red (cold)	HgO, Pb_3O_4
Black (hot); Red-brown (cold)	Fe_2O_3
6	Gas is evolved
Colorless and odorless.	
CO_2-turns lime water milky	$(CaCO_3 \rightarrow CaO + CO_2)$
O_2-rekindle a glowing splinter	Alkali Nitrates $(2KNO_3 \rightarrow 2KNO_2 + O_2)$
N_2	Ammonium nitrite $(NH_4NO_2 \rightarrow N_2 + 2H_2O)$
Colorless gas with odor:	
NH_3 turns red litmus blue and mercurous nitrate paper black	Ammonium salts $(NH_4)_2 SO_4 \rightarrow NH_4HSO_4 + NH_3$
SO_2 - Smell of burning sulfur, turns acidified $K_2Cr_2O_7$ paper green	Sulphites and thiosulphates $CaSO_3$ $CaSO_3 \rightarrow CaO + SO_2$
HCl- Pungent smell, white fumes with ammonia	Hydrated chlorides $MgCl_2.6H_2O \rightarrow MgO + 5H_2O + 2HCl$
Coloured gas:	
	Nitrites and nitrates of heavy metals

NO_2 - Brown turns starch iodide paper blue.	$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$

Dry Tests:

These texts give a clear indication of the presence of certain radicals.

Flame test:

The flame test should not be performed in the presence of As, Sb, Bi, Sn and Pb as these radical form alloy with Pt, and wire may be spoiled.

Colour of Flame	Inference
Pale greenish	Pb
Green with a blue center	Cu
Apple green	Ba
Crimson red	Sr, Li
Brick red	Ca
Pink violet (Lilac)	K
Golden yellow	Na
Violet	Rb, Cs
Livid blue	As, Bi

Borax Bead Test:

- On heating Borax, the colorless glassy bead formed, which consists of sodium metaborate and boric anhydride.

  $Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$

- Oxidising flame: On heating with a colored salt, the glassy bead forms a colored metaborate.

  $CuSO_4 \xrightarrow{\Delta} CuO + SO_3$

  $CuO + B_2O_3 \xrightarrow{\Delta} Cu(BO_2)_2$, copper (II) metaborate, blue

  $Fe_2O_3 + 3B_2O_3 \xrightarrow{\Delta} 2Fe(BO_2)_3$, iron (III) metaborate, yellow

  $Cr_2O_3 + 3B_2O_3 \xrightarrow{\Delta} 2Cr(BO_2)_3$, chromium (III) metaborate, green

  $CoO + B_2O_3 \xrightarrow{\Delta} Co(BO_2)_2$, cobalt (II) metaborate, blue

- Reducing atmosphere: Borax bead test can be carried out in the reducing atmosphere by using a charcoal cavity. The carbon background will act as reducing the atmosphere.

  $CuO + B_2O_3 \rightarrow Cu(BO_2)_2$, blue

  $2Cu(BO_2)_2 + C \rightarrow 2CuBO_2(\text{ white }) + CO + B_2O_3$

  $2CuBO_2 + C \rightarrow 2Cu(\text{red}) + B_2O_3 + CO$

  $FeO + B_2O_3 \rightarrow Fe(BO_2)_2$, green

Oxidizing Flame	Reducing Flame	Metal
Blue	Red	Copper
Yellow	Green	Iron
Green	Green	Chromium
Violet	Colourless	Manganese
Blue	Blue	Cobalt
Red-brown	Grey	Nickel

Identification of Acidic radicals (or) Anions

- Most of the salts are reacted with $dil.H_2SO_4$ (or) dil HCl and $Conc.H_2SO_4$ are release characteristic gas with acidic radicals.
- But some anions are not decomposed either by $dil.H_2SO_4$ or $Conc.H_2SO_4$
- Hence acidic radicals have been classified into three groups, depending upon salt response to a reagent.

Group-I: Contains the radicals which are detected by $dil.H_2SO_4$ (or) dil HCl. They are

a) Carbonates $\left(CO_3^{-2}\right)$

b) Sulphite $\left(SO_3^{-2}\right)$

c) Sulphide $\left(S^{-2}\right)$

d) Nitrite $\left(NO_2^{-1}\right)$

e) Acetate $\left(CH_3COO^{-1}\right)$

Group-II: Contains the radicals which are detected by $Conc.H_2SO_4$

a) Chloride $\left(Cl^{-}\right)$

b) Bromide $\left(Br^{-}\right)$

c) Iodide $\left(I^{-}\right)$

d) Nitrate $\left(NO_3^{-}\right)$

e) Oxalate $\left(C_2O_4^{-2}\right)$

Group-III: Contains the radicals which don't give any characteristic gas with dilute and $Conc.H_2SO_4$.

They are:

a) Sulphate $\left(SO_4^{-2}\right)$

b) Phosphate $\left(PO_4^{-3}\right)$

1. Reaction of $\left(\mathbf{CO_3^{-2}}\right)$ ions:

i) With dilute HCl: gives effervescence, due to the evolution of carbon dioxide. The gas carbon dioxide turns lime water milky white ppt

$$CO_3^{2-} + 2H^{+} \rightarrow CO_2 + H_2O$$

The gas gives turbidity with lime water and baryta water.

$$CO_2 + Ca^{2+} + 2OH^{-} \rightarrow CaCO_3 + H_2O$$

$$CO_2 + Ba^{2+} + 2OH^{-} \rightarrow BaCO_3 + H_2O$$

On prolonged passage of carbon dioxide in lime water, the turbidity sluggishly disappears due to the conformation of answerable hydrogen carbonate.

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

ii) Barium chloride or Calcium chloride solution:

White ppt of barium or calcium carbonate is obtained, which is soluble in mineral acid.

$$CO_3^{2-} + Ba^{2+} \rightarrow BaCO_3 \downarrow$$

$$CO_3^{2-} + Ca^{2+} \rightarrow CaCO_3 \downarrow$$

The ppt is soluble in mineral acids and carbonic acid (soda water).

$$BaCO_3 \downarrow + 2H^{+} \rightarrow Ba^{2+} + CO_2 \uparrow + H_2O$$

$$BaCO_3 \downarrow + CO_2 + H_2O \rightarrow Ba^{2+} + 2HCO_3^{-}$$

iii) Silver nitrate solution:

White ppt of silver carbonate is obtained.

$CO_3^{2-} + 2Ag^+ \rightarrow Ag_2CO_3$

The ppt so attained is soluble in nitric acid and in ammonia.

The ppt becomes brown on addition of excess reagent and the same may also be if the blend is boiled, due to the conformation of tableware oxide

$Ag_2CO_3 \rightarrow AgO + CO_2$

2. Sulphites $\left(SO_3^{-2}\right)$

i) Dilute HCl or Dilute H_2SO_4

decomposes with the evolution of sulfur dioxide

$SO_3^{2-} + 2H^+ \rightarrow SO_2 + H_2O$

The gas has a suffocating odor of burning sulfur.

ii) Acidified potassium dichromate solution:

Turns sludge paper moistened with acidified potassium dichromate result, green due to the conformation of Cr^{3+} ions.

iii) Lime water: On passing the gas through lime water, a milky ppt is formed. The precipitate dissolves on prolonged passage of the gas, due to the conformation of hydrogen sulfite ions.

iv) Barium chloride or Strontium chloride solution: Gives white ppt. of barium or strontium sulfite.

3. Sulphide $\left(S^{-2}\right)$

i) Dil. HCl or Dil. H_2SO_4:

A colorless gas smelling of rotten eggs $\left(H_2S\right)$ is evolved.

$S^{2-} + 2H^+ \rightarrow H_2S$

ii) The gas turns lead acetate paper black

iii) Silver nitrate solution: Black ppt. of silver sulfide insoluble in cold but soluble in hot dil nitric acid.

iv) Sodium nitroprusside solution: Turns sodium nitroprusside solution purple

$Na_2S \ + \ Na_2[Fe(CN)_5 NO] \rightarrow Na_4[Fe(CN)_5 NOS]$

4. Nitrites (NO_2^-)

i) Dil HCl and Dil. H_2SO_4 : Adding to solid nitrite in cold yields pale blue liquid (due to the presence of free nitrous acid HNO_2 or its anhydride N_2O_3 & the evolution of brown fumes of nitrogen dioxide, the latter being largely produced by a combination of nitric oxide with the oxygen of the air

ii) Silver nitrate solution: White crystalline ppt. is obtained

iii) Turns acidified KI - starch paper blue

$2KI + 2NO_2 \rightarrow 2KNO_2 + I_2$

Starch + $I_2 \rightarrow$ Blue colour

5. Acetate (CH_3COO^-)

i) Dilute Sulphuric Acid: A smell of vinegar is observed.

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

The following test is performed with the aqueous salt solution.

ii) Iron (III) Chloride Solution: Gives deep - red coloration

$$3CH_3COONa + FeCl_3 \rightarrow (CH_3COO)_3Fe + 3NaCl$$

Brown color ppt forms

6. Thiosulphates

i) Dil Hydrochloric acid: Gives sulphur & sulphur dioxide

ii) Silver nitrate solution: Gives white ppt. of silver thiosulphate.

The ppt. is unstable, turning dark on standing when silver sulphide is formed.

iii) Lead acetate or Lead nitrate solution: Gives white ppt.

On boiling, it turns black due to the formation of PbS.

7. Chloride (Cl^-)

Conc. H_2SO_4 : decomposes with the evolution of HCl.

$$Cl^- + H_2SO_4 \rightarrow HCl + HSO_4^-$$

Gas so produced

(1) Turns blue litmus paper red

(2) Gives white fumes of NH_4Cl when a glass rod moistened with ammonia solution is brought near the mouth of the test tube.

Silver nitrate solution: White, curdy ppt. of AgCl insoluble in water & in dil .nitric acid, but soluble in dilute ammonia solution.

v) Chromyl chloride test: When a salt containing chloride ion is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 orange-red fumes of chromyl chloride (CrO_2Cl_2) are formed.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \rightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

A sample of chlorine-containing salt is heated with conc H_2SO_4 in presence of $K_2Cr_2O_7$, deep red vapours of chromyl chloride are evolved.

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$

$K_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2KHSO_4 + 2CrO_3 + H_2O$

$CrO_3 + 2HCl \rightarrow CrO_2Cl_2 + H_2O$

Chromyl chloride

(deep red vapour)

When these vapours are passed through a NaOH solution, the solution becomes yellow due to the formation of sodium chromate.

$CrO_2Cl_2 + 4NaOH \rightarrow Na_2CrO_4 + 2NaCl + 2H_2O$

The yellow solution is neutralized with acetic acid and on the addition of lead acetate gives a yellow precipitate of lead chromate.

$Na_2CrO_4 + Pb(CH_3COO)_2 \rightarrow PbCrO_4 + 2CH_3COONa$

8. Bromide (Br^-)

- Conc. H_2SO_4 : Gives reddish-brown vapors of bromine accompanying the hydrogen bromide.
- Manganese dioxide and conc. sulphuric acid: When a mix of solid bromide, MnO_2, and conc. H_2SO_4 is heated reddish-brown vapors of bromine are evolved.

The following tests are performed with the aqueous salt solution.

- Silver nitrate solution: Pale yellow ppt. of silver bromide is obtained. This ppt. is sparingly soluble in dil but readily soluble in conc. ammonia solution and insoluble in dil. HNO_3
- Lead acetate solution: White crystalline ppt. of lead bromide which is soluble in boiling water.

9. Iodide (I^-)

- Conc. H_2SO_4 : Gives violet vapors of iodine
- Silver nitrate solution: Yellow ppt. of silver iodide AgI, very slightly soluble in conc. ammonia solution and insoluble in dil nitric acid.

10. Nitrate (NO_3^-)

- Conc H_2SO_4 : Gives reddish-brown vapors of nitrogen dioxide
- Brown ring test: When freshly saturated solution of iron (II) sulfate is added to nitrate solution and conc. H_2SO_4 is poured slowly down the side of the test - tube, a brown ring is obtained.

On shaking and warming the mix, the brown color disappears, nitric oxide is evolved and a yellow solution of Iron(III) ions remains.

11. Test for Oxalate ion [$C_2O_2^{4-}$]

$CaCl_2 + Na_2C_2O_4 \rightarrow CaC_2O_4$ (White precipitate) + 2NaCl

12. Sulfate (SO_4^{2-})

i) Barium chloride solution: White ppt. of barium sulfate $BaSO_4$ insoluble in warm dil. hydrochloric acid and in dilute nitric acid but moderately soluble in boiling, conc. hydrochloric acid.

ii) Lead acetate solution: Gives white ppt forms

$Na_2SO_4 + (CH_3COO)_2Pb \rightarrow PbSO_4$(white ppt) + $2CH_3COONa$

13. Test for Phosphate ion [$PO_3{}^{4-}$]

Na_2HPO_4 + 12 $(NH_4)_2$ MoO_4 + 23 $HNO_3 \rightarrow (NH_4)_3$ [P $(Mo_3O_{10})_4$] (Canary yellow precipitate) + $2NaNO_3$ + $21NH_4NO_3$ + $12H_2O$

Test for Cations:

Group I (**Pb^{2+}**, **Ag^+**, **Hg^+**)

- $PbCl_2$ gives a yellow ppt. with K_2CrO_4. The ppt. is insoluble in acetic acid but soluble in NaOH

  $PbCl_2 + 2KI \rightarrow PbI_2 + 2KCl$

  $PbCl_2 + 2KI\ (excess) \rightarrow K_2[PbI_4]$

- AgCl is soluble in NH_4OH forming a complex while Hg_2Cl_2 forms a black ppt. with NH_4OH .

2. Group II A

- Cu^{+2} ions in solution give deep blue color with an excess of NH_4OH

  $Cu^{+2} + 4NH_4OH \rightarrow [Cu(NH_3)_4]^{+2} + 4H_2O$

  Cu^{+2} ions give a chocolate precipitate with $K_4Fe(CN)_6$.

  $2Cu^{+2} + K_4Fe(CN)_6 \rightarrow Cu_2[Fe(CN)_6] + 4K^+$

- For Pb^{2+}

  $3PbS + 8HNO_3 \rightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O + 3S$

  $Pb(NO_3)_2 + H_2SO_4 \rightarrow PbSO_4 + 2HNO_3$

  White precipitate of lead sulphate appears in the above reaction. For further confirmation.

  $PbSO_4 + 4CH_3COONH_4 \rightarrow (NH_4)_2$ [Pb $(CH_3COO)_4$] + $(NH_4)_2SO_4$

  $(NH_4)_2$ [$Pb(CH_3COO)_4$] + $K_2CrO_4 \rightarrow PbCrO_4 + 2CH_3COOK + 2(NH_4)_2SO_4$

  The Colour of $PbCrO_4$ is yellow which confirms the presence of Pb^{2+}.

3. Group II B

- As^{+3} ions in solution give a yellow precipitate with ammonium molybdate and HNO_3 on heating.

  $H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow (NH_4)_3AsMo_{12}O_{40} + 21NH_4NO_3 + 12H_2O$

4. Group III A

- White precipitate of $Al(OH)_3$ is soluble in NaOH
- $Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O$
- $Fe(OH)_3$ is insoluble in NaOH
- Brown precipitate of $Fe(OH)_3$ is dissolved in HCl and addition of KCNS to this solution gives blood red color.
- Also on the addition of $K_4Fe(CN)_6$ to this solution, a Prussian blue color is obtained.

  $FeCl_3 + 3K_4Fe(CN)_6 \rightarrow Fe_4[Fe(CN)_6]_3 + 12KCl$

5. Group IV (Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{+2})

- Ni^{+2} after conversion into $NiCl_2$ forms a red ppt with dimethyl glyoxime.
- Co2+ ion forms a yellow ppt in the following reaction.
  $CoCl_2 + 7KNO_2 + 2CH_3COOH \rightarrow K_3[Co(NO_2)_6] + 2KCl + 2CH_3COOK + NO + H_2O$
- Zn^{+2} ions in solution give a white precipitate with NaOH, which dissolves in excess of NaOH.
- Mn^{2+} ions in solution give a pink precipitate with NaOH turning black or brown on heating.

6. Group V (Ba^{2+}, Sr^{2+}, Ca^{2+})

- Ba^{+2} ions in solution give yellow precipitate with K_2CrO_4

  $Ba^{+2} + K_2CrO_4 \rightarrow BaCrO_4 + 2K^+$
- Sr^{+2} ions give a white precipitate with $(NH_4)_2SO_4$.
- Ca^{+2} ions give a white precipitate with $(NH_4)_2C_2O_4$ only.

7. Group VI

For Mg^{2+}, white ppt of Magnesium ammonium phosphate forms as shown in below reaction.

$Mg^{2+} + Na_2HPO_4 \rightarrow Mg(NH_4)PO_4 + NH_4OH + 2Na^+ + H_2O$

8. Group 0

NH_4^+ ion can be formed by the following reaction sequence.

$(NH_4)_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2NH_3 + 2H_2O$

$NH_3 + HCl \rightarrow NH_4Cl$ (white)

$2K_2HgI_4 + NH_3 + 3KOH \rightarrow HgO.Hg(NH_2)I$ (Brown precipitate) $+ 7KI + 2H_2O$