General Principles of Inorganic Qualitative Analysis

3.1 The qualitative analysis of salt mixture

Salt analysis is carried out by systematic method of analysis. Generally or conventionally the anions are first identified and then the cations. The anion tests are carried out on the dry salts as well as on solutions (sodium carbonate extract). Tests on cations are **carried out** using dry salt (charcoal test, flame test) as well as by using salt solutions.

3.2 Basic two physico-chemical principles used in the analysis

In the separation and identifications of cations, two basic physico-chemical principles are employed. These are :

(a) Solubility product K_{sp} principle of salts.

(b) Common ion principle.

(a) Solubility Product K_{sp}

In qualitative analysis of a salt mixture, for metal ions, the salt mixture is brought into solution form using water or dil. HCl. Then the metal ions are separated from the salt solution by using characteristic group reagents as precipitates. These precipitates are chlorides, sulphides and carbonates of the metals generally. A soluble metal ion in the solution is precipitated by adding a suitable anion (mostly Cl^-, S^{2-}, CO_3^{2-}). The metal ion will be precipitated as a salt of the above mentioned anions if only the product of the metal ion concentration in the solution and the anion concentration added exceeds the solubility product M_xX_y of the salt (metal ion + added anion) *ie.*

$$M_xX_y \rightleftharpoons XM^{+y} + yX^{-x}$$

(s) (aq.) (aq.)

$$K_{sp} = [M^{nT}]^x [X^{m-}]^y$$

Solubility Product of a Salt

The product of concentrations of metal ions and the anions in a saturated solution of the salt is called solubility product (K_{sp})

Example : $BaCl_2 : [Ba^{2+}][Cl^-]^2$, $Al_2(SO_4)_3 : [Al^{3+}]^2[SO_4^{2-}]^3$

The solubility products of chlorides, sulphides and carbonates of some metal ions are given in the table 3.1

Table 3.1 Solubility products of some salts

Substance	K_{sp} at 25° C
PbS	1.4×10^{-28}
CdS	1.6×10^{-28}
CuS	8.5×10^{-36}
HgS	4.1×10^{-53}
MnS	1.4×10^{-10}
ZnS	1.2×10^{-28}
NiS	1.5×10^{-24}

[Unit are not given]

Generally the salt is represented as M_xA_y. The solubility of the salt is '*S*'. Then the solubility product K_{sp} is written as follows :

$$M_xA_y \rightleftharpoons xM^{y+} + yA^{x-}$$

$$K_{sp} = [xM^{y+}]^x [yA^{x-}]^y$$

If solubility of the ppt. is '*S*'.

$$K_{sp} = [xS]^x [yA]^y$$

Some examples

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

$BaSO_4$

$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = S \times S = S^2$$

Al_2S_3

$$Al_2S_3 \rightleftharpoons 2Al^{3+} + 3S^{2-}$$

$$= 2S \quad 3S$$

$$K_{sp} = [2S]^2 [3S]^3 = 4S^2 \times 27S^3$$

$$= 108S^5$$

$BaCl_2$

ing generally an anion of the salt. This anion must be the same as the anion of the salt required to be precipitated. *For example* if NaCl is to be precipitated as NaCl from its solution in water, Cl^- is added in excess. Due to the increase in the concentration of the common ion *ie* Cl^-, the solubility of NaCl in the solution decreases and is precipitated. This Common ion effect is very important in the analysis of metal ions.

For example Cu^{2+} as well as Zn^{2+} will be precipitated as their sulphides CuS, ZnS. But the solubility product of CuS and ZnS are different. Solubility product of CuS is less then than that of ZnS. Hence if to a solution of $Cu^{2+} + Zn^{2+}$ ions, S^{2-} ions are added CuS will be precipitated first at lower concentration of added S^{2-}. Generally S^{2-} ions are added in qualitative analysis as H_2S. Hence if H_2S is added in presence of HCl. Due to common ion $[H^+]$ effect, S^{2-} concentration decreases. Hence $[Cu^{2+}][S^{2-}]$ exceeds K_{sp} of CuS but $[Zn^{++}][S^{2-}]$ does not exceed K_{sp} of ZnS. Hence

Similarly Al^{3+}, Mn^{2+} can both be precipitated as their hydroxides $Al(OH)_3$, $Mn(OH)_2$ by adding NH_4OH. But K_{sp} of $Al(OH)_3$ is less than that of $Mn(OH)_2$. So by adding NH_4Cl to NH_4OH the concentration of OH^- in the solution decreases due to common ion NH_4^+. Al^{3+} is precipitated but not Mn^{2+}. As mentioned earlier OH^- ions are added in qualitative analysis in the form of NH_4OH. So if NH_4Cl is added to NH_4OH solution, due to the common ion NH_4^+, the OH^- concentration decreases

$Fe(OH)_3$ is precipitated but not $Mn(OH)_2$.

3.3 Analysis and identification of anions

The anions to be identified are :

1. carbonate (CO_3^{-2})
2. sulphate (SO_4^{-2})
3. chloride (Cl^-)
4. bromide (Br^-)
5. iodide (I^-)
6. acetate (CH_3COO^-)
7. nitrate (NO_2^{-1})
8. borate (BO_3^{-3})
9. phosphate (PO_4^{-3})

These ions are classified into 3 groups :

1. The first group ion reacts with dil HCl or dil H_2SO_4 and liberate gas which can be identified. This gas liberated is CO_2 and the ion is carbonate.
2. The second group ion react with conc. H_2SO_4 alone or in presence of MnO_2, Cu turnings, or dichromate etc. and give characteristic gases.

These can be identified by colour, smell and characteristic chemical tests.

Cl⁻ (in presence of MnO_2)

1. The first group ion reacts with dil HCl or dil H_2SO_4 and liberate gas which can be identified. This gas liberated is CO_2 and the ion is carbonate.
2. The second group ion react with conc. H_2SO_4 alone or in presence of MnO_2, Cu turnings, or dichromate etc. and give characteristic gases.

   These can be identified by colour, smell and characteristic chemical tests.

   Chloride $\rightarrow Cl_2$ (in presence of MnO_2)

   Bromide $\rightarrow Br_2$ (in presence of MnO_2)

   Iodide $\rightarrow I_2$ (in presence of MnO_2)

   Nitrate $\rightarrow NO_2$ (In presence of Cu turnings)

   $CH_3COOH \rightarrow CH_3COOH$ vapours. Borate $\rightarrow$ Ethylborate (in presence of C_2H_5OH)

3. The third group ions do not react with dil. HCl or conc. H_2SO_4. Hence special tests are used.

   These are sulphate and phosphate. Based on the above facts, analysis of salts for anions is carried out by dry and wet tests. These are given in the next section.

The test are conducted in 3 ways :

(i) Heating of the sample of the salt mixture in a dry test tube.

(ii) Action of dil HCl on the sample of the salt.

(iii) Action of conc. H_2SO_4 or conc. $H_2SO_4 + MnO_2$, conc.H_2SO_4 +C turnings conc. $H_2SO_4 + C_2H_5OH$, on the mixture

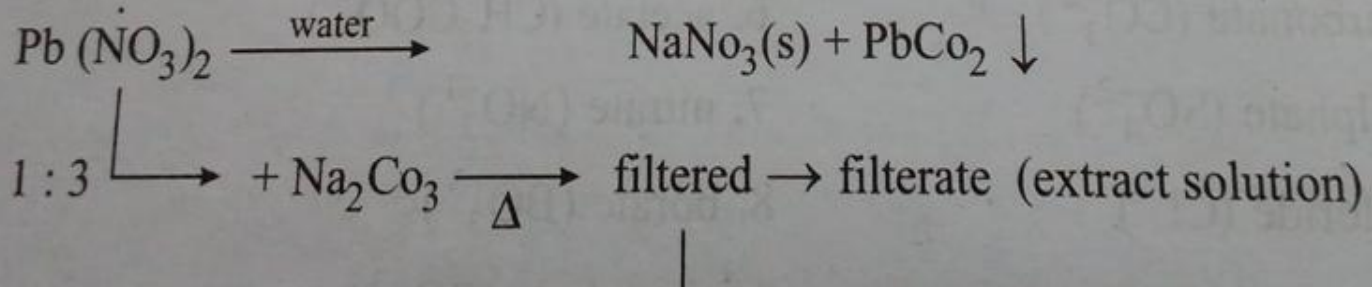
(iv) Some special tests.

Preparation of original Solution :

The salt solution prepared for identification of anions is known as original solution. It may be prepared by dissolving pinch of salt in water and filtered. (heated if necessary)

Generally sodium carbonate extract is prepared for salts which are insoluble in water. 1 : 3 ratio of sample salt and sodium carbonate is mixed and added with water. This solution is boiled and filtered. The supernatant solution (filtrate) is called sodium carbonate extract. In this process anion part is protected and cation part is replaced by sodium which allow the anions to dissolve in water.

Example :



	in a dry test tube	White sublimate	
	2. Action of dil HCl	1. Brisk effevescence with evaluation of colurless gas. The gas gives white precipitate on passing into solution of lime water.	gas is CO_2, may be carbonate
	3. Action of conc. H_2SO_4	1. Colurless gas gives dense white fumes with rod dipped in NH_3 aq.	gas is HCl may be chloride.
		2. Colurless gas which does not give white fumes with NH_3 aq. Smell of vinegar.	gas is CH_3COOH, may be acetate.
		3. Colourless gas + reddish brown gas. Fumes in moist air.	gas is ($HBr + Br_2$) may be bromide.
		4. Violet vapours, turns starch paper blue.	gas is I_2, may be iodide.
	4. Action of conc. $H_2SO_4 + MnO_2$	1. Greenish yellow gas.	gas is Cl_2, may be chloride
		2. Reddish brown vapour	gas is Br_2 may be bromide.

6.	Action of conc. $H_2SO_4 + FeSO_4$	Brown ring	$[FeNO]^{2-}$ ring may be nitrate.
7.	Action of conc. $H_2SO_4 + K_2Cr_2O_7$	Reddish brown vapours	Chromyl chloride vapours may be chloride.
8.	Action of conc. $H_2SO_4 + C_2H_5OH$	gas burning with	gas is ethyl borate, may be borate.

3.5 Chemical reactions underlying the tests Given in section 9.4

(1) Action of dil HCl tests

(a) Carbonate

3.5.1

CO_2 gas is liberated when carbonates are treated with dilute acids. The liberated CO_2 when passed into lime water ($Ca(OH)_2$) it will turns into milky white ($CaCO_3$)

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

$$Ca^{2+} + 2OH^- + CO_2 \longrightarrow CaCO_3 \downarrow \text{white precipitate} + H_2O$$

(b) $$Ba^{2+} + CO_3^{-2} \longrightarrow BaCO_3 \downarrow \xrightarrow{2HCl} BaCl_2 + CO_2 \uparrow + H_2O$$

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

$$NH_3 + HCl \longrightarrow NH_4Cl \text{(dense white fumes)}$$

(b) When bromide reacts with conc. H_2SO_4 reddish-brown vapous of bromine are evolved along with HBr.

$$Br^- + H_2SO_4 \longrightarrow HSO_4^- + HBr$$

$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$

(Brown vapours)

(c) Iodide salts on treatment with conc. H_2SO_4 gives violet Vapours of iodine (I_2)

$$I^- + H_2SO_4 \longrightarrow HI + HSO_4^-$$

$$H_2SO_4 + 2HI \longrightarrow I_2 + SO_2 + 2H_2O$$

Violet Vapours

(d) To the solid nitrite salt if conc. H_2SO_4 is added, a reddish-brown vapours of NO_2 are evolved.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

Greenish yellow gas

(f) Mixture of bromide salt and MnO_2 when reacts withe conc. H_2SO_4 in hot conditions gives reddish brown vapours of bromine.

$$MnO_2 + 4HBr \longrightarrow MnBr_2 + Br_2 + 2H_2O$$

Reddish brown vapours

(g) Solid Iodide salt reacts with conc. H_2SO_4 in presence of MnO_2 to produce iodine (I_2)

$$2I^- + MnO_2 + 2H_2SO_4 \longrightarrow I_2 + Mn^{2+} + 2H_2O + SO_4^{2-}$$

Action of conc. H_2SO_4 + $K_2Cr_2O_7$

(h) When conc. H_2SO_4 is added to the mixture of solid chloride salt and solid potassium dichromate and gently heated, a reddish-brown vapours of chromyl chloride (CrO_2Cl_2) are formed.

$$Cr_2O_7^{2-} + 4Cl^- + 6H_2SO_4 \longrightarrow 2CrO_2Cl_2 + 6HSO_4^- + 3H_2O$$

Reddish

$2NO_3^- + 4H^+ + Cu \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$

Brown vapours

Action of conc. H_2SO_4 + $FeSO_4$ (Brown ring test)

(j) To the salt solution of nitrate when freshly prepared saturated ferrous sulphate solution is added and conc. H_2SO_4 Solution is slowly added by the sides of the test tube a brown ring is $[Fe(NO)]^{2-}$ formed at junction of two layers of solution.

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow 3Fe^{2+} + NO + 2H_2O$$

$$Fe^{2+} + NO \longrightarrow [FeNO]^{2-}$$

Brown ring

Action of conc. H_2SO_4 + C_2H_5OH

(k) On warming Borate salt will react with con. H_2SO_4 and Ethyl alcohol

(a) PO_4^{3-}

With ammonium molyblate an yellow precipitate is formed.

$$HPO_4^{-2} + 12MoO_4^{2-} + 23H^+ + 3NH_4^+ \longrightarrow (NH_4)_3PO_4\,12MoO_3 + 12H_2O$$

yellow precipitate

(b) SO_4^{2-}

With $BaCl_2$ solution, a white precipitate insoluble in conc. HCl

$$SO_4^{2-} + BaCl_2 \longrightarrow BaSO_4 \downarrow + 2Cl^-$$

White precipitate

Flame Test for Metal Ions

The salt is mixed with conc. HCl. and the paste formed is introduced into Bunsen flame

Brick red colour	—	Ca^{2+}
Green colour	—	Ba^{2+}
Lilac colour	—	K^+
Golden yellow colour	—	Na^+

barium, strontium, potassium and ammonium.

These ions are identified by carrying systematic qualitative analysis by precipitating these ions as chlorides, sulphides, hydroxides, carbonates and phosphate. The ions on the basis of these precipitates are divided into 6 groups. For every group a precipitating reagent is used

I Group	—	chlorides	—	reagent : dil HCl
II Group	—	sulphides	—	reagent : dil HCl + H_2S gas
III Group	—	hydroxides	—	reagent : NH_4Cl aq. + NH_4OH solid
IV Group	—	sulphides	—	reagent : NH_4Cl solid + NH_4OH aq. + H_2S gas
V Group	—	carbonates	—	reagent : NH_4Cl solid + NH_4OH aq. + $(NH_4)_2CO_3$ aq.
VI Group	—	phospho-molybdate	—	Ammonium molybdate solution

First of all the groups in which the cations in the salt mixture analysed belong are identified. For this the group reagent, the cations in the group and the precipitates formed are given in the table 3.2. Then systematic analysis group table is used. This is

number			
I	dil HCl	Pb^{2+}	$PbCl_2$ — white
II	dil HCl + H_2S gas	Cd^{3+}, Cu^{2+}	CuS, — black Cds — yellow
III	NH_4Cl solid + NH_4OH soluiton	Al^{3+}, Fe^{3+}	$Al(OH)_3$ — white $Fe(OH)_3$ — yellow
IV	NH_4Cl solid + NH_4OH solution + H_2S (gas)	Mn^{2+}, Zn^{2+}	MnS — Pink coloured ZnS — white
V	NH_4Cl solid + $NH_4(OH)$ solution + $(NH_4)_2CO_3$ saturated solution	Ca^{2+}, Ba^{2+}, Sr^{2+}	$CaCO_3$ — white $BaCO_3$ — white $SrCO_3$ — white
VI	No specific reagent Nessler's reagent	NH_4^+, K^+, Mg^{2+}	

3.5.1. FIRST GROUP (Pb^{2+}, Ag^{+}, Hg_2^{2+})

Precipitation. **The group reagent is dilute hydrochloric acid.** The first group radicals are precipitated as their chlorides (by adding dilute hydrochloric acid) because the solubility product of these chlorides (AgCl, $PbCl_2$ and Hg_2Cl_2) is less than the solubility product of all other chlorides.

$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 \downarrow + 2HNO_3$$

$$AgNO_3 + HCl \longrightarrow AgCl \downarrow + HNO_3$$

$$Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 \downarrow + 2HNO_3$$

Analysis. Out of these three chlorides, only lead chloride is soluble in hot water and therefore can be separated from the two other chlorides and tested as follows.

$$\underset{\text{Ppt.}}{PbCl_2\downarrow} + H_2O \underset{\text{Cold}}{\overset{\text{Hot}}{\rightleftharpoons}} \underset{\text{Soluble}}{PbCl_2} + H_2O$$

Lead (Pb^{2+}). (i) $PbCl_2 + K_2CrO_4 \longrightarrow PbCrO_4\downarrow + 2KCl$

(ii) $PbCl_2 + 2KI \longrightarrow \underset{\textbf{(yellow)}}{PbI_2\downarrow} + 2KCl$

(iii) $PbCl_2 + H_2SO_4 \longrightarrow \underset{\textbf{(white)}}{PbSO_4\downarrow} + 2HCl$

Out of the two chlorides viz. AgCl and Hg_2Cl_2, only the former is soluble in excess of ammonia *owing to the formation of a soluble complex, while the latter forms a black ppt. of mercury and mercuric aminochloride.*

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{Silver ammino chloride}}{[Ag(NH_3)_2]Cl} + 2H_2O$$

$$Hg_2Cl_2 + 2NH_4OH \longrightarrow HgNH_2Cl\downarrow + Hg\downarrow + NH_4Cl + 2H_2O$$

Black

Mercurous (Hg_2^{2+}). The black ppt. is dissolved in aqua regia to give mercuric chloride which is then tested with (i) stannous chloride and (ii) copper turnings.

$$HNO_3 + 3HCl \longrightarrow 2H_2O + NOCl + 2Cl$$

$$Hg + 2Cl \longrightarrow HgCl_2$$

(i) $$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{White}}{Hg_2Cl_2\downarrow} + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\text{Grey}}{2Hg\downarrow} + SnCl_4$$

(ii) $$HgCl_2 + Cu \longrightarrow CuCl_2 + Hg\downarrow$$

Silver (Ag^+)

(i) $$Ag(NH_3)_2Cl + 2HNO_3 \longrightarrow \underset{\text{White}}{AgCl\downarrow} + 2NH_4NO_3$$

(ii) $$Ag(NH_3)_2Cl + KI \longrightarrow \underset{\text{Yellow}}{AgI\downarrow} + KCl + 2NH_3$$

Points to remember. 1. $PbCl_2$ is soluble in hot water (but insoluble in cold water), while AgCl and Hg_2Cl_2 are insoluble.

(a) $PbCl_2$ gives a yellow ppt. with K_2CrO_4. The ppt. is insoluble in acetic acid but soluble in KOH or NaOH.

$$PbCl_2 + K_2CrO_4 \longrightarrow PbCrO_4\downarrow + 2KCl$$

$$PbCrO_4 + 4NaOH \longrightarrow Na_2[PbO_2] + Na_2CrO_4 + 2H_2O$$

(b) $$PbCl_2 + 2KI \longrightarrow PbI_2\downarrow + 2KCl$$

(all in IIB).

The group reagent is hydrogen sulphide in presence of HCl. These radicals are precipitated as their sulphides, while the sulphides of other metals remain in solution because of their high solubility product.

HgS, PbS, Bi_2S_3 and CuS — **Black**

CdS, As_2S_3 and SnS_2 — **Yellow**

SnS — **Brown**

Sb_2S_3 — **Orange**

Function of HCl is to decrease the ionisation of H_2S (due to common ion effect) so that only the solubility product of sulphides of II group radicals is overpowered and not that of III, IV and V groups. Hence III, IV and V group radicals are not precipitated by H_2S in presence of HCl.

$$HgCl_2 + H_2S \longrightarrow \underset{\textbf{Black}}{HgS\downarrow} + 2HCl$$

$$PbCl_2 + H_2S \longrightarrow PbS\downarrow + 2HCl$$

$$CuCl_2 + H_2S \longrightarrow CuS\downarrow + 2HCl$$
Black

$$CdCl_2 + H_2S \longrightarrow CdS\downarrow + 2HCl$$
Yellow

$$2AsCl_3 + 3H_2S \longrightarrow As_2S_3\downarrow + 6HCl$$
Yellow

$$2SbCl_3 + 3H_2S \longrightarrow Sb_2S_3\downarrow + 6HCl$$
Orange

$$SnCl_2 + H_2S \longrightarrow SnS\downarrow + 2HCl$$
Brown

$$SnCl_4 + 2H_2S \longrightarrow SnS_2\downarrow + 4HCl$$
Yellow

It is important to note that sometimes a white or yellow precipitate of sulphur is obtained owing to the oxidation of H_2S by HNO_3 or other oxidising agent like NO_2^-, SO_3^- or Fe^{3+}.

$$2HNO_3 + 3H_2S \longrightarrow 4H_2O + 2NO + 3S\downarrow$$

$$2NaNO_2 + H_2S + 2HCl \longrightarrow 2NaCl + 2NO + S\downarrow + 2H_2O$$

Separation of group II cations into sub-groups II A and II B. The II group sulphides are divided into two sub-groups on the basis that the arsenic, antimony, and tin sulphides (IIB) are dissolved in yellow ammonium sulphide* as soluble thiosalts while the other (II A) remain unaffected.

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*Ordinary ammonium sulphide, $(NH_4)_2 S$ is colourless.

$$As_2S_3 + 3(NH_4)_2S_2 \longrightarrow 2(NH_4)_3AsS_4 + S$$
(soluble)

$$Sb_2S_3 + 3(NH_4)_2S_2 \longrightarrow 2(NH_4)_3SbS_4 + S$$
(soluble)

$$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_3$$
(soluble)

Analysis of II A cations : The precipitates of sulphides of Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+} and Cd^{2+} are treated with nitric acid when all the sulphides **except mercury sulphide** are dissolved as their nitrates.

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

$$Bi_2S_3 + 8HNO_3 \longrightarrow 2Bi(NO_3)_3 + 2NO + 3S\downarrow + 4H_2O$$

$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S\downarrow + 4H_2O$$

$$3CdS + 8HNO_3 \longrightarrow 3Cd(NO_3)_2 + 2NO + 3S\downarrow + 4H_2O$$

The insoluble mercuric sulphide (HgS) is then tested as follows.

Mercuric (Hg^{2+}). Black ppt. of mercuric sulphide (which remains unaffected by HNO_3) is [illegible] and then tested with stannous chloride solution.

$$3HgCl_2 + 2NO\uparrow + 3S\downarrow + 4H_2O$$

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{White}}{Hg_2Cl_2\downarrow} + SnCl_4$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\text{Grey}}{2Hg\downarrow} + SnCl_4$$

The nitrates of Pb^{2+}, Bi^{3+}, Cu^{2-} and / or Cd^{2+} are then treated with sulphuric acid when lead, if present, is precipitated out as lead sulphate while the sulphates of other ions remain in solution.

$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow \underset{\text{White}}{PbSO_4\downarrow} 2HNO_3$$

$$2Bi(NO_3)_3 + 3H_2SO_4 \longrightarrow Bi_2(SO_4)_3 + 6HNO_3$$

$$Cu(NO_3)_2 + H_2SO_4 \longrightarrow CuSO_4 + 2HNO_3$$

$$Cd(NO_3)_2 + H_2SO_4 \longrightarrow CdSO_4 + 2HNO_3$$

White precipitate of lead sulphate are tested as below.

$$Cd(NO_3)_2 + H_2SO_4 \longrightarrow CdSO_4 + 2HNO_3$$

White precipitate of lead sulphate are tested as below.

Lead (Pb^{2+})

$$PbSO_4 \downarrow + 2CH_3COONH_4 \longrightarrow (CH_3COO)_2Pb + (NH_4)_2SO_4$$

$$(CH_3COO)_2Pb + K_2CrO_4 \longrightarrow PbCrO_4 \downarrow + 2CH_3COOK$$

Yellow

Centrifugate containing sulphates of bismuth, copper and/or cadmium is treated with ammonium hydroxide when only bismuth forms insoluble hydroxide and tested separately, while the copper and cadmium ions form soluble tetrammine complex.

$$Bi_2(SO_4)_3 + 6NH_4OH \longrightarrow 2Bi(OH)_3 \downarrow + 3(NH_4)_2SO_4$$

$$CuSO_4 + 4NH_4OH \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$$

Tetrammine copper sulphate

(Blue)

$$CdSO_4 + 4NH_4OH \longrightarrow \underset{\text{Tetrammine cadmium sulphate}}{[Cd(NH_3)_4]SO_4} + 4H_2O$$

Bismuth (Bi^{3+})

$$Bi(OH)_3\downarrow + 3HCl \longrightarrow BiCl_3 + 3H_2O$$

(i)

$$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$$

ppt. with potassium ferrocyanide solution.

$$[Cu(NH_3)_4SO_4] + 4CH_3COOH \longrightarrow CuSO_4 + 4CH_3COONH_4$$

$$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow \underset{\substack{\text{Cuproferrocyanide}\\ \textbf{(Brown)}}}{Cu_2[Fe(CN)_6]\downarrow} + 2K_2SO_4$$

Cadmium complex is decomposed by H_2S to give yellow precipitate of CdS.

$$[Cd(NH_3)_4]SO_4 + H_2S \longrightarrow CdS\downarrow + (NH_4)_2SO_4 + 2NH_3$$

Analysis of II B cations. The centrifugate containing the thiosalts of the three cations is treated with dil. *HCl* when the sulphides are reprecipitated.

$$2(NH_4)_3AsS_4 + 6HCl \longrightarrow \underset{\text{Yellow}}{As_2S_5\downarrow} + 6NH_4Cl + 3H_2S$$

$$2(NH_4)_3SbS_4 + 6HCl \longrightarrow \underset{\text{Orange}}{Sb_2S_5\downarrow} + 6NH_4Cl + 3H_2S$$

$$(NH_4)_2SnS_3 + 2HCl \longrightarrow SnS_2\downarrow + 2NH_4Cl + H_2S$$

$$2HNO_3 \longrightarrow H_2O + 2NO_2 + O$$
$$As_2S_5 + 20[O] \longrightarrow As_2O_5 + 5SO_3$$
$$As_2O_5 + 3H_2O \longrightarrow 2H_3AsO_4$$

Arsenic acid

$$H_3AsO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3AsO_4.12MoO_3\downarrow + 21NH_4NO_3 + 12H_2O$$

Yellow

Antimony (Sb^{3+})

(i)

$$SbCl_3 + H_2O \longrightarrow SbOCl\downarrow + 2HCl$$

$$SbOCl + \begin{matrix} CH(OH)\cdot COOH \\ | \\ CH(OH)\cdot COOH \end{matrix} \longrightarrow \begin{matrix} CH(OH)\cdot COO(SbO) \\ | \\ CH(OH)\cdot COOH \end{matrix} + HCl$$

Antimonyl tartarate

Preparation of sodium stannite.

$$SnCl_2 \xrightarrow{2NaOH} Sn(OH)_2\downarrow \xrightarrow{2NaOH} Na_2SnO_2 + 2H_2O$$

(ii)

$$(COOH)_2 + 2NH_4OH \longrightarrow (NH_4)_2C_2O_4 + 2H_2O$$

$$SbCl_3 + 3(NH_4)_2C_2O_4 \longrightarrow (NH_4)_3[Sb(C_2O_4)_3] + 3NH_4Cl$$

$$(NH_4)_3[Sb(C_2O_4)_3] \rightleftharpoons 3NH_4^+ + [Sb(C_2O_4)_3]^{3-}$$

$$[Sb(C_2O_4)_3]^{3-} \rightleftharpoons Sb^{3+} + 3C_2O_4^{2-}$$

$$2Sb^{3+} + 3H_2S \longrightarrow Sb_2S_3\downarrow + 6H^+$$

Orange

Tin (Sn^{2+})

$$SnCl_4 + Fe \longrightarrow SnCl_2 + FeCl_2$$

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2\downarrow + SnCl_4$$

White

$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\text{Grey}}{2Hg\downarrow} + SnCl_4$$

Points to remember. **1.** Since the solubility products of PbS and CdS are more than the sulphides of other II group radicals, these are precipitated only on dilution.

2. HgS is insoluble in dil. HNO_3, while sulphides of Pb, Bi, Cu and Cd are soluble forming nitrates.

3. $PbSO_4$ is insoluble in water while sulphates of other metals are soluble.

4. $Bi(OH)_3$ is soluble in dil. HCl to form $BiCl_3$ which on dilution gives milky white ppt. of BiOCl.

5. Cu and Cd separation is based upon the fact that in presence of KCN, only Cd is precipitated as sulphide on passing H_2S.

$$2[Cu(NH_3)_4]SO_4 + 10KCN + 8H_2O \longrightarrow 2K_3[Cu(CN)_4] + 2K_2SO_4 + 8NH_4OH + (CN)_2$$

$$[Cd(NH_3)_4]SO_4 + 4KCN + 4H_2O \longrightarrow K_2[Cd(CN)_4] + K_2SO_4 + 4NH_4OH$$

Since second ionisation constant of pot. cadmicyanide is higher than that of pot. cuprocyanide, sufficient Cd^{2+} ions are present in solution and hence only CdS is precipitated on passing H_2S gas.

6. Arsenic sulphide is insoluble in conc. HCl, while Sb and Sn sulphides are soluble.

Radicals are precipitated as their hydroxides.

$$MCl_3 + 3NH_4OH \longrightarrow M(OH)_3 \downarrow + 3NH_4Cl$$

(where M = Fe, Cr, Al)

Importance of nitric acid. Conc. HNO_3 is used to oxidise Fe^{2+} ion into Fe^{3+} because the solubility product of $Fe(OH)_2$ is very high as compared to $Fe(OH)_3$ and in presence of NH_4Cl (group reagent), the ionisation of NH_4OH is suppressed and thus only the solubility product of $Fe(OH)_3$ is reached. It is important to note that iron in the II group filtrate will be present in the ferrous state no matter it was originally in the ferric state. It is because on passing H_2S in II group, Fe^{3+} ion is reduced to Fe^{2+} ion.

Function of NH_4Cl is to suppress the ionisation of NH_4OH so that only the III group radicals ar

precipitated because the solubility product of III group hydroxides is less than that of IV and VI group hydroxides.

Iron (Fe^{3+})

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

(i) $$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow Fe_4[Fe(CN)_6]_3 \downarrow + 12KCl$$

Ferric ferrocyanide

(Deep blue)

(ii) $$FeCl_3 + 3NH_4CNS \longrightarrow Fe(CNS)_3 + 3NH_4Cl$$

Ferric thiocyanate

(Blood red colour)

Aluminium (Al^{3+})

$$Al(OH)_3 \downarrow + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

Sod. meta-aluminate

$$NaAlO_2 + NH_4Cl + H_2O \longrightarrow Al(OH)_3 \downarrow + NaCl + NH_3$$

Chromium (Cr^{3+})

$$2Cr(OH)_3 \downarrow + 4NaOH + 3H_2O_2 \longrightarrow 2Na_2CrO_4 + 8H_2O$$

$$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4 \downarrow + 2CH_3COONa$$

Yellow

1. Excess of NH_4Cl should be added otherwise manganese will be precipitated in III group as $MnO_2 \cdot H_2O$.

2. $(NH_4)_2SO_4$ can't be used in place of NH_4Cl because the SO_4^{2-} will precipitate barium (if present) as $BaSO_4$.

3. NH_4NO_3 can't be used in place of NH_4Cl because NO_3^- ions will oxidise Mn^{2+} to Mn^{3+} and thus $Mn(OH)_3$ will be precipitated in third group.

4. Only $Al(OH)_3$ is soluble in excess of NaOH followed by boiling to form sodium meta-aluminate, while $Fe(OH)_3$ and $Cr(OH)_3$ are insoluble.

$$Al(OH)_3 + NaOH \longrightarrow \underset{\substack{\text{Sod. meta-aluminate} \\ \textbf{(Soluble)}}}{Na[AlO_2]} + 2H_2O$$

$$Cr(OH)_3 \downarrow + NaOH \underset{\text{Cool}}{\overset{\text{Boil}}{\rightleftharpoons}} \underset{\text{(Soluble)}}{Na[CrO_2]} + 2H_2O$$

5. $Cr(OH)_3$ is soluble in NaOH in presence of an oxidising agent (like H_2O_2, bromine wat

This group includes Co^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+}. **The group reagent is hydrogen sulphide in ammonical solution.** Radicals are precipitated as sulphides which are insloluble in NH_4OH.

$$MCl_2 + H_2S \xrightarrow{NH_4OH} MS + 2HCl$$

(where M = Co, Ni, Mn or Zn)

CoS, NiS—**Black;** MnS—**Buff;** ZnS—**White**

Function of amm. hydroxide is to increase the ionisation of H_2S by removing H^+ of H_2S as unionisable water.

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

$$H^+ + OH^- \text{ (from } NH_4OH) \longrightarrow H_2O$$

Thus, excess of sulphide ions will be available and hence the ionic product of IV group sulphides exceeds their solubility product and precipitate will be obtained. In case H_2S is passed through a neutral

$$MCl_2 + H_2S \longrightarrow MS + 2HCl$$

solution, incomplete precipitation will take place due to the formation of HCl which decreases the ionisation of H_2S.

Function of ammonium chloride is to check the precipitation of group V and VI radicals as hydroxides and sulphides because in presence of NH_4Cl, concentration of OH^- ions is fairly low.

Separation. The separation of the sulphides of the fourth group radicals is based upon the following facts.

Manganese (Mn^{2+})

$$MnS\downarrow + 2HCl \longrightarrow MnCl_2 + H_2S$$

$$MnCl_2 + 2NaOH \longrightarrow Mn(OH)_2\downarrow + 2NaCl$$

$$Mn(OH)_2 + 2HNO_3 \longrightarrow Mn(NO_3)_2 + 2H_2O$$

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \longrightarrow \underset{\text{Permanganic acid}}{2HMnO_4} + 5Pb(NO_3)_2 + 2H_2O$$

(Violet colour)

Zinc (Zn^{2+})

$$ZnS\downarrow + 2HCl \longrightarrow ZnCl_2 + H_2S$$

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2\downarrow + 2NaCl$$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{Sod. zincate}}{Na_2ZnO_2} + 2H_2O$$

(a) $$Na_2ZnO_2 + H_2S \longrightarrow \underset{\textbf{(White ppt.)}}{ZnS\downarrow} + 2NaOH$$

presence of NH_4Cl and NH_4OH. These are precipitated as carbonates which are insoluble in NH_4O

$$MCl_2 + (NH_4)_2CO_3 \longrightarrow \underset{\text{(White)}}{MCO_3\downarrow} + 2NH_4Cl$$

(where M = Ca, Ba or Sr)

Function of amm. chloride is to suppress the ionisation of NH_4OH and $(NH_4)_2CO_3$ an check the precipitation of $Mg(OH)_2$ and $MgCO_3$ (along with V group carbonates) because the sol product of $Mg(OH)_2$ and $MgCO_3$ is high. NH_4Cl should also not be added in excess becaus concentration of NH_4^+ ions will decrease the ionisation of $(NH_4)_2CO_3$ to such an extent that su CO_3^{2-} ions will not be present and hence V group carbonates will not be precipitated.

Separation. 1. $BaCO_3$, $SrCO_3$ and $CaCO_3$ are soluble in CH_3COOH forming corres acetate.

$$MCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2M + H_2O + CO_2$$

$CaSO_4$ dissolves in $(NH_4)_2SO_4$ forming soluble complex.

$$(CH_3COO)_2Sr + (NH_4)_2SO_4 \longrightarrow \underset{\textbf{(White ppt.)}}{SrSO_4\downarrow} + 2CH_3COONH_4$$

$$CaSO_4 + (NH_4)_2SO_4 \longrightarrow (NH_4)_2[Ca(SO_4)_2]$$

4. The above soluble complex of calcium gives white ppt. with ammonium oxalate.

$$(NH_4)_2[Ca(SO_4)_2] + (NH_4)_2C_2O_4 \longrightarrow \underset{\textbf{(White ppt.)}}{CaC_2O_4\downarrow} + 2(NH_4)_2SO_4$$

Calcium oxalate ppt. are dissolved in dil. H_2SO_4 to give oxalic acid which discha
O_4 solution colour.

$$CaC_2O_4 + H_2SO_4 \longrightarrow H_2C_2O_4 + CaSO_4$$

$$H_2C_2O_4 + [O] \longrightarrow 2CO_2 + H_2O$$

3.5.6. SIXTH GROUP

The only radical of this group is Mg^{2+} whose reagent is disodium hydrogen phosphate.

$$MgSO_4 + Na_2HPO_4 + NH_4OH \longrightarrow \underset{\substack{\text{Mag. ammonium phosphate}\\ \textbf{(White ppt.)}}}{Mg(NH_4)PO_4 \downarrow} + Na_2SO_4 + H_2O$$

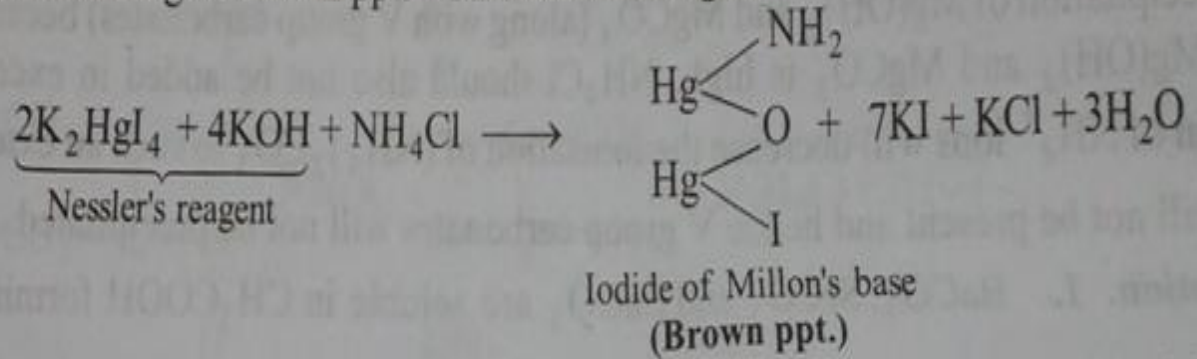
Note. (*i*) The filtrate of group V is first treated with amm. oxalate to remove V group radicals (if any) as oxalates because V group radicals may not be precipitated completely as carbonates due to the presence of excess of NH_4Cl.

3.7. ZERO GROUP (NH_4^+, Na^+ and K^+)

1. Ammonium salts when heated with NaOH solution give ammonia.

$$NH_4Cl + NaOH \longrightarrow NaCl + NH_3\uparrow + H_2O$$

Evolution of NH_3 gas can be detected by the following tests.



Nessler's reagent is obtained by adding excess of KI solution to mercuric chloride solu scarlet ppt. of HgI_2 first formed redissolves. The resulting solution is made alkaline by adding N KOH.

$$HgCl_2 + 2KI \longrightarrow HgI_2 \downarrow + 2KCl$$

$$HgI_2 + 2KI \longrightarrow \underset{\text{Pot. tetra-iodo-mercurate}}{K_2HgI_4}$$

3. *Pot. salts give a yellow ppt. with sod. cobaltinitrite.*

$$Na_3[Co(NO_2)_6] + 3KCl \longrightarrow \underset{\text{Pot. cobaltinitrite}}{K_3[Co(NO_2)_6]} + 3NaCl$$

(Yellow ppt.)

present. Ions white Precipitate $PbCl_2$

Precipitate II group present : Cus — black CdS — yellow

Filtrate : H_2S is boiled off then boiled with conc. HNO_3
NH_4Cl solid and NH_4OH solution are added.

Precipitate III group ions present
$Fe(OH)_3$ — brown
$Al(OH)_3$ — white

Filtrate : H_2S is passed.

Precipitate IV group ions present
ZnS — white
MnS — Buff colour

Filtrate :
NH_4Cl solid + NH_4OH solution + $(NH_4)_2CO_3$ saturated solution

V group cations present
$CaCO_3$ — white

Filtrate : No reagent
+
NH_4, K^+, N

3.9 Interfering anions and some dry tests

(a) Oxalate ion is eliminated before proceeding for the analysis of cation. The salt sample is taken in a china dish and heated strongly. Oxalate decomposes. The residue is dissolved in HCl and used in the analysis.

(b) Phosphate is eliminated before proceeding to the III group. Phosphate was eliminated in earlier days by adding neutral $FeCl_3$ solution to the filtrate in the II group of the main table. But presently this is eliminated by adding NH_4Cl solution + zirconyl chloride solution to the filtrate of II group. Phosphate is eliminated as zinconyl phosphate.

(c) Charcoal test : This is conducted in the case of coloured salts. The salt is mixed with Na_2CO_3 solid. The mixture is placed in the cavity of charcoal piece and heated.

brown residue — Ca^{2+}

yellow residue — Zn^{++}

(d) Borax Beed Test : Borax is taken on a platinum wire and heated to form a beed. This is then dipped in the salt and is again heated. The beed gets

3.10 Conclusions

Thus salt mixture is analysed in a systematic way by the following types of tests.

(1) Dry tests :

(a) Action of heat — NH_4^+, heavy metal nitrates

(b) Flame test — Sr^{2+}, Ba^{2+}, Ca^{2+}, K^+ identified

(c) Charcoal test — Coloured salts, Mn^{2+}

(d) Borax beed test — Mn^{2+}

(2) Wet Tests :

with dil HCl — Pb^{2+}

with cone. H_2SO_4 alone or in presence of MnO_2, $K_2Cr_2O_7$, Cu turnings, $FeSO_4$, C_2H_5OH for Cl^-, Br^-, I^-, NO_3^-, borate respectively.

(3) By systematic analysis of cations through using the group reagents as shown below

I group — dil HCl

II group — dil HCl + H_2S gas

III group — NH_4Cl solid + NH_4OH solution

IV group — NH_4Cl solid + NH_4OH solution + H_2S

V group — NH_4Cl solid + NH_4OH + $(NH_4)_2CO_3$ solution, sat. solution

VI group — NH_4^+ — Nessler's reagent K_2HgI_4 + NaOH solution