30. QUALITATIVE ANALYSIS

1. INTRODUCTION

 $Salt \longrightarrow \underbrace{Cation (C^{+})}_{\text{from base}} + \underbrace{Anion (A^{-})}_{\text{from acid}}$

Determination of quality of any salt mixture is called **Qualitative analysis** or **Salt analysis**.



Flowchart 30.1: Procedure of salt analysis

2. PHYSICAL APPEARANCE

Experiment	Observation	Inference
Color (due to d-d transition of e ⁻ in d-block elements and f-f transition of e ⁻ in f-block elements)	Blue or bluish green Green Reddish brown Pink violet Light pink White	Cu ²⁺ or Ni ²⁺ Ni ⁺² Fe ⁺² Fe ⁺³ Co ⁺² Mn ⁺²
		Absence of above transition metals ions $\begin{bmatrix} Ba^{+2}, Sn^{+2}, Ca^{+2}, Mg^{+2}, AI^{+3}, Zn^{+2} etc \end{bmatrix}$
Smell	Rotten egg Vinegar Ammonical	S ²⁻ CH ₃ COO ⁻ NH ₄ ⁺
Density	Heavy Light powder	Pb^{+2},Ba^{+2} can be CO_3^{2-}

Table 30.1: Physical properties

Deliquescence: Colorless \rightarrow Mg⁺², Al⁺³, Zn⁺²

Colored \rightarrow Cu⁺², Fe⁺³

Deliquescence \rightarrow Substance absorbs moisture from the atmosphere until it dissolves $\overline{}$

in the absorbed water and forms a solution

Hygroscopic \rightarrow Substance absorbs and hold water molecules from the surroundings

(Water of crystallisation)

3. DRY HEATING TESTS

Table 30.2: Dry tests

Observation	Inference
1. Gas evolved:	
Colorless + odorless	CO ₃ ²⁻ ,HCO ₃ ⁻
Colorless	
Rotten egg $(H_2 S \uparrow)$	S ²⁻
Vinegar like CH ₃ COOH	CH₃COO⁻
Burning sulphur	SO ₃ ²⁻ , S ₂ O ₃ ²⁻ , S ²⁻
Ammonical	NH_4^+
Colored (Pungent Smell)	
Reddish brown $(NO_2 \uparrow)$	NO_3^- , NO_2^-
Yellowish green	CI⁻
Reddish brown $(Br_2 \uparrow)$	Br ⁻
Violet black $(I_2 \uparrow)$	I_

Observation	Inference	
2. Sublimate: Decomposition of solid substance and deposition in the upper portion of test-tube.	White \rightarrow NH ₄ Cl,Hg(I),Hg(II) chlorides As(III),Sb(III) or Se(IV) Yellow $\rightarrow S_{\text{free sulphur}}$, As ₂ S ₃ ,Hg(I) / Hg(II)iodides exception to above	
3. Decripitation: Decomposition with crackling sound on heating. Salts not having water of crystallization.	$\left\{ \text{halides of alkali metals, Pb}\left(\text{NO}_3\right)_2 \right\}$	
4. Fusion: Salts with water of crystallization will fuse generally.	CuSO ₄ .5H ₂ O,FeSO ₄ .7H ₂ O	
5. Swelling:	PO ₄ ³⁻ , BO ₃ ³⁻	
6. Residue:		
Yellow when hot and white when cold	ZnO	
Brown when hot and yellow when cold	PbO	
White residue which glows on heating	Ba^{+2} , Sr^{+2} , Ca^{+2} , Mg^{+2}	
Original salt is blue in color, becomes white on heating	Cu ²⁺ or CuSO ₄	
Colored salts become brown or black on heating	Co ⁺² ,Fe ⁺³ ,Fe ⁺² ,Cr ⁺³ ,Cu ⁺² ,Ni ⁺² ,Mn ⁺² ,etc	

4. OTHER DRY TESTS



Figure 30.1: Different regions of flame

Figure 30.2: Diagram showing non luminous and luminous flame

5. CHARCOAL CAVITY TEST

$$ZnSO_4 + Na_2CO_3 \rightarrow ZnCO_3 + \underbrace{Na_2SO_4}_{charcoal will absorb Na_2SO_4}$$

 $ZnCO_3 \rightarrow ZnO + CO_2$

 $\begin{array}{c} {\sf CuSO}_4 \rightarrow {\sf CuO} \rightarrow & \underbrace{{\sf Cu}}_{\substack{ {\sf reddish \ residue} \\ {\sf of \ metallic \ {\sf Cu}}}} \end{array}$

Metal carbonate decompose on heating to form metal oxides and may further get reduced to metal especially if metals are less reactive (e.g Ag, Cu, gold).

Charcoal absorbs the anion formed by Na.



Figure 30.3: Set up for charcoal cavity test

6. COBALT NITRATE TEST

Residue of charcoal cavity test + cobalt nitrate.

If residue in charcoal cavity test is white, then this test is performed.

Table	30.3:	Charcoal	cavity	test
Tubic	50.5.	Charcoar	cuvity	ic si

Test	Inference
Residue + Co(NO ₃) ₂ + Δ	Distinct colour residue is obtained for different metal cations.
E.g. $2\text{Co}(\text{NO}_3)_2 \rightarrow 2\text{CoO} + 4\text{NO}_2 + \text{O}_2$	They are mixed cobalt-metal oxides.
$ZnO + CoO \rightarrow \underbrace{ZnO.CoO}_{\begin{array}{c} CoZnO_2\\ Rinman's green \end{array}}$	
ZnO.CoO	Green
Al ₂ O ₃ .CoO	Blue
MgO.CoO	Pink
SnO.CoO	Bluish

7. FLAME TEST

Generally, alkali and alkaline earth metal salts impart characteristic color to the flame. For this metals only, the electronic de-excitation will be in visible range. To perform this test, the metal salts are converted into their corresponding chlorides [generally, these metal chlorides are volatile] (volatile \rightarrow vaporizes easily)



2. Dip the wire in concentrated HCI



3. Dip the wire salt to be tested



4. Hold sample on the hot flame



Figure 30.4: Steps to preform flame test

Sr. No.	Metals Color of flame		
1	Sr , Li	Crimson Red	
2	Са	Brick Red	
3	Ва	Apple Green	
4	К	Violet (lilac)	
5	Cu	Blue Green	
6	Na	Golden Yellow	
7	Ni	Brown	

Table 30.4: Flame test for transition metals

8. BORAX BEAD TEST

Borax \rightarrow salt of boric acid [Na₂B₄O₇.10H₂O]. The free end of Pt wire is coiled into a small loop. This loop is heated in Bunsen flame until it is red hot and then is quickly dipped into powdered form of solid. The adhering solid is held in the hottest part of the flame. At first, salt loses water of crystallization and shrinks on the loop forming a colorless, transparent glass like bead consisting of mixture of sodium meta borate and boric anhydride.



Figure 30.5: Heating a Pt wire

 $Na_{2}B_{4}O_{7}.10H_{2}O \xrightarrow{\Delta} Na_{2}B_{4}O_{7} \xrightarrow{\Delta} \underbrace{NaBO_{2} + B_{2}O_{3}}_{colorless, tranparent glass like bead.}$

The bead is moistened and dipped into the finely powdered subs. (salt) so that a minute of it sticks to the bead and this bead is heated in lower reducing flame, is allowed to cool and the color is observed. This is then heated in an oxidizing flame, allowed to cooled and color is observed again.

Coloured beads are due to the formation of various coloured transition metal borates. The Bead "R" and Bead "O" is due to the variable oxidation states of the metal ions.

$$CuCO_3 \Delta CuO + CO_2$$

 $CuO + B_2O_3 \rightarrow \underbrace{Cu(BO_2)_2}_{\text{blue colored bead is oxdising flame}}$

 $2Cu(BO_2)_3 + 2NaBO_2 + C \rightarrow CuBO_2 + Na_2B_4O_7 + CO$

Copper(I) metaborate \rightarrow Colorless

 $2Cu(BO_2)_3 + 4NaBO_2 + 2C \rightarrow \underbrace{2CuBO_2}_{\text{Red colored}} + 2Na_2B_4O_7 + 2CO$ bead in reducing flame

Table 30.5:	Colour	of flame	of d	lifferent	ions	during	borax	bead	test

	Color in oxidizing flame		Color in reducing flam	e
Metal	When Hot	When Cold	When Hot	When Cold
Copper	Green	Blue	Colorless	Brown red

	Color in oxidizing flame		Color in reducing flame		
Metal	When Hot When Cold		When Hot	When Cold	
Iron	Brown yellow	Pale yellow	Bottle green	Bottle green	
Chromium	Green	Green	Green	Green	
Cobalt	Blue	Blue	Blue	Blue	
Manganese	Violet	Red	Grey	Grey	
Nickel	Violet	Brown	Grey	Grey	

Non luminous flame = Oxidizing flame.

Luminous flame = Reducing flame.

9. MICROCOSMIC SALT BEAD TEST

 $\underbrace{\underbrace{\mathsf{Na}(\mathsf{NH}_4).\mathsf{HPO}_4.4\mathsf{H}_2\mathsf{O}}_{\substack{\Delta\\ \text{micro\,cosmic}\\ \text{salt}}} \xrightarrow{\Delta} \mathsf{Na}\mathsf{PO}_3 + \mathsf{H}_2\mathsf{O}\uparrow\mathsf{NH}_3\uparrow$

(Ammonium sodium phosphate)

Na(NH₄).HPO₄ when heated first, colorless transparent bead of sodium metaphosphate is obtained.

This combines with metallic oxide to form orthophosphate which are of characteristic colors.

It will have color similar to borax bead test.

 $NaPO_3 + CoO \rightarrow \underbrace{NaCoPO_4}_{(blue \ color)}$ orthophosphate

10. CONFIRMATORY TESTS (WET TESTS)

Table 30.6: Wet tests

Sr. No.	Acid radical	Characteristics
1	CO ₃ ²⁻	All carbonates are ppt. except Na ⁺ ,K ⁺ ,Rb ⁺ ,Cs ⁺ ,NH ⁺ ₄
2	HCO ₃	All bicarbonates are soluble (i.e. are found in soln. phase only). Only alkali metals NH_4^+ bicarbonate can be obtained in solid form or can be isolated.
3	SO ₃ ²⁻	All sulphides are insoluble except group I- NH^+_4
4	S ²⁻	The acid , bisulphide, polysulphides of alkali metal & NH_4^+ are soluble, rest are ppt. Generally S ²⁻ ppt are common. Sn^{2+} HS ⁻ are normally soluble
5	$NO_2^-, NO_3^-, CH_3 COO^-$	All are soluble except AgNO ₂ ,CH ₃ COOAg, CH ₃ COOHg

Sr. No.	Acid radical	Characteristics
6	CI⁻	All soluble except Ag ⁺ , Hg ₂ ²⁺ , Cu ⁺ , BiO ⁺ , SbO ⁺ , <u>Pb⁺²</u> soluble in hot water
7	Br⁻	All except Ag^+ , $\underline{Pb^{+2}}_{soluble in hot water}$, Cu^+ , Hg_2^{+2}
8	Ι-	All soluble except Ag^+ , Hg_2^{2+} , Hg^{+2} , Cu^+ , Bi^{+3} , Pb^{+2}
9	SO ₄ ²⁻	All soluble except Pb ⁺² , Ba ⁺² Sr^{+2} , Ca^{+2} or Hg(II) slightly soluble Basic sulphates of Hg, Bi and Cr are insoluble but these dissolves in dil.HCl or dil. HNO ₃ E.g. HgO. HgSO ₄ \rightarrow insoluble (basic) $(neutral salt)$
10	PO ₄ ³⁻	All phosphates are ppt except $\begin{array}{c} Grp I + NH_{4}^{+} \\ \overbrace{slightly}^{slightly} \end{array}$ Primary phosphates of alkaline earth metals are also soluble (dihydrogen phosphate) E.g. Mg(H ₂ PO ₄) ₂

11. ANALYSIS OF ANIONIC OR ACIDIC RADICAL



Flowchart 30.2: Analysis of anionic or acidic radical

Group A (dil H ₂ SO ₄)					
Sr. No.	Observation	Gases	Inference		
1	Effervescence of a colorless & odorless gas , which turns lime water milky	CO ₂	CO ₃ ²⁻ , HCO ₃ ²⁻		
2	Evolution of colorless, suffocating gas with burning sulphur smell which turns $\rm K_2Cr_2O_7$ paper green	SO ₂	SO ₃ ²⁻		
	$\operatorname{Cr}_2\operatorname{O}_7^{2-} + \operatorname{SO}_2 \to \operatorname{Cr}^{3+}(\operatorname{green})$				
3	Evolution of colorless gas with rotten egg smell which turns lead acetate paper black(PbS)	H ₂ S	S ^{2–}		
4	Evolution of pungent smelling reddish brown gas which turns starch iodide paper blue	NO ₂	NO ₂		
	$I^++NO_2 \rightarrow I_2$ (I_2 +starch-blue complex)				
5	Evolution of colorless gas having vinegar like smell	CH₃COOH	CH ₃ COO ⁻		
Group	A(conc. H ₂ SO ₄)				
1	Colorless, pungent smelling gas which gives white fumes with rod dipped in NH ₃ (conc. H ₂ SO ₄ cant oxidise Cl ⁻ toCl ₂)	HCI	Cl-		
2	Reddish brown gas with pungent smell and intensity of these fumes/ vapours increase on addition of a pinch of MnO_2 & these also turn starch iodide paper orange red.	Br ₂	Br		
3	Evolution of violet vapours which turn starch paper blue	I ₂	ŀ		
4	Evolution of brown fumes, intensity of which increase on addition of Cu pieces/turnings and turns starch iodide paper blue.	NO ₂	NO ₃ -		
Group B	3	Ppt.			
1	Water extract (WE)+sodium carbonate extract+soda extract(SE)+BaCl ₂ (aq)	White insoluble ppt.	SO ₄ ²⁻		
2	$WE+SE+conc.HNO_3(1N \text{ or } 2N)+ammonium molybdate$	Canary yellow ppt.	PO ₄ ³⁻		

Table 30.7: Analysis of group A and group B radicals

12. SODIUM CARBONATE EXTRACT



Figure 30.6: Set up for preparation of sodium carbonate extract

Sodium carbonate reacts with other inorganic salts to form water soluble salt of acid radical and the cation of salt will be ppt. in the form of CO_3^{2-} . SE is used when given salt is partially soluble or insoluble in water. Cation of the salt interfere with the test of acid radical.

Dil.H₂SO₄ grp (CO₃²⁻,CO₂)

C., N.,	Deswort	Observation	Demonto
Sr. NO.	Reagent	Observation	
1	$CO_3^{2-} + H_2SO_4 \rightarrow SO_4^{2-} + \underbrace{H_2O + CO_2}_{H_2CO_3}$	Colorless, Odourless, brisk Effervescence gas	Some carbonates like $FeCO_3$, $MgCO_3$ and $CaCO_3$ should be powdered for appreciable reaction.
2	Lime water $Ca(OH)_2$ $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow$ $Ba(OH)_2 + CO_2 \rightarrow BaCO_3 \downarrow$	White turbidity (For CaCO ₃ , prolonged passage of CO ₂ dissolves the turbidity) CaCO ₃ +CO ₂ \rightarrow Ca(HCO ₃) ₂	White turbidity dissolves in dil. acid liberating CO ₂ gas. CaCO ₃ \downarrow +HCI \rightarrow CaCl ₂ +CO ₂ \uparrow +H ₂ C
3	$MgSO_{4}/BaCl_{2} \text{ soln (colorless)}$ $Mg^{2+}+CO_{3}^{2-} \rightarrow MgCO_{3}$ $Mg^{2+}+2HCO_{3} \rightarrow Mg(HCO_{3})_{2}$ $Mg(HCO_{3})_{2} \xrightarrow{\Delta} MgCO_{3} \downarrow +CO_{2} + H_{2}O$	White	
4	AgNO ₃ soln. $2Ag^{+}+CO_{3}^{2-} \rightarrow AgCO_{3}$ $AgCO_{3} \xrightarrow{\Delta \text{ or}} Ag_{2}O + CO_{2}$ $\xrightarrow{\Delta} 2Ag + \frac{1}{2}O_{2}$	White ppt(dissolves in NH ₃ or HNO ₃) Yellow/brown ppt.	Carbonates are more easily polarized Metal carbonates are generally constant and not stable to heat.
5	HgCl ₂ /Hg(NO ₃) ₂ Hg ²⁺ +HCO ₃ → [•] No reaction Hg ²⁺ +3CO ₃ ²⁻ +3H ₂ O→3HgO.Hg(CO ₃) ₂ .Hg(CO ₃) ₂ (basic mercuric carbonate)	Reddish brown ppt	
6	Phenolphthalein (HPh)	CO_{3}^{2-} +HPh = Pink	
		HCO_3 +HPh = Colo rless	

Table 30.8: Sodium carbonate extract test

ACTION OF HEAT

Bicarbonates $\xrightarrow{\Delta}$ Carbonates

 $2NaHCO_{3} \xrightarrow{\Delta} Na_{2}CO_{3} + CO_{2} \uparrow H_{2}O$ Carbonates $\xrightarrow{\Delta} \underbrace{metal \ oxide + CO_{2}}_{\left(exception \ Na^{+}, \ K^{+}, \ Rb^{+}, \ Cs^{+}\right)}$

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$
; $PbCO_3 \rightarrow PbO + CO_2$

Carbonates of less reactive metals

$$\begin{bmatrix} Ag, Au, Hg, Cu \end{bmatrix} \xrightarrow{\Delta} metal + CO_2 \uparrow +O_2 \uparrow$$
$$Ag_2CO_3 \xrightarrow{\Delta} 2Ag + CO_2 \uparrow + \frac{1}{2}O_2 \uparrow$$

S. No.	Reagent	Observation	Remarks
SO ₃ ^{2−}			
1	Dil.H ₂ SO ₄ SO ₃ ^{2−} + H ₂ SO ₄ (aq) → SO ₂ ↑ + H ₂ O + SO ₄ ^{2−}	Colorless, suffocating burning sulphur smelling gas.	
	Above gas+lime/baryta water Ca(OH) ₂ + SO ₂ \rightarrow CaSO ₃ \downarrow +H ₂ O	Milkiness	If both SO_3^{2-} , CO_3^{2-} are present, then SO_3^{2-} will be oxidized to SO_4^{2-} by $K_2Cr_2O_7$
	On prolonged passage, milkiness disappears $CaSO_3 + H_2O + SO_2 \rightarrow Ca(HSO_3)_2$	No milkiness	(a) and (b) not given by CO ₃ ²⁻
	a) $\underbrace{\text{acidifiedK}_2 Cr_2 O_7}_{\text{moist filter paper}} + SO_2 \xrightarrow{\qquad} \underbrace{Cr^{3+}_3}_{\text{green}} + SO_4^{2-}$	Green	
	b) $SO_2 + IO_3^- \rightarrow I_2^- + SO_4^{2-}$ starchiodate (blue)	Blue	
2	BaCl ₂ Soln. Ba ²⁺ + SO ₃ ^{2−} → BaSO ₃ ↓ On exposure to air, changes to BaSO ₄ . Oxidising agents show such changes. H ₂ O ₂ → H ₂ O;Br ₂ → Br [−] HNO ₃ → NO; MnO ₄ [−] → Mn ⁺²	White ppt.	BaSO ₃ dissolves in- (i) Dil.HCl BaSO ₃ + HCl → SO ₂ +H ₂ O + BaCl ₂ (ii) Dil.H ₂ SO ₄ BaSO ₃ + H ₂ SO ₄ → SO ₃ ²⁻
	Sodium nitroprusside Na[Fe(CN) ₅ NO] + SO ₃ ²⁻ \rightarrow Na ₄ [Fe(CN) ₅ NO]SO ₃	Rosy-red coloration	If both SO_3^{2-} and S^{2-} are present, this test is not used.
3	AgNO ₃ Soln. Ag ⁺ + SO ₃ ²⁻ $\longrightarrow [Ag(SO_3)]^-$ soluble sulphito argentate	No Visible change	
	On adding more AgNO ₃ to the above complex $[Ag(SO_3)]^{-}+Ag^{+} \rightarrow Ag_2SO_3$ Dissolves in excess of SO ₃ ²⁻ $Ag_2SO_3 + SO_3^{-2-} \rightarrow 2[Ag(SO_3)]^{-}(aq)$ $2\left[Ag(SO_3)\right]^{-} \xrightarrow{\Delta} 2Ag \downarrow + SO_4^{2-} + SO_2$	White ppt. Dissolves in NH ₃ and dil. HNO ₃	

Table 30.9: Confirmatory test for sulphite radical

S. No.	Reagent	Observation	Remarks
4	Pb(NO ₃) ₂ / Pb(CH ₃ COO) ₂	White	
	$Pb^{+2} + SO_3^{2-} \rightarrow PbSO_3 \xrightarrow{O_2} PbSO_4$		
5	$Zn + H_2SO_4 (aq)$ $Zn + SO_3^{2-} + H^+ \rightarrow Zn^{+2} + H_2S \uparrow + H_2O$		

Illustration 1: $M_2X.7H_2O(A)$ has water and M_2X (M is monovalent alkaline cation and X is divalent anion) in 1:1 ratio by wt. (A). On reaction with dil. H_2SO_4 gives a gas that turns $K_2Cr_2O_7/H^+$ soln green. Identify (A) and explain.

Sol: Anion \rightarrow SO ₃ ²⁻	M_2SO_3
2x+32+48 =	18x7 = 126
$2x = 46 \implies$	x = 23
$A \rightarrow Na_2SO_3$	

Table 30.10: Confirmatory tests for sulphide and nitrite ion

S ²⁻	Reagent	Observation	Reaction
1	Dil H ₂ SO ₄	Colorless, rotten egg smell.	
	$S^{2-}+H_2SO_4 \rightarrow H_2S+SO_4^{-2-}$		
	(i) Above gas + Pb(NO ₃) ₂ / $\underbrace{Pb(CH_3COO)_2}_{\text{moist filter paper}} \rightarrow PbS \downarrow$	Black	
	(ii) $Cd^{+2} + H_2S \rightarrow CdS \downarrow$	Yellow	
	$(33) \text{ pk}^{+2} = 20 \text{ H}^{-1} \text{ sph}(0.11) + 20.15$	All sulphide	
	(iii) PD \longrightarrow PD(OH) ₂ \checkmark 2OH	One ppt except Al ₂ S ₃ (aq.)	
	$PbS + 2H_2O + 2OH^{-} \xrightarrow{H_2S} \left[Pb((OH)_4 \right]^{2^{-1}}$	H ₂ S+AI(OH) ₃	
2	Oxidising agent	Yellow/white ppt.	
	(i) $MnO_4^{-} \xrightarrow{H_2S} S \downarrow +Mn^{+2}$		
	(ii) $\operatorname{Cr}_2 \operatorname{O}_7^{2-} \xrightarrow{H_2 S} S \downarrow + \operatorname{Cr}^{3+}$		
	(iii) $I_3^- \xrightarrow{H_2S} 3I + S$		
3	Sodium Nitroprusside	Purple colour	
	$S^{2-} + Na_2 \Big[Fe(CN)_5 NO \Big] \rightarrow Na_4 \Big[Fe(CN)_5 NO \Big]$		
4	Methylene blue test	Methylene blue	

$H_{3}C \longrightarrow CH_{3}$ $+ Fe^{3+}(soln.) + H_{2}S \longrightarrow V(CH_{3})_{2}$ $+ Fe^{2^{+}} + NH_{4}^{+} + H^{+}$ $N, N-Dimethyl phenyl diamine$			
NO ₂ -	Reagent	Observation	Reaction
1	Dil.H ₂ SO ₄	Pale blue liquid (contains	
	$Dil.H_2SO_4$ + solid nitrites	$HNO_2 + N_2O_3$) gives reddish brown NO_2 fumes-Pungent smell)	
2	BaCl ₂ soln.		
	$Ba^{2+} + NO_3^- \rightarrow No$ Reaction		
3	Conc.AgNO ₃	White ppt	
	$Ag^+ + NO_2^- \longrightarrow AgNO_2$		
4	KI Sol ⁿ (excess)	Yellow brown vapours	
	$2NO_2^{-} + 3I^- + 4H^+ \Longrightarrow I_3^- + 2NO \uparrow +H_2O$		
5	MnQ_ ⁻ (acidic)	Decolourised by a soln. of	
	$NO_2^- + MnO_4^- \rightarrow NO_3^- + Mn^{+2} (Nogas)$	nitrite	
6	Solid urea		
	$\underbrace{NO_2^-}_{acidified} + urea \rightarrow N_2 \uparrow + CO_2 \uparrow$		
7	Solid thiourea		SCN ⁻ ions can be
	$(NH_2)_2 CS + \underbrace{NO_2^-}_{acidified} \rightarrow H^+ + N_2 \uparrow + SCN^- + H_2O$		with FeCl ₃ + HCl
	$Fe^{3+} + 3SCN^{-} \longrightarrow \downarrow Fe(SCN)_{2}$	Blood red colour	
	(aq.)		

13. BROWN RING TEST

When nitrite solution is added carefully along the sides of test tube to a saturated solution of $FeSO_{4'}$ acidified with acetic acid or dil. $H_2SO_{4'}$ a brown ring is formed due to formation of complex of variable composition best represented as



Figure 30.7: Brown ring test for estimation of unsaturation

 NO_3^- will also give similar test if NO_2^- and NO_3^- both are present, then NO_2^- can be selectively decomposed by using

Sulphamic acid $(NH_2 - SO_3H)$ O \parallel $HO - S - NH_2 + 2HNO_2 \longrightarrow N_2 \uparrow + SO_4^{2-} + 2H^+ + H_2O$ \parallel O

Sodium oxide (NaN₃)

 $NO_2^- + N_3^- + H^+ \rightarrow N_2 \uparrow + SO_4^{2-} + 2H^+ + H_2O$ Boil the mixture with NH_4Cl NO_2^- is decomposed to N_2

 $NaNO_2 + NH_4CI \rightarrow N_2 \uparrow + SO_4^{2-} + 2H^+ + H_2O$

Table 30.11: Confirmatory	y test for acetate ic	on
---------------------------	-----------------------	----

CH ₃ COO-	Test	Observation	Remarks
1	Dil.H ₂ SO ₄ CH ₃ COO [−] + H ⁺ → CH ₃ COOH	Vinegar like smell	All acetate are soluble except. CH ₃ COOAg and CH ₃ COOHg
2	$AgNO_3Soln: CH_3COO^- + Ag^+ \rightarrow CH_3COOAg$	White ppt.	
3	$BaCl_2$ soln: $BaCl_2 + CH_3COO^- \rightarrow No$ reaction		
4	$C_2H_5OH + conc.H_2SO_4$ (2 - 3ml) (1ml) +1gm acetate salt+heat	Fruity smell of an ester	
5	Neutral FeCl ₃ 6CH ₃ COO ⁻ + 3Fe ⁺³ + 2H ₂ O \rightarrow [Fe ₃ (H ₂ O) ₂](CH ₃ COO) ₆	Red blood sol ⁿ	
	Above redblood soln. $\xrightarrow{\Lambda}$ 4H ₂ O	Reddish brown	

Illustration 2: An aqueous solution of salt containing an anion X^{n-} gives the following reactions: It gives the purple or violet coloration with sodium nitroprusside solution. It liberates a colorless, unpleasant smelling gas with dilute H_2SO_4 which turns lead acetate paper black. Identify the anion (X^{n-}) and write the chemical reactions involved.

Sol: X^{n-} is S^{2-} because

 $\left[\mathsf{Fe}(\mathsf{CN})_{5} \mathsf{NO} \right]^{2-} + \mathsf{S}^{2-} \rightarrow \left[\mathsf{Fe}(\mathsf{CN})_{5} \mathsf{NOS} \right]^{4-} \text{ (purple or violet coloration)}$ $\mathsf{S}^{2-} + \mathsf{H}_{2}\mathsf{SO}_{4} \rightarrow \mathsf{H}_{2}\mathsf{S} \uparrow \text{ (colorless, unpleasant smelling)} \mathsf{SO}_{4}^{-2-} + \mathsf{H}_{2}\mathsf{S} + \mathsf{Pb}(\mathsf{CH}_{3}\mathsf{COO})_{2} \rightarrow \mathsf{PbS} \downarrow (\mathsf{black}) + 2\mathsf{CH}_{3}\mathsf{COOH}$

Illustration 3: Sulphite on treatment with dil H₂SO₄ liberates a gas which:

Turns lead acetate paper black

Turns with blue flame

Smells like vinegar

Turns acidified K solution green

Sol: $SO_3^{2-} + H_2SO_4 \rightarrow SO_2 + SO_4^{2-} + H_2O$ SO_2 turns acidified $K_2Cr_2O_7$ solution green $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \rightarrow Cr_2(SO_4)_3$ (Green) + $K_2SO_4 + H_2O$ Therefore , (iv) option is correct.

Illustration 4: A colorless pungent smelling gas (x) is obtained when a salt is reacted with dil. H_2SO_4 . The gas (X) responds to the following properties.

It turns lime water milky

It turns acidified potassium dichromate solution green

It gives white turbidity when H_2S gas is passed through it aqueous solution.

Its aqueous solution in NaOH gives a white ppt. with barium chloride which dissolves in dil HCl liberating (X).

Identify (X) and write the chemical equations involved.

Sol: As gas X turns lime water milky it may be CO_2 or SO_2 . But CO_2 is colorless and odorless , so 'X' may be SO_2 . This is further , confirmed by the following reactions:

 $SO_{3}^{2-} + H_{2}SO_{4} \rightarrow SO_{4}^{2-} + SO_{2} + H_{2}O$ $Ca(OH)_{2} + SO_{2} \rightarrow CaSO_{3}(Milky) + H_{2}O$ $K_{2}Cr_{2}O_{7} + H_{2}SO_{4} + 3SO_{2} \rightarrow K_{2}SO_{4} + Cr_{2}(SO_{4})_{3}(Green) + H_{2}O$ $SO_{2} + 2H_{2}S \rightarrow 3S \downarrow (White) + 2H_{2}O$ $SO_{2} + 2NaOH \rightarrow Na_{2}SO_{3} + H_{2}O$ $Na_{2}SO_{3} + BaCl_{2} \rightarrow BaSO_{3} \downarrow (White) + 2NaCl$ $BaSO_{3} + 2HCl \rightarrow BaCl_{2}(Soluble) + SO_{2} + H_{2}O$

Conc: H₂SO₄ group

Table 30.12: Confirmatory test for chloride ic	n
--	---

[CI-]	Reagent	Observation	Remarks
1	$\begin{array}{c} \underbrace{CI^{-}}_{H_{2}SO_{4}} \rightarrow HCI \uparrow +HSO_{4}^{-} \\ + H_{3}PO_{4} \\ \downarrow \\ HCI \uparrow +H_{2}PO_{4}^{-} \end{array}$	Dipped rod of NH ₃ +HCI=white fumes of NH ₄ CI	Being a stronger oxidizing agent, Cl ₂ is not produced.
2	$MnO(OH)_{2} + 2H_{2}SO_{4} + 2CI^{-} \rightarrow$ $Mn^{+2} + CI_{2} \uparrow + 2SO_{4}^{2-} + 3H_{2}O$	Yellowish green; turns iodide paper blue	Permanently bleaches dyes by oxidation
3	$\begin{array}{c} Ag^{+} + CI^{-} \to AgCI \downarrow \\ \left(AgNO_{3}\right) \end{array}$	White ppt soluble in NH ₃	
	$AgCI + AsO_3^{3-} arsenite \rightarrow Ag_3ASO_3 \downarrow$	Yellow (distinct from AgBr/Agl)	
4	$\underbrace{Pb^{2+}}_{Pb(CH_3COO)_2} + 2CI^- \rightarrow PbCl_2$	White ppt-soluble in hot water) conc.HCl/KCl	
5	Chromyl chloride test $K_2Cr_2O_7 + conc.H_2SO_4 + 4Cl^- \longrightarrow CrO_2Cl_2$	Red vapours	$Cl_2 \& K_2 Cr_2 O_7$.have equal oxidizing power. Br & l'don't give similar test since $Cr_2 O_7^{2-}$ oxidises Br, Kl ⁻ to Br ₂ & l ₂
	$CrO_4^{2-} + Pb^{+2} \rightarrow PbCrO_4 \downarrow$	Bright yellow ppt.	

Illustration 5: Comp X imparts imparts a golden yellow flame and shows following reaction

(1) Zn (powder) when boiled with conc. Ag. Solⁿ of X dissolves and H_2 gas is evolved .

(2) When Ag. Solⁿ of X is added to Ag Solⁿ of SnCl₂, a white ppt is obtain which dissolves in excess of X

When dissolved in Zn which is amphoteric, H₂O gas is evolved which signified Basic nature

 $NaOH + Zn \longrightarrow Na_2ZnO_2$

 $NaOH + ZnCI_2 \longrightarrow Sn(OH)_2 \rightarrow Na_2SnO_2$

Illustration 6: A gaseous mixture of X, Y, Z when passed into acidified $K_2Cr_2O_7$, gas X was absorbed and solⁿ turned green. The remainder mixture was passed through lime which turned milky by absorbing gas Y. The residue gas when passed through alc. pyrogallol solution turned black.

Sol: K₂Cr₂O₇ and lime water to differentiate between SO₂ and CO₂ .pyrogallol is used to absorb O₂ gas Q.

Illustration 7: Colourless salt (A) gives apple green flame with conc. HCl,(A) or reaction with dil. H_2SO_4 gives brown fumes (D) turing KI starch paper blue

(A) + $CH_3COOH + K_2CrO_4 \longrightarrow Yellow ppt$	(A) + $H_2SO_4 \longrightarrow White ppt (C) + (D)$
(D) + $CH_3NH_2 \longrightarrow CH_3OH + H_2O + gas$ (E)	$(E) + Mg \longrightarrow (F)$

Table 30.13: Confirmatory test fe	or bromide ion
-----------------------------------	----------------

Br⁻	Reagent	Observation	Remarks
1	i) $2Br^- + SO_{4+}^{2-} + 4H^+ \rightarrow Br_2 + SO_2 + 2H_2O$ ii) $Br^- + H_3PO_4 \rightarrow HBr + H_2PO_4^-$	Reddish brown Br ₂ vapours and pungent smell	
2	Pinch of MnO_2 added to above test-tube. $Br^- + MnO_2 \rightarrow Br_2 + Mn^{2+} + H_2O$	Intensity of coloured fumes increases. Irritating pungent smell. Bleaches litmus paper. Filter paper dipped in fluorescein dye(yellow) turns red. Turns starch iodide paper blue.	Fluorescence Cl ₂ , Br ₂ , l ₂ , Colourless red violet
3	$Ag^+ + Br^- \rightarrow AgBr ↓$ (AgNO ₃)	Pale yellow ppt. Dissolves in conc. NH ₃ , KCN hypo soln.	
4	$Pb^{+2}+2Br \rightarrow PbBr_2$ (Pb-acetate)	White ppt.Soluble in conc.HBr or conc, KBr	
5	$8HNO_3+6Br \rightarrow 3Br_2\uparrow +NO\uparrow +6NO_3^-+4H_2O$		
6	$K_2Cr_2O_7 + H_2SO_4 + Br^- \longrightarrow Br_2 + Cr^{+3}$		
7	Layer test With Cl_2 water. i) Cl_2 water + $Br^- \rightarrow Br_2 \uparrow$ Dropwise	Br ₂ vapours colours the sol ⁿ orange red.	
	ii) Above soln. +CHCl ₃ +shake	Upper layer: colourless Lower layer: Red brown Greater solubility of Br ₂ in organic solvent	
	iii) Excess of Cl_2 water $Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$ $Br_2 + Cl_2 \rightarrow 2BrCl$	Yellow soln.	

ŀ	Reagent	Observation	Remarks
1	$\begin{array}{c c} HI + HSO_{4}^{-} & I_{2}^{+} + SO_{2}^{-} \uparrow \\ \uparrow & \uparrow \\ I + H_{2}SO_{4}^{-} \\ \downarrow & \downarrow \\ I_{2}^{+} + S^{-} & I_{2}^{-} + H_{2}S^{-} \end{array}$	Violet coloured vapours	All are soluble except Ag ⁺ ,Hg ⁺² , Cu ⁺ , Pb ⁺² , Pb ⁺² = soluble in hot water
	HI is a good reducing agent		
2	$MnO_2 + H_2SO_4 + I^- \rightarrow I_2 + Mn^{+2}$	Intensity of violet vapours increase	
3	$\underbrace{\operatorname{Ag}^{+}}_{\operatorname{AgNO}_{3}} + \mathrm{I}^{-} \rightarrow \operatorname{AgI} \downarrow$	Yellow. Soluble in KCN, Partially soluble in conc. NH _{3.}	
4	$\underbrace{Pb^{+2}}_{Pb-acetate} + 2\mathrm{I}^{-} \rightarrow PbI_{2} \downarrow$	Yellow	
5	$I^- + K_2 Cr_2 O_7 + H_2 SO_4 \rightarrow I_2 + Cr^{3+}$		
6	$KNO_2 + I^- + H_2SO_4 \to I_3^- + NO \uparrow + H_2O$		
7	$HgCI_{2} + 2I^{-} \rightarrow HgI_{2} ↓ + 2CI^{-}$ $HgI_{2} + 2I^{-} \rightarrow [HgI_{4}]^{2-}$	Scarlet Red	$\underbrace{K_2 \left[HgI_4 \right] + KOH}_{Nessler's reagent}$ Used for detection of NH_4^+ and NH_3
8	Iodometric Titrations i) $2Cu^{+2} + 2I^{-} \rightarrow 2Cu^{+} + I_{2}$ ii) $I_{2} + 2S_{2}O_{3}^{2-} \rightarrow 2I^{-} + S_{4}O_{6}^{2-}$		
9	$2\text{FeCl}_3 + 3\text{I}^- \rightarrow 2\text{Fe}^{+2} + \text{I}_3^-$		
10	Layer Test Cl_2 water $+l^- \rightarrow l_2$	Brown soln.	
	Above solution. + CHCl ₃	Upper layer: Colourless lower layer: violet layer	
	Excess of Cl_2 water i) $Cl_2 + I^- \rightarrow Cl^- + I_2$ $I_2 + I^- \rightarrow I_3^-$ ii) $I_3^- + 8Cl_2 + 9H_2O \rightarrow$ $3IO_3^- + 16Cl^- + 18H^+$	Colourless iodic acid formed	

Table 30.14: Confirmatory test for lodide ion

Remark for HgCl₂

 $K_2[Hgl_4] + KOH$ as alkaline solution of K_2Hgl_4 . Is called Nessler's reagent used for detection of NH_4^+ or NH_3^-

NO ₃ ⁻	Reagent	Observation	Remarks
1	i) $NO_3^- + H_2SO_4 \rightarrow HNO_3^-$ + HSO_4^-		All nitrate are soluble
	ii) $2HNO_3 \rightarrow 2NO_2 \uparrow +\frac{1}{2}O_2 \uparrow H_2O$	Reddish Brown	
2	Cu turnings+Above soln. \rightarrow Cu ⁺² + 2NO \uparrow +4SO ₄ ²⁻ + 4H ₂ O	Intensity of above colour increases	
3	Diphenyl /blue ring test $NO_3^- + (C_6H_5)_2 NH \downarrow$ $Ph_2 - N - Ph_2$	Blue complex	
4	Brown Ring Test		

 Table 30.15:
 Confirmatory test for nitrate ion

Brown ring Test

3 - 4 ml conc. $H_2SO_4 + 2ml$ of NO_3 solution +mix+cool the mixture under a stream of cold water+ saturated solution of $FeSO_4$ from the side of the test tube to form a layer on the top of the liquid. A brown ring will formed at the junction of two liquids. This brown ring complex is unstable and decomposes on shaking or on heating into NO and a yellow colour solution of Fe⁺³ ion.

Reduction of NO_3^- or NO_2^- is alkaline medium into NH_4^+ or NH_3 can be done by Zn, Al , Devarda's Alloy(50% Cu, 45% Al, 5% Zn)

 $NO_3^- + 4Zn + 7OH^- + 6H_2O \rightarrow NH_3^+ + 4[Zn(OH)_4]^-$

 $3NO_3^- + 8AI + 5OH^- + 18H_2O \rightarrow 3NH_3^+ + 8[Zn(OH)_4]^-$

Action of heat on nitrate

Alkali metal nitrate $\xrightarrow{\Delta}$ Metal nitrate + O₂

$$NaNO_3 \xrightarrow{\Delta} NaNO_2 + \frac{1}{2}O_2$$

(Except Li)

Metal nitrate $\xrightarrow{\Delta}$ Metal oxide + NO₂ + O₂ (Except Na⁺, K⁺, Rb⁺, Cs⁺)

$$3\text{LiNO}_{3} \xrightarrow{\Delta} \text{Li}_{2}\text{O} + 2\text{NO}_{2} + \frac{1}{2}\text{O}_{2}$$

$$2\text{Cu}(\text{NO}_{3})_{2} \xrightarrow{\Delta} 2\text{CuO} + 4\text{NO}_{2} + \text{O}_{2}$$

$$2\text{Pb}(\text{NO}_{3})_{2} \xrightarrow{\Delta} 2\text{PbO} + 4\text{NO}_{2} + \text{O}_{2}$$

$$2\text{Hg}(\text{NO}_{3})_{2} \xrightarrow{\Delta} 2\text{Hg} + 4\text{NO}_{2} + \text{O}_{2}$$

$$2\text{AgNO}_{3} \xrightarrow{\Delta} 2\text{Ag} + 4\text{NO}_{2} + \text{O}_{2}$$

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

$$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$$

$$N_2H_5NO_2 \xrightarrow{\Delta} N_2H + 2H_2O$$

Nitrogen oxides are supporter of combustion as these fumes in to $\mathrm{N_2}$ and $\mathrm{O_2}$

 $2N_2O \longrightarrow 2N_2 + O_2$ 33.33%Air $\longrightarrow O_2$

Aır —	$\rightarrow 0_{\gamma}$
	لے۔
	20%

Table 30.16: Confirmatory test for sulphate ic	on
--	----

SO ₄ ²⁻	Reagent	Observation	Remarks
1	$\underbrace{Ba^{+2}}_{BaCl_2} + SO_4^{2-} \rightarrow BaSO_4 \downarrow$	White ppt. Insoluble in dil.HCl Soluble in hot, conc. H ₂ SO ₄	All sulphates are soluble except Ba ⁺² ,Pb ⁺² ,Sn ⁺² ,Ag ⁺ ,Ca ⁺² which are partially soluble.
2	$\underbrace{2Ag^{+}}_{AgNO_{3}} + SO_{4}^{2-} \rightarrow Ag_{2}SO_{4} \downarrow$	White ppt.	
3	$\underbrace{Pb^{+2}}_{Pb(NO_3)_2} + SO_4^{2-} \to PbSO_4 \downarrow$	White ppt	
4	$\underbrace{\operatorname{3Hg}^{+2}}_{\operatorname{Hg}(\operatorname{NO}_3)_2} + \operatorname{SO_4^{2-}} + \operatorname{2H_2O} \downarrow \operatorname{2HgO.HgSO_4}$	Yellow ppt.	
5	Match Stick Test Ba ⁺² + SO ₄ ²⁻ \rightarrow BaSO ₄ \downarrow	White ppt	
	Above ppt + Na ₂ CO ₃ (s) paste Apply paste on wooden piece of match stick+Burn in reducing flame+Dip in sodium nitroprusside soln. i) Paste \rightarrow BaCO ₃ + Na ₂ SO ₄ ii) Na ₂ SO ₄ + 4C \rightarrow Na ₂ S + 4CO \uparrow iii) Na ₂ S + Na ₂ [Fe(CN) ₅ NO] <u>S²⁻</u> Na ₄ [Fe(CN) ₅ NOS]	Purple coloration	

PO ₄ ^{3⁻}	Reagent	Observation	Remarks
1	$\underbrace{Ba^{+2}}_{BaCl_2} + PO_4^{3-} \longrightarrow Ba_3(PO_4)_2 \downarrow$	White ppt	
2	$\underbrace{\operatorname{3Ag}}_{\operatorname{AgNO}_3}^{+} + \operatorname{PO}_4^{3-} \longrightarrow \operatorname{Ag}_3\operatorname{PO}_4 \downarrow$	White ppt Soluble in NH ₃ , KCN, hypo, etc.	
3	Magnesia i) $PO_4^{3-} + \underbrace{Mg^{+2}}_{Mg(NO_3)_2} + NH_4^+ + \underbrace{Mg(NH_4)PO_4}_{Hg^+} + Mg^+ \rightarrow Mg_3PO_4^+$	White ppt.	
	ii) $\underbrace{AsO_4^{3-} + Mg^{+2} + NH_4^{+}}_{Mg(NH_4)AsO_4} + Mg^+ \rightarrow Mg_3AsO_4^{\downarrow}$	White ppt Brownish red ppt	
4	PO_4^{3-} + conc.HNO ₃ +ammonium molybdate (excess) (NH ₄) ₂ MoO ₄ △↓ (NH ₄) ₃ PO ₄ .12MoO ₃ ↓ +H ₂ O + NH ₄ NO ₃ + NaNO ₃	Canary yellow ppt.	

Table 30.18: Confirmatory test for borate ion

BO ₃ ³⁻	Reagent	Observation	Remarks
	0.2g salt+Conc. $H_2SO_4(1ml)+C_2H_5OH(4-5ml)+.Ignite on a Bunsen flame. 2Na_3BO_3 \xrightarrow{3H_2SO_4}{-3Na_2SO_4} 2H_3BO_3$	Green edged flame	
Group O	$2H_3BO_3 \xrightarrow{-3H_2O} (C_2H_5)_3BO_3$		
1	$NH_{4}^{+} + dil.NaOH$ \downarrow $NH_{3}^{+} + H_{2}O + Na^{+}$	 Ammoniacal smell White fumes (NH₄Cl) with HCl HgNO₃ on filter paper becomes black (Hg) Red litmus turns blue (MnCl₂+H₂O₂)on filter paper becomes brown black (MnO₂[MnO(OH)₂]) 	
2	$NH_{4}^{+} + K_{2}[HgI_{4}]$ $\underbrace{+OH^{-}}_{Nessler'sreagent}$ \downarrow $HgO.Hg(NH_{2})I$		

3	$3NH_{4}^{+} + Na_{3}\left[Co(NO_{2})_{6}\right]$ \downarrow $\left(NH_{4}\right)_{3}\left[Co(NO_{2})_{6}\right] \downarrow + 3Na^{+}$	Yellow ppt	
4	$2NH_{4}^{+} + Na_{2}[PtCI_{6}]$ \downarrow $(NH_{4})_{2}[PtCI_{6}] \downarrow + 2Na^{+}$	Yellow ppt	NH4 ⁺ salts are insoluble

Illustration 8: A compound (A) of S, Cl and O has vapour density of 67.5 (approx). It reacts with water to form two acids and reacts with KOH to form two salts (B) and (C) while (B) gives white ppt. with $AgNO_3$ solution and (C) gives white ppt. with $BaCl_2$ solution. Identify (A), (B) & (C).

Sol: As mixture gives white ppt. with $BaCl_2$ and $AgNO_3$, it should be SO_4^{2-} and Cl^- ions. As SO_2Cl_2 when dissolves in water gives, a mixture of H_2SO_4 & HCl which then reacts with KOH to form KCl and K_2SO_4 . Therefore (A) is SO_2Cl_2 and (B) & (C) are K_2SO_4 and KCl respectively.

Vapour density of SO_2Cl_2 = molecular weight/2.

Vapour density of $SO_2CI_2 = 135/2 = 67.2$.

Illustration 9: $Na_2S_2O_3 + I_2 \longrightarrow Nal + \dots [X]$, [X] is:

(A) $Na_2S_4O_6$ (B) Na_2SO_4 (C) Na_2S (D) Na_3ISO_4

Sol: $2Na_2S_2O_3 + I_2 \longrightarrow 2NaI + Na_2S_4O_6$

Therefore A is correct option.

Illustration 10: Column I and II contains four entries each. Entries of column I are to be matched with some entries of column II. Each entry of column I may have the matching with one or more than one entries of column II.

Column I	Column II
(A) Colourless gas evolved on addition of dil. H_2SO_4	(p) Cl ⁻
(B) White ppt. on addition of $AgNO_3$	(q) S ²⁻
(C) Ppt. with solution containing Pb ⁺² ions	(r) NO ₂
(D) Its acidified salt solution decolourises pink $KMnO_4$ solution.	(s) SO ₃ ²⁻

 $\textbf{Sol:} \ A \rightarrow p, \ q, \ s; \ B \rightarrow p, \ r, \ s; \ C \rightarrow p, \ q, \ s; \ D \rightarrow p, \ q, \ r, \ s$

(A) $CI^- + H_2SO_4 \rightarrow HCI^+ (Colourless) + HSO_4^-; S^{2-} + 2H^+ \rightarrow H_2S^+ (Colourless)$ $NO_2^- + 2H^+ \rightarrow NO_2^- (Redish brown) + H_2O; SO_3^{2-} + 2H^+ \rightarrow SO_2^- (Colourless) + H_2O$

(B)
$$Ag^+ + CI^- \rightarrow AgCI \downarrow (White); Ag^+ + S^{2-} \rightarrow Ag_2S \downarrow (Black)$$

 $Ag^{+} + NO_{2}^{-} \rightarrow Ag NO_{2} \downarrow (White); 2Ag^{+} + SO_{3}^{2-} \rightarrow Ag_{2}SO_{3} \downarrow (White)$

(C) $Pb^{2+} + 2Cl^{-} \rightarrow PbCl_{2} \downarrow (White); Pb^{2+} + S^{2-} \rightarrow PbS \downarrow (Black)$ $Pb^{2+} + NO_{2}^{-} \rightarrow PbNO_{2}(Soluble); Pb^{2+} + SO_{3}^{2-} \rightarrow PbSO_{3} \downarrow (White)$ $\begin{array}{ll} \text{(D)} & 2\text{MnO}_{4}^{-} + 16\text{HCI} \rightarrow 5\text{CI}_{2} + 2\text{Mn}^{2+} + 6\text{CI}^{-} + 8\text{H}_{2}\text{O} \\ \\ & 2\text{MnO}_{4}^{-} + 5\text{H}_{2}\text{S} + 6\text{H}^{+} \rightarrow \text{Mn}^{2+} + 5\text{S} \downarrow + 8\text{H}_{2}\text{O} \\ \\ & 2\text{MnO}_{4}^{-} + 5\text{NO}_{2}^{-} + 6\text{H}^{+} \rightarrow \text{Mn}^{2+} + 5\text{NO}_{3}^{-} + 3\text{H}_{2}\text{O} \\ \\ & 2\text{MnO}_{4}^{-} + 5\text{SO}_{2}^{-} + 2\text{H}_{2}\text{O} \rightarrow 2\text{Mn}^{2+} + 5\text{SO}_{4}^{2-} + 4\text{H}^{+} \end{array}$

Classification of Cation Radicals: For the purpose of systematic qualitative analysis, the cations are classified into various groups and the classification is based on whether the cation with the given group reagent and forms a ppt or not

Group	Cation	Reagent	Observation
Zero	NH4 ⁺	NaOH or Ca(OH) ₂ , heat if required	Ammonium gas is evolved. AgCl
Ι.	$Ag^{+}Hg_{2}^{+2}Pb^{+2}$	dil. HCl	Hg ₂ Cl ₂ PbCl ₂ White
II (A)	Cu ⁺² , Hg ⁺² , Pb ⁺² , Bi ⁺³ , Cd ⁺²	H ₂ S gas in dil. HCl insoluble in YAS (Yellow Ammonium Sulphide) (NH ₄) ₂ Sn	$ \begin{array}{c} Cu^{+2}\\ Hg^{+2}\\ Hg^{S} \ black\\ Pb^{+2}\\ Bi^{+3}\\ Bi_2S_3\\ CdS \rightarrow yellow \ CdS \end{array} $
II (B)	Sn ⁺² , Sn ⁺⁴ , As ⁺³ , As ⁺⁵ , Sb ⁺³ , Sb ⁺⁵		SnS → Brown ppt. SnS ₂ , As ₂ S ₃ → Yellow Sb ₂ S ₃ → Orange As ₂ S ₅ → Yellow solution Sb ₂ S ₅ → Orange solution
	Fe ⁺³ , Al ⁺³ , Cr ⁺³	NH_4OH in presence of NH_4CI	$Fe(OH)_3$ → Reddish brown Al(OH) ₃ → Gelatinous white Cr(OH) ₃ → Dirty/ grey green
IV	Mn ⁺² , Co ⁺² , Zn ⁺² , Ni ⁺²	H_2S in presence of NH_4OH and NH_4CI	NiS, CoS \rightarrow Black ZnS \rightarrow Dirty black MnS \rightarrow Buff colored (light pink)
(V)	Ba ⁺² , Sr ⁺² , Ca ⁺²	$(NH_4)_2CO_3$ in presence of NH_4OH and $NH_4CI Na_2HPO_4$ in presence of NH_4OH and NH_4CI	$ BaCO_{3} SrCO_{3} CaCO_{3} $ White ppt CaCO_{3} Mg(NH ₄)PO ₄ \downarrow (White)

Table 30.19: Classification of cation radicals

Preparation of Original Solution (O.S): Original solution is used for the analysis if basic radicals except NH₄⁺. It is prepared by dissolving given salt or mixture in a suitable solvent as follows:

1. H₂O 2. Dil. HCl 3. Conc. HCl

Salt or Mixt.+ $H_2O \xrightarrow{\Delta}$ Soluble (then H_2O is suitable solvent)

If given salt or mixture is insoluble in H₂O, then it is dissolved in dil. HCl.

Salt or Mixt.+dil. HCl $\xrightarrow{\Delta}$ Soluble (then dil HCl is taken as solvent)

If given salt or mixture is insoluble in dilute HCl, then it is dissolved in conc. HCl.

Salt or Mixt.+conc. $HCI \xrightarrow{\Delta} Soluble$

In this way after selecting suitable solvent, given salt or mixture is dissolved in small quantity in the solvent and filtered. Obtained filtered is called as original solution (O.S.) and that is used for the detection of basic radicals except NH_a^+ .

Remarks:

- 1. Pb⁺² is placed in both group I and group II because PbCl₂ is soluble is not water and all of Pb⁺² is not separated by addition of HCl.
- 2. In group II, only those sulphides are ppt. which have very low values of K_{sp} for this. H_2S gas is added in acidic medium. Dil. HNO_3 cant be added to prevent oxidation of H_2S to sulphur. (It is yellow and may be confused with CdS). Dil. H_2SO_4 cant be added to prevent the formation of ppt. of sulphates.
- **3.** Before proceeding with test of group III, the solution is boiled to remove dissolved H_2S gas to prevent ppt. of sulphides in group III. Then dil. HNO_3 is added as we don't have to perform tests with Fe^{+2} . HNO_3 oxidises Fe^{+2} to Fe^{+3}
- **4.** NH_4OH is added in presence of NH_4CI to decrease the degree of dissociation of NH_4OH by common ion effect. So, only those salts are ppt. which have low values of Ksp. $(NH_4)_2SO_4$ and $(NH_4)_2CO_3$ cannot be used in place of NH_4CI to prevent the ppt of carbonates and sulphates.
- **5.** For the test of group IV, H_2S is added in presence of NH_4OH to increase the degree of dissociation of H_2S resulting in increase of S^{2-} conc. So that sulphides of higher values of Ksp can be separated.
- 6. We cant use NaCO₃ in test of group V as Na₂CO₃ is highly soluble resulting in high conc. of CO_3^{2-} which may lead to ppt of group VI, Mg⁺² ions.

Group 0:		
Reagent	Observation	Remarks
1. Dil.NaOH	NH_4^+ +dil. NaOH $\longrightarrow NH_3^+ + H_2O + Na$	Ammoniacal smell forms white fumes in presence of HCl. $NH_3(g)$ +HCl $\longrightarrow NH_4Cl(g)$ (dense White fumes)
		Filter paper dipped in HgNO ₃ (aq.) becomes black
		$\begin{array}{c} \text{HgNO}_{3} \xrightarrow{\text{NP3}} \\ \text{Hg} \\ \text{Black} \\ + \underbrace{\text{Hg(NH}_{2})\text{NO}_{3}}_{\underline{\text{white}}} \end{array}$
		Filter paper dipped in red litmus become blue
		Filter paper dipped in MnCl ₂ +H ₂ O ₂ (aq.) Becomes brown black due to formation of MnO ₂ [MnO(OH) ₂]
2. Test with K_2 Hgl ₄	$\underbrace{NH_4^+ + K_2[HgI_4] + OH^-}_{Nesslare's reagent} \longrightarrow \underbrace{Hg(NH_2)I + 2K^\oplus}_{\substack{basic mercuric\\amido iodide}}$	Yellow / brown
3. Test with Na ₃ [Co(NO ₂) ₆]	$3NH_4^+ + Na_3[Co(NO_2)_6] \rightarrow (NH_4)_3[Co(NO_2)_6] + 3Na^+$ Yellow	Yellow ppt.
4. Na ₂ [PtCl ₆] or H ₂ [PtCl ₆] {sodiumchloro palatinate} or {chloropalatinate acid}	$2NH_4^+ + Na_2[PtCl_6] \longrightarrow (NH_4)_2[PtCl_6] \downarrow + 2Na^+$	Yellow ppt Generally, NH_4^+ salts are insoluble.

Table 30.20: Classification of cation radicals

Group I



Flowchart 30.3: Systematic path for the analysis of group I radicals

Pb ²⁺	Test/Reagents	Observation
	Dilute HCl solution: $Pb^{2+} + HCl \rightarrow PbCI_2 \downarrow (white) + 2H^+$ $PbCl_2 \downarrow + 2Cl^- \rightarrow [PbCl_4]^{2-}$ Sodium hydroxide solution $Pb^{2+} + 2OH^- \rightarrow Pb(OH) \downarrow$:	White ppt is formed in cold solution. White ppt is soluble in hot water. White ppt is also soluble in concentrated HCl or concentrated KCl. White ppt is formed which is soluble in excess of the reagent.
	$Pb(OH)_{2} \downarrow +2OH^{-} \rightarrow \left[Pb(OH)_{4}\right]^{2-}$ $\left[Pb(OH)_{4}\right]^{2-} +H_{2}O_{2} \rightarrow PbO_{2} \downarrow +2H_{2}O + 2OH^{-}$ $\left[Pb(OH)_{4}\right]^{2-} +S_{2}O_{8}^{2-} \rightarrow PbO_{2} \downarrow +2H_{2}O + 2SO_{4}^{2-}$	Black/brownish black
	Potassium iodide solution $PbCl_{2} + 2KI \rightarrow Pbl_{2} \downarrow + 2KCI;$ $Pbl_{2} + KI \longrightarrow K_{2} [Pbl_{4}] \downarrow$	A yellow ppt is formed which is soluble in excess more conc.(6M) soln of the reagent. Yellow ppt of Pbl ₂ is moderately soluble in boiling water to give a colourless solution. Yellow ppt reappears on dilution with water. Yellow ppt of Pbl ₂ does not dissolve in excess of dilute solution of KI.
	Potassium chromate solution (in neutral, acetic or ammonia solution) $PbCl_2 + K_2CrO_4 \rightarrow PbCrO_4 \downarrow 2KCl$ $2PbCrO_4 + 2H^+ \rightleftharpoons 2Pb^2 + Cr_2O_7^{-2} + H_2O$ $PbCrO_4 + 4OH \rightleftharpoons \left[Pb(OH)_4\right]^{2^-} + CrO_4^{2^-}$	A yellow ppt is formed. Yellow ppt is soluble in sodium hydroxide and HNO_3 (nitric acid).Both reversible reactions on buffering the solution with ammonia or acetic acid respectively, PbCrO ₄ reprecipitates.
	Ammonia solution $Pb^{2+} + 2NH_4OH \rightarrow Pb(OH)_2 \downarrow + 2NH_4^+$	With ammonia solution, Pb ²⁺ gives a white ppt of lead hydroxide
	Dilute H₂SO₄: PbCl ₂ + H ₂ SO ₄ \rightarrow PbSO ₄ \downarrow +2HCl PbSO ₄ \downarrow +4CH ₃ COO ⁻ \rightarrow [Pb(CH ₃ COO) ₄] ²⁻ +SO ₄ ²⁻ PbSO ₄ \downarrow +2C ₄ H ₄ O ₆ ²⁻ \rightarrow [Pb(C ₄ H ₄ O ₆) ₂] ²⁻ +SO ₄ ²⁻ PbSO ₄ \downarrow +H ₂ SO ₄ \rightarrow Pb ² + 2HSO ₄ ⁻	White ppt is formed which is soluble in more conc. ammonium acetate (6M) solution or ammonium tartrate in the presence of ammonia. Hot,conc.H ₂ SO ₄ dissolves the ppt due to the formation of PbHSO ₄ .

Table 30.21: Analysis of group I and group II radical

Hg ₂ ²⁺	Test/Reagents	Observation
	Dilute HCl solution Hg ₂ ²⁺ + 2HCl \rightarrow Hg ₂ Cl ₂ \downarrow (white) + 2H ⁺	White ppt is formed in cold solution.
	Ammonia solution $2Hg_2CI_2 + 4NH_4OH \rightarrow HgO.Hg(NH_2)CI \downarrow +Hg \downarrow$ $+3NH_4CI + 3H_2O$	A mixture of mercury metal (black ppt) and basic mercury (II) amido chloride (white ppt) is formed.
	Dissolution of white ppt. Hg_2Cl_2 in aquaregia $3Hg_2Cl_2 + 2HNO_3 + 6HCl \rightarrow 6HgCl + 2NO + 4H_2O$ $2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 \downarrow + SnCl_4$; $Hg_2Cl_2 + SnCl_2 \rightarrow 2Hg \downarrow (black) + 2SnCl_4$ $HgCl_2 + KI \rightarrow HgI_2 \downarrow + 2KCl$; $HgI_2 + KI(excess) \rightarrow K_2 [HgI_4](soluble)$ $HgCl_2 + Cu \rightarrow Hg \downarrow + CuCl_2$	 (a) Stannous chloride test: White ppt is formed which finally turns to black. (b) Potassium iodide test: Scarlet/red ppt is formed which is soluble in excess of the reagent. (c) Copper chips test: Shining grey deposition of mercury on copper chips is formed.
	Potassium iodide solution: A green ppt is formed. $Hg_2^{2^+} + 2I^- \rightarrow Hg_2I_2 \downarrow$ $Hg_2I_2 + 2I^- \rightarrow [HgI_4]^{2^-} + Hg \downarrow (finely divided)$ $Hg_2I_2 \rightarrow HgI_2 \downarrow + Hg \downarrow$	Green ppt in excess of reagent undergoes disproportionation reaction and a soluble $\left[\text{Hgl}_{4}\right]^{2_{-}}$ ions and black mercury are formed. Boiling the mercury (I) iodide ppt with water, disproportionation takes place and a mixture of red mercury (II) iodide ppt and black mercury is formed.
	Potassium chromate solution $Hg_2^{2^+} + CrO_4^{2^-} \rightarrow Hg_2CrO_4 \downarrow;$ $Hg_2CrO_4 + 2OH^- \rightarrow Hg_2O \downarrow + CrO_4^{2^-} + H_2O$	A red crystalline ppt is formed which turns black when solution of sodium hydroxide is added.
	Potassium cyanide solution Hg ₂ ²⁺ + 2CN ⁻ \rightarrow Hg \downarrow +Hg(CN) ₂ (soluble)	A black ppt of mercury is obtained
(Ag*)	Dilute hydrochloric acid/soluble chlorides $Ag^{+} + HCI \rightarrow AgCI \downarrow +H^{+}$ $AgCI + CI^{-} \longrightarrow [AgCI_{2}]^{-}$ $AgCI + 2NH_{3} \longrightarrow [Ag(NH_{3})_{2}]^{+} + CI^{-}$ $[Ag(NH_{3})_{2}]CI + 2HNO_{3} \rightarrow AgCI \downarrow +2NH_{4}NO_{3}$	White ppt Soluble in conc.HCl On dilution with water, the equilibrium shifts back to the left and the ppt reappears. Dil.ammonia solution dissolves the ppt forming a soluble complex. Dil.HNO ₃ or HCl neutralizes the excess ammonia and the ppt reappears because the equilibrium is shifted backwards.
	Potassium iodide solution $Ag^{+} + I^{-} \rightarrow AgI \downarrow$ $AgI + 2CN^{-} \rightarrow [Ag(CN)_{2}]^{-} + I^{-};$ $AgI + 2S_{2}O_{3}^{-2} \rightarrow [Ag(S_{2}O_{3})_{2}]^{3-} + I^{-}$	A bright yellow ppt. is formed which is insoluble in dilute ammonia but partially soluble in concentrated ammonia. The yellow ppt. is soluble in KCN and in $Na_2S_2O_3$.

	Potassium chromate solution $2Ag^{+} + CrO_{4}^{2-} \rightarrow Ag_{2}CrO_{4} \downarrow$ $2Ag_{2}CrO_{4} + 2H^{+} \rightleftharpoons 4Ag^{+} + Cr_{2}O_{7}^{2-}$ $2Ag_{2}CrO_{4} + 4NH_{3} \rightarrow 2[Ag(NH_{3})_{2}]^{+} + CrO_{4}^{2-}$	Red ppt. is formed which is soluble in dilute HNO_3 and in ammonia solution.
	Disodium hydrogen phosphate solution $3Ag^{+} + HPO_{4}^{2-} \rightarrow Ag_{3}PO_{4} \downarrow + H^{+}$	In neutral solution a yellow ppt. is formed with the reagent. The yellow ppt. is soluble in nitric acid and ammonia solution.
	Hydrazine sulphate (saturated) $4\left[Ag\left(NH_{3}\right)_{2}\right]^{+} + H_{2}N - NH_{2}H_{2}SO_{4} \rightarrow 4Ag \downarrow + N_{2} \uparrow + 6NH_{4}^{+} + 2NH_{3} + SO_{4}^{2-}$	With diammineargentate (I) reagent forms finely divided silver which adheres to the cleaned glass walls of the test tube forming an attractive mirror.
	Ammonia solution $2Ag^{+} + 2NH_{3} + H_{2}O \rightarrow Ag_{2}O \downarrow + 2NH_{4}^{+}$ $Ag_{2}O \downarrow + 4NH_{3} + H_{2}O \rightarrow 2\left[Ag(NH_{3})_{2}\right]^{+} + 2OH^{-}$	Brown ppt. is formed Ppt. dissolves in ammonia.
Hg ²⁺	Test/Reagents	Observation
	Precipitation with H ₂ S in acidic medium $Hg^{2+} + H_2S \xrightarrow{H^+} HgS \downarrow +2H^+$ $HgS + S^{2-} \rightarrow [HgS_2]^{2-}$ $3HgS + 6HCI + 2HNO_3 \rightarrow$ $3HgCl_2 + 3S \downarrow +2NO \uparrow +4H_2O$ $2HNO_3 + S \rightarrow SO_4^{-2-} + 2H^+ + 2NO \uparrow$ Stannous chloride solution $2HgCl_2 + SnCl_2 \rightarrow SnCl_4 + Hg_2Cl_2 \downarrow$ $HgCl_2 + SnCl_2 \rightarrow SnCl_4 + 2Hg_2 \downarrow$	 Black ppt. is formed. Insoluble in water, hot dilHNO₃, alkali hydroxides, or colourless ammonium sulphide. Na₂S(2M) dissolves the ppt. forming soluble complex. Aqua regia dissolves the ppt. HgCl₂ is undissociated. On heating, white ppt. of sulphur dissolves forming H₂SO₄. When added in moderate amounts silky white ppt. is formed. If more reagent is added, Hg (I) chloride is reduced to black ppt. of mercury.
	Potassium iodide solution $Hg^{2+} + 2I^{-} \rightarrow HgI_{2} \downarrow$ $HgI_{2} + 2I^{-} \rightarrow [HgI_{4}]^{2-}$ Copper chips, sheet or coin	On slow addition red ppt. is formed. Ppt. dissolves in excess of KI forming colourless soluble complex. KCN does not have any effect. A black ppt. of mercury is formed.
	$Hg^{2+} + Cu \rightarrow Hg \downarrow + Cu^{2+}$ Sodium hydroxide solution $Hg^{2+} + 2OH^{-} \rightarrow HgO \downarrow + H_2O$	When added in small quantity brownish-red ppt. of varying composition is formed and in stoichiometric amounts ppt. turns to yellow when Hg (II) oxide is formed. Ppt. is insoluble in excess reagent but dissolves readily in acids and this can be used to differentiate Hg (I) from Hg (II).

	Ammonia solution $2Hg^{2+} + NO_3^{-} + 4NH_3 + H_2O \rightarrow$ $HgO.Hg(NH_2)NO_3 \downarrow + 3NH_4^+$	White ppt. of mixed composition (Mercury (II) oxide+Mercury (II) amido nitrate) is formed with metal nitrate.
	Cobalt (II) thiocyanate test $Hg^{2+} + CO^{2+} + 4SCN^{-} \rightarrow CO^{+2} \left[Hg(SCN)_{4} \right]^{2} \downarrow$	When reagent is added to an aqueous solution of Hg^{2+} ions and the walls of the test tube is stirred with a glass rod, deep-blue crystalline ppt. is formed. In place of Cobalt (II) thiocyanate, Co(CH ₃ COO) and NH ₄ SCN can be added to the aqueous solution of Hg^{2+} ions.
Cu ²⁺	Test/Reagents	Observation
	Precipitation with H ₂ S in acidic medium $Cu^{2+} + H_2S \xrightarrow{H^+} CuS \downarrow + 2H^+$ $3CuS + 8HNO_3 \rightarrow$ $3Cu(NO_3)_2 (blue) + 2NO + 4H_2O + 3S$ $2CuS \downarrow + 8CN^- \rightarrow 2[Cu(CN)_4]^{3-} + S_2^{2-}$	Black ppt. is formed. Ppt. is insoluble in boiling dilute (M) H_2SO_4 (distinction from cadmium), in NaOH, $Na_2Sand(NH_4)_2S$. Ppt. dissolves in hot conc. HNO_3 When boiled for longer, S is oxidized to H_2SO_4 and a clear solution of Cu(NO ₃) ₂ is obtained. KCN dissolves the ppt. forming a clear solution. (disulphide ion)
	Ammonia Solution $2Cu^{2} + SO_{4}^{2-} + 2NH_{3} + 2H_{2}O \rightarrow$ $Cu(OH)_{2}.CuSO_{4} \downarrow + 2NH_{4}^{+}$ $Cu(OH)_{2}.CuSO_{4} + 8NH_{3} \rightarrow$ $2\left[Cu(NH_{3})_{4}\right]^{2+} + SO_{4}^{2-} + 2OH^{-}$	When added sparingly a blue ppt. of basic salt (basic copper sulphate) is formed with $CuSO_4$. It is soluble in excess of reagent forming a deep blue colouration.
	Sodium hydroxide in cold solution $Cu^{2} + 2 OH^{-} \rightarrow Cu(OH)_{2} \downarrow$ $Cu(OH)_{2} \xrightarrow{\text{Heat}} CuO \downarrow (black) + H_{2}O$	A blue ppt. is formed.
	Potassium iodide $2Cu^{2+} + 5I^{-} \rightarrow Cu_{2}I_{2} \downarrow +I_{3}^{-}$ $I_{3}^{-} + 2S_{2}O_{3}^{2-} \rightarrow 3I^{-} + S_{4}O_{6}^{2-}$	It gives a white ppt. of Cu (I) iodide but the solution is intensely brown because of the formation of tri- iodide ions (or iodine). The soln becomes colourless and a white ppt. is visible when excess of sodium thiosulphate solution is added. These reactions are used in quantitative analysis for the iodometric determination of copper.
	Potassium ferrocyanide (Potassium hexacyanidoferrate (II) solution $2Cu^{2+} + K_4Fe(CN)_6 \rightarrow Cu_2[Fe(CN)_6] \downarrow +4K^+$	Cu ²⁺ ions gives brown/chocolate brown ppt.
	$2\left[\operatorname{Fe}(\operatorname{CN})_{6}\right]^{3-} + 3\operatorname{Cu}^{2+} \rightarrow \operatorname{Cu}_{3}\left[\operatorname{Fe}(\operatorname{CN})_{6}\right]_{2} \downarrow$	Green

	Potassium cyanide $Cu^{2+} + 2CN^{-} \rightarrow Cu(CN)_{2} \downarrow$ $2Cu(CN)_{2} \rightarrow 2CuCN \downarrow (white) +$ $(CN)_{2} \uparrow (highlypoisonous)$ $CuCN + 3CN^{-} \rightarrow [Cu(CN)_{4}]^{3-}$	When added sparingly forms first a yellow ppt. which decomposes into CuCN and cyanogen. Excess reagent dissolves the ppt. forming a colourless soluble complex. Complex is so stable that H ₂ S cannot ppt. Cu(l) sulphide (distinction from cadmium).
	Potassium thiocyanate solution $Cu^{+2} + 2SCN^{-} \rightarrow Cu(SCN)_{2} \downarrow$ $2Cu(SCN)_{2} \rightarrow 2CuSCN \downarrow + (SCN)_{2} \uparrow$ $2Cu(SCN)_{2} + SO_{2} + 2H_{2}O \rightarrow$ $2CuSCN + 2SCN^{-} + SO_{4}^{2-} + 4H^{+}$	The Cu^{+2} ions solution initially gives a black ppt. which then slowly decomposes to give white ppt. of Cu (I) thiocyanate. Cu (II) thiocyanate can be immediately converted into Cu (I) thiocyanate by adding a suitable reducing agent like saturated solution of SO ₂ .
Bi ³⁺	Test/Reagents	Observation
	Precipitation with H ₂ S in acidic medium $2Bi^{3+} + 3H_2S \xrightarrow{H^+} Bi_2S_3 \downarrow (black) + 6H^+$ $Bi_2S_3 + 8HNO_3 \rightarrow 2Bi(NO_3)_3 + 2NO + 3S + 4H_2O$ $Bi_2S_3 + 6HCl(boiling, conc.) \rightarrow 2Bi^3 + 6Cl^- + 3H_2S$	Black ppt. is formed which is insoluble in cold dilute HNO_3 and yellow ammonium sulphide.
	Sodium hydroxide $Bi^{3+} + 3OH^{-} \rightarrow Bi(OH)_{3} \downarrow$ $Bi(OH)_{3} + 3H^{+} \rightarrow Bi^{3+} + H_{2}O$ $Bi(OH)_{3} \rightarrow BiO.OH \downarrow + H_{2}O$ $BiO.OH + H_{2}O_{2} \rightarrow BiO_{3}^{-} + H^{+} + H_{2}O$	White ppt. is formed with the reagent, slightly soluble in excess reagent in cold solution but soluble in acids. Ppt. on boiling loses water and turns yellowish white which is oxidised to BiO_3^- by H_2O_2 .
	Ammonia solution $Bi^{3+} + NO_3^{-} + 2NH_3 + 2H_2O \rightarrow Bi(OH)_2 NO_3 \downarrow + 2NH_4^{+}$	White basic salt of variable composition is formed.
	Alkaline sodium stannite (Sodium tetrahydroxidostannate (II)) $Bi^{3+} + 3OH^{-} \rightarrow Bi(OH)_{3} \downarrow$ $2Bi(OH)_{3} + [Sn(OH)_{4}]^{2-} \rightarrow 2Bi \downarrow + 3[Sn(OH)_{6}]^{2-}$	A black ppt. of metallic bismuth is obtained. The reagent must be freshly prepared and test must be carried out in cold solution.
	Dilution with water $Bi^{3+} + NO_3^{-} + H_2O \rightarrow BiO(NO_3) \downarrow + 2H^+$ $Bi^{3+} + CI^- + H_2O \rightarrow \underbrace{BiOCI \downarrow}_{\text{bismuth oxychloride}} + 2H^+$ bismuthoxychloride	Solution of bismuth salts gives white ppt. when water is added in larger quantity. Soluble in mineral acids (dilute) but insoluble in tartaric acid (distinction from antimony) and in alkali hydroxide (distinction from tin).

	Potassium iodide $Bi^{3+} + 3I^{-} \rightarrow BiI_{3} \downarrow$ $BiI_{3} + I^{-} \longrightarrow [BiI_{4}]^{-}$ $BiI_{3} \downarrow +H_{2}O \rightarrow BiOI \downarrow +2H^{+} + 2I^{-}$	When the reagent is added dropwise to a solution containing Bi^{3+} ions, a black ppt. is formed. The ppt. dissolves in excess KI forming orange coloured soluble complex. On dilution the reaction is reversed and black Bil_3 turns orange.
(Cd ²⁺)	Test/Reagents	Observation
	Precipitation with H_2S in acidic medium $Cd^{2+} + H_2S \xrightarrow{H^+} CdS \downarrow +2H^+$ $CdS + 8HNO_3 \rightarrow 3Cd(NO_3)_2 + 4H_2O + 2NO + 3S$	Yellow ppt. is formed which dissolves in hot dil. HNO_{3} . Ppt. does not dissolve in KCN.
	Ammonia solution (Dropwise addition) $Cd^{2+} + 2NH_3 + 2H_2O \longrightarrow Cd(OH)_2 \downarrow + 2NH_4^+$ $Cd(OH)_2 + 4NH_3 \rightarrow [Cd(NH_3)_4]^{2+} + 2OH^-$	Ammonium hydroxide first gives white ppt. of Cd(OH) ₂ which gets dissolve in excess of reagent forming a soluble complex.
	Potassium cyanide $Cd^{2+} + 2CN^{-} \rightarrow Cd(CN)_{2} \downarrow$ $Cd(CN)_{2} + 2CN^{-} \rightarrow [Cd(CN)_{4}]^{2-}$ $[Cd(CN)_{4}]^{2-} + H_{2}S \rightarrow CdS \downarrow + 2H^{+} + 4CN^{-}$	White ppt. of Cd(CN) ₂ is formed which in excess of reagent dissolves forming a soluble complex. The colourless soluble complex is unstable, therefore, reacts with H ₂ S gas forming a yellow ppt. of CdS. KI forms no ppt. (distinction from Copper)
	Sodium hydroxide $Cd^{2+}(aq) + 2NaOH(aq) \rightarrow Cd(OH)_2 \downarrow +2Na^+$	White ppt. is obtained which insoluble in excess of NaOH

Illustration 11: When NaOH solution is mixed with aqueous solution of a salt 'A', and warmed, a black ppt. is formed. Black ppt. is filtered and dissolved in concentrated HNO₃ by boiling. The resulting solution gives a chocolate brown coloured ppt. with potassium ferrocyanide solution. The filtrate obtained after filtering off the black ppt., upon warming with Zn and NaOH evolves an alkaline pungent smelling gas. The resulting solution also responds to the brown ring test. The filtrate does not evolve N₂ gas when it is boiled with urea in the presence of H₂SO₄. Identify the cation and anion present in the salt 'A'.

Sol: $Cu(NO_3)_2 + NaOH \rightarrow Cu(OH)_2 \downarrow (Blue) + 2NaNO_3$ $Cu(OH)_2 \downarrow \xrightarrow{\Delta} CuO \downarrow (Black) + H_2O$ $4Zn + NaNO_3 + 7NaOH \rightarrow 4Na_2ZnO_2 + 2H_2O + NH_3 \uparrow (Pungent smelling alkaline gas)$ $CuO + 2HNO_3 \xrightarrow{\Delta} Cu(NO_3)_2 + H_2O$ $2Cu(NO_3)_2 + K_4 [Fe(CN)_6] \rightarrow Cu_2 [Fe(CN)_6] \downarrow (Chocolate brown) + 4KNO_3$

Illustration 12: A compound on heating with an excess of caustic soda solution liberates a gas (B) which gives while fumes on exposure of HCl. The resultant alkaline solution thus obtained after heating again liberates the same gas (B) when heated with zinc powder. Compound (A) on heating alone gives a neutral oxide of nitrogen not nitrogen gas. Identify (A) and (B) and give the relevant chemical reactions.

Sol: As NH_3 gives white fumes with HCl, therefore, (B) should be NH_3 and (A) should be the salt of ammonium. Further we know that nitrite of ammonium gives a NH_3 with Zn and alkali and when heated alone gives neutral oxide (N₂O) not N₂. Hence the salt should be ammonium nitrate not ammonium nitrite.

 $\begin{aligned} \mathsf{NH}_4\mathsf{NO}_3(\mathsf{A}) + \mathsf{NaOH} &\to \mathsf{NaNO}_3 + \mathsf{H}_2\mathsf{O} + \mathsf{NH}_3 \uparrow \big(\mathsf{B}\big); \mathsf{NH}_3 + \mathsf{HCI} \to \mathsf{NH}_4\mathsf{CI} \left(\mathsf{White fumes}\right) \\ \mathsf{NaNO}_3 + \mathsf{8}\big[\mathsf{H}\big] &\xrightarrow{\mathsf{Zn}/\mathsf{NaOH}} \mathsf{NaOH} + 2\mathsf{H}_2\mathsf{O} + \mathsf{NH}_3; \mathsf{NH}_4\mathsf{NO}_3 \to \mathsf{N}_2\mathsf{O} \left(\mathsf{Neutral}\right) + 2\mathsf{H}_2\mathsf{O} \end{aligned}$

Illustration 13: A certain metal (A) is boiled with dilute HNO_3 to give a salt (B) and an neutral oxide of nitrogen (C). An aqueous solution of (B) gives a white ppt. (D) with brine which is soluble in ammonium hydroxide. An aqueous solution of (B) also gives red/brick red ppt., (E) with potassium chromate solution. Identify (A) to (E) and write the chemical reactions involved.

Sol: As solution of (B) gives white ppt. with NaCl (aq) ppt. is soluble in ammonium hydroxide, it may be of silver salt. Further it gives brick red ppt. with $K_2 CrO_4$, therefore, metal (A) may be silver.

 $\begin{aligned} 3\text{Ag}(A) + 4\text{HNO}_{3} &\rightarrow 3\text{Ag}\text{NO}_{3}(B) + \text{NO}(C) + 2\text{H}_{2}\text{O}; \\ \text{Ag}\text{NO}_{3} + \text{Na}\text{CI} &\rightarrow \text{Ag}\text{CI} \downarrow (\text{White})(D) + \text{Na}\text{NO}_{3} \\ \text{Ag}\text{CI} + 2\text{NH}_{4}\text{OH} \rightarrow \left[\text{Ag}(\text{NH}_{3})_{2}\right]\text{CI}(\text{Soluble}) + 2\text{H}_{2}\text{O} \\ 2\text{Ag}\text{NO}_{3} + \text{K}_{2}\text{CrO}_{4} \rightarrow \text{Ag}_{2}\text{CrO}_{4} \downarrow (\text{Red}/\text{Brickred})(E) + 2\text{KNO}_{3} \end{aligned}$

Illustration 14: Which of the following salt will give white ppt. with the solution containing Pb^{2+} ions?

(A) Na_2CO_3 (B) NaCl (C) Na_2SO_3 (D) All of these

Sol: $Pb^{2+} + CO_3^{2-} \rightarrow PbCO_3 \downarrow (White)$ $Pb^{2+} + 2CI^- \rightarrow PbCI_2 \downarrow (White)$ $Pb^{2+} + SO_3^{2-} \rightarrow PbSO_3 \downarrow (White)$

Therefore, (D) option is correct.

Table 30.22: Some important reactions of group III radicals

Fe ⁺³	Test/Reagents	Observation
	Potassium ferrocyanide (Potassium hexacyanidoferrate (II)) $4Fe^{+3} + 3[Fe(CN)_6]^{4-} \rightarrow Fe_4[Fe(CN)_8]_3 \downarrow$	Intense blue ppt. (Prussian blue) of iron (III) hexacyanidoferrate (II) is formed.
	$Fe_{4}[Fe(CN)_{8}]_{3} + 12OH^{-} \rightarrow Fe(OH)_{3} \downarrow + 3[Fe(CN)_{6}]^{4-}$	This is insoluble in dilute acids but decomposes in concentrated HCl. A large excess of the reagent dissolves it partly or entirely, when an intense blue solution is obtained. Sodium hydroxide turns the ppt. red. Oxalic acid also dissolves Prussian
		blue forming a blue-solution.

Important:

If iron (III) chloride is added to an excess of potassium hexacyanidoferrate (II), a product with the composition of $KFe\left[Fe(CN)_{6}\right]$ is formed. This tends to form colloidal solutions ('soluble Prussian blue') and can not be filtered.

$$\label{eq:production} \begin{array}{|c|c|} \hline Potassium ferricyanide (Potassium hexacyanidoferrate (III)) \\ Fe^{3+} + \left[Fe(CN)_{6}\right]^{3-} \rightarrow Fe\left[Fe(CN)_{6}\right]^{4-} \\ Fe^{2+} + \left[Fe(CN)_{6}\right]^{3-} \rightarrow Fe + \left[Fe(CN)_{6}\right]^{4-} \\ 4Fe^{3+} + 3\left[Fe(CN)_{6}\right]^{4-} \rightarrow Fe_{4} + \left[Fe(CN)_{6}\right]_{3}^{4-} \\ Fe^{2+} + \left[Fe(CN)_{6}\right]^{4-} \rightarrow Fe_{4} + \left[Fe(CN)_{6}\right]_{3}^{4-} \\ Fe^{2+} gives dark blue ppt. with potassium ferricyanide. First hexacyanidoferrate (II) on rom (III), when hexacyanidoferrate (II) is formed. \\ And these ions combine to form a ppt. called Turnbull's blue. \\ \hline Note: Composition of this ppt. is identical to that of Prussian blue. Earlier the composition suggested was \\ Fe_{3}\left[Fe(CN)_{6}\right]_{2}^{-}, hence different name. \\ 3Fe^{2+} + 2K_{3}\left[Fe(CN)_{6}\right] \rightarrow Fe_{3}\left[Fe(CN)_{6}\right]_{2} (Ferrous ferric cyanide) + 6K^{+} \\ Turnbull's blue \\ Fe (II) in ammonical solution gives red solution with DMG-colouration fades on standing due to the oxidation of iron (II) complex. Fe (III) does not give such complex. \\ In complex descence of air, Fe (II) ions produces white ppt. with potassium hexacyanidoferrate (II). \\ Fe^{2} + 2K^{+} + \left[Fe(CN)_{6}\right]^{4-} \rightarrow K_{2}Fe\left[Fe(CN)_{6}\right] \downarrow \\ \hline \end{array}$$

Under ordinary atmospheric conditions a pale-blue ppt. is formed.

Cr ⁺³	Test/Reagents	Observation
	Acidified H ₂ O ₂ test	
	$Na_{2}CrO_{4} + H_{2}SO_{4} \rightarrow Na_{2}SO_{4} + H_{2}CrO_{4};$ $H_{2}CrO_{4} + 2H_{2}O_{2} \xrightarrow{\text{Amylalchohol}} CrO_{5} + H_{2}O$ $4CrO_{5} + 6H_{2}SO_{4} \rightarrow 2Cr_{2}(SO_{4})_{3} + 7O_{2} + 6H_{2}O$	Blue colouration On acidifying the yellow solution with dil.H ₂ SO ₄ +few drops of ether/amyl alcohol +H ₂ O ₂ = Blue
		colouration ,can be extracted into the organic layer by gently shaking. Blue colouration fades slowly due to the decomposition of perchromic acid (or chromium peroxide) with the liberation of oxygen.
	Tests for: $AI(OH)_3 + NaOH \rightarrow NaAIO_2 + 2H_2O$ $NaAIO_2 + H_2O + NH_4CI \rightarrow AI(OH)_3 + NaCI + NH_3$	In excess of NaOH. Sodium meta-aluminate (soluble). White gelatinous ppt.

Fe ³⁺	Test/Reagents	Observation
	Tests for	
	$Fe(OH)_3 + 3HCI \rightarrow FeCl_3 + 3H_2O$	Red brown $Fe(OH)_3$ dissolves in dil. HCl as
	$4\text{FeCl}_{3} + 3\text{K}_{4}\left[\text{Fe}(\text{CN})_{6}\right] \rightarrow \text{Fe}_{4}\left[\text{Fe}(\text{CN})_{6}\right]_{3} + 12\text{KCI}$	Reaction with $K_4 \left[Fe(CN)_6 \right]$:
	$FeCl_3 + KSCN \rightarrow Fe(SCN)Cl_2 + KCl$	Ferric ferrocyanide (Dark Blue)
	5 () 2	Reaction with KCNS:
		Ferrithiocyanate (dark red colour)
Cr³⁺	Test/Reagents	Observation
	Tests for	On boiling with
	(CH ₃ COO) ₂ Pb / CH ₃ COOH	NaOH / Br ₂ , Cr(OH) ₃ gives
	$2NaOH + Br_2 \rightarrow NaOBr + NaBr + H_2O$	sodium chromate which gives yellow ppt. of PbCrO ₄ with
	$2Cr(OH)_{3} + 4NaOH + 3[O] \rightarrow 2Na_{2}CrO_{4} + 5H_{2}O$	Yellow solution
	Yellow solution Na ₂ CrO ₄ + (CH ₃ COO) ₂ Pb \rightarrow PbCrO ₄ \downarrow +2CH ₃ COONa	Yellow ppt.
	Yellowppt.	Yellow solution
	$2Cr(OH)_{3} + 2Na_{2}CO_{3} + 3KNO_{3} \rightarrow 2Na_{2}CrO_{4} + 3KNO_{2} + 3H_{2}O + 2CO_{2}$	
	Yellow solution	Yellow ppt.
	$Na_2CrO_4 + (CH_3COO)_2Pb \rightarrow PbCrO_4 \downarrow + 2CH_3COONa$	
	Yellowppt.	

Illustration 15: A black coloured compound (A) on reaction with dil. H_2SO_4 gives a gas (B) and a green colour solution. The gas (B) on passing in a solution of an acid (C) gives a white/yellow turbidity (D). Gas (B) when passed in acidified solution of (E) gives a ppt. (F) soluble in dil HNO₃. After boiling this solution when excess of NH_4OH is added, a blue coloured compound (G) is formed. To this solution on addition of acetic acid and aqueous potassium ferrocyanide a chocolate coloured ppt. (H) is obtained. On addition of an aqueous solution of $BaCl_2$ to an aqueous solution of (E), a white ppt. insoluble in HNO_3 is obtained. Green colour solution on reaction with ammonium hydroxide in presence of air gives reddish brown ppt.. Identify (A) to (H).

Sol:
$$FeS(A) + H_2SO_4 \rightarrow FeSO_4 + H_2S(B)$$

 $HNO_3(C) \rightarrow NO_2 + H_2O + O; H_2S + O \rightarrow H_2O + S \downarrow (D)$
 $CuSO_4(E) + H_2S \rightarrow CuS \downarrow (F) + H_2SO_4$
 $3CuS + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO \uparrow +4H_2O + 3S \downarrow$
 $Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+}(G)$
 $2Cu^{2+} + K_4Fe(CN)_6 \rightarrow Cu_2[Fe(CN)_6] \downarrow (H) + 4K^+$



Flowchart 30.4: Systematic path for the analysis of group IV radicals

14. REACTIONS OF Ni²⁺ (NICKEL) AND Co²⁺ (COBALT)

The black ppt. is dissolved in aqua-regia.

 $3\text{NiS} + 6\text{HCI} + 2\text{HNO}_3 \rightarrow 3\text{NiCl}_2 + 2\text{NO} + 3\text{S} + 4\text{H}_2\text{O}$ $3\text{CoS} + 6\text{HCI} + 2\text{HNO}_3 \rightarrow 3\text{CoCl}_2 + 2\text{NO} + 3\text{S} + 4\text{H}_2\text{O}$

The solution is evaporated to dryness and residue extracted with dilute HCl. It is divided into three parts.

Part I	Part II	Part III
Excess NH ₄ OH+ dimethyl glyoxime = rosy red ppt. if nickel is present	CH ₃ COOH (excess)+KNO ₂ =yellow ppt. confirms the presence of cobalt. KNO ₂ + CH ₃ COOH → CH ₃ COOK + HNO ₂ CoCl ₂ + 2KNO ₂ → Co(NO ₂) ₂ + 2KCl Co(NO ₂) ₂ + 2HNO ₂ → Co(NO ₂) ₃ + NO + H ₂ O Co(NO ₂) ₃ + 3KNO ₂ → K ₃ [Co(NO ₂) ₆]	Solution containing either nickel or cobalt is treated with NaHCO ₃ and bromine water. Appearance of apple green colour confirms the presence of cobalt. If no apple green colour is observed, the solution is heated when black ppt. is formed, which shows the presence of nickel. $CoCl_2 + 2NaHCO_3 \rightarrow Co(HCO_3)_2 + 2NaCl$ $Co(HCO_3)_2 + 4NaHCO_3 \rightarrow Na_4Co(CO_3)_3 3H_2O$ $+3CO_2Br_2 + H_2O \rightarrow 2HBr + O$ $2Na_4Co(CO_3)_3 + H_2O + O \rightarrow 2Na_3Co(CO_3)_3 + NaOH$ Sod. cobalt carbonate (Green colouration) $NiCl_2 + 2NaHCO_3 \rightarrow NiCO_3 + 2NaCl + H_2O + CO_2$ $2NiCO_3 + O \rightarrow Ni_2O_3 + 2CO_2$ Black

Table 30.23: Some important reaction of group IV

Zn²⁺ (zinc)

The sulphide dissolves in HCl.

 $ZnS + 2HCI \rightarrow ZnCI_2 + H_2S$

When the solution is treated with NaOH, first a white ppt. appears which dissolves in excess of NaOH

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

Whiteppt.
 $Zn(OH)_2 + 2NaOH \rightarrow Na_2ZnO_2 + 2H_2O$
Soluble

On $passing H_2S$, white ppt. of zinc sulphide is formed,

 $Na_2ZnO_2 + H_2S \rightarrow ZnS + 2NaOH$ Whiteppt

Mn²⁺ (manganese)

Manganese sulphide dissolves in HCI.

 $MnS + 2HCI \rightarrow MnCl_2 + H_2S$

On heating the solution with NaOH and $\mathrm{Br}_{_{2}}$ -water, manganese dioxide gets ppt..

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



Flowchart 5: For the analysis of group V radical

GROUP V (Ba (II), Sr (II), Ca (II))

Ammonium carbonate ppt. V group radicals in the form of carbonates. These carbonates are soluble in acetic acid.

Ba ²⁺	Test/Reagents	Observation
	$Ba(CH_{3}COO)_{2} + K_{2}CrO_{4} \rightarrow BaCrO_{4} \downarrow + 2CH_{3}COOK$ $Ba(CH_{3}COO)_{2} + (NH_{4})_{2}SO_{4} \rightarrow BaSO_{4} \downarrow + 2CH_{3}COONH_{4}$	White ppt.
	$Ba(CH_{3}COO)_{2} + (NH_{4})_{2}C_{2}O_{4} \rightarrow BaC_{2}O_{4} \downarrow + 2CH_{3}COONH_{4}$ Sr(CH_{3}COO)_{2} + (NH_{4})_{2}SO_{4} \rightarrow SrSO_{4} \downarrow + 2CH_{3}COONH_{4}	White ppt.
	Sr(CH ₃ COO) ₂ (NH ₄) ₂ C ₂ O ₄ \rightarrow SrC ₂ O ₄ \downarrow +2CH ₃ COONH ₄	White ppt.
	$Ca(CH_{3}COO)_{2} + (NH_{4})_{2}C_{2}O_{4} \rightarrow CaC_{2}O_{4} \downarrow + 2CH_{3}COONH_{4}$	Calcium chlorate and calcium sulphate are soluble.
	White ppt.	

Table 30.24: Confirmatory test for group V radicals

VITH GROUP

Table 30.25: Confirmatory test for group VI radical

Mg ²⁺	Test/Reagents	Observation
	Disodium hydrogen phosphate solution $Mg^{2} + NH_{3} + HPO_{4}^{2-} \rightarrow Mg(NH_{4})PO_{4} \downarrow$ $Mg^{2} + HPO_{4}^{2-} \rightarrow MgHPO_{4} \downarrow$	White crystalline ppt. is formed in presence of NH_4Cl prevent precipitation of $Mg(OH)_2$ and NH_3 soln white flocculent ppt.
	Ammonia solution $Mg^{2} + 2NH_{4}OH \rightarrow Mg(OH)_{2} \downarrow + 2NH_{4}^{+}$ $Mg(OH)_{2} \longrightarrow Mg^{+2} + 2OH^{-}$ $NH_{4}CI \rightarrow NH_{4}^{+} + CI^{-};$ $NH_{4}^{+} + OH^{-} \rightarrow NH_{4}OH(weak base)$	White gelatinous ppt is sparingly soluble in water but readily soluble in ammonium salts. NH_4^+ ions 'remove' OH ⁻ causing the hydroxide to dissolve more. Not possible with NaCl.
	Ammonium carbonate solution $5Mg^{2+} + 6CO_3^{2-} + 7H_2O \rightarrow 2MgCO_3.Mg(OH)_2.5H_2O \downarrow + 2HCO_3^{-}$ $NH_4^{+} + CO_3^{2-} \longrightarrow NH_3 + HCO_3^{-}$	Absence of NH_4^+ salts. In the presence of NH_4^+ salts no precipitation occurs, because the equilibrium is shifted towards the formation of HCO_3^- ions. K_{sp} of the ppt. being high (K_{sp} of pure MgCO_3 is 1×10^{-5}), the concentration of carbonate ions necessary to produce a ppt. is not attained.
	4-(4-Nitrophenyl azo resorcinol) or Magneson I $MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 + 2NaCI$ Magneson reagent = p-nitrobenzene-azo resorcinol, a dye stuff, absorbed over Mg(OH) ₂ to give a blue coloured lake.	Ppt. is dissolved in dilute HCI (min.) +NaOH +0.5ml magneson-l reagent = Blue lake

Titan yellow (a water soluble yellow dyestuff)	Deep red colour or ppt.
It is adsorbed by Mg(OH) ₂	
Dissolve ppt. in dil.HCl(min.)+1 drop of NaOH soln (2M) + 1 drop titan yellow soln	Deep red colour solution or ppt. is obtained.
	Ba^{2+} and Ca^{2+} do not react but intensify the colour.

Table 30.26: Action of heat on different compounds

(a) Some oxides liberate O ₂ :	(e) Some sulphates liberate SO ₂ :
$2HgO \xrightarrow{Heat} 2Hg + O_2 \uparrow$	$2MgSO_4 \xrightarrow{Heat} 2MgO + 2SO_2 + O_2$
(Red) (Silvery deposit)	$2ZnSO_4 \xrightarrow{\text{Heat(hightemp)}} 2ZnO + 2SO_2 + O_2$
$2Pb_3O_4 \xrightarrow{\text{Heat}} 6PbO + O_2 \uparrow$	$2BeSO_4 \xrightarrow{Heat} 2BeO + 2SO_2 + O_2$
(Red) (Yellow)	(f) Some sulphates lose water of crystallization:
$2PbO_2 \rightarrow 2PbO + O_2$	$2(CaSO_4.2H_2O) \xrightarrow{Heat} 2(CaSO_4.H_2O) + 2H_2O$
$2Ag_2O \longrightarrow 4Ag + O_2 \uparrow$	$ZnSO_{}7H_{2}O \xrightarrow{70^{\circ}C} ZnSO_{}6H_{2}O \xrightarrow{100^{\circ}C}$
(b) Some carbonates liberate CO:	$-H_{20} + H_{20} + $
$CuCO_3 \xrightarrow{Heat} CuO + CO_2 \uparrow$	$2 \text{IISO}_4.\text{H}_2\text{O} \xrightarrow{-\text{H}_2\text{O}} 2 \text{IISO}_4$
(Green) (black)	(g) Some nitrates liberate NO_2 and O_2 :
$ZnCO_3 ZnO + CO_2 \uparrow$	$2Zn(NO_3)_2 \xrightarrow{\text{Heat}} 2ZnO + 4NO_2 + O_2$
(white) Yellow(hot) white(cold)	white Brown
$2Ag_2CO_2 \xrightarrow{\text{Heat}} 4Ag + 2CO_2 \uparrow +O_2 \uparrow$	$2Cu(NO_3)_2 \xrightarrow{\text{Heat}} 2CuO + 4NO_2 + O_2$
$G_2 \xrightarrow{3} G_3 \xrightarrow{4} G_3 \xrightarrow{4} G_3 \xrightarrow{2} G_2 \xrightarrow{2} G_2 \xrightarrow{2} G_3 \xrightarrow{2} G$	$2Pb(NO_3)_2 \xrightarrow{\text{Heat}} 2PbO + 4NO_2 + O_2$
$MgCO_3 \xrightarrow{Heat} MgO + CO_2 \uparrow$	$2Mg(NO_3)_2 \xrightarrow{Heat} 2MgO + 4NO_2 + O_2$
$Li_2CO_3 \xrightarrow{Heat} Li_2O + CO_2 \uparrow$	$2Ca(NO_3)_2 \xrightarrow{Heat} 2CaO + 4NO_2 + O_2$
(c) Some bicarbonates liberate CO ₂ :	$2\text{LiNO}_3 \xrightarrow{\text{Heat}} \text{Li}_2\text{O} + 2\text{NO}_2 + 1/2\text{O}_2$
$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$	$Hg(NO_3)_2 \xrightarrow{Heat} Hg + 2NO_2 + O_2$
$NH_4HCO_3 \rightarrow NH_3 + CO_2 + H_2O$	$2AgNO_3 \xrightarrow{Heat} 2Ag + 2NO_2 + O_2$
(d) Some sulphates liberate SO ₃ :	$2Co(NO_3)_2 \xrightarrow{\text{Heat}} 2CoO + 4NO_2 + O_2$
$CuSO_4.5H_2O \xrightarrow{Heat}{-5H_2O} CuSO_4;$	(h) Some nitrates liberate O ₂ :
$\xrightarrow{\text{Heat}} \text{CuO} + \text{SO}_2$	$2NaNO_3 \xrightarrow{Heat} 2NaNO_2 + O_2$
$2\text{FeSO}_4 \xrightarrow{\text{Heat}} \text{Fe}_2\text{O}_3 + \text{SO}_2 + \text{SO}_3$	$2AgNO_3 \xrightarrow{Heat} 2AgNO_2 + O_2$
$AI_2(SO_4)_3 \xrightarrow{\text{RedHot}} AI_2O_3 + 3SO_3$	

(i) Some nitrates liberate N ₂ O:	(k) Some chlorides decompose as:
$NH_4NO_3 \xrightarrow{Heat} N_2O + 2H_2O$	$2\text{FeCl}_3 \xrightarrow{\text{Heat}} 2\text{FeCl}_2 + \text{Cl}_2$
	$2CuCl_2 \xrightarrow{Heat} Cu_2Cl_2 + Cl_2$
(j) Hydrated chlorides liberate HCI:	$NH_4CI \xrightarrow{Heat} NH_3 + HCI$
$2\left[\operatorname{AICI}_{3}.6\operatorname{H}_{2}\operatorname{O}\right] \xrightarrow{\operatorname{Heat}} \operatorname{AI}_{2}\operatorname{O}_{3} + 6\operatorname{HCI} + 9\operatorname{H}_{2}\operatorname{O}_{3}$	$Hg_2CI_2 \xrightarrow{Heat} HgCI_2 + Hg$
$\operatorname{NigCl}_{2}.\operatorname{OH}_{2}O \longrightarrow \operatorname{NigO} + 2\operatorname{HCl} + \operatorname{SH}_{2}O$ $\operatorname{ZnCl}_{2}.2\operatorname{H}_{2}O \longrightarrow \operatorname{Zn}(OH)\operatorname{Cl} + \operatorname{HCl} + \operatorname{H}_{2}O$	(I) Some other salts decompose as:
$2(\text{ZnCl}_2.\text{H}_2\text{O}) \xrightarrow{\text{Heat}} \text{Zn}_2\text{OCl}_2 + 2\text{HCl} + \text{H}_2\text{O}$	$\left(NH_{4}\right)_{2}Cr_{2}O_{7} \xrightarrow{Heat} N_{2} + Cr_{2}O_{3} + 4H_{2}O$
$2[FeCl_2.6H_2O] \xrightarrow{Heat} Fe_2O_2 + 6HCl + 9H_2O$	orange Green
$\operatorname{SnCl}_2H_{2}O \xrightarrow{\text{Heat}} \operatorname{Sn}(OH)Cl + HCl + H_{2}O$	$4K_2Cr_2O_7 \xrightarrow{\text{Heat}} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$
	$NH_4NO_2 \xrightarrow{Heat} N_2 + 2H_2O$
	$NH_4NO_3 \xrightarrow{Heat} N_2 + 2H_2O$
	$2Mg(NH_4)PO_4 \xrightarrow{Heat} Mg_2P_2O_7 + H_2O + 2NH_3$
	$2Zn(NH_4)PO_4 \xrightarrow{Heat} Zn_2P_2O_7 + H_2O + 2NH_3$
	$(CH_3COO)_2 Pb \xrightarrow{Heat} PbCO_3 + CH_3COCH_3$
	$\operatorname{FeC}_2O_4 \xrightarrow{\operatorname{Heat}} \operatorname{FeO} + \operatorname{CO}_2 + \operatorname{CO}$
	$SnC_2O_4 \xrightarrow{Heat} SnO + CO_2 + CO$
	$CaC_2O_4 \xrightarrow{Heat} CaCO_3 + CO$
	$K_4[Fe(CN)_6] \xrightarrow{\text{Heat}} 4KCN + Fe + 2C + N_2$
	$H_3BO_3 \xrightarrow{100^{\circ}C} HBO_2 \xrightarrow{160^{\circ}C} H_2B_4O_7;$
	$\xrightarrow{\text{Red Hot}} B_2O_3$
	$2\text{KCiO}_3 \xrightarrow{\text{Heat}} 2\text{KCI} + 3\text{O}_2$
	$2KMnO_4 \xrightarrow{Heat} K_2MnO_4 + MnO_2 + O_2$
	$Na_2B_4O_7.10H_2O \xrightarrow{Heat}{-10H_2O} Na_2B_4O_7;$
	$\xrightarrow{\text{Heat}} 2\text{NaBO}_2 + \text{B}_2\text{O}_3$
	(Glassy bead)
	$Na(NH_4) HPO_4 \longrightarrow NH_3 + NaPO_3 + H_2O$

Table 30.27: Different colored inorganic compou	nc	ł
---	----	---

Black Coloured	Blue Coloured Compounds	Green Coloured Compounds	Yellow Coloured
Compounds			Compounds
	Light Blue		
1. PbS	1. Cu(OH) ₂	1. Ni(OH) ₂ (Green ppt.)	1. As ₂ S ₃
2. Ag ₂ S	2. Cu(NO ₃) ₂	2. Hg ₂ l ₂ (Green ppt.)	2. As ₂ S ₅
3. CuS	3. CuCl ₂	3. Cr ₂ O ₃ (Green solid)	3. CdS
4. Cu ₂ S	4. $CuSO_4.5H_2O$ (Blue vitrol)	4. Cr ₂ (SO ₄) ₃	4. SnS ₂ (Artificial gold)

Black Coloured Compounds	Blue Coloured Compounds	Green Coloured Compounds	Yellow Coloured Compounds
5. NiS	5. Zn ₂ [Fe(CN) ₆] (Bluwish white	5. CrCl ₃	5. FeS ₂ (Fool's gold)
6. CoS	ppt)	6. FeSO _{4.} 7H ₂ O	6. $(NH_4)_2S_x$ (where X=2 to 5)
7. HgS	6. Co(OH) ₂	7. FeCl ₂	7. PbCrO ₄
8. FeS		8. FeSO _{4.} (NH ₄)2SO ₄ .6H ₂ O	8. BaCrO ₄
9. NiO	Deep Blue	(Mohr's salt)	9. SrCrO ₄
10. MnO	1. [Cu(NH ₃) ₄]SO ₄ (Swizzer's	9. Na ₂ MnO ₄	10. AgBr (light yellow)
11. FeO	reagent)	10. K ₂ MnO ₄	11 AgI (Dark yellow)
12. CuO	2. $[Cu(NH_3)_4](NO_3)_2$	11. $B(OC_2H_5)_3$ (Burns with green	12. Pbl ₂
13. PbO ₂	3. Fe ₄ [Fe(CN) ₆] ₃ (Prussian's blue)	edge flame)	13. PbO (in Cold)
14. MnO ₂	4. $\operatorname{Fe}_{3}[\operatorname{Fe}(\operatorname{CN})_{6}]_{2}$ (Turnbull's blue)	12. CoO.ZnO (Riemann's green)	14. ZnO (in Hot)
15. Mn ₃ O ₄	5. Na ₄ [Fe(CN) ₅ (NOS)] (Violet)		15. HgO(Yellow ppt.)
16. Fe ₃ O ₄			16. Na ₂ O ₂ (Pale yellow)
17. Co ₃ O ₄			17. Ag ₃ PO ₄
18. Ni(OH) ₃			18. Ag ₂ CO ₃
19. Cu ₃ P ₂			19. Ag ₃ AsO ₄
20. Bil ₃			20. Cu(CN) ₂
21. Hg+Hg(NH ₂)Cl			21. K ₃ [Co(NO ₂) ₆]
			22. (NH ₄) ₃ PO ₄ .12MoO ₃
			23. (NH ₄) ₃ AsO ₄ .12MoO ₃
			24. Na ₂ CrO ₄
			25. CrO ₄ ²⁻ (Yellow in solution)

Red Coloured	Brown Coloured Compounds	Orange Coloured	Pink Coloured
1 Ag CrO (Brick red)	1 SpS		
$1. Ag_2 CIO_4 (blick red)$	1. 5115	1. 30233	
2. Hg ₂ CrO ₄ (Brick red)	2. Bi ₂ S ₃	2. Sb_2S_5	MnS
3. Hgl ₃ (Scarlet red)	3. CdO	3. KO ₃	MnO ₄ -
4. Pb ₃ O ₄ (2PbO + PbO ₂)	4. PbO ₂	4. CsO ₂	(pink or purple in aq.soln)
5. CrO ₂ Cl ₂ (Reddish Brown)	5. Fe(OH) ₃ (Reddish Brown)	5. $Cr_2O_7^{2-}$ (orange in aq. soln)	Co(CN) ₂
6. Fe(CH ₃ COO) ₃	6. Fe ₂ O ₃ (Reddish Brown solid)		(NH ₄) ₂ SnCl ₆
(Blood red)			CoCl ₂ .6H ₂ O
7. Fe(SCN) ₃ (Blood Red)	7. Fe ₂ (CO ₃) ₃		
8. Asl ₃	8. Cu ₂ O (Reddish Brown)		
9. Sbl ₃	9. Ag ₃ AsO ₄ (Reddish Brown)		
10. Snl ₂	10. $Cu_2I_2 + I_3^-$ (Brown ppt.)		
11 CuBr ₂	11 Cu ₂ [Fe(CN) ₆] (Chocolate Brown)		
12. [Ni(DMG) ₂] (Rosy red)	12. NO ₂ (Brown gas)		
	13. [Fe(H ₂ O) ₅ (NO)]SO ₄ (Brown ring)		

POINTS TO REMEMBER

An aqueous solution containing :



Solved Examples

JEE Main/Boards

Example 1: A colourless solid (A) liberates a brown gas (B) on acidification, a colourless alkaline gas (C) on treatment with NaOH and a colourless non-reactive gas (D) on heating. If heating of (A) is continued, it completely disappears. Identify the compounds (A) to (D).

Sol: (A) From the given data it appears to be NH_4NO_2 .

This can be explained by the following reaction

With mineral acid NH_4NO_2 yields Nitrous acid which eventually gets converted to Nitric acid liberating NO.

NO with oxygen forms brown coloured NO₂ gas.

(1) $NH_4NO_2 + HCI \longrightarrow NH_4CI + HNO_2$ (A) Nitrous acid $3HNO_2 \longrightarrow HNO_3 + H_2O + 2NO$ (Nitric acid)

 $2NO + O_2 \longrightarrow 2NO_2$ (Brown gas) (B)

 NH_4NO_2 with NaOH gives out Sodium nitrite and ammonia gas.

(2) $NH_4NO_2 + NaOH \longrightarrow NaNO_2 + NH_3 \uparrow + H_2O$ (C) Ammonia gas

On heating it gives off colourless Nitrogen gas and water.

(3) $NH_4NO_2 \xrightarrow{\Delta} N_2 \uparrow + 2H_2O$ Non-reactive (D)

*** Both NO₂ and Br₂ are brown gases. How can they be identified if placed separately in two containers?

[Hint: Water is added in both the container. Br₂ forms yellow solution whereas NO₂ forms colourless solution.]

Example 2: An aqueous solution of gas (X) shows the following reactions

(a) It turns red litmus blue.

(b) When added in excess to a copper sulphate solution, a deep blue colour is obtained.

(c) On addition of FeCl_3 solution, a brown ppt., soluble in dilute HNO_3 is obtained. Identify (X) and give equations for the reactions at step (b) and (c).

Sol: Gas X is soluble in water forming basic solution because it turns red litmus blue. Hence, the gas may be NH_3

 $NH_3 + H_2O \longrightarrow NH_4OH$ $CuSO_4 + 4NH_4POH \longrightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$ (Tetra- amine cupric sulphate) Deep blue

Ferric chloride gives brown ppt. of Fe(OH)₃

 $FeCI_3 + 3NH_4OH \longrightarrow Fe(OH)_3 + 3NH_4CI$ (Brown precipitate)

Brown ppt. is soluble in HNO₃

 $Fe(OH)_3 + 3HNO_3 \longrightarrow Fe(NO_3)_3 + 3H_2O$ (Soluble complex)

*** NaCl on heating with conc. H_2SO_4 gives HCl whereas NaBr and Nal gives Br_2 and I_2 respectively. Why?

[Hint: NaCl + $H_2SO_4 \longrightarrow NaHSO_4 + HCl$ NaBr + $H_2SO_4 \longrightarrow NaHSO_4 + HBr$ 2HBr + $H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$

HBr and HI are reducing agent whereas H_2SO_4 is oxidising agent and thus Br_2 and I_2 are formed.]

Example 3: A compound (A) on heating with an excess of caustic soda solution liberates a gas (B) which gives white fumes on exposure of HCl. Heating it continued to expel the gas completely. The resultant alkaline solution again liberates the same gas (B) when heated with zinc powder. However the compound (A), when heated alone does not give nitrogen. Identify (A) and (B).

Sol: We all know that NH_3 with HCl gives white fumes of NH_4Cl with popping noise.

Hence it should be NH_3 . Thus, compound (A) must be an ammonium salt.

Also we know that nitrates and nitrites on heating with Zn and alkali liberate NH_3 gas. Hence the compound (A) should be ammonium nitrate or nitrite

But compound (A) does not give $\rm N_{2}$ on heating hence it may not be ammonium nitrite.

Reactions involved:

$$NH_4NO_3 + NaOH \longrightarrow NaNO_3 + H_2O + NH_3 \uparrow$$
(A)

 $NH_3 + HCI \longrightarrow NH_4CI$

(White fumes)

$$NaNO_3 + 8[H] \xrightarrow{Zn/NaOH} NaNO_3 + 2H_2O + NH_3 \uparrow$$

*** Why original solution is not prepared in conc. HNO₃?

[Hint: HNO₃ is an oxidising agent which on decomposition gives oxygen. A yellow ppt. of sulphur is obtained in presence of HNO₃ when H₂S is passed for detecting the radicals of group II and group IV. $H_2S + 2HNO_2 \longrightarrow 2NO_2 + 2H_2O + S$]

Example 4: An inorganic compound (A) shows the following reactions.

(i) It is white solid and exists as dimmer; gives fumes of (B) with wet air.

(ii) It sublimes on 180° C and forms monomer if heated to 400° C.

(iii) Its aqueous solution turns blue litmus to red.

(iv) Addition of NH_4OH and NaOH separately to a solution of (A) gives white ppt. which is however soluble in excess of NaOH.

Sol: (i) (A) is a characteristic dimerized compound which sublimes on 180° C and forms monomer if heated to 400° C and thus, (A) is (AlCl₃)₂ or Al₂Cl₆

$$\mathsf{Al}_2\mathsf{Cl}_{6(s)} \xrightarrow{180^\circ\mathsf{C}} \mathsf{Al}_2\mathsf{Cl}_{6(v)} \xrightarrow{400^\circ\mathsf{C}} 2\mathsf{AlCl}_3$$

(ii) It fumes with wet air

 $Al_2Cl_6 + 6H_2O \longrightarrow 2Al(OH)_3 + 6HCI \uparrow$ Fumes (B)

(iii) Its solution in water is acidic due to hydrolysis

 $2\text{AICl}_3 + 6\text{H}_2\text{O} \longrightarrow 2\text{AI(OH)}_3 + 6\text{HCl}_{(aq)}$

(iv) (A) gives white ppt. with NH_4OH , soluble in excess of NaOH.

 $AI_2CI_6 + 6NH_4OH \longrightarrow 2AI(OH)_3 + 6NH_4CI$

 $Al_2Cl_6 + 6NaOH \longrightarrow 2AIOH + 6NaCI$

Example 5: (i) Solution salt of an acid (A) is formed on boiling white phosphorus with NaOH solution.

(ii) On passing chlorine through phosphorus kept fused under water, another acid (B) is formed which on strong heating gives metaphosphoorus acid.

(iii) Phosphorus on treatment with conc. HNO_3 gives an acid (C) which ais also formed by the action of dilute H_2SO_4 on powdered phosphorite rock.

(iv) (A) on treatment with a solution of $HgCl_2$ first gives a white ppt. of compound (D) and then grey ppt. (E).

Identify (A) to (E) and write balanced chemical equations for the reactions at step (i) to (iv)

Sol: (i) $P_4 + 3NaOH + 3H_2O \longrightarrow 3NaH_2PO_2 + PH_3$ (Sodium hypophosphate)

Thus, acid (A) is H₃PO₂ i.e., hypophosphorus acid

(ii) $2P + 3Cl_2 + 6H_2O \longrightarrow 2H_3PO_3 + 6HCl$ (Phosphorus acid)

Thus, acid (B) is H₃PO₃

(iii)
$$P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

(C)
 $P_4 + 10HNO_3 \longrightarrow 4H_3PO_4 + 10NO_2 + 4H_2O$

Thus acid (C) is H₃PO₄

(iv)
$$H_3PO_2 + 2H_2O \longrightarrow H_3PO_4 + 4H$$

 $HgCl_2 + 2H \longrightarrow Hg_2Cl_2 + 2HCl$ (white)(D)

$$Hg_2CI_2 + 2H \longrightarrow 2Hg + 2HCI$$
(Grey)(E)

*** During testing of Cl⁻ and Br⁻ by chloroform test, CHCl₃ layer first turns violet and then brown, confirming the presence of l⁻ and Br⁻ respectively. When layer turns brown then violet colour disappears or not and why?

[Hint: Violet and brown colours are due to oxidation of I^{-} to I_{2} and Br to Br₂ respectively. The violet colour of I_{2} disappears when layer is brown due to formation of (IO_{3}^{-}) (iodate ion) which is colourless.] **Example 6:** (i) A black coloured compound (B) is formed on passing hydrogen sulphide through the solution of a compound (A) in NH₄OH.

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

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

(iv) The compound (C) is changes 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 some time, a green colour compound (E) is formed. No change is observed on heating. Identify (A) to (E) and gives chemical equations for the reactions at steps (i) to (v).

Sol: Here it is given that a black coloured compound (B) is formed on passing hydrogen sulphide through the solution of a compound (A) in NH_4OH .

This indicates that (A) is salt of the IV group radicals $(Co^{2+}, Ni^{2+}or Zn^{2+})$.

Further it is given that on treatment with potassium cyanide (A) gives a buff coloured ppt. which dissolves in excess of this reagent forming a compound (C).

Which appears to be a cobalt salt (CoCl₂)

(i)
$$CoCl_2 + 2NH_4OH + H_2S \longrightarrow CoS + 2NH_4Cl + 2H_2O$$

(A) (B)

(ii)
$$CoS + 2HCI + O \xrightarrow{(B)} CoCI_2 + H_2O + S$$

(from KCIO₃)

$$2\text{KCIO}_3 \longrightarrow 2\text{KCI} + 3\text{O}_2$$

(iii)
$$CoCl_2 + 2KCN \longrightarrow Co(CN)_2 \downarrow + 2KCI$$

buff coloured

$$CO(CN)_2 + 4KCN \longrightarrow K_4[Co(CN)_6]$$

(iv)
$$2K_4[CO(CN)_6] + O + H_2O \longrightarrow 2K_3[Co(CN)_6] + 2KOH$$

(D)

(v)
$$\operatorname{CoCl}_2 + 6\operatorname{NaHCO}_3 \longrightarrow \operatorname{Na}_4[\operatorname{Co}(\operatorname{CO}_3)_3] + 2\operatorname{NaCl} + 3\operatorname{CO}_2 + 3\operatorname{H}_2\operatorname{O}_2$$

 $2Na_{4}[Co(CO_{3})_{3}] + 2NaHCO_{3} + O \longrightarrow$ $2Na_{3}[Co(CO_{3})_{3}] + 2Na_{2}CO_{3} + H_{2}O$

(E)

Note: *** Subquestions placed after the answers

JEE Advanced/Boards

Example 1: (i) An ore (A) on roasting with sodium carbonate and lime in the presence of air gives two compounds, (B) and (C).

(ii) The solution of (B) in conc. HCl on treatment with potassium ferricyanide gives a blue colour or ppt. of compound (D).

(iii) The aqueous solution of (C) on treatment with conc. H_2SO_4 gives a yellow coloured compound (E).

(iv) Compound (E) when treated with KCl gives an orange-red compound (F) which is used an oxidizing reagent.

(v) The solution of (F) on treatment with oxalic acid and then with an excess of potassium oxalate gives blue crystals of compound (G).

Identify (A) to (G) and give balanced chemical equations for reactions at steps (i) to (v).

Sol: (a) Reaction (i) suggests that the ore contains Fe.

(b) Reaction (ii) and (iv) suggests that the ore also contains chromium.

Reaction (i), (iii) and (IV) are involved in the preparation of $K_2Cr_2O_7$ from chromite ore, $FeOCr_2O_3$.

Hence the given reactions can be written as below

(i)
$$4\text{FeO.Cr}_2\text{O}_3 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \xrightarrow[(\text{Rosting})]{\text{lime}} 2\text{Fe}_2\text{O}_3 \downarrow$$

Chromite ore (A) (B)

$$\cdot 8Na_2CrO_4 + 8CO_2 \uparrow$$
(C)

(ii) $Fe_2O_3 + 6HCI \longrightarrow 2FeCI_3 + 3H_2O$

$$4\text{FeCl}_3 + 3\text{K}_4[\text{Fe(CN)}_6] \longrightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 + 12\text{KCl}$$

Blue(D)

(iii)
$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_6O_3 + Na_2SO_4 + H_2O$$

soluble (C) Yellow colour (E)

(iv)
$$Na_2Cr_2O_7 + 2KCI \longrightarrow K_2Cr_2O_7 + 2NaCI$$

(E) (F)

 $K_2 Cr_2 O_7$ (F) is well known oxidizing agent.

(v)
$$\operatorname{Cr}_2(\operatorname{C}_2\operatorname{O}_4)_3 + 3\operatorname{K}_2\operatorname{C}_2\operatorname{O}_4 \longrightarrow$$

 $2K_3[Cr(C_2O_4)_3] + Cr_2(C_2O_4)_3$ Potassium trioxalatochromium Blue crystals (G) *** Chromyl chloride test for chlorides is not performed if mixture contain chlorates, why?

[Hint: Because ClO_3^- ions react with H_2SO_4 to form chlorine dioxide (yellow greenish gas) which dissolves in H_2SO_4 forming orange-yellow solution. This solution is highly explosive.

$$3\text{KCIO}_3 + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{CIO}_2 + \text{CIO}_4^- + 3\text{SO}_4^{2-} + 4\text{H}^+ + 3\text{K}^+ + \text{H}_2\text{O}$$

Example 2: (i) A black mineral (A) on heating in presence of air gives a gas (B).

(ii) The mineral (A) on reaction with dilute H_2SO_4 gives a gas (C) and solution of a compound (D).

(iii) On passing gas (C) into an aqueous solution of (B) a white turbidity is obtained.

(iv) The aqueous solution of compound (D) on reaction with potassium ferricyanide gives a blue compound (E).

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

Sol: Summary of the given statement can be written as:

Gas C + Solution of D $\leftarrow dilH_2SO_4 \rightarrow Black mineral$

$$A \xrightarrow{O_2} Gas B \xrightarrow{i)H_2O} White turbidity$$

$$D \\ K_3[Fe(CN)_6]$$

Blue compound E

Compound D foms blue coloured solution of E by ton treatment of potassium ferricyanide. This indicates that compound D contains Fe^{2+} ion which is also the constituent ion of the compound A. Further it is given that A, is a black mineral of Fe^{2+} ion, so it has to be ferrous sulphide (FeS) which is confirmed by following reaction:

(i)
$$4 \operatorname{FeS} + 7 \operatorname{O}_2 \longrightarrow 2 \operatorname{Fe}_2 \operatorname{O}_3 + 4 \operatorname{SO}_2$$

(A) (B)
(ii) $\operatorname{FeS} + \operatorname{H}_2 \operatorname{SO}_4 \longrightarrow \operatorname{FeSO}_4 + \operatorname{H}_2 \operatorname{S} + \operatorname{S}$
(A) (D) (C)
(iii) a) $\operatorname{SO}_2 + \operatorname{H}_2 \operatorname{O} \longrightarrow \operatorname{H}_2 \operatorname{SO}_3$
b) $2\operatorname{H}_2 \operatorname{S} + \operatorname{H}_2 \operatorname{SO}_3 \longrightarrow 3\operatorname{S} + 3\operatorname{H}_2 \operatorname{O}$
(C) Turbidity

(iv)
$$FeSO_4 + K_3[Fe(CN)_6] \longrightarrow KFe[Fe(CN)_6] + K_2SO_4$$

(D) (E)

Example 3: A white substance A reacts with dilute H_2SO_4 to produce a colourless gas B and a colourless solution C. The reaction between B and acidified $K_2Cr_2O_7$ solution produces a green solution and a slightly coloured participate D. The substance D burns in air to produce a gas E which reacts with B to yield D and a colourless liquid. Anhydrous copper sulphate is turned blue on addition of this colourless liquid. Addition of aqueous NH₃ or NaOH to C produces first a participate which dissolves in the excess of the respective reagent to produce a clear solution in each case. Identify A, B, C, D and E. Write the equation of the reactions involved.

Sol:

A
$$\xrightarrow{\text{dil.H}_2\text{SO}_4}$$
 B↑ + C
(White) (Colourless) (Colourless solution)
 \downarrow $K_2\text{Cr}_2\text{O}_7/\text{H}^+$
Green solution + D↓ (Burns in air to form E)
(Coloured)
E↑ + B↑ → D + Colourless liquid $\xrightarrow{\text{CuSO}_4}$ Blue

$$C \xrightarrow{Aq.NH_3} Precipitate \xrightarrow{Excess of} Clear solution$$

The above set leads to following conclusions.

(i) Because Gas (B) is colourless and turns acidified $K_2Cr_2O_7$ solution green, it appers to be H_2S .

(ii) H_2S gas is obtained by the reaction of dil. H_2SO_4 on A, thus A must be a sulphide.

(iii) Zns sulphide is white thus it indicates that A is ZnS

$$ZnS + H_2SO_4(dil) \longrightarrow ZnSO_4 + H_2S^{\uparrow}$$
(A)
(C)
(B)
$$3H_2S + K_2Cr_2O_7 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$
(B)
(green)
(D)
(E)
(Colourless liq)
(D)
(E)
(Colourless liq)
(D)
(E)
(CuSO_4(white)
(CuSO_4. 5H_2O (blue)
ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2 \downarrow \xrightarrow{2NaOH} Na_2ZnO_2 + 2H_2O
(C)
(Soluble)

*** Before testing II group, iodide ions are separated. Why?

[Hint: Because I⁻ ions react with air to form I₂ which reacts with H₂S and give white or light yellow ppt. of sulphur i.e., why I⁻ are removed by boiling original solution with NaNO₂.

$$4HI + O_2 \longrightarrow 2H_2O + 2I_2$$
; $I_2 + H_2S \longrightarrow 2HI + S$]

Example 4: A black coloured compound (A) on reaction with dilute sulphuric 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 acidified solution of a compound (E) gives a ppt. (F) soluble in dilute nitric acid. 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 ppt. (H) is obtained. On addition of an aqueous solution of barium chloride to an aqueous solution (E), a white ppt. insoluble in HNO₃ is obtained. Identify from (A) to (H).

Sol: Summary we can draw from the given Data:



(i) Aqueous solution of compound E with $BaCl_2$ to give white ppt. which is insoluble in nitric acid indicates that the salt (E) contains SO_4^{2-} ions.

(ii) Compound (G) with potassium ferricyanide in presence of acidic acid to give chocolate ppt. (H) this indicates that (G) must contain Cu^{2+} and hence (H) has to be cupric ferricyanide, Cu_2 [Fe (CN) ₆].

(iii) As compound (G) is derived from (F), compound (F) also contains Cu^{2+} . Further since (F) is derived from the reaction of the gas (B) and compound (E), (E) must contain Cu^{2+} ion. Ppt. of Cu^{2+} ion soluble in dilute nitric

acid should be CuS; hence (F) must be CuS and thus (B) is H_2S .

(iv) According to first point compound (E) contains SO_4^{2-} hence (E) must be $CuSO_4$.

(v) Gas (B) (identified as H_2S) is obtained by the decomposition of black coloured compound (A) with dil. H_2SO_4 . Hence (A) must be sulphide of Cu, Pb, Hg, and Fe. Co, Ni, etc.

Thus the various compounds from (A) to (H) and their reactions can be written as below.

 $\begin{array}{c} \text{FeS} & + \text{H}_2\text{SO}_4 \longrightarrow & \text{FeSO}_4 & + & \text{H}_2\text{S} \uparrow \\ \text{Ferrous sulphide (A)} & & \text{Hydrogen sulphide (B)} \end{array}$

$$H_2S$$
 + HNO_3 ------> $2H_2O + 2NO_2$ + Hydrogen sulphide (B) Nitric acid(C)

$$\underbrace{\text{CuSO}_4}_{\text{Copper sulphide(E)}} + \underbrace{\text{H}_2\text{S}}_{\text{(B)}} \xrightarrow{\text{ in presence}}_{\text{ of dil.HCl}} \xrightarrow{\text{CuS}}_{\text{Copper sulphide(F)}} \downarrow + \underbrace{\text{H}_2\text{SO}_4}_{\text{2}}$$

$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2C$$

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

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

Cupric ammonium sulphate
(blue compound (G))

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

$$(G)$$

$$2CuSO_4 + K_4[Fe(CN)_6] \longrightarrow Cu_2[Fe(C)_6] \downarrow + 2K_2SO_4$$

$$\underbrace{\mathsf{CuSO}_4 + \mathsf{BaCl}_2 \longrightarrow \mathsf{BaSO}_4}_{(E)} \xrightarrow{\mathsf{Barium sulphate}}_{(insoluble in water)} \downarrow +\mathsf{CuCl}_2$$

Thus the compounds (A) to (H) are

- A = Ferrous sulphide, FeS,
- $B = Hydrogen sulphide, H_2S,$
- $C = Nitric acid, HNO_{2}$
- D = sulphur, S,
- $E = Copper sulphate, CuSO_{4}$
- F= Copper sulphide, CuS,
- G = Cupric ammonium sulphate, $[Cu(NH_3)_4]SO_4$
- $H = Cupric ferricyanide, Cu_2[Fe(CN)_6]$

*** An original solution is prepared in conc. HCl. When diluted a while ppt. is formed. What does it indicate?

[Hint: Formation of White ppt indicates the Presence of Sb⁺³ or Bi⁺³. Their chlorides hydrolyse to oxychlorides in presence of excess of water.

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

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

Example 5: (i) The yellow coloured ppt. of compound (A) is formed on passing H_2S through a neutral solution of salt (B).

(ii) (A) is soluble in hot dilute HNO_3 but insoluble in yellow ammonium sulphide.

(iii) The solution of (B) on treatment with small quantity of NH_3 gives a white ppt. which become soluble in excess of its forming a compound (C).

(iv) The solution of (B) gives white ppt. with small concentration of KCN which becomes soluble in excess of this reagent forming a compound (D).

(v) The solution of (D) on treatment with H_2S gives (A).

(vi) The solution of (B) in dil. HCl on treatment with a solution of $BaCl_2$ gives a white ppt. of compound (E) which is insoluble in conc. HNO₃.

Identify (A) to (E) and give chemical equations for the reactions at steps (a) to (c) to (f)

Sol: Yellow ppt. of CdS is (A)

(i)
$$CdSO_4 + H_2S \longrightarrow CdS + H_2SO_4$$

(B) (A)

(ii) $CdS+2HNO_3 \longrightarrow Cd(NO_3)_2 + H_2S$ soluble

CdS ----- Insoluble in yellow ammonium sulphide.

$$CdSO_4 + 2NH_4OH \longrightarrow Cd(OH)_2 + (NH_4)_2SO_4$$

(iii)
$$Cd(OH)_2 + 4NH_4OH \longrightarrow [Cd(NH_3)_4](OH)_2 + 4H_2O$$

(C)

(iv)
$$CdSO_2 + 2KCN \longrightarrow Cd(CN)_2 + K_2SO_4$$

white

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

(D) soluble

(v)
$$K_2[Cd(CN)_4] + H_2S \longrightarrow CdS + 2KCN + 2HCN$$

(vi) $CdSO_4 + BaCl_2 \longrightarrow BaSO_4 + CdCl_2$
(E)

Example 6: A substance X dissolves in hot conc. HCl to give solution which when treated with caustic soda solution gives a white ppt. which however dissolves in excess of caustic soda solution giving a strongly solution. On heating X with sulphur, a brown powder Y is formed which dissolved on warming with yellow ammonium sulphide solution. The solution gives a grey ppt. with HCl. When X is heated in air, a white powder Z is obtained which can be dissolved in conc. H_2SO_4 . When Z is fused with NaOH, extracted with hot water, then treated with mineral acid, white gelatinous ppt. is obtained. Identify X, Y, Z and give the reactions involved.

Sol:

X –	Solution—	NaOH →	White ppt	NaOH	→Solution
					(Strongly
					reducing)
X –	Brown powder - Y	(NH ₄) ₂	⁵ → Solutior	ו <u>HCI</u>	→Grey ppt.
v	air Milette reserved en	i)NaOH	Calution	HCI	- I - 4 ¹

X
$$\xrightarrow[heat]{heat}$$
 White powder $\xrightarrow[ii]hot water}$ Solution $\xrightarrow[heat]{Heat}$ Gelatinous ↓
Z(soluble only white
in conc.H₂SO₄)

(i) Solution of X (with HCl) reacts with NaOH and forms white ppt.This ppt dissolves in excess of NaOH to give solution which has strongly reducing nature. This reducing properties of this solution points out that the solution might be containing sodium stannite and here X must be tin.

(ii) The nature of X as tin is confirmed by its reaction with S forming SnS_2 which dissolves in yellow ammonium sulphide but regenerates in presence of HCl.

Thus the various reactions and nature of X, Y, and Z can be written as below.

(i)
$$Sn_{(X)} + 2HCI \longrightarrow SnCl_2 + H_2$$

 $SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCI$
 $Sn(OH)_2 + 2NaOH \longrightarrow Na_2SnO_2 + 2H_2O$
 $Sodium stannite$
 $(Strongly reducing)$
(ii) $Sn + 2S \longrightarrow SnS_2$
 $SnS_2 + (NH_4)_2 S \longrightarrow (NH_4)_2 SnS_3$

 $(NH_4)_2 SnS_3 + 2HCI \longrightarrow SnS_2 + 2NH_4CI + H_2S$

(iii) Sn+O₂ \longrightarrow SnO₂ (Soluble only in conc. H₂SO₄) SnO₂ + 2NaOH \longrightarrow Na₂SnO₃ + H₂O Na₂SnO₃ + 2HCI \longrightarrow H₂SnO₃ \downarrow +2NaCl Stannic acid

Example 7: A colourless solid A on heating gives a white solid B and a colourless gas, C; B gives off reddish brown fumes on treatment with dilute acids. On heating with NH_4Cl , B gives a colourless gas D and a residue E. The compound A also gives a colourless gas F on heating with ammonium sulphide and white residue G. Both E and G impart bright yellow colour to Bunsen flames. The gas C forms white powder with strongly heated magnesium metal. The white powder forms magnesium hydroxide with water. The gas D, on the other hand, is absorbed by heated calcium which gives off ammonia on hydrolysis. Identify the substance A to G and gives reactions for the changes involved.

Sol: It is advisable to summarize the given facts in the form of a chart.

 $A \xrightarrow{(NH_4)_2 SO_4}_{Heat} \xrightarrow{G} G + F_{Colourless gas}$ $A \xrightarrow{(NH_4)_2 SO_4}_{Heat} \xrightarrow{G} F_{Colourless gas}$ $A \xrightarrow{(I)}_{Colourless solid} \xrightarrow{Heat}_{Colourless solid} \xrightarrow{Heat}_{Colourless gas} = C_{Colourless residue} + F_{Residue}$ $B \xrightarrow{Dil, HCl}_{Heat} \xrightarrow{D}_{Reddish brown fumes}$ $C \xrightarrow{C}_{Colourless residue} + Mg \xrightarrow{Heat}_{Colourless gas} = Mg(OH)_2$

 $\underset{\text{Colourless residue}}{\text{D}} + \text{Ca (Heated)} \xrightarrow{\text{H}_2\text{O}} \text{NH}_3$

The above reactions lead to the following conclusions.

(A) And (D) on reaction with calcium forms a compound which on hydrolysis gives ammonia, this indicates that D must be nitrogen.

Compound (B), Residues E and G burns with yellow flame this indicates that these are sodium salts. Hence compound B (which give E) and A (which give G) must be sodium salts.

(C) The colourless solid B with dilute acid gives reddish brown fumes, the reddish brown fumes are probably of NO_2 .

Hence compound B must be nitrite

(Remember: NO_2^- ions are not attacked by dil. Acids.).

Consequently, A must be compound of NO_3^- which can give NO_3^- (B) on heating.

Thus compound A is NaNO₃.

Reactions are as follows:

$$3HNO_2 \longrightarrow HNO_3 + H_2O + 2NC$$

$$BNO + O_2 \longrightarrow 2NO_2 \uparrow$$
Re ddish brown fumes

(iv)
$$2NaNO_3 + (NH_4)_2SO_4 \longrightarrow Na_2SO_4 + 2NH_3 \uparrow + 2HNO_3$$

(G) (F)

(iii)
$$\operatorname{NaNO}_2 + \operatorname{NH}_4 \operatorname{Cl} \xrightarrow{\text{heat}} \operatorname{NaCl} + \operatorname{N}_2 \stackrel{\uparrow}{(\mathsf{E})} + 2\operatorname{H}_2 \operatorname{C}$$

(iv) $2 \text{NaNO}_2 + (\text{NH}_4)_2 \text{SO}_4 \longrightarrow \text{Na}_2 \text{SO}_4 + 2 \text{NH}_3 \uparrow + 2 \text{HNO}_3$ (G) (F)

(v)
$$2Mg + O_2 \longrightarrow 2MgO_{(C)} White powder$$

$$MgO + H_2O \longrightarrow 2Mg(OH)_2$$

(vi)
$$3Ca + N_2 \longrightarrow Ca_3 N_2$$

(D) $Ca_3 N_2 + 6H_2 O \longrightarrow 2Ca(OH)_2 + 2NH_3 \uparrow$

Thus substance (A) to (G) can be represented as

Note: *** Subquestions placed after the answers

JEE Main/Boards

Exercise 1

Q.1 Sometimes, a white ppt. is obtained even in the absence of members of 1st group on the addition of HCl. Explain it.

Q.2 Give examples and explain with equations:

(i) Two colourless solution give a black ppt. on mixing.

(ii) Two colourless solution give a red ppt. on mixing, soluble in excess of one of them.

(iii) Two colourless solutions give a white ppt. on mixing, soluble in ammonium hydroxide.

(iv) Two colourless solution give a yellow ppt. on mixing.

Q.3 What is yellow ammonium sulphide? Why is yellow ammonium sulphide and not ordinary ammonium sulphide used for the separation of II A and II B subgroups?

Q.4 A certain inorganic compound (X) shows the following reactions:

(i) On passing H_2S through an acidified solution of (X) a brown ppt. is obtained.

(ii) The ppt. obtained at step (i) dissolve in excess of yellow ammonium sulphide.

(iii) On adding an aqueous solution of NaOH to a solution of (X), first a white ppt. is obtained which dissolves in excess of NaOH.

(iv) The aqueous solution of (X) reduce ferric chloride.

Identify the cation of (X) and give chemical equations for reactions at steps (i), (iii) and (iv)

Q.5 A mixture of the three gases A, B and C is passes first into an acidified dichromate solution when A is absorbed turning the solution green. The remainder of the gas is passed through an excess of lime water which turns milky, resulting in the absorption of B. The residual gas C is absorbed by an alkaline pyrogallol solution. However, the original gaseous mixture does not turn lead acetate paper black. Identify A, B and C.

Q.6 You are given unlabelled four packets of white substance of zinc, namely ZnO, $Zn(OH)_2$, $ZnCO_3$ and ZnS. How will you proceed to identify each of them?

Q.7 Explain, while performing qualitative analysis of basic radicals of third group, why ammonium chloride is added in excess before adding ammonium hydroxide?

Q.8 What happens when

(i) Copper sulphate is treated with excess of NH₄OH

(ii) Bismuth chloride is treated with sodium stannite in presence of NaOH

(iii) Stannous chloride is treated with mercuric chloride

(iv) Excess of water is added to concentrated solution of antimony chloride

Q.9 (i) What is the function of concentrated HNO_3 in third group?

(ii) Will you add HNO_3 in third group even if iron is given in ferric state in the mixture?

(iii) Can you use NaCl and NaOH instead of NH_4Cl and NH_4OH in third group?

Q.10 Identify compounds A to G from the following reactions

A (white crystals)
$$\xrightarrow{\text{heat}} B + C_{gas}; C \xrightarrow{KI} I_2 A$$

$$B \xrightarrow{HNO_3} Solution D \xrightarrow{NaOH} E \xrightarrow{brown} \xrightarrow{NH_3}$$

SolutionF $\xrightarrow{H \text{ CO OH}}$ Black precipitate

Q.11 Complete the following

(i) PbS+ Acid
$$\longrightarrow$$
 Gas $\xrightarrow{Acid}_{(B)}$ \xrightarrow{C} Yellow ppt.

(ii)
$$A + H_2S \xrightarrow{NH_4OH} White ppt.+ 2HCI$$

$$A + NaOH \xrightarrow[(C)]{} ppt. \xrightarrow[(D)]{} solution$$

(iii) Pbs
$$\xrightarrow{\text{heat in air}} A + PbS \xrightarrow{B} Pb + SO_2$$

Q.12 Explain the following:

(i) Lead (Pb²⁺) is placed in the first as well as second group of qualitative analysis.

(ii) The colour of mercurous chloride, Hg_2CI_2 , change from white to black when treated with ammonia.

(iii) During the qualitative analysis of a mixture containing Cu^{2+} and Zn^{2+} ions, H_2S gas is passes through an acidified solution containing these ions in order to test Cu^{2+} alone. Explain briefly.

Q.13 Identify the unknown species and complete the following:

- (i) (A)+BaCl₂ \longrightarrow White ppt.
- (ii) NaOH+(B) \longrightarrow NH₂ gas
- (iii) (C)+MnO₂+H₂SO₄ \longrightarrow Violet vapours
- (iv) (D)+ $K_2Cr_2O_7$ + H_2SO_4 Green coloured solution
- (v) (E) $\xrightarrow{\text{Heat}}$ Yellow compound solid

Q.14 Fill in the blanks

(a) Lime water is used for the test of.....

(b) Acetates are..... in water.

(c) Nitrates when treated with conc. H_2SO_4 evolve...... gas.

(d) Chromyl chloride test is performed for.....

(e) Chlorides of are insoluble in dilute HCl.

(f) H₂S is used as a group reagent in...... group in..... medium while in...... group in.....medium.

(g) HgS is..... in dilute HNO₃

(h) Yellow ammonium sulphide dissolves sulphides of.....

(i) Group reagent for third group radicals is.....

(j) If metal ions of group III are ppt. by NH_4CI medium and NH_4OH without prior oxidation by concentrated HNO_3 is not completely ppt..

(k) colour of zinc sulphide is

(I) In V group, K_2CrO_4 is used for the test of.....

(m) ppt. is formed when Na_2HPO_4 is added to magnesium salt in presence of NH_4OH .

(n) Ammonium thiocyanate is used in the detection of.....

Q.15 A compound on heating with an excess of caustic soda solution liberates a gas (B), which gives white fumes on exposure to HCl. Heating is continued to expel the gas completely. The resultant alkaline solution again liberates the same gas (B), when heated with zinc powder. However, the compound (A), when heated alone, does not give nitrogen. Identify (A) and (B).

Q.16 A certain metal (A) is boiled in dilute nitric acid to give a salt (B) and an oxide of nitrogen (C). An aqueous solution of (B) with brine gives a ppt. (D) which is solution in ammonium hydroxide. On adding aqueous solution of (B) to hypo solution, a white ppt. (E) is obtained. (E) on standing turns to a black compound (F). Identify (A) to (F).

Q.17 A yellow solid (A) is unaffected by acids and bases. It is not soluble in water. It dissolves slowly in hot conc. HNO_3 and a brown gas (B) is released. The solid (A) dissolves only in a boiling solution of sodium sulphite giving a clear solution (C). Acidification (C) causes a colourless gas (D) to be liberated, accompanied by an appearance of a milky ppt. (E) in the solution. Identify (A) to (E).

Q.18 State, whether the following statements are true or False:

(a) AgCl dissolve in NH_4OH .

(b) Sb_2S_3 is yellow in colour.

(c) Copper suplhate forms a violet colour with potassium ferrocyanide solution.

(d) Both phosphate and arsenic ions give yellow ppt. when heated with nitric acid and ammonium molybdate.

(e) Addition of ammonium chloride to a sodium containing ferric and magnesium ions is essential for selective precipitation of ferric hydroxide by aqueous ammonia.

(f) Ammonium sulphate can be used in place of ammonium chloride in third group.

(g) lodine is liberated when an iodine in heated with conc. H_2SO_4

(h) It is not necessary to use HNO_3 in the third group if ferric compound is given in a mixture.

(i) In the test of acetate radical, neutral ferric chloride is used.

(j) Nessler's reagent is the alkaline solution of K_2 Hgl₄.

(k) The solubility product of cadmium sulphide is highest amongst the sulphides of second group.

(I) Cobalt can be tested with dimethyl glyoxime.

(m) Cobalt salt with $\mathrm{KNO}_{\mathrm{2}}$ and acetic acid gives yellow ppt..

(n) The carbonates of barium, strontium and calcium are soluble in acid.

Q.19 Explain with proper reasoning.

(a) The aqueous solution of ferric chloride can not be stored. It is always acidified with hydrochloric acid.

(b) The aqueous solution of FeCl_3 , possesses yellow colour. The colour becomes green on passing H₂S gas.

(c) The aqueous solution of $K_2Cr_2O_7$, is orange. On adding an alkali, it turns yellow.

(d) In the test of oxalate, the evolved gas burns with blue flame inly initially.

(e) Why yellow ammonium sulphide is used in group (II) sulphides separation?

(f) Why zinc sulphide is not ppt. when H_2S is passed through ZnCl₂ solution.

(g) $CaSO_4$ is insoluble but it is not ppt. when excess of $(NH_4)_2SO_4$ is added to $CaCl_2$

(h) Why (NH₄CI+NH₄OH) and not $[(NH_4)_2SO_4+NH_4OH]$ is used in group (III) analysis?

(i) Why is it necessary to added few drops of conc. HNO_3 to the filtrate of group (II) before the use of NH_4CI+NH_4OH .

(j) Why NaOH cannot be used to separate $AI(OH)_3$ and $Zn(OH)_2$?

Q.20 A certain salt (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.

Identify the salt (X) and give the equations for the reactions.

Q.21 An aqueous solution of a gas (X) shows the following reactions.

(i) It turns red litmus blue.

(ii) When added in excess to copper sulphate solution deep blue colour is obtained.

(iii) On addition to a ferric chloride solution a brown ppt. soluble in dilute nitric acid is obtained. Identify (X) and give equations for the reactions at steps (ii) and (iii).

Exercise 2

Single Correct Choice Type

Q.1 Which of the following gives a suffocating gas when treated with dilute HCI?

(A) Carbonate	(B) Sulphite
(C) Sulphate	(D) Borate

Q.2 The acidic solution of a salt produces blue colour with KI starch solution. The salt may be

(A) Sulphite	(B) Bromide

(C) Nitrite (D) Chloride

Q.3 Sulphite on treatment with dil, H_2SO_4 liberates a gas which

(A) Turns lead acetate paper black

(B) Burns with blue flame

(C) Smells like vinegar

(D) Turns acidified $K_2Cr_2O_7$ paper green

Q.4 A gas is evolved which burns with blue flame when the mixture is heated with conc. H_2SO_4 . The mixture contains.

(A) Carbonate	(B) Oxalate
(C) Nitrate	(D) Nitrite

Q.5 Mercurous chloride turns black on treatment with ammonium hydroxide. This is due to the formation of

(A) Hg(NH ₂)Cl	(B) Hg ₂ Cl ₂ .NH ₄ OH
(C) Hg and HgNH ₂ Cl	(D) HgCl ₂ .NH ₄ OH

Q.6 Bromine vapours turn starch iodide paper

(A) Violet (B) Blue
--------------	---------

(C) Yellow (D) Red

Q.7 A mixture when heated with dil. H_2SO_4 does not evolve brown vapours but when heated with conc. H_2SO_4 , brown vapours are obtained. The vapours when brought in contact with silver nitrate solution do not give any ppt.. The mixture contains.

(A)	NO_2^-	(B)	NO ₂
• •	/	• • •	ר

(C) Cr (D) Br⁻

Q.8 Ammonium dichromate is used in some fireworks. The green coloured powder blown in air is due to

(A) CrO_{3} (B) $Cr_{2}O_{3}$ (C) Cr (D) $CrO(O_{2})$

Q.9 A mixture, on heating with conc. H_2SO_4 and $MnO_{2'}$ liberates brown vapours of

(A) Br_2 (B) NO_2 (C) HBr (D) I_2

Q.10 A white solid is first heated with dil. H_2SO_4 and then with conc. H_2SO_4 . No action was observed in wither case. The solid salt contains.

(A) Sulphide	(B) Sulphite

(C) Thiosulphate (D) Sulphate

Q.11 A light yellow ppt. is formed in the second group of the qualitative analysis on passing H_2S even when no radical of second group is present. This is due to presence of in the mixture:

(A) Phosphate	(B) Acetate
(C) Oxalate	(D) Nitrate

 $\ensuremath{\textbf{Q.12}}$ On adding water to $\ensuremath{\text{BiCl}_{\scriptscriptstyle 3}}$ solution in HCl, the compound formed is

(A) Bi_2O_3	(B) Bi(OH) ₃
(C) BiOCI	(D) BiOCl ₂

Q.13 The sulphide which is insoluble in 30% HNO₃ is

(A) HgS (B) CuS (C) PbS (D) CdS

Q.14 NiS is separated from ZnS by treating with

(A) NaOH

(B) Conc.HCl

(C) Yellow ammonium sulphide

(D) Aqua-regia

Q15.Soda extract is prepared by

(A) Fusing soda and mixture and then extracting with water

(B) Dissolving NaHCO₃ and misture in dil. HCl

(C) Boiling Na₂CO₃ and mixture in dil. HCl

(D) Boiling Na₂CO₃ and mixture in distilled water

Q.16 When dimethyl glyoxime solution is added to an aqueous solution of nickel (II) chloride followed by ammonium hydroxide:

(A) No ppt. is obtained

(B) A blue coloured ppt. is obtained

(C) A red coloured ppt. is obtained

(D) A black coloured ppt. is obtained

Q.17 An organic salt when heated evolves a coloured gas which bleaches moist litmus paper. The evolved gas is

(A) NO_2 (B) Cl_2 (C) Br_2 (D) l_2

Q.18 Which of the following metal oxides is white in colour but becomes yellow in heating?

(A) AgO (B) Ag₂O (C) FeO (D) ZnO

Q.19 A white ppt. obtained in the analysis of a mixture becomes black on treatment with NH₄OH. It may be.

(A) $PbCl_2$ (B) AgCl (C) $HgCl_2$ (D) Hg_2Cl_2

Q.20 Which one among the following soluble in excess of NaOH?

(A) Fe(OH) ₃	(B) AI(OH) ₃
(C) Cr(OH) ₃	(D) Mn(OH) ₂

Q.21 Which compound does not dissolve in hot dil. HNO_3

(A) HgS (B) PbS (C) CuS (D) CdS

Q.22 An aqueous solution of $FeSO_4Al_2(AO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are

- (A) A colourless filtrate and a green residue
- (B) A yellow filtrate and green residue
- (C) A yellow filtrate and a brown residue
- (D) A green filtrate and a brown residue

Q.23 All ammonium salts liberate ammonia when

- (A) Heated
- (B) Heated with caustic soda
- (C) Heated with H_2SO_4
- (D) Heated with HaNO₂

Q.24 One of the following compounds gives a white ppt. with aqueous AgNO₃ and a green flame test.

(A) NaCl (B) KCl (C) BaCl₂ (D) CaCl₂

Q.25 Which one of the following pairs of ions cannot be separated by H₂S in dilute hydrochloric acid?

(A) Bi ³⁺ , Sn ⁴⁺	(B) Al ³⁺ , Hg ²⁺
(C) Zn ²⁺ Cu ²⁺	(D) Ni ²⁺ , Cu ²⁺

Q.26 When H_2S is passes through an ammonium salt solution X, a white ppt is obtained. The X can be

(A) Cobalt salt	(B) Nickel salt
-----------------	-----------------

(C) Manganese salt (D) Zinc salt

Q.27 The best explanation for the solubility of MnS in dil. HCl in salt

(A) Solubility product of MnCl₂ is less than that of MnS

(B) Concentration of Mn²⁺ is lowered by the formation of complex ions with chloride ions.

(C) Concentration of sulphide ions is lowered by oxidation to free sulphur.

(D) Concentration of sulphide ions is lowered by formation of the weak acid H_2S

Q.28 A white solid is first heated with dilute H_2SO_4 and when with concentrated. No action is observed in either case. The solid contains.

(A) Sulphide	(B) Sulphide
--------------	----	------------

(C) Sulphate (D) Thiosulphate

Q.29 The salt used for performing 'bead test' in qualitative inorganic analysis is

(A) K ₂ SO ₄ .Al ₂ (SO ₄) ₃ .24H ₂ O	
(B) FeSO ₄ .(NH ₄) ₂ SO ₄ .6H ₂ O	
(C) Na(NH ₄)HPO ₄ .4H ₂ O	
(D) CaSO ₄ .2H ₂ O	

Q.30 The only cation present in a slightly acidic solution are Fe^{3+} , Zn^{2+} and Cu^{2+} . The reagent which when added in excess to this solution would identify and separate Fe^{3+} in one step is

(A) 2MHCl	(B) 6 M NH ₃
(C) 6 M NaOH	(D) H ₂ S gas

Q.31 Concentrated aqueous sodium hydroxide can separate a mixture of

(A) AI^{3+} and Sn^{2+}	(B) AI^{3+} and Fe^{3+}
(C) Al ³⁺ and Zn ²⁺	(D) Zn ²⁺ and Pb ²⁺

Q.32 Potassium ferricyanide [potassium hexacyano ferrate (III)] has

(A) Fe(II) (B) Fe(III) (C) Cu(II) (D) Cd(II)

Q.33 Which of the following sulphate is insoluble in water?

(A) $CuSO_4$ (B) $CdSO_4$ (C) $PbSO_4$ (D) $Bi_2(SO_4)_3$

Q.34 Calcium burns in nitrogen to produce a white powder which dissolve in sufficient water to produce a gas (A) and an alkaline solution. The solution on exposure to air produces a thin solid layer of (B) on the surface. Identify the compounds A and B.

(A) C_2H_2 , $CaCO_3$	(B) NH ₃ , CaCO ₃
(C) NH ₃ , Ca(OH) ₂	(D) CH ₄ , CaCO ₃

Q.35 A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white ppt.. The saturated aqueous solution also dissolve magnesium ribbon with the evolution of a colourless gas 'Y'. Identify 'X' and 'Y'.

(A) $X = CO_{2'} Y = CI_{2}$	(B) X=Cl ₂ , Y=CO ₂
(C) X=Cl ₂ , Y=H ₂	(D) $X_2 = H_2$, $Y = CI_2$

Previous Years' Questions

Q.1 A gas 'X' is passed through water to form a saturated solution. The aqueous solution on treatment with silver nitrate gives a white ppt.. The saturated aqueous solution also dissolves magnesium ribbon with evolution of a colourless gas 'Y'. Identify 'X' and 'Y'. (2002)

Q.3 A sodium salt of an unknown anion when treated with MgCl₂ gives white ppt. only on boiling. The anion is **(2004)**

(A)
$$SO_4^{2-}$$
 (B) HCO_3^{-} (C) CO_3^{2-} (D) NO_3^{-}

Q.4 $(NH_4)_2Cr_2O_7$ on heating gives a gas is also given by (2004)

(A) Heating NH_4NO_2 (B) Heating NH_4NO_3 (C) $Mg_3N_2+H_2O$ (D) Na(comp.)+ H_2O_2

Q.5 A metal nitrate reacts with KI to give a black ppt. which on addition of excess of KI convert into orange colour solution. The cation of metal nitrate (2005)

(A) Hg^{2+} (B) Bi^{3+} (C) Sm^{2+} (D) Pb^{2+}

Q.6 A solution when diluted with H_2O and boiled, it gives a white ppt. On addition of excess NH_4CI/NH_4OH , the volume of ppt. decreases leaving behind a white gelatinous ppt. Identify the ppt which dissolves in NH_4OH/NH_4CI . (2002)

(A) Zn(OH) ₂	(B) Al(OH) ₃
(C) Mg(OH) ₂	(D) Ca(OH)

(A) If both assertion and reason are true and reason is the correct explanation of assertion, then mark (a)

(B) If both assertion and reason are true but R is not the correct explanation of assertion, then mark (b)

(C) If assertion is true but reason is false, then mark (c)

(D) If both assertion and reason are false, then mark (d)

Q.7 Statement-I: A very dilute acidic solution of Cd²⁺ and Ni²⁺ gives yellow ppt. of CdS on passing H₂S.

Statement-II: Solubility product of CdS is more than that of NiS. (1989)

Q.8 Statement-I: Sulphate is estimated as BaSO₄, not as MgSO₄.

Statement-II: Ionic radius of Mg²⁺ is smaller than that of Ba²⁺ (1998)

Q.9 An aqueous solution $FeSO_4$. $Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtaining are **(1996)**

(A) A colourless filtrate and a green residue

(B) A yellow filtrate and a green residue

(C) A yellow filtrate and a brown residue

(D) A green filtrate and brown residue

Q.10 In nitroprusside ion the iron and NO exist as Fe (II) and NO⁺ rather than Fe(III) and NO. These forms can be differentiated by (1998)

(A) Estimating the concentration of iron

(B) Measuring the concentration of CN

(C) Measuring the solid state magnetic moment

(D) Thermally decomposing the compound

Q.11 An aqueous solution if a substance gives a white ppt. on treatment with dilute hydrochloride acid, which dissolves on heating. When hydrogen sulphide is passed through the hot acid solution, a black ppt. is obtained. The substance is a **(2000)**

(A) Hg_3^{2+} salt	(B) Cr ²⁺ salt
(C) Ag^+ salt	(D) Pb ²⁺ salt

JEE Advanced/Boards

Exercise 1

Q.1 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 NH_4OH is brought near to it.

(iii) An acidic solution of (X) on addition of NH_4CI and NH_4OH gives a ppt. which dissolves in NaOH solution.

(iv) An acidic solution of (X) does not give a ppt. with H_2S . Identify (X) and give chemical equations for reactions at steps (i) to (iii).

Q.2 An aqueous solution of salt (A) gives white ppt. (B) with NaCl solution. The filtrate gives black ppt., (C) when H_2S is passed into it. Compound (B) dissolves in hot water and the solution gives a yellow ppt., (D) on treatment with sodium iodide and cooling. The compound (A) does not give any gas with dilute HCl but liberates a reddish-brown gas on heating. Identify the compounds (A) to (D).

Q.3 A mixture of two salts was treated as follows:

(a) The mixture was heated with manganese dioxide and concentrated H_2SO_4 when yellowish green gas was liberated.

(b) The mixture on heating with NaOH solution gave a gas which turn red litmus blue.

(c) Its solution in water gave blue ppt. with potassium ferricyanide and red colouration with NH_4CNS .

Q.4 An unknown inorganic compound (X) loses its water of crystallization on heating and its aqueous solution gives the following reactions.

(i) It gives a white turbidity with dilute hydrochloric acid solution.

(ii) It decolourises a solution of iodine in potassium iodide.

(iii) It gives white ppt. with silver nitrate solution which turns black on standing.

Q.5 Identify the compound (X) and give chemical equations for the reactions at steps (i), (ii) and (iii). A certain compound (X) shows the following reactions.

(i) When KI is added to an aqueous suspension of (X) containing acetic acid, iodine is liberated.

(ii) When CO_2 is passed through an aqueous suspension of (X) the turbidity transforms to a ppt..

(iii) When a paste of (X) in water is heated with ethyl alcohol a product of anesthetic use is obtained. Identify (X) and write down chemical equation for reactions at steps (i), (ii) and (iii).

Q.6 Identify the unknown species and complete the following

(i) (A) + dil.H₂SO₄ + K₂Cr₂O₇ \rightarrow (B) green coloured (A) + dil.H₂SO₄ + (C) \rightarrow (B) MnSO₄ (A) + O₂ $\xrightarrow{H_2O}$ (D) (D) + BaCl₂ \rightarrow White ppt. (ii) (A)aq. + Zn \xrightarrow{Heat} (B)gas

(A) aq. + (C)
$$\xrightarrow{\text{Heat}} \text{PH}_3$$

(A) aq. + NH₄Cl $\xrightarrow{\text{Heat}}$ (D) gas

Q.7 (i) A black coloured compound (B) is formed on passing hydrogen sulphide through the solution of a compound (A) in NH_4OH .

(ii) (B) on treatment with hydrochloric acid and KCIO_3 gives (A).

(iii) (A) on treatment with potassium cyanide gives a buff colored ppt. 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 boiled.

(v) The solution of (A) was treated with excess of sodium bicarbonate and then with bromine water. On cooling and shaking for same time, 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 (a) to (e).

Q.8 A colourless solid (A) on hydrolysis produces a heavy white ppt. (B). Solid (A) gives a clear solution in conc. HCl; however, when added to large amount of water, it again gives ppt. (B). When H_2S is passed through a suspensions of (A) or (B), a brown black ppt. of (C) is obtained. Compound (A) liberates a gas (D) on treating with H_2SO_4 . The gas (D) is water soluble and gives white ppt. (E) with solution of mecurous salt but not with mercuric salt. Identify (A) to (E). Also report (A), (B), (C) if (C) is orange ppt..

Q.9 Identify the unknown species and complete the following

- (i) (A) + NaOH $\xrightarrow{\text{Heat}}$ NaCl + NH₃ + H₂O. (ii) NH₃ + CO₂ + H₂O \rightarrow (B). (iii) (B) + NaCl \rightarrow (C) + NH₄Cl.
- (iv) (C) $\xrightarrow{\text{Heat}} Na_2CO_3 + H_2O + (D)$.

Q.10 Element A burns in nitrogen to give an ionic compound B. Compound B reacts with water to give C and D. A solution of C becomes 'milky' on bubbling carbon dioxide. Identify A, B, C and D.

Q.11 An inorganic compound (A) in its aqueous solution produced a white ppt. With NaOH, which gets dissolved in excess of NaOH. The aqueous solution of (A) also produced white ppt. With NH_4OH which also dissolved in excess of NH_4OH . Also its aqueous solution produced light yellow ppt. with $AgNO_3$ solution, soluble in dil. HNO_3 , identify (A).

Q.12 (i) An aqueous solution of a compound (A) is acidic towards litmus and (A) is sublimed at about 300°C.

(ii) (A) on treatment with an excess of NH_4SNC gives a red coloured compound (B) and on treatment with a solution of $K_4[Fe(CN)_6]$ gives a blue coloured compound (C). (iii) (A) on heating with excess of $K_2Cr_2O_7$ in presence of concentrated H_2SO_4 evolves deep red vapours of (D).

(iv) On passing the vapours of (D) into a solution of NaOH and then adding the solutions of acetic acid and lead acetate, a yellow ppt. of compound (E) is obtained.

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

Q.13 An aqueous solution of gas (X) gives the following reactions.

(i) It decolourizes on acidified $K_2Cr_2O_7$ solution.

(ii) On boiling it with H_2O_2 , cooling it and then adding an aqueous solution of $BaCl_2$ a ppt. insoluble in dilute hydrochloric acid is obtained.

(iii) On passing H_2S in the solution, a white turbidity is obtained.

Identify (X) and gives equations for the reactions at steps (i),(ii) and (iii).

Q.14 A colourless solid A, when placed into water, produces a heavy white ppt. B. Solid A gives a clear solution in conc. HCl; however when added to large amount of water, it again gives ppt. of B which dissolves in dilute HCl. When H_2S is passed through the suspension of A or B, a brown black ppt. (C) is obtained. Compound A liberates a gas D with conc. H_2SO_4 . The gas D is water soluble and gives white ppt. E with solution of mercurous salts but not with mercuric salts. Identify A to E.

Q.15 (i) A blue coloured compound (A) on heating gives two products, (B) and (C).

(ii) A metal (D) is deposited on passing hydrogen through heated (B).

(iii) The solution of (B) in HCl on treatment with $K_4Fe(CN)_6$ gives a chocolate brown coloured ppt. of compound (E).

(iv) (C) turns lime water milky which disappears on continuous passage of (C) forming a compound (F). Identify (A) to (F) and give chemical equations for the reactions at steps (i) to (iv).

Q.16 (i) An inorganic compound (A) is formed on passing a gas (B) through a concentrated liquor containing sodium sulphide and sodium sulphite.

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

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

Q.17 A metal chloride (X) shows the following reactions:

(i) When H_2S is passed in an acidified aqueous solution of (X), a black ppt. is obtained.

(ii) The ppt. obtained at step (i) is not soluble in yellow ammonium sulphide.

(iii) When a solution of stannous chloride is added to an aqueous solution of (X) a white ppt. is obtained which turns grey on addition of more of stannous chloride.

(iv) When an aqueous solution of KI is added to an aqueous solution of (X) a red ppt. is obtained which dissolves on addition of excess of KI.

Identify (X) and write down the equations for the reactions at steps (i), (iii) and (iv).

Q.18 A well known orange crystalline compound (A) when burnt imparts violet colour of fame. (A) on treating with (B) and conc. H_2SO_4 gives red gas (C) which gives red yellow solution (D) with alkaline H_2SO_4 gives red gas (C) which gives red yellow solution (D) with alkaline water. (D) on treating with acetic acid and lead acetate gives yellow ppt. (E). (B) sublimes on heating. Also on heating (B) NaOH, gas (F) is formed which gives white fumes with HCl. What are (A) to (F)?

Q.19 Complete and balance the following chemical equations:

- (i) $Au + HCI + HNO_3 \rightarrow \dots + H_2O$
- (ii) $C + HNO_3(conc.) \rightarrow CO_2 + \dots + H_2O$

(iii)
$$Sn + KOH(hot) + H_2O \rightarrow \dots + \dots$$

(iv) $Cu(OH)_2 + NH_4NO_3 + NH_4OH_{(aq)} \rightarrow \dots + H_2O$

Q.20 A gaseous mixture containing (X), (Y) and (Z) gases, when passed into acidified $K_2Cr_2O_7$ solution, gas (X) was absorbed and the solution was turned green. The remainder gas mixture was then pass through lime water, which turns milky by absorbing gas (Y). The residual gas when passed through alkaline pyrogallol solution, it turned black. Identify gas (X), (Y) and (Z) and explain the reaction involved.

Exercise 2

Single Correct Choice Type

Q.1 Which compound does not dissolve in hot dil. HNO_3 ?

(A) HgS (B) PbS (C) CuS (D) CdS

Q.2 An aqueous solution of $FeSO_4Al_2(SO_4)_3$ and chrome alum is heated with excess of Na_2SO_3 and filtered. The materials obtained are

(A) A colorless filtrate and a green residue

(B) A yellow filtrate and a green residue

(C) A yellow filtrate and a brown residue

(D) A green filtrate and a brown residue

Q.3 Magnesium carbonate does not ppt. with the carbonates of group V radicals in presence of NH_4OH and NH_4CI because

(A) MgCO₃ is soluble in water.

(B) MgCO₃ is soluble in NH_4OH

(C) MgCO₃ is soluble in NH_4CI

(D) MgCO₃ is soluble in $(NH_4)_2CO_3$

Q.4 The extent of splitting in d-orbitals is more when the chromium in the solution is in

(A) +1 oxidation state	(B) +2 oxidation state
(C) +3 oxidation state	(D) +6 oxidation state

Assertion Reasoning Type

(A) If both assertion and reason are true and reason is the correct explanation of assertion, then mark (A)

(B) If both assertion and reason are true but reason is not the correct explanation of assertion, then mark (B)

- (C) If assertion is true but reason is false, then mark (C)
- (D) If both assertion and reason are false, then mark (D)

Q.5 Assertion: Ammonium phosphomolybdate is a yellow coloured ppt.

Reason: Yellow colour of compound is due to ammonium ions.

Q.6 Assertion: Ring test for nitrates is performed from the water extract of the salt.

Reason: All nitrates are generally soluble in water.

Q.7 Assertion: In the analysis of group III-radicals NaOH can also be used as group reagent.

Reason: NaOH can be used only in the presence of NaCl as ppt. agent for group III.

Q.8 Assertion: In charcoal cavity test in intimate mixture of salt and Na₂CO₃ is heated on a charcoal block.

Reason: Charcoal cavity test is meant only for coloured salts

Q.9 Assertion: Match-stick test is meant for all sulphur containing radicals.

Reason: Match-stick test is not given by Na₂S.

Q.10 Assertion: CdS and As₂S₃ both have yellow colour.

Reason: CdS and As_2S_3 can be separated by yellow ammonium sulphide.

Comprehension Type

The following observation were made on Na_2CrO_4 and $Na_2Cr_2O_7$

(A) When CO_2 was passed over Na_2CrO_4 , then $Na_2Cr_2O_7$ was formed.

(B) When Zn is added to acidic solution of $Na_2Cr_2O_7$, the colour changes from orange to green, then to blue and then back to green.

(C) Na_2CrO_4 when added to a nitrate salt solution gave a yellow coloured ppt. which after separation and drying followed by flame test gave a green coloured flame.

Q.11 What is the function of CO₂ in the first observation?

(A) Acts as an oxidising agent

- (B) Acts as a reducing agent
- (C) Produces chromium and oxygen
- (C) Makes the solution acidic

Q.12 The reason for the colour $Na_2Cr_2O_7$ solution to first change from orange to green on adding Zn is because

- (A) Zn is reducing agent and changes Cr⁺⁴ to Cr⁺³
- (B) Zn is a reducing agent and changes Cr⁺⁶ to Cr⁺³
- (C) Zn is a reducing agent and it reduces Cr⁺⁶ to Cr⁺²
- (D) None of these

Q.13 The second change in colour in the solution that is from green to blue is due to the conversation of

(A) Cr ⁺³ to Cr ⁺¹	(B) Cr ⁺³ to Cr
(C) Cr ⁺³ to Cr ⁺²	(D) Cr ⁺³ to Cr ⁺⁴

Q.14 The nitrate salt which gives a yellow ppt. with Na_2CrO_4 and yellow ppt. gives green flame with bunsen burner

(A) Pb^{2+} (B) Ca^{2+} (C) Mg^{2+} (D) Ba^{2+}

Previous Years' Questions

Q.1 MgSO₄ on reaction with NH₄OH and Na₂HPO₄ forms a white crystalline ppt. What is its formula? (2006)

(A) Mg(NH ₄)PO ₄	(B) Mg ₃ (PO ₄)
(C) MgCl ₂ . MgSO ₄	(D) MgSO ₄

Q.2 A solution of metal ion when treated with KI gives a red ppt. which dissolves in excess KI in excess KI to give a colourless solution. Moreover, the solution of metal ion on treatment with a solution of cobalt (II) thiocyanate gives rise to a deep blue crystalline ppt. The metal ion is **(2007)**

(A) Pb²⁺ (B) Hg²⁺ (C) Cu²⁺ (D) Co²⁺

Q.3 Passing H_2S gas into a mixture of Mn^{2+} , Ni^{2+} , Cu^{2+} , and Hg^{2+} ions in an acidified aqueous solution ppt. *(2011)*

(A) CuS and HgS	(B) MnS and CuS
(C) MnS and NiS	(D) NiS and HgS

Q.4 The reagents, NH_4CI and aqueous NH_3 will ppt. (1991)

(A) Ca ²⁺	(B) Al ³⁺	(C) Bi ³⁺	(D) Mg ²⁺
(E) Zn ²⁺			

Q.5 Which of the following statement (s) is (are) correct with reference to the ferrous and ferric ions? **(1998)**

(A) Fe³⁺ gives brown colour with potassium ferricyanide

(B) Fe²⁺ gives blue ppt. with potassium ferricyanide

(C) Fe³⁺ gives red colour with potassium ferricyanide

(D) Fe²⁺ gives brown colour with ammonium thiocyanate

Q.6 A solution of colourless salt H on boiling with excess NaOH produces a non-flammable gas. The gas evolution ceases after sometime. Upon addition of Zn dust to the same solution, the gas evolution restarts. The colourless salt (s) H is (are) (2008)

(A) NH_4NO_3	(B) NH_4NO_2
(C) NH ₄ Cl	(D) (NH ₄) ₂ SO ₄

Paragraph 1: p- amino –N, N- dimethylaniline is added to a strongly acidic solution of X. The resulting solution is treated with a few drops of aqueous solution of Y to yield blue colouration due to the formation of methylene blue. Treatment of the aqueous solution of Y with the reagent potassium hexacyanoferrate (II) leads to the formation of an intense blue ppt.. The ppt. dissolves on excess addition of the reagent. Similarly, treatment of the solution of Y with the solution of potassium hexacyanoferrate (III) leads to a brown colouration due to formation of Z.

Q.7 The comp	ound X, i	S	(2009)	
(A) NaNO ₃	(B) NaC	(C) Na ₂ SO ₄	(D) Na ₂ S	
Q.8 The comp	ound Y, is	5	(2009)	
(A) MgCl ₂	(B) FeCl ₂	(C) FeCl ₃	(D) ZnCl ₂	
Q.9 The comp	ound Z, i	S	(2009)	
(A) Mg ₂ [Fe(CN	I) ₆]	(B) Fe[Fe(CN) ₆]		
(C) Fe ₄ [Fe(CN)	6] ³	(D) $K_2 Zn_3 [Fe(CN)_6]_2$		
Q.10 Fe ³⁺ — Se	Q.10 $Fe^{3+} \xrightarrow{SCN^{-}(excess)} Blood red (A)$			
	_	$F^{-}(excess) \rightarrow Colourle$	ess (B)	

Identify A and B. (a) Write IUPAC name of A and B. (b) Find out spin only magnetic moment of B. **(2005)**

Q.11



Identify the metal M and hence, MCl_4 . Explain the difference in colours of MCl_4 and A. (2005)

Paragraph 2: An aqueous solution of a mixture of two inorganic salts, when treated with dilute HCl, gave a precipitate (P) and a filtrate (Q). The precipitate P was found to dissolve in hot water. The filtrate (Q) remained unchanged, when treated with H_2S in a dilute mineral acid medium. However, it gave a precipitate (R) with H_2S in anammoniacal medium. The precipitate R gave a coloured solution (S), when treated with H_2O_2 in an aqueous NaOH medium.

Q.12 The pre	(2013)		
(A) Pb ²⁺	(B) Hg ²⁺	(C) Ag^+	(D) Hg ²⁺

Q.13 The coloured solution S contains (2013)

(A) $\operatorname{Fe}_2(\operatorname{SO}_4)_3$	(B) CuSO ₄
(C) ZnSO ₄	(D) Na ₂ CrO ₄

Q.14 The reagent(s) that can selectively precipitate S^{2-} from a mixture of S^{2-} and SO_{-4}^{2-} in aqueous solution is (are) (2016)

(A) CuCl₂ (B) BaCl₂

(C) $Pb(OOCCH_3)_2$ (D) $Na_2[Fe(CN)_5 NO]$

Q.15 In the following reaction sequence in aqueous solution, the species X, Y and Z, respectively, are

$$S_{2}O^{2}_{3} \xrightarrow{Ag^{+}} X \xrightarrow{Ag^{+}} Y_{\text{White precipitate}} (2016)$$

$$\xrightarrow{\text{With time}} Z_{\text{Black precipitate}}$$

$$(A) \left[Ag(S_{2}O_{3})_{2}\right]^{3-}, Ag_{2}S_{2}O_{3}, Ag_{2}S$$

$$(B) \left[Ag(S_{2}O_{3})_{2}\right]^{5-}, Ag_{2}S_{2}O_{3}, Ag_{2}S$$

$$(C) \left[Ag(SO_{3})_{2}\right]^{3-}, Ag_{2}S_{2}O_{3}, Ag$$

$$(D) \left[Ag(SO_{3})_{3}\right]^{3-}, Ag_{2}S_{2}O_{4}, Ag$$

PlancEssential Questions

JEE Main/Boards

JEE Advanced/Boards

Exercise 1			Exerci	Exercise 1		
Q.2	Q.3	Q.10	Q.1	Q.4	Q.6	
Q.19 (f,i))		Q.11	Q.15	Q.18	
Exercise 2		Exerci	Exercise 2			
Q.2	Q.7	Q.15	Q.5			
Q.24	Q.30					
		Previous Years Questions				
Previous Years' Questions		Q.5	Q.10	Q.11		
Q.2	Q.6					

Answer Key

JEE Main/Boards

Exercise 2

Single Correct Choice Type

Q.1 B	Q.2 C	Q.3 D	Q.4 B	Q.5 C	Q.6 B
Q.7 B	Q.8 B	Q.9 A	Q.10 D	Q.11 A	Q.12 C
Q.13 A	Q.14 B	Q.15 D	Q.16 C	Q.17 A	Q.18 D
Q.19 D	Q.20 B	Q.21 A	Q.22 C	Q.23 B	Q.24 C
Q.25 A	Q.26 D	Q.27 D	Q.28 C	Q.29 C	Q.30 B
Q.31 B	Q.32 B	Q.33 C	Q.34 B	Q.35 C	

Previous Years Questions

Q.1 X-Cl ₂ , Y-H ₂	Q.2 A	Q.3 B	Q.4 A	Q.5 B	Q.6 A
Q.7 C	Q.8 B	Q.9 C	Q.10 C	Q.11 D	

JEE Advanced/Boards

Exercise 2

Single Correct (Choice Type						
Q.1 A	Q.2 C	Q.3 C	Q.4 D				
Assertion Reaso	oning Type						
Q.5 C	Q.6 A	Q.7 D	Q.8 C	Q.9 C	Q.10 B		
Comprehension Type							
Q.11 D	Q.12 B	Q.13 C	Q.14 D				
Previous Years Questions							
Q.1 A	Q.2 B	Q.3 A	Q.4 B, C	Q.5 B, C	Q.6 A, B		
Q.7 D	Q.8 C	Q.9 B	Q.12 A	Q.13 D	Q.14 A, C		
Q.15 A							

Solutions

JEE Main/Boards

Exercise 1

Single Correct Choice Type

Sol 1: It due to the formation of PbCl₂.

Sol.2 (i) Lead salt + sulphide \rightarrow PbS (black)

E.g Pb(CH₃COO)₂ + Na₂S \rightarrow PbS + 2CH₃COONa (ii) HgCl₂ + 2KI \rightarrow Hg I₂ + KCl red Hg I₂ + KCI \rightarrow K₂HgI₄ (soluble) (iii) AgNO₃ + NaCl \rightarrow AgCl + NaNO₃ AgCl + 2NH₄OH \rightarrow Ag(NH₃)₂Cl + 2H₂O (iv) Pb(NO₃)₂ + 2KI \rightarrow Pb I₂ + 2KNO₃

Sol 3: Yellow ammonia sulphide.

YAS = yellow ammonium sulphide $(NH_4)_2 S_x$

The group II A and II B elements are differentiated on the basis of their solubility in YAS.

The group 2A elements are insoluble in YAS and 2B elements soluble in YAS, whereas they are all insoluble in sulphides.

Sol 4: $X + H_2S + acid gas \rightarrow Brown ppt.$

Brown ppt \rightarrow soluble in YAS

 $X + NaOH \rightarrow white ppt \xrightarrow{excess}{NaOH} soluble$

 $X(aq) + FeCl_3 \rightarrow FeCl_2 + \dots$

X is a group 2B salt which gives a brown sulphide $\therefore\,$ X is $Sn^{\scriptscriptstyle +2}$

 $SnCl + NaOH \rightarrow Sn(OH)_2 + 2NaCl$

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

(Strongly reducing)

 $Sn^{+2} + 2FeO_3 \rightarrow Sn^{4+} + 2FeCl_2$

Sol 5: A + $K_2Cl_2O_7 \rightarrow$ Green soluble A = SO_3/H_2S B + Ca(OH)₂ → White ppt ∴ B = CO₂ C + Alkaline pyrogallol → Absorbed ∴ C = O₂ A + B + C + Lead acetate → Does not turn black ∴ A = SO₂; B = CO₂; C = O₂

Sol 6: ZnO, Zn (OH)₂, ZnCO₃ and ZnS

 $Zn(OH)_2 \xrightarrow{\Delta} H_2O + ZnO$ (Yellow when hot

white when cold)

$$ZnCO_3 \rightarrow CO_2 + ZnO$$

 \downarrow
 $Ca(OH)_2 \longrightarrow CaCO_3$

(turns lime water milky)

 $ZnO \xrightarrow{\Delta} no gas$

ZnS $\xrightarrow{\Lambda}$ with dil H₂SO₄ gives H₂S

Sol 7: To decrease the conc. of (OH^{-}) ion in solution as if (NH_{4}^{+}) ion, conc. is high. Due to common ion effect, the conc. of OH^{-} ions is maintained low.

Sol 8: (i) $CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$ $Cu(OH)_2 + (NH_4)_2 SO_4 + 2NH_4OH \rightarrow Cu(NH_3)_4 SO_4 + 2H_2O$ (ii) $BiCl_3 + 2Na_2SnO_2 + 6NaOH \rightarrow 2Bi + 3Na_2SnO_3 + 6NaCl + 3H_2O$ (iii) $2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$ $HgCl_2 + SnCl_2 \rightarrow 2Hg + SnCl_4$ (iv) $SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$

Sol 9: Conc. HNO₃ is added for the (i) Oxidation of metal to its highest oxidation state (ii) No (iii) No. NaOH is a strong base $\therefore \text{ It has high conc of OH} \text{ ions.}$ Sol 10: A(White crystals) $\xrightarrow{\Delta} B_{\text{solid}} + C_{\text{solid}} + C_{\text{so$

Acid (A) : dil HCl of H_2SO_4 $B = H_2S$ $C = \text{conc. HNO}_3$ D = S (yellow ppt)(ii) $A + H_2S \xrightarrow{NH_4OH}$ White ppt. + 2HCl $A = ZnCl_2 + H_2S \xrightarrow{NH_4OH}$ ZnS + 2HCl $ZnCl_2 + NaOH \rightarrow Zn(OH)_2 \xrightarrow{NaOH} Na_2ZnO_2$ (iii) PbS $\xrightarrow{\Delta \text{ in}}_{air} A + PbS \rightarrow Pb + SO_2$ A = PbO

Sol 12: (i) $PbCl_2$ is formed after Ist group partly soluble in water and hence Pb^{2+} ions pass to the first group filtrate, i. e. to the II group and is detected in the test for IInd group as well.

(ii)
$$Hg_2Cl_2 \xrightarrow{NH_4OH} Hg(NH_2)Cl + Hg_{Black}$$

(iii) K_{cn} (CuS) < K_{cn} (ZnS)

lonisation of H_2S is further suppressed in presence of acid (common ion effect).

 \therefore So, when H₂S gas is passed through acidified solution contain Cu²⁺ and Zn²⁺ only. Cu²⁺ ions will precipitate out due to low conc, of S²⁻ ion.

Sol 13: (a) A + BaCl₂ \rightarrow White ppt $A = H_3SO_4$ or some sulphate (b) NaOH + B \rightarrow NH₃(g) $B = NH_4^+$ salt (c) C + MnO⁻₄ + H₂SO₄ \rightarrow Violet vapours C = iodide(d) D + $K_2Cr_2O_7 + H_2SO_4 \rightarrow Green soluble$ D = Some reducing agent (e) E $\xrightarrow{\Delta}$ Yellow component E = ZnO**Sol 14:** (a) CO₃²⁻ (b) Soluble (c) NO_2 (d) Chloride ions (e) Ist group (Pb²⁺ Ag⁺ Hg⁺) (f) II group \rightarrow Acidic medium IV group \rightarrow Alkaline medium (g) Insoluble (h) Group IIB (i) NH₄OH (j) Fe (iron) (k) White (I) Ba²⁺↑ (m) White (n) Co²⁺ + Fe³⁺ ion Sol 15: A $\xrightarrow{\Delta}$ B \uparrow + C $B \xrightarrow{HCI}$ white green $\therefore B = NH_3$ $C \xrightarrow{Zn} B$

$$A \xrightarrow{\Delta} No N_2$$
; $A = NH_4NO_2$

Sol 16: $A = AgNO_3$ $Ag + DilHNO_3 \rightarrow AgNO_3 + NO$ $AgNO_3 + Brine \rightarrow AgCl$ $AgCl \xrightarrow{NH_4OH} Ag (NH)_3Cl$

$$AgNO_{3} + H_{2}S_{2}O_{3} \rightarrow Ag_{2}S_{2}O_{3}$$

$$Ag_{2}S_{2}O_{3} \rightarrow Ag_{2}S$$

$$\therefore A = Ag \qquad B = Ag NO_{3}$$

$$C = NO \qquad D = Ag CI$$

$$E = Ag_{2}S_{2}O_{3} \qquad F = Ag_{2}S$$

Sol 17:

A = sulphur

$$S = \xrightarrow{\text{hot conc HNO}_3} NO_2 + H_2SO_4$$

S $\xrightarrow{\text{Na}_2SO_3} Na_2S_2O_3$ (C)

$$\label{eq:Na2S2O3} \begin{split} \text{Na_2S_2O_3}(\text{acidified}) & \rightarrow \ \underset{\text{white}}{\text{Na2S4O_6} + \text{NaOH}} \end{split}$$

Sol 18: (a) AgCl
$$\xrightarrow{NH_4OH}$$
 Ag(NH₃)₂Cl (soluble)

true

(b) Sb₂S₃ (is orange in colour) false

(c)
$$CuSO_4 + K_4FeCN_6 \rightarrow CuFeCN_6 + K_2SO_4$$

False

(d) True

(e) True

(f) False, sulphates of V group radicals will be precipitated

(g) $I^- \xrightarrow{\text{conc. H}_2SO_4} I_2$ true

(h) False IInd group ferric salts are reduced as H_2S . Hence it is always necessary to use HNO_3 in IIIrd grp.

(i) True 3(CH₃COO⁻)₂Ca + FeCl₃ \rightarrow 2Fe (CH₃COO)₃ + 3CaCl₂

(j) K₂HgI₄ alkaline true

(k) True

(I) False Ni can be tested with dimethyl glyoxime as it forms a colored complex.

(m) Co^{2+} + KNO₃ + acetic acid \rightarrow Yellow ppt.

 $CoCl_2 + KNO_3 \rightarrow K_3[Co(NO_2)_6]$ Yellow

(n) $BaCO_3$, $SnCO_3$, $CaCO_3$ are soluble in acid to give corresponding sulphates or chloride. True

Sol 19: (a) FeCl_3 is a salt of weak base and a strong acid. It readily hydrolyses to form $\text{Fe}(\text{OH})_3$

 $FeCI_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCI$ addition of HCI prevents hydrolysis (b) $\operatorname{FeCl}_3 + \operatorname{H}_2 S \rightarrow 2\operatorname{FeCl}_2 + 2\operatorname{HCl} + S$ yellow green

Due to the reduction of $\mathsf{FeCl}_{\scriptscriptstyle 3^\prime}$ the colour changes.

(c) $K_2Cr_2O_7$ + alkali $\rightarrow CrO_4^{2-}$ + H_2O

the dichromate changes to yellow colored chromate.

(d) CO is evolved along with CO_2 . CO_2 burns with blue flame while CO_2 prevents burning

$$H_2C_2O_4 \xrightarrow{\Lambda} H_2O + CO + CO_2$$

CO diffuses faster than CO_2 . Once CO burns with blue flame, it is put off by CO_2 which diffuse later.

(e) YAS possess excess free sulphur. It combines with group 2B sulphide which convert it and forms Sulphates from soluble complex will $(NH_4)_2S$

E.g: SnS + S
$$\rightarrow$$
 SnS₂
SnS₂ + (NH₄)₂S \rightarrow (NH₄)₂SnS₃

(f) Reaction of $ZnCl_2$ with H_2S produces HCl which dissolve ZnS.

(g) $CaSO_4 \xrightarrow{dissolves} forming a stable complex$

 $CaSO_4 + (NH_4)_2 \rightarrow (NH_4)_2 Ca(SO_4)_2$

(h) Presence of SO_4^{2-} brings preicipitation of group V ion such as Ca^{2+} , Ba^{2+} etc.

(i) Adding of conc. HNO₃ serves 2 purposes

(1) It precipitates the dissolved H₂S

(2) It convert $Fe^{2+} \rightarrow Fe^{3+}$ ions

(j) Al(OH)₃ and Zn(OH)₂ dissolve in NaOH

$$AI(OH)_{3}+NaOH \rightarrow NaAIO_{2} + 2H_{2}O$$
soluble
$$Zn(OH)_{2}+2NaOH \rightarrow Na_{2}ZnO_{2} + 2H_{2}O$$
soluble

Sol 20: X (aq) $\xrightarrow{\Delta}$ Alkaline

 $A \xrightarrow{\Delta} Swells$ to give glassy material

 $X \xrightarrow{Conc, H_2SO_4} Crystals$

X is an alkali metal salt and as it swells up to give a glassy mass, it may be borax.

$$\therefore X \text{ is borax}$$

$$Na_{2}B_{4}O_{7} + 7H_{2}O \rightarrow 2NaOH + 4H_{3}BO_{3}$$

$$Na_{2}B_{4}O_{7} \cdot 10H_{2}O \rightarrow Na_{2}B_{4}O_{7} + 10H_{2}O$$

$$Na_{2}B_{4}O_{7} \xrightarrow{\Delta} 2NaBO_{2} + B_{2}O_{3}$$
glassy mass

 $Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$ weak acid

Sol 21: $X(aq) \rightarrow Red litmus blue$

∴ X is basic

X $\xrightarrow{\text{excess}}$ Deep blue colour X + FeCl₃ → Brown ppt (Soluble in dil. HNO₃) \therefore X must be NH₃ as X + CuSO₄ → Deep blue solution CuSO₄+4NH₃ → Cu(OH)₃ + 3NH₄Cl 3NH₃ + 3H₂O + FeCl₃ → Fe(OH)₃ + 3NH₄Cl Fe(OH)₃+3HNO₃ → Fe(NO₃)₃+H₂O

Exercise 2

Single Correct Choice Type

Sol 1: (B) Sulphite + HCl \rightarrow S (Suffocating)

Sol 2: (C) CuNO₃ + KI(Starch) \rightarrow blue

Sol 3: (D)
$$SO_3^- + dil H_2SO_4 \rightarrow SO_2$$

 \downarrow
 $K_2Cr_2O_7$
Green

Sol 4: (B) Oxalate
$$\xrightarrow{\Delta}$$
 CO + CO₂
 $(C_2O_4^{2^-})$

burns with blue flame

Sol 5: (C)
$$Hg_2CI_2 + NH_4OH \rightarrow Hg + [HgNH_2CI]$$

Sol 6: (B) $Br_2 + KI \rightarrow Blue$

Sol 7: (B) X + dil. $H_2SO_4 \xrightarrow{\Lambda}$ do not evolve brown vapour

X+conc. $H_2SO_4 \xrightarrow{\Delta}$ brown vapours \downarrow AgNO₃ no ppt. Brown vapours = NO₂ X \rightarrow Nitrate NO₃⁻ Sol 8: (B) (NH₄)₂Cr₂O₇ \rightarrow Cr₂O₃

Sol 9: (A) Only brown gas was Br₂

Sol 10: (D)

White solid + dil H₂SO₄
$$\longrightarrow$$

Conc. H₂SO₄
 Δ
No action observed

Salt contains sulphate

Sol 11: (A) IInd group MS (is yellow) When no radical of group II is present ∵ Phosphate is present in mix.

Sol 12: (C) $BiCl_3 + H_2O \rightarrow BiOCl$

Sol 13: (A) HgS is insoluble in dil. HNO₃

Sol 14: (B) NiS and ZnS are seperated by Conc. HCl ZnS dissolved in dil HCl Where ZnS + 2HCl \rightarrow ZnCl₂ + H₂S NiS is insoluble in dil HCl.

Sol 15: (D) Heating Na₂CO₃ mix in distilled water.

Sol 16: (C) Dimethyl glyoxime + Ni \rightarrow Red coloured complex ppt.

Sol 17: (A) NO₂ bleaches moist litmus paper.

Sol 18: (D) $Z_{nO} \xrightarrow{\Delta} Z_{nO}$ white $\xrightarrow{\Delta}$ yellow

Sol 19: (D) White ppt + $NH_4OH \rightarrow black$ Compound is Hg_2Cl_2 $Hg_2Cl_2 + NH_4OH \rightarrow Hg + [HgNH_2Cl]$

Sol 20: (B) $Al(OH)_3 + NaOH (excess) \rightarrow Na[Al(OH)_4]$ Soluble complex

Sol 21: (A) HgS does not dissolve in hot dil. HNO₃.

Sol 22: (C) An aqueous solution of $FeSO_4Al_2(AO_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The materials obtained are a yellow filtrate and a brown residue

Sol 23: (B) NH_{4}^{+} (salt) + NaOH $\xrightarrow{\Delta}$ NH_{3}

Sol 24: (C) Green frame :. Cation is Ba²⁺

 $BaCl_2 + 2Ag^+ \rightarrow 2AgCl + Ba^{2+}$ White

Sol 25: (A) Bi and Sn both belong to IInd group. Both give precipitate.

Sol 26: (D) $H_2S + NH_4OH + X \rightarrow$ White ppt.

ZnCl₂

 \therefore X = Zinc salt

Sol 27: (D) Conc. of S^{2-} ion is covered by formation of weak acid H_2S .

Sol 28: (C) A white solid is first heated with dilute and when with concentrated. No action is observed in either case. The solid contains sulphate.

Sol 29: (C) Bead's test's salt is Na(NH₄)HPO₄. 4H₂O

Sol 30: (B) To separate Fe from Zn and Cu, use excess NH_{3}

Sol 31:(B) Al and Fe can be separated by NaOH excess Al + NaOH \rightarrow Al(OH)₃

 $AI(OH)_3 + NaOH \rightarrow NaAIO_2$

Sol 32: (B) K₄[Fe(CN)₆], Fe⁺³ ferricyanide

Sol 33: (C) $PbSO_4$ is water insoluble.

Sol 34: (B) Ca + N₂ \rightarrow Ca₃N Ca₃N + 6H₂O \rightarrow 3Ca(OH)₂ + NH₃ Ca(OH)₂ + CO₂ \rightarrow CaCO₃ \therefore gas = NH₃ and solid = CaCO₃

Sol 35: (C) $X + H_2O \rightarrow$ Saturated solution X(ag) + AgNO₃ \rightarrow White ppt. AgCl X(ag) + Mg \rightarrow Colourless gas MgCl₂ X = Cl₂; Y = H₂

Previous Years' Questions

Sol 1:
$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

'X'
 $HCl + AgNO_3 \longrightarrow AgCl \downarrow (White) + HNO_3$
 $2HCl + Mg \longrightarrow MgCl_2 + H_2(g) \uparrow Y$
y

Sol 2: (A)
$$SO_3^{2-} + H_2SO_4 \longrightarrow SO_2^{2-} + H_2O + SO_4^{2-}$$

SO₂ is a colourless gas with irritating odour.

$$SO_2 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

Green
solution

Sol 3: (B) A sodium salt of an unknown anion when treated with MgCl gives white precipitate (MgCO₃) only on boiling. Hence, the action must be HCO_3^- ion.

Sol 4: (A) Both $(NH_4)_2Cr_2O_7$ and NH_4NO_2 on heating gives nitrogen gas.

Sol 5: (B) $Bi^{3+} + 3I^{-} \longrightarrow BiI_{3} \downarrow \xrightarrow{I^{-}}_{Black} BiI_{4}]^{-} \xrightarrow{Canage}_{Solution}$

Sol.6: (A) $Zn^{2+} + 2H_2O \longrightarrow Zn(OH)_2 \downarrow + 2H^+$ White

Sol 7: (C) Cation Cd^{2+} belongs to group II white Ni^{2+} belongs to group I of analytical group. Group II radicals are precipitated by passing $H_2S(g)$ through acidic solution of salt but radicals of group III are precipitated by passing $H_2S(g)$ in NH_3/NH_4Cl buffer solution of salt due to greater solubility products of later salts.

Sol 8: (B) As $MgSO_4$ is soluble in water, so not used for estimation of SO_4^{2-} ion.

Sol 9: (C) Yellow filtrate contain CrO_5 and brown residue contain Fe_2O_3 .

Sol 10: (C) Fe(II) and Fe(III) will have different values of magnetic moment due to different number of unpaired electrons in their d-orbitals.

Sol 11: (D) $PbCl_2$ is soluble in hot water and PbS (black) is formed on passing $H_2S(g)$ through acidic solution.

JEE Advanced/Boards

Exercise 1

Sol 1: X (Lewis acid \rightarrow fumes in moist air)

 $X + NH_4OH \rightarrow$ fumes intensity increases

X (acidic) + NH_4CI + $NH_4OH \rightarrow ppt \rightarrow soluble in NaOH$ X + $H_3S \rightarrow No ppt$.

X is some chloride as its fumes increases in presence of NH_4OH

 $X + NH_4CI + NH_4OH \rightarrow ppt \rightarrow soluble in NaOH$

 \therefore X = AlCl₃ or ZnCl₂

But X is a Lewis acid \therefore X = AlCl₃

Sol 2: $A(aq) \xrightarrow{NaCl} B(ppt) + O$ solution

 $C \xrightarrow{H_2S} Black ppt$

 $\mathsf{B} \xrightarrow{\mathsf{hot water} + \mathsf{Na I}_2} \to \mathsf{Yellow ppt.}$

A $\xrightarrow{\text{dil. HCl}}$ X no gas reddish brown gas

 $A = Pb(NO_3)_2$

$$B = PbCl_2$$

Pb $\xrightarrow{H_2S}$ PbS (black)

 $Pb^{2+} + KI \rightarrow Pbl_2$ yellow

Sol 3: Salt + MgO₂ $\xrightarrow{\text{Conc. H}_2\text{SO}_4}$ Yellow greenish gas Mix + NaOH $\xrightarrow{\Delta}$ Red litmus blue X (aq) \rightarrow Blue ppt K₄(Fe₃CN₃)

and let NH₄CNS

Mix $\xrightarrow{K_2HgI_4}$ brown ppt.

The mixture contains $Fe^{_{+2}}$ and $Fe^{_{+3}}$ (from NH_4^+) (from test b and d) and Cl^- from test A.

: The reactions are Cl⁻ + MgO $\xrightarrow{\text{Conc, H}_2\text{SO}_4}$ Cl₂

$$NH_4^+ + NaOH \longrightarrow NH_3$$

$$Fe^{+2} \rightarrow K_4 FeCN_3$$

 $Fe^{+3} \rightarrow Blue ppt will be K_4 FeCN_6$

$$NH_3 \xrightarrow{K_2HgI_4} Brown ppt.$$

Sol 4: X . nH₂O
$$\xrightarrow{\Delta}$$
 X + nH₂O

 $X(aq) \xrightarrow{\text{with dil HCI}} White turns brown$

 $KI + X \rightarrow Decolourises$

Ag NO₃ + X
$$\rightarrow$$
 White ppt
black or strong

X containing $S_2O_3^{2-}$ as it decolourises I⁻ which also coincides with the other 2 statement I and (II)

hence the compound is $Na_2S_2O_3$. $5H_2O$

$$Na_2S_2O_3$$
. $5H_2O \xrightarrow{\Delta} Na_2S_2O_3 + 5H_2O^{\uparrow}$

(i)
$$Na_2S_2O_3 + 2HCI \rightarrow 2NaCI + H_2O$$

(ii)
$$2Na_2S_2O_3+I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

(iii)
$$Na_2S_2O_3 + 2AgNO_3 \rightarrow Ag_2S_2O_3\downarrow + 2NaNO_3$$

White ppt.

$$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S\downarrow + H_2SO_4$$

Black

Sol 5: $X + CH_3COO^- + KI \rightarrow I_2$ $CO_2 + aq(X) \rightarrow ppt.$ $X (H_2O) + ethyl alcohol \rightarrow$ Product = Ester $X = CaOCl_2$ bleaching powder (i) $CaOCl_2 + CH_3COOH \rightarrow (CH_3COO)_2 Ca + Cl_2 + H_2O$ $2KI + Cl_2 \rightarrow 2KCl + I_2$ (ii) $CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$ (iii) $CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2$

```
C_2H_5OH + Cl_2 \rightarrow CH_3CHO + 2HCl
CH_3CHO + 3Cl_2 \rightarrow CCl_3CHO + 3HCl
CCI_3CHO + 2Ca(OH)_2 \rightarrow CHCI_3 + (HCOO)_2Ca
Sol 6: A = SO<sub>2</sub>
SO_2 + dil. H_2SO_4 + K_2Cr_2O_7 \rightarrow K_2SO_4 + Cr_2(SO_4)_3
SO_2 + dil. H_2SO_4 + KMnO_4 \rightarrow MnSO_4
SO_2 + O_2 \rightarrow H_2SO_4
H_2SO_4 + BaCl_2 \rightarrow BaSO_4
A = SO_2
B = Cr_2(SO_4)_3
C = KMnO_{4}
D = H_2SO_4
Sol 7: (i)A(aq) + Zn \xrightarrow{\text{heat}} B
A(aq) + C \xrightarrow{heat} PH_{2}
A(aq) + NH_{A}CI \rightarrow (D) gas
(ii) A = NaOH/KOH C = P_A
B = H_{2}
                                   D = NH_{2}
      : CoS
CO
 \downarrow
                               \downarrow
A + H_2S \xrightarrow{NH_4OH} B (black)
B CoS + HCI + KCIO_3 \rightarrow A(CoCl_2)
A_{(COCl_2)} + KCN buff coloured ppt.
       А
     Excess
     reagent
   C
Co(CN)<sub>6</sub>
A_{COCI_2}(aq) \xrightarrow{\Delta} B
A + NaHCO<sub>3</sub> (excess) \rightarrow \xrightarrow{Br_2}_{H_2O}
A = CoCl_2
B = CoS
C = K_{A}[Co(CN)_{c}]
E = 2Na_3Co(CO_3)_3 Green
CoCl_2 + H_2S + NH_4OH \rightarrow CoS (black)
CoS + HCI + KCIO_3 \rightarrow CoCI_2
CoCl_2 + KCN \rightarrow K_3 [Co(CN)_6]
```

 $CoCl_2 + NaHCO_3 \rightarrow Na_4Co(CO_3)_3 + H_2O + 3CO_2$ $Br_2 + H_2O \rightarrow HBr + O$ $2Na_4Co(CO_3)_3 + H_2O + O \rightarrow 2Na_3Co(CO_3)_3 + NaOH$ sod. cobalt carbonate (green) **Sol 8:** A + H₂O $\xrightarrow{\Delta}$ White ppt. (B) A + conc. HCl \rightarrow Clear solution Excess H₂O B precipitate A/B $\xrightarrow{H_2S}$ Brown / Black ppt. (C) $A + H_2SO_4 \rightarrow D$ $D + Hg^{+}(Salt) \rightarrow White E$ \therefore D = Cl₂, E = Hg₂Cl₂ $A = BiCl_2$, B = BiOCl, C = BiS $D = HCI, E = Hg_2CI_2$ $BiCl_3 + H_2O \rightarrow Bi(OH)_3 + 2HCl$ $Bi(OH)_3 + HCI \rightarrow Clear BiCl_3$ $BiCl_3 + H_2O$ (Excess) $\rightarrow BiOCl$ $BiCl_3 + H_2S \rightarrow BiS$ (Brownish black) $D = HCl and E = Hg_2Cl_2$ **Sol 9:** A = NH₂Cl $B = NH_{A}HCO_{2}$ $C = NaHCO_3$ $NH_{A}CO_{3} + NaCI \rightarrow NaHCO_{3} + NH_{A}CI$ $NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$ $D = CO_2$. **Sol 10:** $A + N_2 \rightarrow B$ $B = H_2O \rightarrow C + D$ $C + CO_2 \rightarrow Milky sol^n$ \therefore C = Ca(OH)₂ A = Ca $B = Ca_{3}N_{3}$ $C = Ca(OH)_{2}$ $D = NH_{2}$

A contains $S_2O_3^{2-}$ ion from (ii) and A = Na₂S₂O₃ SO_2 + conc. EtOH + NaS + NaSO₂ \rightarrow Na₂S₂O₃ $Na_2S_2O_3 + dil AgNO_3 \rightarrow Ag_2S_2O_3$ White ppt. AgS (Black) $FeCl_3 + 3Na_2S_2O_3 \rightarrow Fe_2(S_2O_3)_3 + 3NaCl_3$ Violet $CuCl_2 + Na_2S_2O_3 \rightarrow NH_4[Cu_6(S_2O_3)_5]$ Sol 17: MCI MCl + H_2S (acidified) \rightarrow black ppt (not soluble in YAS) .:. MS is group IIA $SnCl_2 + X \rightarrow White ppt. \xrightarrow{SnCl_2} Grey$ $KI + X \rightarrow Red ppt. \xrightarrow{Excess} Dissolve$ Acc. To these facts, $X = HgCl_2$ $\mathsf{HgCl}_{_2} + \mathsf{H}_{_2}\mathsf{S} \xrightarrow[]{\mathsf{H}^+} \mathsf{HgS} + 2\mathsf{HCl}$ $2\text{HgCl}_2 + \text{SnCl}_2 \rightarrow \frac{\text{Hg}_2\text{Cl}_2 + \text{SnCl}_4}{\text{White}}$ $\operatorname{HgCl}_{2} + \operatorname{SnCl}_{2} \rightarrow \operatorname{Hg}_{\operatorname{Grev}} + \operatorname{SnCl}_{4}$ $\mathrm{HgCl}_{_{2}} + 2\mathrm{KI} \rightarrow \mathrm{HgI}_{_{2}} + 2\mathrm{KCI}_{_{\mathrm{Red}}}$ Hg I₂ + 2KI \rightarrow K₂HgI₄ **Sol 18:** A $\xrightarrow{\Delta}$ Violet colour flame .: A contains Cr A + B + conc. $H_2SO_4 \rightarrow C$ (Red gas) $C + alk H_2SO_4 \rightarrow Red yellow solution D$ $D + CH_2COOH \rightarrow$ Yellow ppt. $B + NaOH \rightarrow F$ (fumes) \therefore F = NH₂ B = NH₄Cl $C = CrO_2Cl_2$ $D = Na_2CrO_4$

 $E = PbCrO_4$ $A = K_2Cr_2O_7$

Sol 19: (i) Au + HCl + HNO₃ \rightarrow HAuCl₄ + 3NO₂ + 3H₂O (ii) C + 4HNO₃ (conc) \rightarrow CO + 4NO₂ + 2H₂O (iii) Sn + 2KOH (hot) + H₂O \rightarrow K₂SnO₃ + 2H₂ (iv) Cu(OH)₂ + 2NH₄NO₃ + 2NH₄OH \rightarrow Cu(NH₃)₄(NO₃)₂ + 4H₂O

Sol 20: $K_2Cr_2O_7 + (Mix) \rightarrow X$ absorbed solution green solution $(Y + Z) + Ca(OH) \rightarrow Milky$ (Z) Alkali pyragallol \rightarrow Black $\therefore Z = O_{2'}Y = CO_2X = SO_2$ (i) $3SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow H_2SO_4 + Cr_2(SO_4)_3 + H_2O$ (ii) $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$ (iii) $O_2 + Pyragallol \rightarrow Absorbed$

Exercise 2

Single Correct Choice Type

Sol 1: (A) Theoretical : HgS does not dissolve in hot dil. HNO_3 .

Sol 2: (C) FeSO₄. Al₂(SO₄) and chrome alum + Na₂SO₃ $\xrightarrow{\Delta}$ (C) a yellow filtrate and brown residue.

Sol 3: (C) MgCO₃ is soluble in NH₄Cl forming MgCl₂.

Sol 4: (D) Excess of splitting ∞ oxidation state.

Assertion Reasoning Type

Sol 5: (C) Yellow colour of compound is not due to NH_4^+ ion (as NH_4^+ ion does not impart colour to its molecules).

Sol 6: (A) (A) Both statements are true.

Sol 7: (D) both statements are false as NaOH will react with salt and not form ether hydroxide.

Sol 8: (C) Charcoal cavity test can only be used for non coloured salt,.

Sol 9: (C) All S containing molecules give match state test.

Sol 10: (B) Both Statement true but reason does not explain assertion.

Comprehension Type

Sol 11-14: (D, B, C, D)

(a)
$$Na_2CrO_4 + CO_2 \rightarrow Na_2Cr_2O_7$$

(b) Zn + acidic
$$Na_2Cr_2O_7 \rightarrow Green Cr_2O_3$$

Orange

I

 CO_2 acts to make the solution acidic $H_2O + CO_2 \rightarrow H_2CO_3$ Zn is the reducing agent Cr^{+6} to Cr^{+3} Cr^{+3} to Cr^{+2} (blue in colour)

Previous Years' Questions

Sol 1: (A) $MgSO_4 + NH_4OH + Na_2HPO_4 \longrightarrow$ $Mg(NH_4)PO_4 \downarrow + Na_2SO_4 + H_2O_{white}$

Sol 2: (B) $Hg^{2+} + 2I^{-} \longrightarrow HgI_{2}$ (red)

 $\begin{array}{l} \mathsf{HgI}_{2} + 2\mathsf{KI} \longrightarrow \mathsf{K}_{2}[\,\mathsf{HgI}_{4}]\\ \mathsf{Hg}^{2+} + \mathsf{Co}(\mathsf{SCN})_{2} \longrightarrow \mathsf{Co}[\,\mathsf{Hg}(\mathsf{SCN})_{4}]\\ \end{array}$

Sol 3: (A) In acidic medium, H_2S is very feebly ionized giving very small concentration of sulphide ion for precipitation. Therefore, the most insoluble salts CuS and HgS are precipitated only.

Sol 4: (B, C) Both Al^{3+} and Bi^{3+} are precipitated as their hydroxides.

Sol 5: (B, C) The blue precipitate of Fe^{2+} ion with potassium ferricyanide is due to formation of Turnbull's blue KFe[Fe(CN)₆].

 $Fe^{2+} + K_{3}[Fe(CN)_{6}] \longrightarrow KFe[Fe(CN)_{6}] + 2K^{+}$

The red colour of Fe^{3+} ion with potassium thiocyanate is due to formation of $[Fe(SCN)_3]$.

 $Fe^{3+} + 3KSCN \longrightarrow [Fe(SCN)_3] + 3K^+$ red coloured

Sol 6: (A, B) $NH_4NO_3 + NaOH \longrightarrow NaNO_3 + NH_3 + H_2O$

 $NH_4NO_2 + NaOH \longrightarrow NaNO_2 + NH_3 + H_2O$

Sol 7: (D) Sol 8: (C) Sol 9: (B)

The comprehension describing methylene-blue test.





Blue solution

Therefore,

```
1. X is Na<sub>2</sub>S
```

```
2. Y is FeCl<sub>3</sub>
```

3. Compound Z is Fe[Fe(CN)₆]

Sol 10: (a) $Fe^{3+} + 3SCN^{-} \longrightarrow [Fe(SCN)_{3}]$ (blood red colouration)

 $\operatorname{Fe(SCN)}_{3} + \operatorname{F}^{-}(\operatorname{excess}) \longrightarrow \operatorname{[FeF_{6}]}^{3-} + \operatorname{3SCN}^{-}_{R}$

(b) Magnetic moment (μ_s) = $\sqrt{n(n+2)}$ BM

 $=\sqrt{3S}$ BM

= 5.92 BM

Sol 11: $MCl_4 \xrightarrow{Zn}$ Purple coloured compound (A) $M \xrightarrow{moist} B$ (white fumes)

tr. metal air

$$\Rightarrow$$
 M = Ti, A=[Ti(H₂O)₆]³⁺; B = TiO₂

Ti (IV) contains no d-electron, while d-d transition of single electron of Ti (III) will cause colour change.

Sol 12: (A)
$$Pb^{+2} + 2HCI \rightarrow PbCI_2 \xrightarrow{Hot} Soluble$$

Sol 13: (D)
 $Pb^{+2} + 2HCI \rightarrow PbCI_2 \xrightarrow{Hot} Soluble$
 $Cr^{+3} \xrightarrow{H_2S} Cr(OH)_3 \downarrow$
 $Cr(OH)_3 \xrightarrow{NaOH} Na_2CrO_4$
 $Yellow solution$
Sol 14: (A, C) (A) $CuCI_2 + S^{-2} \rightarrow CuS_{Black ppt} \downarrow + 2CI^-$
 $CuCI_2 + SO_4^{-2} \rightarrow No. ppt$
(B) $BaCI_2 + S^{-2} \rightarrow BaSO_4 \downarrow 2CI^-$
 $White ppt$
(C) $Pb(OAc)_2 SO^{-2} \rightarrow PbSO_4 \downarrow + 2CH_3 - COO^-$
 $Pb(OAc)_2 + S^{-2} \rightarrow PbSO_4 \downarrow + 2CH_3 - COO^-$
 $Black ppt$
PbS can be selective ppt out first as K is much less the selective ppt of the se

PbS can be selective ppt out first as $\rm K_{sp}$ s much less than $\rm K_{sp}$ of $\rm PbSO_4$

Sol 15: (A)

$$S_2O^{2-3} \xrightarrow{Ag^+} \left[Ag(S_2O_3)_2\right]^{3-}$$

 $\xrightarrow{Ag^+} Ag_2S_2O_3 \rightarrow Ag_2S$ (Black ppt)
(Y)