Inorganic Qualitative Analysis

Inorganic Qualitative Analysis involve indentification of cationic part and anionic part of a salt by using dry test and wet test. Identification of cationic part is called as basic radical analysis while identification of anionic part is called as acid radical analysis.

IDENTIFICATION OF ACIDIC/BASIC RADICALS — Section - 1

[A] Physical Appearance of salt :

1. Colour :

(a)	Blue	Copper salts
(b)	Green	Salt of Fe, Ni, Cu or Cr
(c)	Dark green	Chromium salt
(d)	Light yellow or brown	Ferric salts
(e)	Reddish brown	Fe_2O_3
(f)	Dark brown	PbO_2, Bi_2S_3
(g)	Light pink	Manganese salt
(h)	Pink	Cobalt salt
(i)	Red	HgO, HgI_2, Pb_3O_4
(j)	Orange red	Sb_2S_3

2. Feel of Salt :

WET	$CaCl_2$, $ZnCl_2$, $MgCl_2$, $MnCl_2$, nitrites, nitrates
HEAVY	Salts of Pb, Hg, Ba
LIGHT	Carbonates of Bi, Mg, Al, Zn, Ca, Sr

[B] Effect of Heating on Salts :

1. When a gas is evolved :

(a) Coloured gas :

(i) NO_2, (Brown) turns starch Iodine paper blue.
Substance : Nitrites and Nitrates of heavy metals

e.g., $2Cu(NO_3)_2 \xrightarrow{\Delta} CuO + 4NO_2\uparrow + O_2$

(ii) Br_2 (Reddish Brown) turns starch paper yellow.
Substance : Bromide

e.g., $2CdBr_2 + O_2 \xrightarrow{\Delta} 2CdO + 2Br_2\uparrow$

(iii) I_2 (Violet) turns starch paper blue

Substance : Iodides

e.g., $2CdI_2 + O_2 \xrightarrow{\Delta} 2CdO + 2I_2\uparrow$

(iv) Cl_2 (Greenish Yellow) bleaches moist litmus paper.

Substance : Chlorides

e.g., $CuCl_2 + \underset{\text{(moisture)}}{H_2O} \xrightarrow{\Delta} [CuO + 2HCl] \longrightarrow Cu + H_2O + 1/2Cl_2$

(b) Colourless gas (odourless) :

(i) O_2 –supports glowing.
Alkali nitrates

$$2KNO_3 \xrightarrow{\Delta} 2KNO_2 + O_2\uparrow$$

(ii) CO_2 –turns lime water milky.
Carbonates/Oxalates

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2\uparrow$$

(iii) CO– burns with blue coloured flame.

$$CaC_2O_4 \xrightarrow{\Delta} CaO + CO\uparrow + CO_2\uparrow$$

(c) Colourless gas (with odour) :

(i) NH_3 –turns red litmus blue.
Ammonium salts

$$(NH_4)_2SO_4 \xrightarrow{\Delta} NH_4HSO_4 + NH_3\uparrow$$

(ii) SO_2 – Smell of burning sulphur, turns acidified $K_2Cr_2O_7$ paper green.
Sulphites, thiosulphates

$$CaSO_3 \xrightarrow{\Delta} CaO + SO_2 \quad ; \quad \underset{\text{Acidified}}{K_2Cr_2O_7} \xrightarrow{SO_2} Cr_2(SO_4)_3$$

(iii) HCl– pungent smell, white fumes with ammonia
Hydrated Chlorides

$$CaCl_2.6H_2O \longrightarrow Ca(OH)_2 + 4H_2O + 2HCl\uparrow$$

(iv) H_2S – Smell of rotten egg, turns lead acetate paper black $\quad \underset{\text{Lead Acetate}}{Pb(CH_3COO)_2} \xrightarrow{H_2S} PbS$

Sulphides

$$Na_2S + 2H_2O \xrightarrow{\Delta} 2NaOH + H_2S\uparrow$$

2. A residue (oxide) is left and colour :

(i)	Yellow (on hot) and white (on cold)	ZnO
(ii)	Reddish brown (hot) yellow (cold)	PbO
(iii)	Black (hot) Red (cold)	HgO, Pb_3O_4
(iv)	Black (hot) Red Brown (cold)	Fe_2O_3

[C] Properties of Gases :

1.	Hydrogen, H_2	Colourless, odourless, tasteless, lightest gas, sparingly soluble in water, combustible and burns in air or oxygen with pale blue flame, neutral, can be liquefied and solidified.
2.	Carbon monoxide, CO	Colourless, odourless, tasteless, nearly equal to density of air, slightly soluble in water burns in air with blue flame, neutral and poisonous in nature
3.	Carbon oxide, CO_2	Colourless, odourless, heavier than air (1.5 times) and can be poured downward like water, fairly soluble in water. Acidic and non-poisonous can be liquefied, solidified.
4.	Nitrogen, N_2	Colourless, odourless, tasteless, slightly lighter than air, slightly soluble in water, neutral and non-poisonous and can be liquefied.
5.	Nitrogen, N_2O	Colourless, faint pungent smell, fairly soluble in cold water but not in hot water, (laughing gas) heavier than air, neutral and poisonous in nature.
6.	Nitric oxide, NO	Colourless, slightly heavier than air, sparingly soluble in water, neutral and paramagnetic in nature can be liquefied but with great difficulty.
7.	Dinitrogen trioxide, N_2O_3	Reddish brown gas which on cooling (–30°C) gives a deep blue liquid.
8.	Nitrogen dioxide, NO_2	Brown gas having pungent smell and paramagnetic in nature. NO_2 is mixed anhydride of nitrous acid and nitric acid.
9.	Ammonia, NH_3	Colourless, characteristic pungent smell, lighter than air, extremely soluble in water, brings tears in eyes and basic in nature can be liquefied and solidified.
10.	Phosphine, PH_3	Colourless, pungent garlic-like or rotten fish odour, heavier than air and sparingly soluble in water, poisonous in nature, weaker base than NH_3 but neutral to litmus.
11.	Oxygen, O_2	Colourless, odourless, tasteless, slightly heavier than air, slightly soluble in water, can be liquefied and solidified, non-inflammable and paramagnetic in nature

12.	Ozone, O_3	Pale-blue gas with pungent fishy smell, heavier than air, slightly soluble in water, poisonous due to its destructive action on tissues, can be, liquefied, turns starch iodide paper blue, Hg loses its meniscus property in contact with O_3. In liquid form O_3 is deep blue liquid and in solid form violet black.
13.	Hydrogen Sulphide, H_2S	Colourless, rotten eggs smell, slightly heavier than air, slightly soluble in water, poisonous in nature.
14.	Sulphur dioxide, SO_2	Colourless, pungent and suffocating odour, heavier than air, soluble in water and poisonous in nature

[D] Flame Test :

Some salts, especially the chlorides, of the groups 1 and 2 (except Be and Mg) of the periodic table, when placed in the flame, get volatilised and impart characteristic colour to the flame. The test is carried out by placing a mixture of the salt and concentrated HCl (so as to convert the salt into the chloride) in a flame with the help of a platinum wire.

The platinum wire used for the test must be clean. It is cleaned by dipping it in concentrated HCl and placing it in a flame. The process is repeated till the wire imparts no colour to the flame.

The clean wire is again moistened with a fresh sample of concentrated HCl. Then it is made to touch the given inorganic sample so that some of it adheres to the wire, and is finally placed in the flame. The colour impacted to the flame is noted.

	Colour of Flame	Ion
(i)	Golden yellow	Na^+
(ii)	Purple (Lilac)	K^+
(iii)	Brick red	Ca^{2+}
(iv)	Apple green	Ba^{2+}
(v)	Crimson red	Sr^{2+}
(vi)	Green	Cu^{2+} BO_3^-

3. Substance melts : Salts of alkali metals and salts having water of crystallization.

4. Substance makes crackling noise : NaCl, KI, $Pb(NO_3)_2$, $Ba(NO_3)_2$

5. Substance Swells : Alums, borates and phosphates

6. Substance sublimes and colour of sublimate is :

(a)	White	$HgCl_2$, Hg_2Cl_2, $AlCl_3$, As_2O_3, Sb_2O_3
(b)	Yellow	As_2S_3, HgI_2 turns red on rubbing with glass rod
(c)	Blue Black or Violet	Iodides.

[E] Borax Bead test and Microcosmic Bead test :

Borax Bead test

Coloured salts like those of copper, iron, chromium, manganese, cobalt and nickel respond to this test. The free end of clean platinum wire is made into a loop by curling it around a pencil or ball-pen tip. The wire is placed in a Bunsen flame and the red-hot loop is introduced into a bulk of solid borax. The solid clings to the loop. On being heated in the flame, the solid first swells due to the loss of water of crystallization (in the form of vapour) and then forms a colourless, transparent bead upon the loop, called the borax bead.

$$Na_2B_4O_7\cdot 10H_2O \xrightarrow[-10H_2O]{\text{heat}} Na_2B_4O_7 \xrightarrow{\text{heat}} \underbrace{\underset{\text{Sodium metaborate}}{2NaBO_2} + \underset{\text{Boron(III) oxide}}{B_2O_3}}_{\text{Borax bead}}$$

A borax bead is thus a solid solution of sodium metaborate and boron(III) oxide. The hot bead is made to touch the sample so that a small particle of the latter adheres to the bead. On being heated again in the uppermost part of the flame, the bead becomes coloured due to the formation of the coloured metaborate of the corresponding metal.

$$CuO + B_2O_3 \rightarrow \underset{\substack{\text{Copper(II) metaborate}\\ \text{Blue}}}{Cu(BO_2)_2}$$

$$Fe_2O_3 + 3B_2O_3 \rightarrow \underset{\substack{\text{Iron(III) metaborate}\\ \text{Yellow}}}{2Fe(BO_2)_3}$$

$$FeO + B_2O_3 \rightarrow \underset{\substack{\text{Iron(II) metaborate}\\ \text{Green}}}{Fe(BO_2)_2}$$

$$Cr_2O_3 + 3B_2O_3 \rightarrow \underset{\substack{\text{Chromium (III) metaborate}\\ \text{Green}}}{2Cr(BO_2)_3}$$

$$CoO + B_2O_3 \rightarrow \underset{\substack{\text{Cobalt(II) metaborate}\\ \text{Blue}}}{Co(BO_2)_2}$$

A more detailed analysis can be made by heated the bead in the different zone of the flame— oxidiaing and reducing– and then looking at the colour of the bead when cooled. The different colour, when they arise, are due to the different oxidation state of the metal. For example, a copper salt will give a blue bead due to the formation of copper(II) metaborate in the oxidising flame, but a red opaque bead due the reduction of copper to the metallic state in the reducing flame. Similarly, an iron salt gives a yellow bead in an oxidising flame [due to the formation of iron (III) metaborate], but a green bead in the reducing flame [due to the formation of iron (II) metaborate]. The colours of the beads in oxidising and reducing flames for various metals are given in Table 1.

Microcosmic Bead test :

Sodium ammonium hydrogenphosphate tetrahydrate, $Na(NH_4)HPO_4\cdot 4H_2O$, called microcosmic salt, gives on fusion a similar glassy, colourless bead as borax does. The bead consists of sodium metaphosphate.

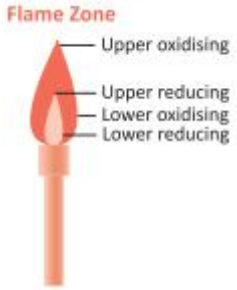
The test is carried out in the same manner as the boraxbead test. The beads are coloured due to the formation of coloured orthophosphates, the colours for the corresponding metals being the same as those of borax beads (Table 1).

$$Na(NH_4)HPO_4 \cdot 4H_2O \xrightarrow{heat} \underset{\text{Sodiummetaphosphate}}{NaPO_3} + NH_3\uparrow + 5H_2O\uparrow$$

$$CuO + NaPO_3 \xrightarrow{heat} \underset{\substack{\text{Sodium Copper(II) orthoposphate}\\ \text{Blue}}}{NaCuPO_4}$$

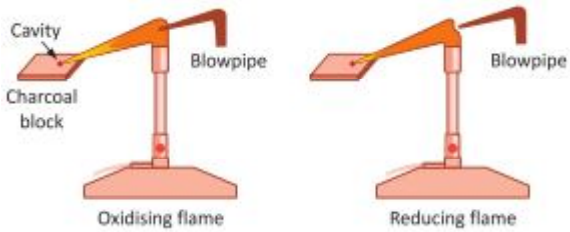
Table 1 : Colours of Borax and Microcosmic Salt Beads

Oxidising flame	Reducing flame	Metal
Blue	Red opaque	Copper
Yellow	Green	Iron
Green	Green	Chromium
Violet	Colourless	Manganese
Blue	Blue	Cobalt
Red-brown	Grey	Nickel



Charcoal Cavity Tests :

A small amount of the sample is thoroughly mixed with twice its bulk of Na_2CO_3 or fusion mixture (an equimolar mixture of Na_2CO_3 and K_2CO_3 ; this has a lower melting point than Na_2CO_3). A cavity is made in a charcoal block with the help of a small coin. The mixture is placed in the cavity and made to settle with the help of a drop of water. Two such blocks are prepared —one for being heated in an oxidising flame and the other in a reducing flame.



Heating in an oxidising flame (Cobalt nitrate test)

An oxidising flame is played over the mixture with help of a blow pipe. If the mass glows, a drop of $Co(NO_3)_2$ solution is added to it and the mass is again heated for a few seconds.

Colour	Cation
Blue (Thenard's blue)	Al^{3+}
Green (Rinnmann's green)	Zn^{2+}
Pink	Mg^{2+}

The colour of the mass is noted.On being heated, the salt reacts with Na_2CO_3 (or fusion mixture) to form the oxide of the corresponding metal. $Co(NO_3)_2$ decomposes to CoO. The oxides of Al, Zn and Mg form coloured compounds or solid solutions with CoO.

$$Al_2(SO_4)_3 + 3Na_2CO_3 \longrightarrow Al_2O_3 + 3Na_2SO_4 + 3CO_2 \qquad CoO + Al_2O_3 \longrightarrow CoAl_2O_4$$

$$ZnSO_4 + Na_2CO_3 \longrightarrow ZnO + Na_2SO_4 + CO_2$$

$$MgSO_4 + Na_2CO_3 \longrightarrow MgO + Na_2SO_4 + CO_2$$

$$Co(NO_3)_2 \longrightarrow CoO + 2NO_2 + \frac{1}{2}O_2$$

$$CoO + ZnO \longrightarrow CoZnO_2$$

$$CoO + MgO \longrightarrow CoMgO_2$$

Heating in a reducing flame :

The mixture is subjected to a reducing flame (using a blow pipe) consistently for a couple of minutes. One reaction with fusion mixture, lead and copper salts form PbO and CuO, which are reduced to the respective metals.

Pb appears as a white metallic bead which, when washed with water and rubbed on a piece of paper, leaves a pencil mark on it. Cu appears as very small, red-brown particles in the charcoal cavity.

Fe appears as black magnetic mass in the classical cavity.

[F] Solubility Table :

1.	NO_3^- and NO_2^-	All metal salts of these ions are soluble.
2.	CH_3COO^-	All metal salt except CH_3COOAg are soluble.
3.	Cl^-	All chloride salts are soluble except $AgCl$, Hg_2Cl_2, $PbCl_2$
4.	Br^-	All bromide salts are soluble except $AgBr$, Hg_2Br_2, $PbBr_2$, $HgBr_2$
5.	I^-	All iodide salts are soluble except AgI, Hg_2I_2, HgI_2, PbI_2
6.	SO_4^{2-}	All sulphate salts are soluble except $CaSO_4$, $SrSO_4$, $BaSO_4$, $PbSO_4$, Hg_2SO_4, Ag_2SO_4
7.	S^{2-}	All sulphide salts are insoluble except group 1 (alkali metal) and group 2(alkaline earth metal)metal ion and NH_4^+ salts are soluble
8.	CO_3^{2-}	All carbonate salts are insoluble except group 1 (alkali metal) metal ion and NH_4^+ salts
9.	PO_4^{3-}	All phosphate salts are insoluble except group 1 (alkali metal) metal ion and NH_4^+ salts are soluble
10.	HO^-	All hydroxide salts are insoluble except group 1 (alkali metal) metal ion and NH_4^+ salts are soluble

Illustration - 1 *Give reasons for the following : Liquid oxygen sticks to the poles of a magnet but liquid nitrogen does not.*

SOLUTION :

Based on molecular orbital theory, electronic configuration of O_2 is

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \pi 2p_y^2, \pi 2p_z^2, \pi^* 2p_y^1, \pi^* 2p_z^1, \sigma^* 2p_x^0$$

Thus, oxygen molecule has two unpaired electrons in its molecular orbitals and hence it is paramagnetic and sticks to the poles of magnet.

Electronic configuration of N_2 is $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \pi 2p_y^2, \pi 2p_z^2, \sigma 2p_x^2, \pi^* 2p_y^0 \pi^* 2p_z^0, \sigma^* 2p_x^0$

All molecular orbitals are completely filled. Thus, nitrogen molecule is diamagnetic and therefore does not stick to the poles of the magnet.

Illustration - 2 *A white solid (X) on heating upto $300^\circ C$ decomposes into its constituent elements (Y) and (Z). (Y) is black violet solid at RTP while (Z) is a gas with a paramagnetic moment of about 2.8 B.M. (X) can be reduced to (Y) by colourless poisonous gas (A). (Y) dissolves completely in hypo solution to give a colourless solution and turns starch paper blue. Identify the unknowns.*

SOLUTION :

$$X_{(solid)} \xrightarrow[300^\circ C]{\Delta} Y_{(solid)} + \underset{\mu = 2.8 B.M.}{Z_{(gas)}} \qquad X + \underset{\text{Colourless \& poisonous}}{A(g)} \xrightarrow[X]{\text{reduction of}} Y$$

$$\text{Blue} \xleftarrow[\text{Paper}]{\text{Strach}} Y \xrightarrow{\text{hypo}} \text{Colourless solution}$$

The set of properties of (Y) says that it is white colour solid compound of iodine and may be I_2O_5.

A colourless poisonous gas which can reduce I_2O_5 into iodine is CO as

$$I_2O_5 + 5CO \rightarrow I_2 + 5CO_2$$

In this circumstances Z must be oxygen. We know that oxygen molecule has two unpaired electrons in its antibonding molecular orbital, so it must be of dipole moment equal to $\sqrt{2(2+2)}$ B.M. i.e. 2.82 B.M.

So (X) = I_2O_5 (Y) = I_2 (A) = CO (Z) = O_2

Illustration - 3 *An orange solid (A) on heating gives a green residue (B), a colourless gas (C) and water vapour. The dry gas (C) on passing over heated Mg gave a white solid (D). (D) on reaction with water gave a gas (E) which formed dense white fumes with HCl. Identify (A) to (E) giving reactions.*

SOLUTION :

According to question,

$$\underset{(A)}{\text{Orange solid}} \xrightarrow{\Delta} \underset{(B)}{\text{Green residue}} + \underset{(C)}{\text{Colourless gas}} + H_2O$$

$$(C) \xrightarrow{\text{heated Mg}} \text{white solid}(D) \xrightarrow{H_2O} \text{gas}\,(E) \xrightarrow{HCl} \text{white dense fumes}$$

(i) Since HCl forms dense white fumes on reaction with gas (E), (E) should be ammonia.

(ii) On hydrolysis of white solid (D), NH_3 is formed. So, (D) should be Mg_3N_2.

(iii) Since, compound (D) is formed by the reaction of gas (D) with Mg. So, the colourless gas (C) must be nitrogen.

(iv) (A) must be ammonium dichromate (orange colour). On heating it, green residue is obtained, which must be Cr_2O_3.

Reactions Involved :

$$\underset{(A)}{(NH_4)_2Cr_2O_7} \xrightarrow{\Delta} \underset{(C)}{N_2} + \underset{(B)}{Cr_2O_3} + 4H_2O \qquad N_2 + 3Mg \xrightarrow{\Delta} \underset{(D)}{Mg_3N_2}$$

$$\underset{(D)}{Mg_3N_2} + 6H_2O \xrightarrow{\Delta} 3Mg(OH)_2 + \underset{(E)}{2NH_3} \qquad \underset{(E)}{NH_3} + HCl \xrightarrow{\Delta} NH_4Cl$$

Illustration - 4 *A certain slat (X) gives the following tests :*

(i) *Its aqueous solution is alkaline to litmus.*

(ii) *On strongly heating it swells to give glassy material.*

(iii) *When concentrated H_2SO_4 is added to a hot concentrated solution of (X), white crystals of a weak acid separate out. Identify (X) and write down the chemical equations for reactions at steps (i), (ii) and (iii).*

SOLUTION :

(i) Aqueous solution of salt (X) is alkaline to litmus. So, (X) may be an alkali metal salt.

(ii) On strong heating, salt (X) swells to give glassy material. So, it may be borax.

(iii) Further, when (X) is treated with conc. H_2SO_4, white crystal of weak acid (i.e. boric acid) separates out. This fact also supports that salt (X) is borax.

Hence, salt (X) is borax $(Na_2B_4O_7 \cdot 10H_2O)$

The chemical equations for reactions at steps (i), (ii) and (iii) are shown below:

(i) $\underset{(X)}{Na_2B_4O_7} + 7H_2O \rightarrow 2\underset{\text{alkali}}{NaOH} + 4H_3BO_3$

(ii) $Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\text{heat}} Na_2B_4O_7 + 10H_2O$ $\qquad$ $Na_2B_4O_7 \xrightarrow{\text{heat}} \underbrace{2NaBO_2 + B_2O_3}_{\text{Glassy material}}$

(iii) $Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + \underset{\text{Weak acid}}{4H_3BO_3}$

Illustration - 5 *When 20.02 gm of a white solid (X) is heated, 4.4 gm of an acid gas (A) and 1.8 gm of neutral gas (B) are evolved leaving behind a solid residue (Y) of weight 13.8 gm. (A) turns lime water milky and (B) condenses into liquid which changes anhydrous copper sulphate blue. The aqueous solution of (Y) is alkaline to litmus and gives 19.7 gm of white ppt. (Z) with barium chloride solution. (Z) gives carbon dioxide with an acid. Identify (A), (B), (X), (Y) and (Z).*

SOLUTION :

According to question,

$$\underset{20.02\,gm}{X} \xrightarrow{\Delta} \underset{4.4\ gm}{(A)} + \underset{1.8\,gm}{(B)} + \underset{13.8\,gm}{(Y)}$$

(i) (A) turns lime water milky, so it may be CO_2 or SO_2.

(ii) The neutral gas (B) condenses into liquid which changes anhydrous copper sulphate blue. So (B) is H_2O.

(iii) The aqueous solution of (Y) is alkaline and gives white ppt. (Z) with barium chloride solution. Solution, (Y) is metal carbonate.

(iv) Since, (Y) and (A) are formed from (X). So (X) is a metal bicarbonate.

$$\underset{(X)}{2MHCO_3} \xrightarrow{\Delta} \underset{(A)}{CO_2} + \underset{(B)}{H_2O} + \underset{(Y)}{M_2CO_3}$$

$\therefore$ $4.4\,gm\ CO_2$ is obtained from $20.02\ gm\ MHCO_3$

$\therefore$ $44\ gm\ CO_2$ is obtained $\dfrac{20.02}{4.4} \times 44\,gm\ MHCO_3 = 200.2\,gm$

$\therefore$ Molecular weight of $MHCO_3 = \dfrac{200.2}{2} = 100.1$

$\therefore$ $M + 1 + 12 + (16 \times 3) = 100.1$ or $M = 100.1 - 61 = 39.1$

Hence, atomic weight of M is 39.1 and the metal is potassium.

Reaction Involved : $\underset{(X)}{2KHCO_3} \xrightarrow{\Delta} \underset{(A)}{CO_2} + \underset{(B)}{H_2O} + \underset{(Y)}{K_2CO_3}$

ACID RADICALS — Section - 2

Radicals tested by dilute HCl/H_2SO_4 :

Gas evolved	Radicals	
CO_2	CO_3^{2-}	Carbonate
SO_2	SO_3^{2-}	Sulphite
H_2S	S^{2-}	Sulphide
$NO_2 + NO$	NO_2^-	Nitrite
CH_3COOH vapours	CH_3COO^-	Acetate

Radical tested by concentrated H_2SO_4 :

Gas evolved	Radicals	
HCl	Cl^-	Chloride
$HBr + Br_2$	Br^-	Bromide
$HI + I_2$	I^-	Iodide
NO_2	NO_3^-	Nitrate
$CO + CO_2$	$C_2O_4^{2-}$	Oxalate
HF	F^-	Fluoride

(A) Major Reactions in detection of Acid Radicals :

1. Carbonate : (CO_3^{2-})

$$CO_3^{2-} + \text{dil } HCl/H_2SO_4 \longrightarrow CO_2$$

$$CO_2 \text{ with } Ca(OH)_2 \longrightarrow \text{milky solution}$$

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2 \uparrow$$

Confirm :

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

(White or milky solution)

➤ If excess of CO_2 is there :

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

Colourless

2. Sulphite : (SO_3^{2-})

$$SO_3^{2-} \xrightarrow{\text{dil } H_2SO_4} \text{gives } SO_2\uparrow$$

(suffocating smell)

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2\uparrow$$

Confirm :

(a) $SO_2 + H_2SO_4 + K_2Cr_2O_7 \longrightarrow Cr_2(SO_4)_3$

(b) $SO_2 + Ca(OH)_2 \longrightarrow \underset{\text{(Milky)}}{CaSO_3} + H_2O$

3. Sulphide : (S^{2-})

$S^{2-} \xrightarrow{dil\ H_2SO_4} H_2S \uparrow$ (Pungent smelling)
(smell like ratten eggs.)

$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S\uparrow$

$Na_2S + H_2SO_4 \rightarrow Na_2SO_4 + H_2S \uparrow$

Confirm :

(a) $(CH_3COO)_2Pb \xrightarrow{H_2S} PbS \downarrow$
(Lead acetate) paper

(b) $Na_2S \xrightarrow{Na_2[Fe(CN)_5(NO)]} Na_4[Fe(CN)_5\ NOS]$

(c) $CdCO_3 + Na_2S \longrightarrow CdS \downarrow + Na_2CO_3$

4. Nitrite : (NO_2^-)

On treatment with dil acid, a nitrite salt decomposes to give NO, which in contact with air forms reddish-brown NO_2 gas.

$NO_2^- \xrightarrow{dil\ H_2SO_4} NO_2 \uparrow$ $\qquad 2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$

$3HNO_2 \longrightarrow HNO_3 + 2NO \uparrow + H_2O$ $\qquad 2NO + \underset{\text{(air)}}{O_2} \longrightarrow 2NO_2$

Confirm :

(a) Brown ring test : $FeSO_4 + NO \longrightarrow \underset{\text{Brown Ring}}{Fe(NO)SO_4}$

(b) $2KI + 2NO_2 \longrightarrow 2KNO_2 + I_2$

$I_2 + \text{starch} \longrightarrow$ starch iodide complex (blue)

5. Acetate : (CH_3COO^-)

$CH_3COO^- \xrightarrow{dil\ H_2SO_4}$ acetic acid (vapours smelling of vinegar)

$2CH_3COONa + H_2SO_4 \longrightarrow Na_2SO_4 + 2CH_3COOH$ (acetic acid)

Confirm :

$CH_3COONa(aq) + FeCl_3 \longrightarrow (CH_3COO)_3Fe + 3NaCl$

6. Chloride : (Cl^-)

$$Cl^- \xrightarrow[H_2SO_4]{\text{conc.}} HCl\uparrow$$

$$NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl\,, \qquad \underset{\text{conc.}}{NH_4OH + HCl} \longrightarrow \underset{\text{white fumes}}{NH_4Cl} + H_2O$$

Confirm :

(a) $AgNO_3 + HCl \longrightarrow AgCl\downarrow + HNO_3$ [$AgCl\downarrow$ white ppt dissolved in NH_4OH]

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{(Soluble complex)}}{Ag(NH_3)_2Cl} + 2H_2O$$

$$Ag(NH_3)_2Cl + 2HNO_3 \longrightarrow \underset{\text{(ppt. appears again)}}{AgCl\downarrow} + 2NH_4NO_3$$

(b) Chromyl Chloride Test :

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$

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

$$2HCl + CrO_3 \longrightarrow CrO_2Cl_2 + H_2O$$

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

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

$$Na_2CrO_4 + BaCl_2 \longrightarrow BaCrO_4\downarrow + 2NaCl$$

$$Na_2CrO_4 + 2AgNO_3 \longrightarrow Ag_2CrO_4 + 2NaNO_3$$

Note : Chromyl chloride test is not shown by insoluble chlorides.

7. Bromide : (Br^-)

$$Br^- \xrightarrow{\text{conc. } H_2SO_4} HBr + Br_2\uparrow \qquad 2KBr + H_2SO_4 \longrightarrow K_2SO_4 + 2HBr\uparrow$$

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

Confirm :

(a) $NaBr + AgNO_3 \longrightarrow AgBr\downarrow + NaNO_3$

$$AgBr + NH_4OH \longrightarrow \underset{\text{partially soluble}}{[Ag(NH_3)_2]Br} + 2H_2O$$

(b) $2KBr + Cl_2(water) \longrightarrow 2KCl + Br_2$

Br_2 + chloroform $\longrightarrow$ Reddish Brown coloured chloroform.

To differentiate between Br_2 and NO_2 as both redish brown in colour.

(i) Brown vapour of Br_2 on passing on passing in H_2O, gives brown colour, but NO_2 does not impart colour to water.

(ii) Cl_2 water liberates Br_2 from bromide which dissolves in $CHCl_3$ or CCl_4 to impart it orange brown colour.

$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$

$Br_2 + CHCl_3 \longrightarrow$ Reddish Brown coloured chloroform layer

8. Iodide (I^-)

$$I^- \xrightarrow[H_2SO_4]{\text{conc.}} I_2 \uparrow$$

$2KI + H_2SO_4$ (conc.) $\longrightarrow K_2SO_4 + 2HI$ $\quad 2HI + H_2SO_4 \longrightarrow 2H_2O + SO_2 + I_2$

$2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2 \uparrow$

Confirm :

(a) I_2 + starch $\longrightarrow$ Blue coloured complex

(b) $NaI + AgNO_3 \longrightarrow AgI \downarrow + NaNO_3$ $\qquad AgI \downarrow + NH_4OH \longrightarrow$ Insoluble

(c) $KI + Cl_2$ water $\longrightarrow 2KCl + I_2$ $\quad I_2$ + chloroform $\longrightarrow$ Violet coloured chloroform. (layer)

9. Oxalate : ($C_2O_4^{2-}$)

$$C_2O_4^{2-} \xrightarrow{\text{conc. } H_2SO_4} CO + CO_2$$

(i) Oxalates are decomposed by conc. H_2SO_4 to give CO_2 and CO. The latter burns with blue flame, while the former turns lime water milky.

$$\begin{matrix} COONa \\ | \\ COONa \\ \text{Sod.oxalate} \end{matrix} + H_2SO_4 \rightarrow Na_2SO_4 + \begin{matrix} COOH \\ | \\ COOH \\ \text{Oxalic acid} \end{matrix} \qquad \begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{\Delta} CO + CO_2 + H_2O$$

$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$

(ii) Oxalate salt on reaction with dil. H_2SO_4 and MnO_2 gives more intensive effervescence of CO_2.

$Na_2C_2O_4 + 2H_2SO_4$ (dil) + $MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + 2CO_2\uparrow + 2H_2O$

Confirm :

(a) CO burns with blue flame ($2CO + O_2 \longrightarrow CO_2$).

(b) $Na_2C_2O_4 + CaCl_2 \longrightarrow CaC_2O_4\downarrow + 2NaCl$

(c) Oxalate decolourises acidified $KMnO_4$ solution.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

colourless

$$H_2C_2O_4 + 5[O] \text{ (acidified } KMnO_4) \longrightarrow 10\ CO_2\uparrow + 5H_2O$$

10. Fluoride (F^-)

$$F^- \xrightarrow[H_2SO_4]{\text{conc.}} HF\uparrow \qquad NaF + H_2SO_4 \longrightarrow Na_2SO_4 + 2HF\uparrow$$

Confirm :

(a) $SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$ (Glass is soluble in aqueous solution of HF)

(glass)

$$3SiF_4 + 3H_2O \longrightarrow 2H_2SiF_6 + H_4SiO_4 \text{ (waxy deposit)}$$

Soluble Hydrofluorosilicic Acid

(b) $NaF + CaCl_2 \longrightarrow CaF_2\downarrow + 2NaCl$

11. Phosphate : (PO_4^{3-})

$$PO_4^{3-} \xrightarrow{HNO_3\,(\text{amm.molybdate})} \text{yellow ppt.}$$

$$Ba_3(PO_4)_2 + 6HNO_3 \longrightarrow 3Ba(NO_3)_2 + 2H_3PO_4$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21\ HNO_3 \longrightarrow (NH_4)_3PO_4.12MoO_3\downarrow + 12H_2O + 21NH_4NO_3$$

Ammonium molybdate Ammonium phosphomolybdate

12. Sulphate : (SO_4^{2-})

(a) $Na_2SO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow + 2NaCl$ $\qquad BaSO_4 + HNO_3 \longrightarrow$ Insoluble

$BaSO_4$ is in soluble in hot water and hot conc. HNO_3

(b) $Na_2SO_4 + (CH_3COO)_2Pb \longrightarrow PbSO_4\downarrow + 2CH_3COONa$

$PbSO_4$ is soluble in ammonium acetate solution.

13. Nitrate (NO_3^-)

$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$ $\qquad 4HNO_3 \longrightarrow 4NO_2\uparrow + O_2 + 2H_2O$

Confirm : Brown Ring test (same as nitrite)

$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

$6FeSO_4 + 3H_2SO_4 + 2HNO_3 \longrightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$

$FeSO_4 + NO \longrightarrow [Fe(NO)]SO_4$

Note : Since, both nitrite and nitrate are responding to ring test, nitrite is removed (when both are present together) by heating with NH_4Cl or with urea/dil H_2SO_4.

$NaNO_2 + NH_4Cl \longrightarrow NaCl + NH_4NO_2$ $\qquad NH_4NO_2 \longrightarrow N_2\uparrow + 2H_2O$

Illustration - 6 *A well known orange crystalline compound (A) when burnt impart violet colour to the flame. (A) on treating with (B) and conc.* H_2SO_4 *gives red gas (C) which gives yellow solution (D) with alkaline water. (D) on treatment with acetic acid and lead acetate gives yellow precipitate. (E). (B) sublimes on heating. Also, on heating (B) with NaOH gas (F)is formed which gives white fumes with HCl. What are (A) to (F) ?*

SOLUTION :

(i) Since, (B) sublimes on heating and also gives gas (F) with NaOH which forms white fumes with HCl. So (B) is NH_4Cl.

(ii) (A) on treatment with (B) and conc. H_2SO_4 gives red gas (C) i.e. CrO_2Cl_2. So, (A) is $K_2Cr_2O_7$.

Reaction Involved

(i) $K_2Cr_2O_7 + 4\,NH_4Cl + 3\,H_2SO_4 \rightarrow K_2SO_4 + 2\,CrO_2Cl_2 + 2(NH_4)_2\,SO_4 + 3\,H_2O$ (C)

(ii) $CrO_2Cl_2 + 4\,NaOH \rightarrow Na_2CrO_4 + 2\,NaCl + 2\,H_2O$ (D)

(iii) $Na_2CrO_4 + (CH_3COO)_2\,Pb \rightarrow PbCrO_4\downarrow + 2\,CH_3COONa$ (E)

(iv) $NH_4Cl(s) \xrightarrow{\Delta} NH_4Cl(g)$

(v) $NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + NH_3 + H_2O$ (F)

(vi) $NH_3 + HCl \rightarrow NH_4Cl$ (F)

GROUP OF BASIC RADICALS AND REAGENTS — Section - 3

Group	Reagent	Radicals
Zero	NaOH (for NH_4^+)	NH_4^+, Na^+, K^+
I.	Dil HCl	Ag^+, Hg_2^{2+}, Pb^{2+}
II.A	Dil HCl + H_2S	Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}
II.B	Dil HCl + H_2S	As^{3+}, Sb^{3+}, Sn^{2+}, Sn^{4+}
III.	NH_4Cl(excess) + NH_4OH	Fe^{3+}, Cr^{3+}, Al^{3+}
IV.	$NH_4Cl + NH_4OH + H_2S$	Mn^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+}
V.	$NH_4Cl + NH_4OH + (NH_4)_2CO_3$	Ba^{2+}, Sr^{2+}, Ca^{2+}
VI.	$NH_4OH + Na_2HPO_4$	Mg^{2+}

(A) Precipitation of Group Radicals

Zero Group radicals are not precipitated.

I. Group radicals are precipitated in the form of their chlorides.

$AgCl$ $PbCl_2$ Hg_2Cl_2

II. Group radicals are precipitated in the form of their sulphides.

II.A HgS PbS CuS CdS Bi_2S_3 or Bi_2S_3

II.B As_2S_3 Sb_2S_3 SnS SnS_2

Sulphides of II.A not soluble while sulphides II.B soluble in yellow ammonimum sulphide.

III. Group radicals are precipitated in the form of their hydroxides.

$Fe(OH)_3$ $Cr(OH)_3$ $Al(OH)_3$

IV. Group radicals are precipated in the form of their sulphides.

MnS CoS ZnS NiS

V. Group radicals are precipated in the form of their carbonates.

$BaCO_3$ $SrCO_3$ $CaCO_3$

VI. Group radicals is precipitated in the form of its Ammonium Phosphate.

$Mg(NH_4)PO_4$

(B) Basic Radicals

Zero Group NH_4^+, K^+, Na^+

1. Ammonium salts when heated with NaOH gives off ammonia.

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

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

Evolution of NH_3 is confirmed by :

(a) A paper soaked in $CuSO_4$ solution becomes deep blue by NH_3 due to complex formation.

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

(b) $$Hg_2(NO_3)_2 + 2NH_3 \longrightarrow \underbrace{Hg(NH_2)NO_3 + Hg}_{\text{Black}} + NH_4NO_3$$

***Note* : 1.** **All nitrates and nitrites on reduction will give ammonia**

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2[H]$$
Lucas Reagent

$$NaNO_3 + 8[H] \longrightarrow NH_3 + 2H_2O + NaOH$$

$$NaNO_2 + 6[H] \longrightarrow NH_3 + H_2O + NaOH$$

2. **All nitrates on decomposition give oxygen, metal oxide, O_2**
Exception :

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$

$$2AgNO_3 \xrightarrow{\Delta} 2Ag + 2NO_2 + O_2$$

$$2NaNO_3 \xrightarrow{\Delta} 2NaNO_2 + O_2$$

3. **All nitrites on decomposition give nitrogen.**
Exception :

$$N_2H_5NO_2 \xrightarrow{\Delta} N_3H + 2H_2O$$

2. Ammonium salts give brown precipitate with Nessler's reagent (K_2HgI_4).

$$2K_2HgI_4 + 4KOH + NH_4Cl \rightarrow I\text{–}Hg\text{–}O\text{–}Hg\text{–}NH_2 + 7KI + KCl + 3H_2O$$

Nessler's reagent :

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

$$HgI_2 + 2KI \; K_2HgI_4 \xrightarrow{NH_4OH} \underset{\text{Iodide of Million's base}}{[HgO.HgNH_2]^+ I^-}$$

Heating effect on ammonium salts :

[If anionic part is oxidising in nature, then N_2 will be the product (some times N_2O)]

[If anionic part is weakly oxidising or non oxidising in nature then NH_3 will be the product.]

$(NH_4)_2Cr_2O_7 \rightarrow N_2 + Cr_2O_3 + 4H_2O$

$NH_4NO_2 \rightarrow N_2 + 2H_2O$

$NH_4NO_3 \rightarrow N_2O + 2H_2O$

$2NH_4ClO_4 \rightarrow N_2 + Cl_2 + 2O_2 + 4H_2O$

$2NH_4IO_3 \rightarrow N_2 + \underset{\text{Purple}}{I_2} + O_2 + 4H_2O$

$(NH_4)_2HPO_4 \rightarrow HPO_3 + H_2O + 2NH_3$

$(NH_4)_2SO_4 \rightarrow NH_3 + H_2SO_4$

$2(NH_4)_3PO_4 \rightarrow 2NH_3 + P_2O_5 + 3H_2O$

$(NH_4)_2CO_3 \rightarrow 2NH_3 + H_2O + CO_2$

Complex formation reaction :

$AgOH(s) + 2NH_4OH \rightarrow [Ag(NH_3)_2]OH + 2H_2O$

$$CuSO_4 + NH_4OH \rightarrow Cu(OH)_2 \xrightarrow{NH_4OH} \underset{\text{Switzer's reagent}}{[Cu(NH_3)_4]SO_4}$$

$$Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$$

$$2CuO + \underset{\text{Glucose}}{C_6H_{12}O_6} \rightarrow Cu_2O + \underset{\text{Gluconic Acid}}{C_6H_{12}O_7}$$

$$CdSO_4 + NH_4OH \rightarrow Cd(OH)_2 \rightarrow \underset{\text{Soluble complex}}{[Cd(NH_3)_4SO_4} + H_2O$$

$NiCl_2 + NH_4OH \rightarrow Ni(OH)_2 \rightarrow [Ni(NH_3]_6Cl_2 + H_2O$

$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$

$SnCl_4 + 2NH_4Cl \rightarrow (NH_4)_2SnCl_6$ (Pink salt : used as mordant)

$CrCl_3 + 3NH_4OH \rightarrow Cr(OH)_3 + 3NH_4Cl$

$AlCl_3 + 3NH_4OH \rightarrow Al(OH)_3 + 3NH_4Cl$

$FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl$

$HgCl_2 + 2NH_4OH \rightarrow Hg(NH_2)Cl + NH_4Cl + 2H_2O$

$Na_2Cr_2O_7 + 2NH_4OH \rightarrow (NH_4)_2Cr_2O_7 + 2NaOH$

$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} Cr_2O_3 + N_2 + 4H_2O$

$3Mg + N_2 \rightarrow Mg_3N_2$

$Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

3. Potassium salts gives yellow precipitate with sodium cobaltinitrite.

$$Na_3[Co(NO_2)_6] + 3KCl \longrightarrow K_3[Co(NO_2)_6] + 3NaCl$$

4. Sodium salts give thick white precipitate with potasium dihydrogen antimonate.

$$KH_2SbO_4 + NaCl \longrightarrow NaH_2SbO_4 \downarrow + KCl$$

Illustration - 7 *The gas liberated on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline solution of K_2HgI_4. The aqueous solution of the mixture on treatment with $BaCl_2$ gives a white precipitate which is sparingly soluble in conc. HCl. On heating the mixture with $K_2Cr_2O_7$ and conc. H_2SO_4, red vapours (A) are produced. The aqueous solution of the mixture gives as deep blue colouration (B) with potassium ferricyanide. Identify the radical in the given mixture and write the balanced equations for the formation of A and B.*

SOLUTION :

(i) The gas liberated on heating a mixture of two salts with NaOH gives a reddish brown ppt. with K_2HgI_4. So, the gas is NH_3 and the salt is an ammonium salt.

(ii) The aqueous solution gives white ppt. with $BaCl_2$ (sparingly soluble in HCl). So, the mixture contain SO_4^{2-} ion.

(iii) On heating the mixture with $K_2Cr_2O_7$ and conc. H_2SO_4. red vapours of CrO_2Cl_2 are produced. This shows the presence of Cl^- ion.

(iv) Formation of blue colour by aqueous solution with $K_3[Fe(CN)_6]$ indicates the presence of Fe^{2+} ion.

Reaction Involved :

(i) $NH_4Cl + NaOH \rightarrow NH_3 + NaCl + H_2O$

$2K_2HgI_4 + 4KOH + NH_4Cl \rightarrow I-Hg-O-Hg-NH_2 + 7KI + KCl + 3H_2O$

(ii) $FeSO_4 + BaCl_2 \rightarrow BaSO_4 + FeCl_2$

(iii) $4NH_4Cl + K_2Cr_2O_7 + 3H_2SO_4 \rightarrow 2CrO_2Cl_2 + K_2SO_4 + 3H_2O + 2(NH_4)_2SO_4$

(iv) $3FeSO_4 + 2K_3[Fe(CN)_6] \rightarrow Fe_3[Fe(CN)_6]_2 + 3K_2SO_4$

$HgCl_2 + 2NH_4OH \rightarrow Hg(NH_2)Cl.Hg + NH_4Cl + 2H_2O$

Ist Group Ag^+, Pb^{2+}, Hg_2^{2+} (Mercurous)

Group Reagent : Dilute HCl

The radicals are precipitated as their chlorides because the solubility product of these chlorides ($AgCl$, $PbCl_2$,Hg_2Cl_2) is less than the solubility product of all other chlorides which remain is solution.

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

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

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

Confirm :

1. $PbCl_2$ is soluble in hot water whereas $AgCl$ and Hg_2Cl_2 are insoluble in hot water.

2. $PbCl_2$ gives yellow precipitate with K_2CrO_4. The precipitate is insoluble in acetic acid but soluble in NaOH.

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

$$2Ag^+ + CrO_4^{-2} \longrightarrow Ag_2CrO_4$$

$$Ag^+ + KI \longrightarrow AgI + K^+$$

$$Ag^+ + 2Na_2S_2O_3 \longrightarrow [Ag(S_2O_3)_2]^{3-} + 4Na^+$$

3. $PbCl_2 + KI \longrightarrow PbI_2 + 2KCl$

$$PbI_2 \xrightarrow[\text{Excess}]{KI} K_2[PbI_4] \text{ soluble}$$

4. $AgCl$ is soluble in NH_4OH : $AgCl + NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O$

5. Hg_2Cl_2 forms black precipitate with NH_4OH. Black precipitate is dissolved in aqua-regia.

$$HgCl_2 + 2NH_4OH \rightarrow Hg(NH_2)Cl.Hg + NH_4Cl + 2H_2O$$

$HNO_3 + 3HCl(\text{aqua regia}) \rightarrow NOCl + 2H_2O + 2[Cl]$

1 : 3

$Hg(NH_2)Cl \cdot Hg + 6[Cl] \rightarrow 2HgCl_2 + N_2 + 4HCl$

$HgCl_2 + 2KI \rightarrow HgI_2 + 2KCl$

$HgI_2 + 2KI \rightarrow \underset{\text{Nessler's reagent}}{K_2HgI_4}$

$Hg_2(NO_3)_2 + K_2CrO_4 \rightarrow Hg_2CrO_4 + 2KNO_3$

Confirm :

(a) $2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$

$Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg\downarrow + SnCl_4$

(b) $HgCl_2 + Cu \rightarrow CuCl_2 + Hg_2Cl_2$

$Hg_2Cl_2 + Cu \rightarrow 2Hg + CuCl_2$

IInd Group II A : $Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}$

II B : $As^{3+}, Sb^{3+}, Sn^{2+}, Sn^{4+}$

Group Reagent : $H_2S(g)$ 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. HCl acts as a source of H^+ and thus decreases the concentration of S^{2-} (common-ion-effect). Hence the decreased concentration of S^{2-} is sufficient to precipitate the IInd group metals due to their low k_{sp} values. (Group IV metals have high solubility products)

HgS PbS CuS CdS Bi_2S_3 or Bi_2S_3

As_2S_3 Sb_2S_3 SnS SnS_2

1. PbS, CdS are precipitated in dilution only due to higher K_{sp}..

$\underset{\text{White}}{PbCl_2} \xrightarrow{\text{hot water}} \text{Disolved} \xrightarrow{\text{cooling}} \text{ppt of } PbCl_2 \text{ mreappears}$

$$Pb^{+2} + CrO_4^{-2} \longrightarrow PbCrO_4$$

$$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4$$

$$Pb^{+2} + OH^- \rightarrow Pb(OH)_2 \xrightarrow[(XS)]{NaOH} Na_2PbO_2 \xrightarrow{Oxidised} Na_2PbO_3$$

$$PbS + 3/2O_2 \xrightarrow{300°C} PbO + SO_2$$

$$PbO \xrightarrow{900°C} PbO$$

***Note* : (i)** Colour change on heating due to the change in crystal structure.

(ii) $Pb(NO_3)_2$ decomposes with cracking noise

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2 + O_2 \quad , \quad 2PbCO_3 \xrightarrow{\Delta} 2PbO + 2CO_2$$

$$\underset{\text{White lead}}{Pb(OH)_2 \cdot 2\,PbCO_3} \xrightarrow{<470°C} Pb_3O_4 + CO_2 + CO + H_2O, \quad Pb_3O_4 \xrightarrow{<470°C} 3\,PbO + \frac{1}{2}O_2$$

$$\underset{\text{(sugar of lead)}}{(CH_3COO)_2\,Pb} \xrightarrow{\Delta} \underset{\text{(Acetone)}}{CH_3 - CO - CH_3} + Pb + CO_2$$

2. IIA sulphides are insoluble in yellow ammonium sulphides and IIB sulphides are soluble in it.
3. HgS is insoluble in dilute HNO_3 while PbS, Bi_2S_3, CuS, CdS are soluble in it.
4. In water, Bi_2S_3, CuS, CdS etc are soluble to give respective hydroxides, but $PbSO_4$ is not soluble.
5. Hydroxides formed above in (4) :

   $Bi(OH)_3$ is insoluble in NH_4OH.

   $Cu(OH)_2$ and $Cd(OH)_2$ form soluble complexes.

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

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

$$[Cu(NH_3)_4]SO_4 + 4CH_3COOH \longrightarrow CuSO_4 + 4CH_3COONH_4$$

$$CuSO_4 + K_4Fe(CN)_6 \longrightarrow Cu_2[Fe(CN)_6]\downarrow + 2K_2SO_4$$

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

$$[Cd(NH_3)_4]\,SO_4 + H_2S \longrightarrow CdS\downarrow + (NH_4)_2\,SO_4 + 2NH_3$$

Note : HgS is only sulphide of second group which does not disolve in conc. HNO_3
So we need Aquaregia ($HCl + HNO_3$) to disolve it.

3 : 1

$$3HgS + 6HCl + 2HNO_3 \rightarrow 3HgCl_2 + 2NO + 3S + 4H_2O$$

Sample : 1 $2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 \downarrow + SnCl_4$

$Hg_2Cl_2 \downarrow + SnCl_2 \rightarrow 2Hg \downarrow + SnCl_4$

Sample : 2 $Hg_2Cl_2 + 2KI \rightarrow HgI_2 \downarrow + 2KCl$

$HgI_2 \downarrow + 2KI \rightarrow \underset{\text{Nessler's reagent}}{K_2HgI_4}$

Pb^{2+}

1. $Pb(NO_3)_2 + K_2CrO_4 \rightarrow PbCrO_4 + 2KNO_3$

$PbCrO_4 \downarrow + 4NaOH \rightarrow Na_2PbO_2 + Na_2CrO_{4(aq)} + 2H_2O$

2. $Pb(NO_3)_2 + K_2SO_4 \rightarrow PbSO_4 + 2KNO_3$

$PbSO_4$ is soluble in ammonium acetate

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

Cu^{2+}

1. $2Cu(NO_3)_2 + K_4[Fe(CN)_6] \rightarrow Cu_2[Fe(CN)_6] + 4KNO_3$

2. $Cu(NO_3)_2 + 2KI \rightarrow CuI_2 \downarrow + 2KNO_3$ $\qquad 2CuI_2 \downarrow \xrightarrow{\Delta} Cu_2I_2 + I_2$

$Cu_2I_2 + 3KI \rightarrow K_3[CuI_4]$ $\qquad I_2 + KI \rightarrow KI_3$

3. $Cu(NO_3)_2 + 2NaOH \rightarrow Cu(OH)_2 \downarrow + 2NaNO_3$

$Cu(OH)_2 \downarrow \xrightarrow{\Delta} CuO \downarrow + H_2O$

$2CuO \downarrow + C_6H_{12}O_6 \rightarrow Cu_2O \downarrow + C_6H_{12}O_7$

4. $2Cu(NO_3)_2 + 2Na_2S_2O_3 \rightarrow Cu_2(NO_3)_2 + Na_2S_4O_6 + 2NaNO_3$

$Cu_2(NO_3)_2 + Na_2S_2O_3 \rightarrow Cu_2S_2O_3 + 2NaNO_3$

$$3Cu_2S_2O_3 + 2Na_2S_2O_3 \rightarrow Na_4[Cu_6(S_2O_3)_5]$$
465 complex

For remembrance 465 complex

4	6	5
Na	Cu	S_2O_3

5. Cu^{2+} and Cd^{2+} separation is based on fact that in presence of KCN, only Cd^{2+} is precipitated as sulphides on passing H_2S.

6. Arsenic sulphides is insoluble in conc. HCl while Sb^{3+}, Sn^{2+} sulphides are soluble. Sb_2S_3 can be precipitated in presence of oxalic acid.

7. $CuSO_4 + 2KCN \rightarrow Cu(CN)_2 + K_2SO_4$

$2Cu(CN)_4 \rightarrow Cu_2(CN)_2 + (CN)_2$ [CN^- is a pseudo halide ion and $(CN)_2$ is pseudo halogen known as Cyanogen.]

$Cu_2(CN)_2 + 6KCN \rightarrow K_3[Cu(CN)_4]$

➢ Properties :

▪ Effect of Heat :

$$CuSO_4 \cdot 5H_2O \xrightarrow[-H_2O]{\Delta} CuSO_4 \cdot 4H_2O \xrightarrow[-H_2O]{100^\circ C} CuSO_4 \cdot 2H_2O \xrightarrow[-2H_2O]{230^\circ C} CuSO_4$$

$$CuSO_4 \xrightarrow[720^\circ C]{\Delta} CuO + SO_2 + \frac{1}{2}O_2$$

$$2CuO \xrightarrow{1100^\circ C} Cu_2O + \frac{1}{2}O_2$$

Bi^{3+} $Bi(OH)_3$ is soluble in dilute HCl to form $BiCl_3$ which is tested in two ways.

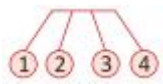
$$Bi(OH)_3 + 3HCl \rightarrow BiCl_3 + 3H_2O$$

(a) $BiCl_3 + H_2O \rightarrow BiOCl\downarrow + 2HCl$

(b) $2BiCl_3 + 2Na_2SnO_2 + 6NaOH \rightarrow 2Bi\downarrow + 3Na_2SnO_3 + 6NaCl + 3H_2O.$

cd^{2+}

Tests : $3CdS + 8HNO_3 \rightarrow 3Cd(NO_3)_2 + 3S + 4H_2O$
Yellow



Sample : 1 $2Cd(NO_3)_2 + K_4[Fe(CN)_6] \rightarrow Cd_2[Fe(CN)_6] + 4KNO_3$

Sample : 2 $Cd(NO_3)_2 + 2\,NH_4OH \rightarrow Cd(OH)_2 \downarrow + 2\,NH_4NO_3$

$Cd(NO_3)_2 + 6\,NH_4OH \rightarrow [Cd(NH_3)_4(OH)_2] + 2\,NH_4NO_3 + 4\,H_2O$

$[Cd(NH_3)_2]\,(OH)_2 + H_2S \rightarrow CdS \downarrow + 4\,NH_3 + 2\,H_2O$

Sample : 3 $Cd(NO_3)_2 + 2\,KCN \rightarrow Cd(CN)_2 + 2\,KNO_3$

$Cd(CN)_2 + 2\,KCN \rightarrow K_2[Cd(CN)_4]$

$K_2[Cd(CN)_4] + H_2S \rightarrow CdS \downarrow + 2\,KCN + 2\,HCN$

Sample : 4 $Cd(NO_3)_2 + 2\,NaOH \rightarrow Cd(OH)_2 \downarrow + 2\,NaNO_3$

$Cd(OH)_2 \downarrow \xrightarrow{\Delta} CdO \downarrow + H_2O$

As^{3+}

Tests : As_2S_3 (soluble in ammonium sulphide)

Sb^{3+}

Sample : 1 $Sb_2S_3 + 2(NH_4)_2S_2 \rightarrow \underset{\text{Soluble}}{Sb_2S_5} + 2(NH_4)_2S$

Sample : 2 $SbCl_3 + H_2O \rightarrow SbOCl + 2\,HCl$

Sample : 1 $2\,SbCl_3 + 3\,H_2S \rightarrow Sb_2S_3 + 6\,HCl$

Sn^{2+} and Sn^{4+}

Test : $SnS \downarrow + (NH_4)_2S_2 \rightarrow SnS_2 \downarrow + (NH_4)_2S$

$SnS_2 \downarrow (NH_4)_2S \rightarrow (NH_4)_2SnS_3$

$SnS_2 \downarrow + 4\,HCl \rightarrow SnCl_4 + 2\,H_2S \uparrow$

$SnCl_2 \downarrow + Fe \rightarrow FeCl_2 + SnCl_2$

$SnCl_2 + HgCl_2 \rightarrow Hg_2Cl_2 \downarrow + SnCl_4$

$Hg_2Cl_2 + SnCl_2 \rightarrow Hg \downarrow + SnCl_4$

$SnCl_4 + 2\,NH_4Cl \rightarrow (NH_4)_2SnCl_6$

Note : $(NH_4)_2SnCl_6$ or pink salt is used as mordant which holds the dyes in clothes.

IIIrd Group Fe^{3+}, Al^{3+}, Cr^{3+}

Reddish brown precipitate $Fe(OH)_3$	Green precipitate $Cr(OH)_3$	White precipitate $Al(OH)_3$
Dissolve the ppt. in dilute HCl and divide into two parts : Part I : $K_4[Fe(CN)_6]$ solution. Prussian blue solution or ppt. Part II + KCNS solution. Red colouration. Fe^{3+} confirmed	ppt. + NaOH + Br_2 water Yellow solution. Acidify the yellow solution with acetic acid and add lead acetate solution, yellow ppt. Cr^{3+} confirmed	Dissolve the ppt. in dil HCl. Add NaOH solution White ppt. appears which then dissolves in excess of NaOH. Treat this solution with solid ammonium chloride Gelatinous white precipitate. Al^{3+} confirmed

Fe^{+2} (Some imporant reaction)

$$FeSO_4 + NO \longrightarrow FeSO_4.NO$$

Nitrosoferrous sulphate

Note : Oxidation state of NO is + 1 in Fe compound. so the oxidation state of Fe in $FeSO_4.NO$ is + 1. It is paramagnetic, its magnetic moment is 3.87 and it is coloured due to the odd electron of NO is fluctuating in between Fe^+ and NO.

$$FeSO_4.7H_2O + NO \longrightarrow [Fe(H_2O)_5NO]SO_4 + 2H_2O$$

$$\xrightarrow{\Delta} FeSO_4 + 5H_2O + NO$$

(This reaction is employed fop separation of NO gas from other gases)

Group Reagent : NH_4OH in presence of NH_4Cl

Metals ions are precipitated as Hydroxides. NH_4Cl is added to suppress the concentration of NH_4OH by common-ion effect, so that only IIIrd group radicals are precipitated. The K_{sp} value of IIIrd group hydroxides is less as compared to IV/VI group hydroxides.

1. Excess of NH_4Cl should be added otherwise manganese will be precipitated in IIIrd group as $MnO_2.H_2O$.
2. $(NH_4)_2SO_4$ cannot be used in place of NH_4Cl since SO_4^{2-} will precipitate Barium (if present) as $BaSO_4$.
3. NH_4NO_3 can't be used otherwise NO_3^- will oxidise Mn^{2+} to Mn^{3+} and thus $Mn(OH)_3$ will be precipitated.
4. Only $Al(OH)_3$ is soluble in excess of NaOH followed by boiling to form sodium metal aluminate, while $Fe(OH)_3$ and $Cr(OH)_3$ are insoluble.

$$Al(OH)_3 + NaOH \longrightarrow Na[AlO_2] + 2H_2O$$

(Aluminate, soluble)

5. $Cr(OH)_3$ is soluble in NaOH and bromine water forming sodium chromate while $Fe(OH)_3$ is insoluble.

$$Cr(OH)_3\downarrow + NaOH \longrightarrow \underset{\text{soluble}}{Na[CrO_2]} + 2H_2O$$

Fe^{3+} ion

(a) $FeCl_3 + 3KCNS \longrightarrow \underset{\text{Potassium thiocyanate}}{} \quad \underset{\text{Ferric thiocyanate}}{Fe(CNS)_3} + 3KCl$

(b) $4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{Ferriferrocyanate}}{Fe_4[Fe(CN)_6]_3} + 12\ KCl$

IVth Group CO^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}

Group Reagent : H_2S in ammonical solution, NH_4OH (NH_4Cl is also added)

Radicals are precipitated as sulphides which are insoluble in NH_4OH.

CoS ; NiS ; MnS ; ZnS

Mn^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} $\xrightarrow[NH_4OH + H_2S]{NH_4Cl}$ MnS, ZnS, CoS, NiS

Black precipitate NiS or CoS	Buff coloured precipitate, MnS	White precipitate ZnS
Wash the ppt. with hot water and dissolve it in aqua regia and heat it to dryness. Extract the residue with water or dilute HCl. Divide it into two parts. Part I + dimethyl glyoxime + NH_4OH → Rose red. Ni^{2+} confirmed Part II + NH_4SCN (solid) + Acetone → Blue layer Co^{2+} confirmed	Dissolve in HCl (dil.) add NaOH to the clear solution and then Br_2 water. Boil and filter. The ppt. is treated with conc. HNO_3 and PbO_2 or Pb_3O_4 (red lead). The contents are heated. Keep the test tube for sometime → purple coloured solution. Mn^{2+} confirmed	Dissolve the ppt. in dilute HCl and add NaOH drop by drop. The precipitate formed dissolves in NaOH. Pass H_2S gas through the solution → Appearance of white ppt. Zn^{2+} confirmed

(Ammonium hydroxide increases the concentration of S^{2-} by increasing the ionisation of H_2S by removing H^+ ions in the form of H_2O)

➤ Now the excess of S^{2-} ions are available and hence the ionic product of IV group sulphides exceeds their solubility product and thus a precipitate will be obtained.

➤ NH_4Cl is used to check the precipitation of V and VI group radicals as hydroxide and sulphides because in presence of NH_4Cl, concentration of OH^- is fairly Low.

1. ZnS and MnS are soluble is cold dilute HCl, while NiS and CoS are insoluble.

2. $Zn(OH)_2$ is soluble in excess of NaOH forming sodium Zincate while $Mn(OH)_2$ insoluble.

$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2\downarrow 2NaCl \; ; \quad Zn(OH)_2 + 2NaOH \longrightarrow \underset{\text{(Soluble Zincate)}}{Na_2ZnO_2} + 2H_2O$$

Mn^{+2} MnS Buff Colour

$$MnS\downarrow +2HCl \xrightarrow{\Delta} MnCl_2 + H_2S\uparrow$$

$$MnCl_2 + 2\,NaOH \rightarrow Mn(OH)_2 + 2\,NaCl$$

$$Mn(OH)_2 + \frac{1}{2}O_2 \rightarrow MnO_2 + H_2O$$

$$MnO_2 + PbO_2 + HNO_3 \rightarrow HMnO_4 + Pb(NO_3)_2 + H_2O$$

$$MnSO_4 + \underbrace{2\,Na_2CO_3 + 2\,KNO_3}_{\text{fusion mixture}} \xrightarrow{\Delta} Na_2MnO_4 + 2\,KNO_2 + 2\,CO_2 + Na_2SO_4$$

$$3\,Na_2MnO_4 + 4\,H_2SO_4 \rightarrow 2\,NaMnO_4 + 4\,NaHSO_4 + MnO_2 + 2\,H_2O$$

Zn^{2+}

Zn^{2+} ion is tested in two ways.

(a) $$Na_2ZnO_2 + H_2S \rightarrow ZnS\downarrow +2\,NaOH$$

(b) $$Na_2ZnO_2 + CH_3COOH \rightarrow (CH_3COO)_2\,Zn + 2\,NaOH$$

$$2(CH_3COO)\,Zn + \underset{\text{Pot. ferrocyanide}}{K_4[Fe(CN)_6]} \rightarrow \underset{\text{Zinc ferrocyanide}}{Zn_2[Fe(CN)_6]} + 4\,CH_3COOK$$

3. Separation of Co^{2+} and Ni^{2+} : Sulphides of Co^{2+} and Ni^{2+} are soluble in aqua-regia.

Co^{2+} and Ni^{2+} chlorides form soluble complexes with KCN.

$$3CoS + 6HCl + 2HNO_3 \longrightarrow 3CoCl_2 + 2NO + 3S + 4H_2O$$

$$3NiS + 6HCl + 2HNO_3 \longrightarrow 3NiCl_2 + 2NO + 3S + 4H_2O$$

(a) $CoCl_2 + 2KCN \longrightarrow Co(CN)_2 + 2KCl$

$$Co(CN)_2 + 4KCN \longrightarrow \underset{\text{Pot.cobaltocyanide}}{K_4[(Co(CN)_6]} \xrightarrow[KCN]{[O]} K_3[Co(CN)_6]$$

(b) $NiCl_2 + 2KCN \longrightarrow Ni(CN)_2 + 2KCl$

$$Ni(CN)_2 + 2KCN \longrightarrow \underset{\text{Pot. nickelocyanide}}{K_2[Ni(CN)_4]}$$

When NaOH and Br_2 water is treated with potassium cobaltocyanide, it is oxidised to very stable complex, potassium Cobalticyanide.

$$2NaOH + Br_2 \longrightarrow NaBr + NaOBr + H_2O \qquad (NaOBr \longrightarrow NaBr + O)$$

$$2K_4[CO(CN)_6] + (O) + H_2O \longrightarrow \underset{\text{Stable}}{2K_3[Co(CN)_6]} + 2KOH$$

- Nickel complex decomposes forming black Nickel oxide.

  $2K_2[Ni(CN)_4] + 4NaOH + [O] \longrightarrow Ni_2O_3 \downarrow + 4NaCN + 4KCN + 2H_2O$

  Nickel salts react with dimethyl glyoxime in presence of NH_4OH to give rose red precipitate of Nickel dimethyl Glyoxime.

- Cobalt salts give blue colour with ammonium thiocynate (not KSCN)

  $CoCl_2 + 4NH_4SCN \longrightarrow (NH_4)_2[Co(SCN)_4] + 2NH_4Cl$

Cobalt salt solution in acetic acid gives a bright yellow precipitate yellow precipitate of potassium cobaltinitrite with KNO_2.

Vth Group Ba^{2+}, Sr^{2+}, Ca^{2+}

1st part + K_2CrO_4 soln. Yellow precipitate	If Ba^{2+} is absent, use 2nd part Add $(NH_4)_2SO_4$ solution White precipitate	If Ba^{2+} and Sr^{2+} both are absent, use the 3rd part. Add $(NH_4)_2C_2O_4$ White precipitate
Ba^{2+} present	Sr^{2+} present	Ca^{2+} present

Group Reagent : $(NH_4)_2CO_3$ in NH_4Cl and NH_4OH

Radicals are precipitated as carbonates insoluble in NH_4OH. NH_4Cl is used to suppress the ionisation of NH_4OH and $(NH_4)_2CO_3$ this is to check the precipitation of $Mg(OH)_2$ and $MgCO_3$ since solubility product of $Mg(OH)_2$ and $MgCO_3$ is high. NH_4Cl should not be added in excess since high concentration of NH_4^+

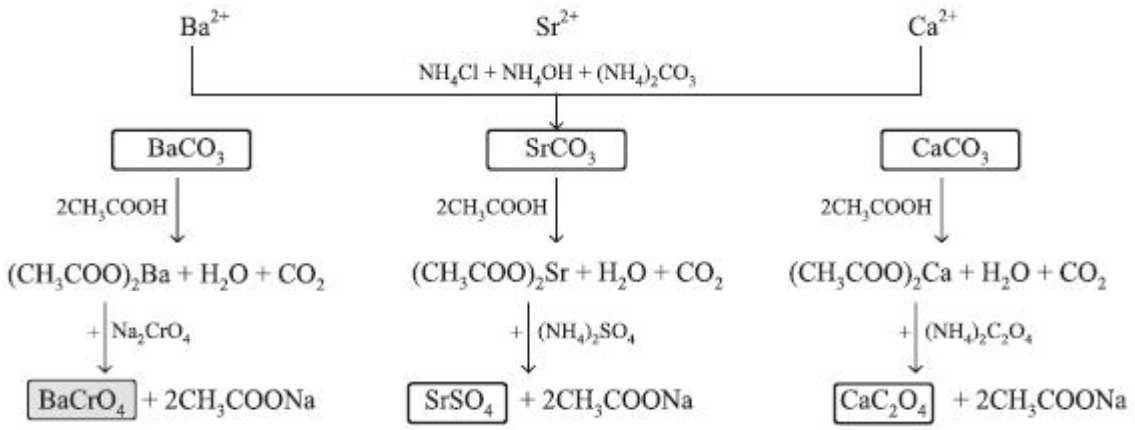
ions will decrease the ionisation of $(NH_4)_2CO_3$ to such an extent that the sufficient CO_3^{2-} ions will not be present even to precipitate Vth group.

1. $BaCO_3$, $SrCO_3$ and $CaCO_3$ are soluble in CH_3COOH forming acetates.

$$MCO_3 + 2\,CH_3COOH \longrightarrow (CH_3COO)_2\,M + H_2O + CO_2$$

$M = Ba^{2+}, Ca^{2+}, Sr^{2+}$ acetate

Tests



Note : This is done in B(Ba).S(Sr).C(Ca) trend only, otherwise all be precipitated at same time. BaC_2O_4,SrC_2O_4 is white ppt and $BaSO_4$, $SrSO_4$ is also white ppt.

2. Potassium Chromate treatment results in formation of insoluble barium chromate. (Others are soluble).

$$(CH_3COO)_2\,Ba + K_2CrO_4 \longrightarrow BaCrO_4\downarrow + 2CH_3COOK$$

3. Ammonia sulphate results in precipitation of strontium sulphate and calcium sulphate. $CaSO_4$ formed is dissolved in ammonia sulphate.

$$(CH_3COO)_2Sr + (NH_4)_2SO_4 \longrightarrow SrSO_4\downarrow + 2CH_3COONH_4$$

$$\underset{\text{formed}}{CaSO_4} + (NH_4)_2SO_4 \longrightarrow \underset{\text{soluble}}{(NH_4)_2\,[Ca(SO_4)_2]}$$

4. Soluble complex $(NH_4)_2[Ca(SO_4)_2]$ gives a white precipitate with ammonium oxalate.

$$(NH_4)_2[Ca(SO_4)_2] + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4\downarrow + 2(NH_4)_2SO_4$$

$$Ca^{2+} + K_4[Fe(CN)_6] \longrightarrow K_2Ca[Fe(CN)_6\downarrow$$

VIth Group Mg^{2+}

Reagent : Disodium hydrogen phosphate, Na_2HPO_4

$$MgSO_4 + Na_2HPO_4 + NH_4OH \longrightarrow Mg(NH_4)PO_4\downarrow + N_2SO_4 + H_2O$$

Mg^{+2}

Test :

1. $MgCl_2 + NH_4OH + Na_2HPO_4 \longrightarrow Mg(NH_4)PO_4 + 2NaCl + H_2O$

2. $MgCO_3 \xrightarrow[-CO_2]{\Delta} MgO + CoO \rightarrow MgO \cdot CoO\,(\text{Cobalt pink})$

$Co(NO_3)_2 \rightarrow CoO + 2NO_2 + 1/2\,O_2$

$MgO + CoO \rightarrow MgO \cdot CoO\,(\text{Cobalt pink})$

Illustration - 8 *An inorganic lewis acid (X) shows the following reactions :*

(i) *It fumes in moist air.*

(ii) *The intensity of fumes increases when a rod dipped in ammonia solution is brought near to it.*

(iii) *An acidic solution of (X) on addition of NH_4Cl and NH_3 solution gives a precipitate which dissolves in $NaOH$ solution.*

(iv) *An acidic solution of* (X) *does not give a precipitate with H_2S.*

Identify (X) *and give chemical equation for steps* (i) *to* (iii).

SOLUTION :

According to question, an organic Lewis acid (X) fumes in moist air the intensity of fumes increase when a rod dipped in NH_3 solution is brought near to it. These reactions clearly indicates that (X) is a metal chloride which is hydrolysed in moist air giving hydrochloric acid and fumes becomes dense when a rod dipped in NH_3 solution is brought near it due to the formation of NH_4Cl. An acidic solution of (X) on addition of NH_4Cl and ammonia solution gives a ppt. soluble in NaOH solution. This means that the metal chloride must be $AlCl_3$ which does not give ppt. When H_2S is passed in acidic solution of (X). Hence (X) is $AlCl_3$ a lewis acid.

The chemical equations for the reaction at step (i), (ii) and (iii) are as follows :

(i) $AlCl_3 + 3H_2O(\text{from mosit air}) \rightarrow \underset{\text{Fumes}}{3HCl} + Al(OH)_3$

(ii) $HCl + NH_3 + H_2O \rightarrow \underset{\text{Dense}}{NH_4Cl} + H_2O$

(iii) $AlCl_3 + 3NH_3 + 3H_2O \rightarrow Al(OH)_3 + 3NH_4Cl$

$Al(OH)_3 + NaOH \rightarrow \underset{\text{Soluble}}{NaAlO_2} + 2H_2O$

Illustration - 9 *On the basis of following reactions identify* (A), (B), (C) *and* (D) *and write down their chemical formulae.*

(i) $(A)\ aq. + Zn \xrightarrow{heat} (B)\ gas$ **(ii)** $(A)\ aq + (C) \xrightarrow{heat} PH_3$

(iii) $(A)\ aq. + NH_4Cl \xrightarrow{heat} (D)\ gas$

SOLUTION :

(i) (A) is an alkali or a mineral acid because Zn is an amphotric metal and evolve H_2 gas. So, the equation is

$$\underset{(A)}{2\,NaOH} + Zn \xrightarrow{heat} \underset{(B)}{Na_2ZnO_2} + H_2 \qquad \text{or} \qquad Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2$$

(ii) We known that, PH_3 gas is obtained from the reaction of phosphorus and alkali. So (A) is NaOH and (C) is phosphorus and the equation is

$$\underset{(A)}{3\,NaOH} + 3\,H_2O + \underset{(C)}{P_4} \xrightarrow{heat} PH_3 + 3\,NaH_2PO_2$$

(iii) (A) i.e. NaOH reacts with NH_4Cl to give a gas D (i.e. NH_3). So, the equation is

$$\underset{(A)}{NaOH} + NH_4Cl \xrightarrow{heat} \underset{(D)}{NH_3} + NaCl + H_2O$$

Illustration - 10 **(i)** *An inorganic compound* (A) *is formed on passing a gas* (B) *through a concentrated liquor containing sodium sulphite.*

(ii) *On adding* (A) *into a dilute solution of silver nitrate, a white precipitate appears which quickly changes into a black coloured compound* (C).

(iii) *On adding two or three drops of ferric chloride into excess of solution of* (A), *a violet coloured compound* (D) *is formed. This colour disappears quickly.*

(iv) *On adding solution of* (A) *into the solution of cupric chloride a white precipitate is first formed which dissolves on adding excess of* (A) *forming a compound* (E).

Identify (A) *to* (E) *and give chemical equations for the reactions at steps* (i) *to* (iv).

SOLUTION :

(i) An inorganic compound, $Na_2S_2O_3$ (sodium thiosulphate) is formed by the reaction of concentrated solution of Na_2S and Na_2SO_3 with I_2 vapours.

$$\underset{(B)}{Na_2S} + Na_2S_2O_3 + I_2 \rightarrow \underset{(A)}{Na_2S_2O_3} + 2\,NaI$$

(ii) When $Na_2S_2O_3$ solution is added into a dilute solution of silver nitrate, a white precipitate of $Ag_2S_2O_3$ (silver thiosulphate) is formed which quickly changes into a black coloured compound i.e. Ag_2S (silver sulphide).

$$2\,AgNO_3 + Na_2S_2O_3 \rightarrow 2\,NaNO_3 + Ag_2S_2O_3$$

$$Ag_2S_2O_3 + H_2O \rightleftharpoons \underset{(A)}{Ag_2S} + H_2SO_4$$

(iii) When two or three drops of ferric chloride is added into the solution of $Na_2S_2O_3$, a violet coloured compound is formed i.e. $Fe_2(S_2O_3)_3$.

$$3\,Na_2S_2O_3 + 2\,FeCl_3 \rightarrow \underset{(D)}{Fe_2(S_2O_3)_3} + 6\,NaCl$$

But violet colour disappear quickly due to the formation of $FeCl_2$.

$$2\,Na_2S_2O_3 + 2\,FeCl_3 \rightarrow 2\,NaCl + 2\,FeCl_2 + Na_2S_4O_6$$

(iv) When solution of $Na_2S_2O_3$ is added into a solution of $CuCl_2$, a white precipitate of $Cu_2S_2O_3$ is first formed which dissolves on adding excess of $Na_2S_2O_3$ solution due to the formation of a compound $Na_4[Cu_6(S_2O_3)_5]$.

$$2\,CuCl_2 + 2\,Na_2S_2O_3 \rightarrow \underset{\text{or}}{2\,CuCl} + Na_2S_4O_6 + 2\,NaCl$$

$$Cu_2Cl_2$$

$$Cu_2Cl_2 + Na_2S_2O_3 \rightarrow Cu_2S_2O_3 + 2\,NaCl$$

$$2\,CuCl_2 + 3\,Na_2S_2O_3 \rightarrow Cu_2S_2O_3 + Na_2S_4O_6 + 4\,NaCl$$

$$3\,Cu_2S_2O_3 + 2\,Na_2S_2O_3 \rightarrow \underset{(E)}{Na_4[Cu_6(S_2O_3)_5]}$$

Illustration - 11 *An unknown solid mixture contains one or two of the following :* $CaCO_3, BaCl_2, AgNO_3, Na_2SO_4, ZnSO_4$ *and* $NaOH$. *The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein. When dilute hydrochloric acid is gradually added to the above solution, a precipitate is formed which dissolves with further addition of the acid. What is (are) present in the solid? Give equations to explain the appearance of the precipitate and its dissociation.*

SOLUTION :

(i) The solution gives pink colour with phenolphthalein, so it must contain NaOH as one of the constituent.

(ii) $ZnSO_4$ forms soluble sodium zincate in the presence of NaOH only

$$ZnSO_4 + 4\,NaOH \rightarrow \underset{\text{Soluble}}{Na_2ZnO_2} + Na_2SO_4 + 2\,H_2O$$

(iii) When dil. HCl is added to soluble Na_2ZnO_2, a white ppt. of $Zn(OH)_2$ is formed

$$Na_2ZnO_2 + 2\,HCl \rightarrow 2\,NaCl + Zn(OH)_2$$

(iv) On adding more of dil. HCl, $Zn(OH)_2$ ppt. dissolves and soluble $ZnCl_2$ is formed.

$$Zn(OH)_2 + 2\,HCl \rightarrow \underset{\text{Soluble}}{ZnCl_2} + 2\,H_2O$$

If other pairs of the given compounds are taken into consideration, then the above reaction will not be possible. This is because $CaCO_3$ is insoluble in water, $BaCl_2$ and $AgNO_3$ if present together would give ppt. of AgCl on adding water. $BaCl_2$ and Na_2SO_4 would give a ppt. of $BaSO_4$ on adding water.

Illustration - 12 **(i)** *A black coloured compound (B) is formed on passing hydrogen sulphide through the solution of a compound (A) in NH_3 solution.*

(ii) *(B) on treatment with hydrochloric acid and potassium chlorate gives (A).*

(iii) *(A) on treatment with potassium cyanide gives a buff coloured precipitate which dissolves in excess of this reagent forming a compound (C).*

(iv) *The compound (C) is changed into a compound (D) when its aqueous solution is boiled.*

(v) *The solution of (A) was treated with excess of sodium bicarbonate and then with bromine water. On cooling and shaking for sometime, a green colour of compound (E) is formed. No change is observed on heating. Identify (A) to (E) and give chemical equations for the reactions at steps (i) to (v)*

SOLUTION :

(i) A black coloured compound CoS is formed on passing hydrogen sulphide through the solution of a compound, $CoCl_2$ to ammonia solution

$$CoCl_2 + H_2S \xrightarrow{NH_3 + H_2O} CoS\downarrow + 2\,HCl$$

(ii) CoS on treatment with HCl and $KClO_3$ again gives $CoCl_2$

$$CoS + 2\,HCl + KClO_3 \rightarrow CoCl_2 + KCl + H_2O + SO_2\uparrow$$

(iii) $CoCl_2$ on treatment with potassium cyanide, gives a buff coloured precipitate of $Co(CN)_2$ which dissolves excess of this reagent forming a complex compound potassium cobaltocyanide.

(iv) The above formed compound is changed into a compound potassium cobaltocyanide when its aqueous solution is boiled.

$$CoCl_2 + 2\,KCN \rightarrow Co(CN)_2 + 2\,KCl$$

$$Co(CN)_2 + 4\,KCN \rightarrow \underset{\substack{\text{Potassium Cobaltocyanide}\\(D)}}{K_4[Co(CN)_6]}$$

(v) When the solution of $CoCl_2$ is treated with excess of $NaHCO_3$ and then with Br_2 water and after cooling and shaking, a green coloured compound is formed.

$$CoCl_2 + 2\,NaHCO_3 \rightarrow Co(HCO_3)_2 + 2\,NaCl$$

$$Co(HCO_3)_2 + 4\,NaHCO_3 \rightarrow Na_4[Co(CO_3)_3] + 3H_2O$$

$$Br_2 + H_2O \rightarrow 2\,HBr + [O]$$

$$Na_4[Co(CO_3)_3] + H_2O + [O] \rightarrow \underset{[E]}{Na_2[Co(CO_3)_3]} + 2\,NaOH$$

Sodium Tricarbonatocobaltate(III)

Illustration - 13 *A white crystalline compound (A) swells up on heating and give violet colour flame on burning. Its aqueous solution gives :*

(A) *White ppt. with* $BaCl_2$

(B) *White gelatinous ppt. with excess of* NH_4OH *which dissolves in NaOH but reappears on boiling with conc.* NH_4Cl *solution.*

SOLUTION :

(i) Since, (A) gives violet colour flame on burning, it must be containing K^+ ions.

(ii) Aqueous solution of (A) gives white ppt. with $BaCl_2$. So, it also contains SO_4^{2-} ions.

(iii) Again, since aqueous solution of (A) gives gelatinous ppt. with excess ammonia solution, it also contains Al^{3+} ions.

Hence, (A) which contains K^+, Al^{3+} and SO_4^{2-} ions with swelling properties (on heating) must be $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

Reactions Involved :

(i) $SO_4^{2-} + BaCl_2 \rightarrow BaSO_4 + 2\,Cl^-$

(ii) $Al^{3+} + 3\,NH_3 + 3\,H_2O \rightarrow Al(OH)_3 + 3\,NH_4^+$

$$Al(OH)_3 + NaOH \rightarrow \underset{\text{(Soluble)}}{NaAlO_2} + 2\,H_2O$$

Illustration - 14 *An aqueous solution of an unknown compound (X) gives the following reactions :*

(i) *It gives brown ppt. with alkaline* $KMnO_4$ *solution.*

(ii) *It forms HCl and evolves* O_2 *when reacted with* Cl_2 *gas.*

(iii) *It liberates* I_2 *from an acidified KI solution.*

(iv) *It gives orange yellow colour with acidified titanic sulphate solution.*

Identify (X) and give the chemical equations for the reactions (i), (ii), (iii).

SOLUTION :

From reaction (iv), it is clear that the unknown compound (X) is H_2O_2.

$$Ti(SO_4)_2 + 2H_2O + \underset{(X)}{H_2O_2} \rightarrow \underset{\text{Pertitanic acid}}{H_2TiO_2} + 2H_2SO_4$$

(i) $2KMnO_4 + 2KOH \rightarrow 2K_2MnO_4 + H_2O + O$

$$\underset{(X)}{H_2O_2} + O \rightarrow H_2O + O_2$$

or $2KMnO_4 + 2KOH + \underset{(X)}{H_2O_2} \rightarrow 2K_2MnO_4 + 2H_2O + O_2$

$$2K_2MnO_4 + 2H_2O \rightarrow 2MnO_2 + O_2 + 4KOH$$

(ii) $H_2O_2 + Cl_2 \rightarrow 2HCl + O_2$

(iii) $\underset{(X)}{H_2O_2} + 2KI + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O + I_2 \uparrow$

So, the unknown compound (X) is H_2O_2.

Illustration - 15 *When gas (A) is passed through dry KOH at low temperature, a deep red coloured compound (B) and a gas (C) are obtained. The gas (A) on reaction with but-2-ene following by treatment with* Zn / H_2O *yields acetaldehyde.*

Identify (A), (B) and (C).

SOLUTION :

Since, the gas (A) on reaction with but-2-ene followed by treatment with Zn / H_2O yields acetaldehyde, (A) is ozone (O_3).

$$\underset{(A)}{O_3} + CH_3-CH=\underset{\text{but-2-ene}}{CH-CH_3} \rightarrow CH_3-\underset{\underset{O}{|}}{CH}-O-\underset{\underset{O}{|}}{CH}-CH_3 \xrightarrow[Zn/H_2O]{\text{Hydrolysis}} \underset{\text{Acetaldehyde}}{2CH_3CHO}$$

Mono ozonide

When gas (A) (i.e. O_3) is passed through dry KOH at low temperature, a deep coloured compound (B), KO_3, and a gas (C), O_2, are obtained. The reaction is shown below :

$$5O_3 + 2KOH \rightarrow \underset{\text{(B)}}{2KO_3} + H_2O(g) + \underset{\text{(C)}}{5O_2}$$

Potassium ozonide

Hence, A = O_3, B = KO_3, C = O_2

Illustration - 16 *Gradual addition of KI solution to $Bi(NO_3)_3$ solution initially produce a dark brown precipitate which dissolve in excess of KI to give a clear yellow solution. Write chemical equation for the above reactions.*

SOLUTION :

$Bi(NO_3)_3$ hydrolyses to give HNO_3 (oxidising agent) which produce a dark brown ppt. I_2, from KI solution. I_2 dissolve in excess of KI to give a clear yellow solution (KI_3).

$$Bi(NO_3)_3 + H_2O \rightarrow [Bi(OH)(NO_3)_2] + HNO_3$$

$$NO_3^- + 2I^- + 4H^+ \rightarrow I_2 + NO + 2H_2O$$

$$I_2 + KI \rightarrow KI_3$$

Illustration - 17 *An inorganic compound (X), which is transparent like glass is a strong reducing agent. Its hydrolysis in water gives a white turbidity (Y). Aqueous solution of (X) give a white ppt. (Z) with aqueous NaOH, which is soluble in excess NaOH. (X) reduces auric chloride to produce purple of cassius. (X) also reduces I_2 and gives chromyl chloride test.*

Identify (X), (Y) and (Z) and give the reactions involved.

SOLUTION :

(i) Since, (X) gives chromyl chloride test, it must be containing Cl^- ion.

(ii) (X) also gives white ppt. with aqueous NaOH, soluble in excess NaOH. So (X) may be containing Zn^{2+}, Sn^{2+} or Al^{3+} ion.

(iii) (X) is also a strong reducing agent. So, (X) is $SnCl_2$

Reaction Involved :

(i) $\underset{\text{(X)}}{SnCl_2} + H_2O \rightarrow \underset{\text{(Y)}}{Sn(OH)Cl} + HCl$

(ii) $SnCl_2 + 2\,NaOH \rightarrow \underset{(Z)}{Sn(OH)_2} + 2\,NaCl$

$Sn(OH)_2 + NaOH \rightarrow Na_2SnO_2 + 2\,H_2O$

(iii) $3SnCl_2 + 2\,AuCl_3 \rightarrow 3SnCl_4 + \underset{\substack{\text{Purple of cassius}\\ \text{(Colloidal gold)}}}{2\,Au}$

(iv) $SnCl_2 + 2\,HCl + I_2 \rightarrow SnCl_4 + 2\,HI$

IN-CHAPTER EXERCISE - B

Subjective Type :

1. *When a white powder (A) is strongly heated, it gives off a colorless, odourless gas (B)which turns lime water milky (C) and if the passage of this gas is continued, the milkiness disappears and gives a solution (D). The solid residue (E) is yellow when hot but turns white on cooling. Identify (A) to (E) with the help of equations.*

2. *A compound on heating with an excess of caustic soda solution liberates a gas (B) which gives white fumes on the exposure to HCl. Heating is continued to expel the gas completely. The resultant alka line solution again liberates the same gas (B) when heated with Zinc powder. However; the com pound (A), when heated alone, does not give nitrogen. Identify (A) and (B).*

3. *An aqueous solution of salt (A) gives a white crystalline precipitate (B) with NaCl solution. The filtrate gives a black precipitate (C) when H_2S is passed into it. The compounds (A) does not give any gas with dilute HCl but liberates a reddish brown gas on heating. Identify compounds from (A) to (D) with help of equations.*

4. *A white substance (A) on heating with excess of dil. HCl gave an offensive smelling gas (B) and a solution (C). The solution (C) on treatment with aqueous ammonia did not give any precipitate but on treatment with NaOH solution gave a precipitate (D) which dissolves in excess of NaOH solution. (A) on strong heating in air gave a strong smelling gas (E) and a solid (F). Solid (F) dissolved completely in HCl and the solution gave a precipitate with $BaCl_2$ in acid solution. Identify (A) to (F) and give the chemical equations.*

5. *An unknown solid mixture contains one or two of the following $CaCO_3, BaCl_2, AgNO_3, Na_2SO_4, ZnSO_4$ and $NaOH$. The mixture is completely soluble in water and the solution gives pink colour with phenolphthalein.*

When dil. HCl acid is gradually added to the above solution a precipitate is formed which dissolved with further addition of the acid. Give composition of mixture and equation.

6. *Compound (A) is greenish solid which gives the following :*

(i) *The addion of $BaCl_2$ solution to a solution of (A) results in the formation of white precipitate (B) which is insoluble in dil HCl.*

(ii) *on heating, water vapours and two oxides of sulphur (C) and (D) are liberated leaving a red brown residue (E).*

(iii) *Compound (E) dissolves in warm concentrated HCl to give a yellow solution (F).*

(iv) *With H_2S gas, the solution (F) yields a yellow white ppt. (G) which when filtered leaves greenish filtrate (H)*

Identify the compounds (A) to (H).

7. *A hydrated metallic salt (A), light green in colour, on careful heating gives a white anhydrous residue (B). (B) is soluble with water and its aqueous solution reacts with NO to give a dark brown compound (C). (B) On strong heating gives a brown residue (D) and a mixture of two gases (E) and (F). The gaseous mixture when passed through acidified permanganate discharges the pink colour and when passed through acidified $BaCl_2$ solution gave a white precipitate. Identify (A) to (F).*

8. *An unknown inorganic compound (X) loses its water of crystallization on heating an its aqueous solution gives the following reactions.*

(i) *It gives turbidity with dil HCl acid*

(ii) *It decolourises a solution of iodine in KI*

(iii) *It gives a white precipitate with $AgNO_3$ which turns black on standing.*

Identify the compound (X) with help of reaction.

9. *The compound (A) is light green solid. It gives the following tests.*

(i) *It dissolved in dil H_2SO_4. NO gas is produced.*

(ii) *A drop of $KMnO_4$ is added to the above solution. The pink colour disappears.*

(iii) *Compound (A) is heated strongly Gases (B) & (C) with pungent smell come out (A brown residue (D) is left behing).*

(iv) *The gas mixture (B) and (C) is passes into dichromate solution. The solution turns greens.*

(v) *The green solution from step (iv) gives a white precipitate (E) with a solution of barium nitrate.*

(vi) *Residue (D) from step (iii) is heated on charcoal in a reducing flame it gives a magnetic substance.*

Identify the various compounds.

10. *A white amorphous powder (A) on heating yields a colourless, non combustible gas (B) and a solid (C). The latter compound assumes a yellow colour on heating and changes to white on cooling. Compound (C) dissolves in dulute acids and the resulting solution gives a white precipitate on add-*

ing $K_4[Fe(CN)_6]$ solution. The compound (A) dissolved in dil HCl with the evolution of gas which is identical in all respects with (B). The gas (B) turns lime water milky but the milki-ness disappears with the continuous passage of the gas. The solution of (A) as obtained above, gives a white precipi tate (D) on the addition of excess of NH_4OH and passing H_2S. Another portion of the solution gives initially a white precipitate (E) on the addition of NaOH solution which dissolved on further addition of the base. Identify (A) to (E) with equations.

11. *An Unknown inorganic compound (A) gave the following reactions*

(i) *(A) on heating gave a residue, oxygen and an oxide of nitrogen.*

(ii) *Aqueous solution of (A) on addition of tap water gave a turbidity which did not dissolve in nitric acid.*

(iii) *The turbidity dissolved in ammonium hydroxide. Identify (A) and gave all balanced reactions.*

12. *A certain inorganic compound (A) on heating loses its water of crystallization. On further heating a blackish brown powder (B) and two oxides of Sulphur (C) and (D) are obtained. The powder (B) on boiling with HCl acid gives a yellow solution (E) on treatment with thiocyanate ions gives a blood red coloured compound (H). Identify (A) to (H).*

13. *A mixture of two salts was treated as follows*

(i) *The mixture was heated with manganese dioxide and concentrated sulphuric acid, when yellow greenish gas was liberated.*

(ii) *The mixture on heating with NaOH solution gave a gas which turned red litmus blue.*

(iii) *Its solution in water gave blue precipitate with potassium ferrocyanide and red colouration with the ammonium thiocyanate.*

(iv) *The mixture was boiled with potassium hydroxide and the liberated gas was bubbled through an alkaline solution of K_2HgI_4 to give brown precipitate. Identify two salts. Give ionic equations for reactions in step (i), (ii) and (iii).*

14. *When 16.8g of a while solid (X) was heated 4.4 g (A) that turned lime water milky was driven off together with 1.8 g of a gas (B)which condensed to a colour less liquid. The solid that remained (Y) dissolved in water to give an alkaline solution, which with excess of $BaCl_2$ solution a white precipitate (Z). The precipitate effervesced with acid giving off CO_2 gas. Identify (A), (B) and (Y) and write down equation for thermal decomposition of (X).*

15. *When a white crystalline compound (X) is heated with $K_2Cr_2O_7$ and concentrated H_2SO_4, a reddish brown gas (A) is evolved. On passing (B) into caustic soda solution, a yellow coloured solution of (B) is obtained. Neutralizing the solution of (B) with acetic acid and on subsequent addition of lead acetate, a yellow precipitate (C) is obtained. When (X) is heated with NaOH solution, a colourless*

gas is evolved and on passing this gas into K_2HgI_4 solution, a reddish brown precipitated (D) is formed. Identify (A), (B), (C), (D) and (X). Also give the equations involved.

16. *An aqueous solution of an inorganic compound (X) yielded a white precipitate when treated with dil HNO_3 acid and silver nitrate. Another sample of solution of (X) when treated with NaOH gave a white precipitate first, which dissolved in the excess of NaOH yielding colourless solution, when H_2S gas was passed through that solution a white precipitate was obtained . Identify the compound (X) and give all reactions.*

17. *A black coloured compound (A) on reaction with dil. H_2SO_4 acid gives a gas (B) which on passing in a solution of an acid (C) gives a white turbidity (D). Gas (B) when passed in an acidified solution of a compound (E) gives a precipitate (F) soluble in dil. HNO_3. After boiling this solution when an excess of ammonium hydroxide is added., a blue coloured compound (G) is formed. To this solution on addition of acetic acid and aqueous potassium ferrocyanide a chocolate precipitate (H) is obtained. On addition of an aqueous solution of barium chloride to an aqueous solution of (E) a white precipitate insoluble in HNO_3 is obtained. Identify (A) to (H).*

18. *A mixture of three X,Y,Z are passed first into an acidified dichromate solution when (X) is absorbed turning the solution green. The remainder of the mixture is passed through an excess of lime water which turns milky, resulting in the absorption of (Y). The residue gas (Z) is absorbed by an alkaline pyrogallol solution. However the original gaseous mixture does not turn lead acetate paper black. Identity X,Y,Z.*

19. *A green solution (A) of a metal chloride on treatment with NaOH and H_2O_2 gives a yellow solution (B) which turns orange on acidification. The solution (orange) on crystallization gives a solid (C), which on heating with NaCl and conc. H_2SO_4 yields a red volatile liquid (D). On adding ammonia to orange crystals of (E) are formed. (E) decomposes on heating to give steam, N and green solid (F). Identify (A) to (F).*

20. *A pale yellow compound (A) is insoluble in mineral acid but soluble in conc. aq. NH_3 forming (B), (A) also reacts with conc. H_2SO_4 and MnO_2 to give brown fumes of (D). If the solution of (C) is boiled, a black ppt. (E) is obtained (E) can be dissolved in HNO_3 giving solution (F) which on treatment with HCl yields white ppt. (G) which can be dissolved in aqueous NH_3 giving solution (H). Identify from (A) to (H).*

21. *A white solid (A) loses on heating one sixth of us weight and becomes a yellow solid (B). (B), on heating in air gains weight and gives a red solid (C). (C) is partly soluble in dil. HNO_3 leaving a brown residue (D). (A) is soluble in dil HNO_3 giving effervescence to give a solution (E). (E) reacts*

with NaOH followed by Cl_2 water to give (D). (A) does not appreciably dissolve in dil HCl or H_2SO_4. Identify (A) to (E).

22. *An inorganic white crystalline solid (A) is soluble in H_2O. Its solution gives black ppt. (B) with H_2S gas which on dissolution in HNO_3 (conc.) again forms (A). (A), reacts with H_2SO_4 to give white solid (C) which dissolves in ammonium acetate to give (D). This solution gives a yellow ppt (E) with KI. The compound (A) on heating with copper turnings and conc. H_2SO_4 evolves a brown gas (F). (A) reacts with cold $FeSO_4$ and conc. H_2SO_4 to give a brown substance (G) which becomes colourless on heating. Identify the compounds (A) to (G).*

23. *From the reaction below, identify A, B, C, D,* _____

(a) **(i)** $A \xrightarrow[+\ H_2SO_4]{dil} B(Green)$; $K_2Cr_2O_7$ A is _____

(ii) $A + dil\ H_2SO_4 + C \longrightarrow MnSO_4$ B is _____

(iii) $A + O_2 \xrightarrow[H_2O]{} D \xrightarrow{Ba_2Cl} E \downarrow white$ C is _____

(b) **(i)** $A(aq) + Zn \xrightarrow{\Delta} B(gas)$ A is _____

(ii) $A(aq) + C \xrightarrow{\Delta} PH_3$ B is _____

(iii) $A(aq) + NH_4Cl \xrightarrow{\Delta} D(gas)$ C is _____

D is _____

(C) NaOH

$\xrightarrow{A} NaCl + NaOCl$

$\xrightarrow{B} NaNO_2 + NaNO_3$

$\xrightarrow{C} NaHSO_3 \xrightarrow{D} Na_2SO_3 \xrightarrow{E} Na_2S_2O_3 \xrightarrow{I_2} X + Y$

24. *You are given an unknown solution that may contain one or more of given ions.*

$$Cr^{3+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Ag^{+}, Zn^{2+}, Hg_2^{2+}, Hg^{2+}$$

(i) *Addition of HCl gives no ppt. which of the ions must be present ?*

(ii) *Subsequent addition of* H_2S *and heating in acid produces a black ppt, insoluble in* HNO_3, *which of the ions must be present?*

(iii) *Filtering off the ppt (in II) removing* H_2S *by boiling and after neutralizing the acid (by ammonia), a greenish ppt. is obtained, which is soluble in excess of NaOH. Which ion must be present ?*

25. *A colour salt (A) when heated with alkali gives a gas (B). (A) on reaction with* $CaCl_2$ *solution give a white precipitate (A). The gas (B) gives white fumes with HCl and (C) decolourises acidified* $KMnO_4$. *Identify A, B and C. Give all the reactions involved.*

26. *A salt (A) on heating gives a colourless gas (B) which dissolves in water to give a neutral solution & leaves no residue. (A) on warming with NaOH gives a pungent smelling gas (C) which turns mercurous nitrate paper black. The solution after warming with NaOH and on treatment with Al Powder gives a further supply of gas (C). Identify A, B, C.*

27. *A salt (A) on warming with NaOH solution gives out a pungent smelling gas (A). which when passed through a solution of copper sulphate gives it a deep blue solution. To the alkaline solution of above, when* $A\ell$ *powder is added, a further quantity of (B) evolves. (A) when heated carefully to a temperature above* $240°C$ *decomposes completely without leaving any residue into two gases (C) and (D). (D) exists as a liquid below* $100°C$ *and (C) can be liquefied by applying pressure at room temperature. The gas (C) when moderately inhaled induces laughter. Identify A, B, C, D. Name the analytical reagent (E) formed by addition of mercuric chloride to excess of KI solution. Indicate the colour of ppt. that the gas (B) would form with (E).*

28. *The solution of salt (A) answers the brown ring test and gives a black ppt. with* H_2S *in HCl. It gives with alkali a yellow ppt. and a scarlet red ppt. with KI dissolving in excess of KI. What is (A) ? What happens when :*

(i) *A is heated ?*

(ii) *If solution of (A) treated with* $SnCl_2$ / HCl *in hot & cold conditions*

29. *There black powders (A), (B), (C) are kept in three dishes. (A) dissolves in dil* H_2SO_4 *to give a blue solution. Moistened with HCl, (A) gives a green colour in flame test. (A) does not dissolve in dil HCl but when boiled with conc. HCl, dissolves giving chlorine. This solution with* H_2S *in ammoniacal*

solution produces of flesh coloured ppt. (C) does not dissolved in HCl but when heated with KNO_3, burns away evolving a gas which turns lime water milky. What are (A), (B), and (C) ?

30. *A certain alloy is dissolved in hot conc. HNO_3 and the solution evaporated till the residue is just moist. Water and HCl are then added and thus the solution obtained is treated with H_2S. A black ppt. is obtained which, filtered off, dissolves in hot dil. HNO_3 to yield a blue solution which become deep blue on adding NH_4OH. The filtrate after treatment with H_2S yields a black ppt. with ammonia. But if the filtrate is thoroughly boiled and treated with dimethyl glyoxime in NH_4^+ solution, a rose red ppt is formed, Identify the metals of alloy.*

31. *A white crystalline solid, dissolves in water. The solution effervesces with $NaHCO_3$ and decolourises $KMnO_4 / H^+$. Conc. H_2SO_4 decomposes the solid without blackening, yielding a mixture of gases, one of which turns lime water milky and the other burns with a blue flame and is not only poisonous but absorbed by ammoniacal Cu_2Cl_2. Identify the solid.*
Determine its equivalent weight as reducing and oxidizing agent.

NOW ATTEMPT IN-CHAPTER EXERCISE-B FOR REMAINING QUESTIONS IN THIS EBOOK

NOW ATTEMPT OBJECTIVE WORKSHEET BEFORE PROCEEDING AHEAD IN THIS EBOOK

SOLUTIONS - IN-CHAPTER EXERCISE - B

1. $A \rightarrow ZnCO_3$; $B \rightarrow CO_2$; $C \rightarrow CaCO_3$; $D \rightarrow Ca(HCO_3)_2$; $E \rightarrow ZnO$

2. $A \rightarrow NH_4NO_3$; $B \rightarrow NH_3$

3. $A \rightarrow Pb(NO_3)_2$; $B \rightarrow PbCl_2$; $C \rightarrow PbS$; $D \rightarrow PbI_2$;

$$Pb(NO_3)_2 \xrightarrow{\Delta} \underset{\text{Reddish brown}}{2NO_2} + PbO + \frac{1}{2}O_2$$

4. $A \rightarrow ZnS$; $B \rightarrow H_2S$; $C \rightarrow ZnCl_2$; $D \rightarrow Zn(OH)_2$;

$$ZnS + O_2 \xrightarrow{\Delta} \underset{(F)}{ZnSO_4} + \underset{(E)}{SO_3}\uparrow$$

5. $ZnSO_4$ and $NaOH$

6. $A \rightarrow FeSO_4 \cdot 7H_2O$; $B \rightarrow BaSO_4$; $C \rightarrow SO_2$; $D \rightarrow SO_3$
$E \rightarrow Fe_2O_3$; $F \rightarrow FeCl_3$; $G \rightarrow S$; $H \rightarrow FeCl_2$

7. $A \rightarrow FeSO_4 \cdot 7H_2O$; $B \rightarrow FeSO_4$; $C \rightarrow FeSO_4.NO$ or $[Fe(H_2O)_5\,NO]SO_4$

$D \rightarrow Fe_2O_3$; $E \rightarrow SO_2$; $F \rightarrow SO_3$

8. $Na_2S_2O_3 \cdot 5H_2O$; $Na_2S_2O_3 \cdot 5H_2O \xrightarrow{\Delta} Na_2S_2O_3 + 5H_2O$;

$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 + \underset{\text{turbidity}}{S} + H_2O$

$2Na_2S_2O_3 + \underset{\substack{\text{(Solution of}\\ \text{iodine in KI)}}}{KI_3} \longrightarrow 2NaI + KI + Na_2S_4O_6$;

$Na_2S_2O_3\ 2AgNO_3 \longrightarrow \underset{\text{(while)}}{Ag_2S_2O_{3(s)}} + 2NaNO_3$

$Ag_2S_2O_3 + H_2O \longrightarrow \underset{\text{(black)}}{Ag_2S_{(s)}} + H_2SO_4$

9. $A \rightarrow FeSO_4 \cdot 7H_2O$; $B \rightarrow SO_2$, $C \rightarrow SO_3$; $D \rightarrow Fe_2O_3$; $BaSO_4$;

$FeSO_4 + H_2SO_4 \longrightarrow \text{No action}$

$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O$

$2FeSO_4 \cdot 7H_2O \xrightarrow{\Delta} Fe_2O_{3(s)} + SO_{2(g)} + SO_{3(g)} + 14H_2O_{(g)}$

$SO_{2(g)} + SO_{3(g)} + K_2Cr_2O_7 \longrightarrow K_2SO_4 + \underset{\text{green solution}}{Cr_2(SO_4)_3}$

$Cr_2(SO_4)_3 + Ba(NO_3)_2 \longrightarrow BaSO_{4(s)} + Cr(NO_3)_{3(aq)}$;

$3Fe_2O_3 + C \longrightarrow \underset{\text{Magnetic substance}}{2Fe_3O_4} + CO$

10. $A \rightarrow ZnCO_3$; $B \rightarrow CO_2$; $C \rightarrow ZnO$; $D \rightarrow ZnS$; $E \rightarrow Zn(OH)_2$

$ZnCO_3 \xrightarrow{\Delta} ZnO_{(s)} + CO_{2(g)}$; $ZnO_{(s)} + 2HCl_{(aq)} \longrightarrow ZnCl_{2(aq)} + H_2O_{(\ell)}$

$2ZnCl_{2(aq)} + K_4[Fe(CN)_6] \longrightarrow \underset{\text{White}}{Zn_2[Fe(CN)_6]_{(s)}} + 4KCl_{(aq)}$

$CO_2 + Ca(OH)_2 \longrightarrow \underset{\text{Milkiness}}{CaCO_{3(s)}}$; $CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_{2(aq)}$

$ZnCl_{2(aq)} + 2NH_4OH_{(aq)} + H_2S_{(g)} \longrightarrow \underset{\text{White}}{ZnS_{(s)}} + 2NH_4Cl + 2H_2O$

$ZnCl_{2(aq)} + 2NaOH \longrightarrow Zn(OH)_{2(s)} + 2NaCl$;

$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_{2(aq)} + 2H_2O$

11. $A \rightarrow AgNO_3$; $AgNO_3 \xrightarrow{\Delta} Ag_{(s)} + \frac{1}{2}O_{2(g)} + NO_{2(g)}$;

$AgNO_{3(aq)} + \underset{\substack{\text{From tap water because of presence of bleaching powder}}}{Cl^-_{(aq)}} \longrightarrow \underset{\text{Turbidity}}{AgCl_{(s)}}$

$AgCl_{(s)} + 2NH_4OH_{(aq)} \longrightarrow [Ag(NH_3)_2]Cl_{(aq)} + 2H_2O$

12. $A \rightarrow FeSO_4 \cdot 7H_2O$; $B \rightarrow Fe_2O_3$; $C \rightarrow SO_2$; $D \rightarrow SO_3$
$E \rightarrow FeCl_3$; $F \rightarrow S$; $G \rightarrow FeCl_2$; $H \rightarrow Fe(SCN)_3$

$FeSO_4 \cdot 7H_2O \xrightarrow{\Delta} FeSO_4 + 7H_2O$; $2FeSO_4 \longrightarrow Fe_2O_3 + SO_2 + SO_3$

$Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$; $2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + S + 2HCl$

$FeCl_3 + SCN^- \longrightarrow Fe(SCN)_3 + 3Cl^-$

13. NH_4Cl ; $FeCl_3$; $4FeCl_3 + 6H_2SO_4 + 3MnO_2 \longrightarrow Fe_2(SO_4)_3 + 3MnCl_2 + 6H_2O + 3Cl_2$

$4NH_4Cl + 2H_2SO_4 + MnO_2 \longrightarrow 2(NH_4)_2SO_4 + MnCl_2 + Cl_2 + 2H_2O$

$NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + NH_3(g)$

$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{Blue precipitate}}{Fe_4[Fe(CN)_6]_{3(s)}} + 12KCl$

$FeCl_3 + 3NH_4SCN \longrightarrow \underset{\text{Red colouration}}{Fe(SCN)_3} + 3NH_4Cl$

14. $X \rightarrow NaHCO_3$; $A \rightarrow CO_2$; $B \rightarrow H_2O(g)$; $Y \rightarrow Na_2CO_3$; $Z \rightarrow BaCO_3$

$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3(s) + CO_2(g) + H_2O(g)$

15. $X \rightarrow NH_4Cl$; $A \rightarrow CrO_2Cl_2$; $B \rightarrow Na_2CrO_4$; $C \rightarrow PbCrO_4$

$4NH_4Cl + K_2Cr_2O_7 + 5H_2SO_4 \rightarrow 4NH_4HSO_4 + K_2SO_4 + 2CrO_2Cl_2 + 3H_2O$

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

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

16. $ZnCl_2$; $ZnCl_2 + 2AgNO_3 \rightarrow Zn(NO_3)_2 + 2AgCl(s)$

$ZnCl_2 + NaOH \rightarrow Zn(OH)_2(s) + 2NaCl$

$Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2(aq) + H_2O$; $Na_2ZnO_2 + H_2S \rightarrow ZnS(s) + Na_2S + H_2O$

17. $A \rightarrow CuS$; $C \rightarrow H_2SO_3$; $E \rightarrow CuSO_4$

$B \rightarrow H_2S$; $D \rightarrow S$; $G \rightarrow [Cu(NH_3)_4]SO_4$; $H \rightarrow Cu_2[Fe(CN)_4]$

18. $X \rightarrow SO_2$; $Y \rightarrow CO_2$; $Z \rightarrow O_2$

19. $A \rightarrow CrCl_3$; $B \rightarrow Na_2CrO_4$; $C \rightarrow Na_2Cr_2O_7$; $D \rightarrow CrO_2Cl_2$

$E \rightarrow (NH_4)_2Cr_2O_7$; $F \rightarrow Cr_2O_3$

20. $A \rightarrow AgBr$; $B \rightarrow [Ag(NH_3)_2]Br$; $C \rightarrow Ag_2S_2O_3$; $E \rightarrow Ag_2S$

$F \rightarrow AgNO_3$; $G \rightarrow AgCl$; $H \rightarrow [Ag(NH_3)_2]Cl$

21. $A \rightarrow PbCO_3$; $B \rightarrow PbO$; $C \rightarrow Pb_3O_4$; $D \rightarrow PbO_2$; $E \rightarrow Pb(NO_3)_2$

22. $A \rightarrow AgNO_3$; $B \rightarrow Ag_2S$; $C \rightarrow Ag_2SO_4$; $D \rightarrow CH_3COOAg$.

$E \rightarrow AgI$; $F \rightarrow NO_2$; $G \rightarrow [Fe(H_2O)_5NO]SO_4$

23. **(1)** $A \rightarrow SO_2$; $B \rightarrow Cr_2(SO_4)_3$; $C \rightarrow KMnO_4$; $D \rightarrow H_2SO_4$; $E \rightarrow BaSO_4$

(2) $A \rightarrow NaOH$; $B \rightarrow H_2$; $C \rightarrow P_4$; $D \rightarrow NH_3$

(3) $A \rightarrow Cl_2$; $B \rightarrow NO_2$; $C \rightarrow SO_2$; $D \rightarrow Na_2CO_3$; $E \rightarrow S$

$X \rightarrow NaI$; $Y \rightarrow Na_2S_4O_6$

24. **(i)** Cr^{3+}, Mn^{2+} Fe^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}

(ii) Hg^{2+}

(iii) Cr^{3+}

25. $A \rightarrow (NH_4)_2\, C_2O_4$; $B \rightarrow NH_3$; $C \rightarrow CaC_2O_4$

26. $A \rightarrow NH_4NO_3$; $B \rightarrow N_2O$; $C \rightarrow NH_3$

27. $A \rightarrow NH_4NO_3$; $B \rightarrow NH_3$; $C \rightarrow N_2O$; $D \rightarrow H_2O$; $E \rightarrow$ Nessler's Reagent

(B) + (E) $\rightarrow$ Brown coloured ppt.

28. $A \rightarrow Hg(NO_3)_2$

$Hg(NO_3)_2 \xrightarrow{\Delta} Hg + 2NO_2 + O_2$

$2Hg(NO_3)_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + Sn(NO_3)_4$

29. $A \rightarrow CuS$

$B \rightarrow MnO_2$

$C \rightarrow$ Charcoal

30. Cu and Ni

31. $Na_2C_2O_4$

$E_{\text{Reducing agent}} = \dfrac{Mo}{2}$

My Chapter Notes