

Chapter

Analytical chemistry deals with qualitative and quantitative analysis of substances.

Qualitative analysis: A salt consists of two parts known as radicals. The positively charged part of a salt (cation) which has been derived from a base is termed as basic radical and the negatively charged part of salt (anion) which has been derived from an acid is termed as acidic radical. In qualitative inorganic analysis, the given compound is analysed for the basic and acid radicals (*i.e.*, the cations and the anions), that it contains. For example zinc blende is analysed for the Zn^{2+} and S^{2-} ions that it contains.

Test for Different Gases

(1) Colourless gases

(i) Tests for ${\it CO}_2$: It is colourless and odourless gas. It gives white ppt. with lime water which dissolves on passing excess of ${\it CO}_2$.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$$
Lime water White ppt.

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

White ppt. Excess So lub le

- (ii) *Test for CO*: It is colourless and odourless gas. It burns with a blue flame. $2CO + O_2 \rightarrow 2CO_2$
- (iii) *Test for O_2*: It is colourless and odourless gas. It rekindles a glowing splinter.

(iv) Tests for H_2S : It is a colourless gas with a smell of rotten eggs. It turns moist lead acetate paper black.

$$(CH_3COO)_2Pb + H_2S \rightarrow 2CH_3COOH + PbS_{Black}$$

(v) **Tests for SO_2:** It is a colourless gas with a suffocating odour of burning sulphur. It turns acidified $K_2Cr_2O_7$ solution green.

$$3SO_2 + K_2Cr_2O_7 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O_{Green}$$

(vi) *Tests for NH*₃: It is a colourless gas with a characteristic ammonical smell. It gives white fumes of NH_4Cl with HCl, $NH_3 + HCl \rightarrow NH_4Cl$. With Nessler's

reagents, it gives brown ppt.

$$2K_2[HgI_4] + NH_3 + KOH \rightarrow NH_2HgOHgI + 7KI + 2H_2O$$
Nessler's reagent

lodine of Millon's base
(Brownpp)

It gives deep blue colour with $CuSO_4$ solution, $CuSO_4 + 4NH_3 \rightarrow \left[Cu(NH_3)_4\right]SO_4$. NH_3 dissolves in $O(NH_3)$

water to give NH_4OH , which being basic, turns red litmus blue, $NH_3 + H_2O \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$.

(vii) **Tests for HCl gas**: It is colourless gas with a pungent irritating smell. It turns moist blue litmus paper red i.e., it is acidic in nature. It gives white ppt. with $AgNO_3$ solution. This white ppt. is soluble in NH_4OH . $HCl + AgNO_3 \rightarrow AgCl + HNO_3$;

$$AgCl + 2NH_4OH \rightarrow \left[Ag(NH_3)_2\right] + 2H_2O$$
.
Soluble

(viii) *Test for CH*₃*COOH vapours* : These vapours are colourless with a vinegar like smell.

(2) Coloured gases

- (i) **Tests for Cl₂:** It is a greenish yellow gas with a pungent smell. In small quantity it appears almost colourless. It bleaches a moist litmus paper, $Cl_2 + H_2O \rightarrow 2HCl + [O]$; $Colour + [O] \rightarrow Colourless$. Blue litmus paper first turns red and then becomes colourless.
- (ii) *Tests for Br_2*: Brown vapours with a pungent smell. It turns moist starch paper yellow.
- (iii) *Tests for I_2*: Violet vapours with a pungent smell. It turns moist starch paper blue.
- (iv) $\textit{Tests for NO}_2$: Brown coloured pungent smelling gas. It turns moist starch KI paper blue

$$2KI + 2NO_2 \rightarrow 2KNO_2 + I_2$$
; $I_2 + Starch \rightarrow Blue\ colour$.

It turns ferrous sulphate solution black,

$$3FeSO_4 + NO_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + FeSO_4 \cdot NO + H_2O_4 \cdot NO +$$

Systematic Procedure for Qualitative Analysis of Inorganic Salts

It involves the following steps: (1) Preliminary tests (2) Wet tests for acid radicals and (3) Wet tests for basic radicals.

(1) Preliminary tests

(i) **Physical examination**: It involves the study of colour, smell, density etc.

Table: 21.1 Colour

Colour	Salt		
Black	Oxides: MnO_2 , FeO , CuO , Co_3O_4 , Ni_2O_3		
	Sulphides :		
	Ag_2S , CuS , Cu_2S , FeS , CoS , NiS ,		
	PbS , HgS , Bi_2S_3 (blackish brown)		
Blue	Hydrated $CuSO_4$, anhydrous $CoSO_4$		
Orange	KO_2 , some dichromate $(K_2Cr_2O_7)$, Sb_2S_3 ,		
	ferricyanides		
Green	Nickel salts, hydrated ferrous salts,		
	potassium permanganate (KMnO_4) , some		
	copper (II) salts		
Brownish	SnS		
yellow			

Dark brown	PbO_2 , Ag_2O , CdO , Fe_2O_3 , $CuCrO_4$, $FeCl_3$ (but yellow in aq. solution)
Pale brown	MnCO ₃
Light pink	Hydrated manganese salts
Reddish pink	Hydrated cobalt (II) salts
Red	HgI_2, Pb_3O_4
Yellow	CdS , PbI_2 , AgBr , AgI , chromates

(ii) $\ensuremath{\textit{Dry heating}}$: Substance is heated in a dry test tube.

Table : 21.2

Observation	Result
(a) A gas or vapour is	Compounds with water
evolved.	of crystallisation
Vapour, evolved, test	Ammonium salts, acid
with litmus paper.	salts, and hydroxides.
	(usually accompanied by
	change of colour)
The vapour is alkaline.	Ammonium salts.
The vapour is acidic.	Readily decomposable
	salts of strong acids.
Oxygen is evolved	Nitrates,chlorates and
	certain oxides.
Dinitrogen oxide	Ammonium nitrate or
	nitrate mixed with an ammonium salt.
Dark-brown or reddish	Nitrates and nitrites of
fumes (oxides of	heavy metals.
nitrogen), acidic in	neavy metais.
reaction.	
CO ₂ is evolved, lime	Carbonates or hydrogen
water becomes turbid.	carbonates.
NH ₃ is evolved which	Ammonium salts.
turns red litmus blue.	
SO ₂ is evolved, which	Sulphates and
turns acidified $K_2Cr_2O_7$	thiosulphates.
green, decolourises	
fuschin colour.	
H_2S is evolved, turns	Hydrates, sulphides or
lead acetate paper black,	sulphides in the presence
or cadmium acetate	of water.
yellow.	
Cl_2 is evolved, yellowish	Unstable chlorides e.g.,
	copper chlorides in the

green gas, bleaches	presence of oxidising
litmus paper, turns KI -	agents.
starch blue, poisonous.	
Br_2 is evolved (reddish	Bromides in the presence
brown, turns fluorescent	of oxidising agents.
paper red).	
I_2 is evolved, violet	Free iodine and certain
vapours condensing to	iodides
black crystals	
(b) A sublimate is formed	Ammonium and mercury
	salts.

White sublimate	As_2O_3 , Sb_2O_3
Grey sublimate	Нд
Steel grey, garlic odour	As
Yellow sublimate	S , As_2S_3 $HgI_2(\text{Re }d)$

Action of heat on different compounds: Many inorganic salts decomposes on heating, liberating characteristic gases. A few such reactions are tabulated as follows,

Table : 21.3

$2HgO \xrightarrow{\Delta} 2Hg + O_2$ (Red) (Silvery deposit)	$2Pb_3O_4 \xrightarrow{\Delta} 6PbO + (Yellow)$	\mathcal{O}_2	$2PbO_2 \xrightarrow{\Delta} 2PbO + O_2$ (Brown)
$CuCO_{3} \xrightarrow{\Delta} CuO + CO_{2}$ (Green)	$ZnO_3 \xrightarrow{\Delta} ZnO + CO_2$ $(White) \xrightarrow{White(cold)} Vhite(cold)$		$CuSO_{4}.5H_{2}O \xrightarrow{\Delta} CuSO_{4} + 5H_{2}O$ (White)
$CuSO_4 \xrightarrow{\Delta} CuO + SO_3$	$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + S$	$SO_2 + SO_3$	$2Ag_2O \rightarrow 4Ag + O_2$
$2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$ (White) (Brown)	$2AgNO_3 \xrightarrow{450^{\circ}C} 2Ag +$	$2NO_2 + O_2$	$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2$
$2Ag_2CO_3 \rightarrow 4Ag + 2CO_2 + O_2$	$2Pb(NO_3)_2 \rightarrow 2PbO + 4$	$NO_2 + O_2$	$ (NH_4)_2 Cr_2 O_7 \rightarrow N_2 + Cr_2 O_3 + 4H_2 O $ (Orange) (Green)
$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$	$NH_4HCO_3 \rightarrow NH_3 + C$	$O_2 + H_2O$	$CaCO_3 \rightarrow CaO + CO_2$
$2NaNO_3 \rightarrow 2NaNO_2 + O_2$	$MgCO_3 \rightarrow MgO + CO_2$		$2NH_3 \xrightarrow{\text{Red hot}} N_2 + 3H_2$
$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$	$2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$		$Al_2(SO_4)_3 \xrightarrow{\text{Red hot}} Al_2O_3 + 3SO_3$
$2CaSO_4.2H_2O \rightarrow 2CaSO_4.H_2O + 2H_2O$ (Plaster of Paris)	$2AlCl_3.6H_2O \rightarrow Al_2O_3 + 6HCl + 9H_2O$		$2BeSO_4 \xrightarrow{\Delta} 2BeO + 2SO_2 + O_2$
$2AgNO_3 \xrightarrow{350^{o}C} 2AgNO_2 + O_2$	$2MgSO_4 \xrightarrow{\Delta} 2MgO + 1$	$2SO_2 + O_2$	$2ZnSO_4 \xrightarrow{\Delta} 2ZnO + 2SO_2 + O_2$
$(COO)_2 Sn \xrightarrow{\Delta} SnO + CO_2 + CO$	$CaC_2O_4 \rightarrow CaCO_3 + Co$	9	$NH_4NO_2 \rightarrow N_2 + 2H_2O$
$NH_4NO_3 \rightarrow N_2O + 2H_2O$	$2KClO_3 \rightarrow 2KCl + 3O_2$		$2FeCl_3 \rightarrow 2FeCl_2 + Cl_2$
$Li_2CO_3 \rightarrow Li_2O + CO_2$	$(COO)_2 Fe \rightarrow FeO + CO$	+ <i>CO</i> ₂	$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$
$MgCl_2.6H_2O \rightarrow HgCl_2 + Hg$	$NH_4Cl \rightarrow NH_3 + HCl$		$2LiNO_3 \rightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$
$Hg(NO_3)_2 \rightarrow Hg + 2NO_2 + O_2$	$2CuCl_2 \xrightarrow{\Delta} Cu_2Cl_2 +$	- Cl ₂	$2Co(NO_3)_2 \xrightarrow{\Delta} 2CoO + 4NO_2 + O_2$
$4K_2Cr_2O_7 \to 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$		$2Mg(NH_4)PO_4$ —	$\xrightarrow{\Delta} Mg_2P_2O_7 + H_2O + 2NH_3$
$2Zn(NH_4)PO_4 \xrightarrow{\Delta} Zn_2P_2O_7 + H_2O + 2NH_3$		$K_4 Fe(CN)_6 \xrightarrow{\Delta} 4KCN + Fe + 2C + N_2$	
$ZnCl_2.2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$		$2(ZnCl_2.H_2O) \xrightarrow{\Delta} Zn_2OCl_2 + 2HCl + H_2O$	
$2[FeCl_3.6H_2O] \xrightarrow{\Delta} Fe_2O_3 + 9H_2O + 6HCl$		$2ZnSO_4 - 800^{\circ}C$	$\rightarrow 2ZnO + 2SO_2 + O_2$
$Na_2B_4O_7.10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$ (Glassy bead)			

$$H_3BO_3 \xrightarrow{100^{\circ}C} HBO_2 \xrightarrow{160^{\circ}C} H_2B_4O_7 \xrightarrow{\text{Red hot}} B_2O_3$$

$$ZnSO_4.7H_2O \xrightarrow{70^{\circ}C} ZnSO_4.6H_2O \xrightarrow{100^{\circ}C} ZnSO_4.H_2O \xrightarrow{450^{\circ}C} ZnSO_4.H_2O \xrightarrow{450^{\circ}C\phantom$$

(iii) Flame test

 ${\it Characteristic\ flame\ colour}$: Certain metals and their salts impart specific colours to Bunsen burner flame.

- (a) Pb imparts pale greenish colour to the flame.
- (b) Cu and Cu salts impart blue or green colour to the flame.
 - (c) Borates also impart green colour to the flame.
- (d) Ba and its salts impart apple green colour to the flame.
 - (e) *Sr* imparts crimson red colour to the flame.
 - (f) Ca imparts brick red colour to the flame.
 - (g) Na imparts yellow colour to the flame.
- (h) K imparts pink-violet (Lilac) colour to the flame.
- (i) *Li* imparts crimson-red, *Rb* imparts violet and *Cs* imparts violet colours to the flame.
 - (j) Livid- blue flame is given by As, Sb and Bi.
- (iv) **Borax bead test:** The transparent glassy bead $(NaBO_2 + B_2O_3)$ when heated with inorganic salt and the colour produced gives some idea of cation present in it.

Table: 21.4

Colour of bead in oxidising flame	Colour of bead in reducing flame	Basic radical present
Greenish when hot, blue in cold.	Red and opaque	Си
Dark green in hot and cold	Same	Cr
Deep - blue	Deep blue	Со
Yellow when hot	Green	Fe
Violet in hot and cold	Colourless	Mn
Brown in cold	Grey or black or opaque	Ni

Microcosmic salt bead test: Microcosmic salt, $Na(NH_4)HPO_4.4H_2O$ is also used to identify certain cations just like borax. When microcosmic salt is heated in a loop of platinum wire, a colourless transparent bead of sodium metaphosphate is formed.

$$Na(NH_4)HPO_4.4H_2O \rightarrow Na(NH_4)HPO_4 + 4H_2O$$

$$Na(NH_4)HPO_4 \rightarrow NaPO_3 + NH_3 + H_2O$$

Now $NaPO_3$ reacts with metallic oxides to give coloured orthophosphates.

$$NaPO_3 + CuO \rightarrow NaCuPO_4$$
 (Blue);

$$NaPO_3 + CoO \rightarrow NaCoPO_4$$
 (Blue);
 $NaPO_3 + Cr_2O_3 \rightarrow NaPO_3.Cr_2O_3$ (Green)

(v) Charcoal cavity test

Table : 21.5

(a) Compound fused in cavity directly		
Nature and colour of bead	Cation	
Yellow, brittle bead	Bi^{3+}	
Yellow, soft bead which marks on paper	Pb ²⁺	
White, brittle	Sb ³⁺	
White yellow when hot	ZnO	
White garlic odour	As_2O_3	
Brown	CdO	
Grey metallic particles attracted by magnet	Fe, Ni, CO	
Maleable beads	Ag and Sn (White), Cu (Red flakes)	

(b) Compound mixed with Na_2CO_3 Crystalline

Sustance
Decrepitates

Salts, NaCl, KCl;

Substance
deflagrate s

Oxidising agents like
NO3, NO3 chlorates

Substance infusible, perform test (a)

(vi) Cobalt Nitrate test

Table : 21.6

Colour	Composition	Result
Blue residue	$CoO.Al_2O_3$	Al
Green residue	CoO . ZnO	ZnO
Pink dirty residue	CoO . MgO	MgO
Blue residue	NaCoPO 4	PO_4^{3-} in
		absence of <i>Al</i> .

(2) Wet tests for acid radicals : Salt or mixture is treated with dil. H_2SO_4 and also with conc. H_2SO_4

separately and by observing the types of gases evolved. Confirmatory tests of anions are performed.

Table : 21.7 Observations with Dilute $\,H_2SO_4\,$

Tuble (21), Obbol Vations With Ditate 17,500 4		
Observations	Acid Radical	Confirmatory test
Brisk effervescence with evolution of colourless and odourless gas.	CO_3^{2-} (carbonate)	Gas turns lime water milky but milkyness disappears on passing gas inexcess, $Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$ $Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$ $lime water milky$ $CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$ soluble
Brown fumes	NO_2^- (Nitrite)	Add KI and starch solution blue colour $2NaNO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$; $HNO_2 \longrightarrow NO$ (colourless); $2NO + O_2$ (air) $\longrightarrow 2NO_2$ (brown) $2KI + H_2SO_4 + 2NHO_2 \longrightarrow K_2SO_4 + 2H_2O + 2NO + I_2$ $I_2 + \text{starch} \longrightarrow \text{blue colour}$
Smell of rotten eggs $(H_2S \text{ smell})$ on heating	S ²⁻ (sulphide)	Gas turn lead acetate paper black Sodium carbonate extract $(SE)^*$ + sodium nitroprusside – purple colour, $Na_2S + H_2SO_4 \longrightarrow H_2S + Na_2SO_4$ $H_2S + (CH_3COO)_2Pb \longrightarrow PbS_{\text{(black)}} + 2CH_3COOH$ $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NOS]$ sodium nitroprusside (purple)
Colourless gas with pungent smell of burning sulphur	SO 3 ²⁻ (sulphite)	Gas turns acidified $K_2Cr_2O_7$ solution green [different from CO_3^{2-}] since gas also turns lime water milky $Na_2SO_3 + H_2SO_4 \xrightarrow{\Delta} Na_2SO_4 + H_2O + SO_2$ $Cr_2O_7^{2-} + 3SO_2 + 2H^+ 2Cr_3^{3+} + 3SO_4^2 + H_2O$ $(green)$ $Ca(OH)_2 + SO_2 CaSO_3$ $(milky)$
Solution gives smell of vinegar	CH ₃ COO ⁻ (acetate)	Aq. Solution + neutral $FeCl_3 \rightarrow blood$ red colour $3CH_3COONa + FeCl_3 \longrightarrow Fe(CH_3COO)_3 + 3NaCl$ neutral (red)
White or yellowish white turbidity on warming	$S_2O_3^{2-}$ (thiosulphate)	Aq. Solution + $AgNO_3$ \rightarrow white ppt. changing to black (viii) on warming $, Na_2S_2O_3 + 2AgNO_3 - \longrightarrow Ag_2S_2O_3 + 2NaNO_3$ white ppt. $Ag_2S_2O_3 + H_2O - \longrightarrow Ag_2S + H_2SO_4$ black ppt.

Table : 21.8 Observation with concentrated $\ensuremath{\mathit{H}_2SO_4}$

Observation	Acid Radical	Confiramatory Test
Colourless pungent gas giving white fumes with	` ,	Add MnO_2 in the same test tube and heat-pale green Cl_2 gas (i)

aq. NH ₄ OH		$S.E. + HNO_3 + AgNO_3$ solution –white ppt. soluble in aq. NH_3 (ii)	
		Chromyl chloride test (iii)	
Reddish brown fumes	Br^- (bromide)	Add Mn_2O and heat -yellowish brown Br_2 gas (iv)	
		$S.E. + HNO_3 + AgNO_3$ solution -pale yellow ppt. partially soluble aq. NH_3 (v)	
		Layer test (vi)	
Violet pungent vapours turning starch paper blue.	I⁻ (iodide)	$S.E. + HNO_3 + AgNO_3 \rightarrow \text{yellow ppt. insoluble in aq. } NH_3 \text{ (vii)}$ Layer test (vi)	
Brown pungent fumes intensified by the addition of <i>Cu</i> - turnigs.	NO ₃ (nitrate)	Ring test (viii)	
Colourless gases turning lime water milky and burning with blue flame.	$C_2 O_4^{2-}$ (oxalate)	Acidified KMnO_4 solution is decolorised (ix) $S.E. + \mathit{CH}_3\mathit{COOH} + \mathit{CaCl}_2 \text{ white ppt. decolorising acidified } \mathit{KMnO}_4$ solution (x)	

Reactions

Chloride

Chloride : (i)
$$KCl + \operatorname{conc.} H_2SO_4 \longrightarrow KHSO_4 + HCl$$

$$HCl + NH_3 \longrightarrow NH_4Cl$$

$$4HCl + MnO_2 \xrightarrow{\Delta} MnCl_2 + Cl_2 + 2H_2O$$

(ii)
$$KCl + AgNO_3 \longrightarrow AgCl \downarrow + KNO_3$$
white ppt.

$$AgCl + aq. 2NH_3 \longrightarrow [Ag(NH_3)_2]Cl$$

(iii) Chromyl- chloride test:

Chloride

 $K_2Cr_2O_7(\text{solid}) + \text{conc. H}_2SO_4 \xrightarrow{\text{heat}} \text{reddish}$ brown vapours of chromyl-chloride (CrO_2Cl_2) . Pass these vapours into NaOH, when yellow Na2CrO4 solution is formed. On adding CH3COOH and (CH3COO)2 Pb, yellow ppt. of lead chromate (*PbCrO*₄) is formed.

$$\begin{split} &KCl + \mathrm{conc.} \, H_2SO_4 \stackrel{\Delta}{\longrightarrow} KHSO_4 + HCl \; ; \\ &K_2Cr_2O_7 + 2H_2SO_4 \stackrel{\Delta}{\longrightarrow} 2KHSO_4 + 2CrO_3 + H_2O \\ & \longrightarrow CrO_2Cl_2 + 2H_2O \\ & \longrightarrow Na_2CrO_4 + 2NaCl + 2H_2O \\ & \longrightarrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \longrightarrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow Pb \stackrel{\Delta}{\longrightarrow} PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \searrow PbCrO_4 \downarrow PbCrO_4 \downarrow + 2CH_3COONa \\ & \nearrow PbCrO_4 \downarrow PbCrO_4 \downarrow PbCrO_4 \downarrow PbCrO_4 \downarrow PbCrO_4 \\ & \nearrow PbCrO_4 \downarrow PbCrO_4 \downarrow PbCrO_4 \\ & \nearrow PbCrO_4 \downarrow PbCrO_4 \\ & \nearrow PbCrO_4 \downarrow PbCrO_4 \\ & \nearrow Pb$$

Bromide : (iv)
$$KBr + \text{conc. } H_2SO_4 \xrightarrow{\Delta} KHSO_4 + H$$
;
 $4HBr + MnO_2 \xrightarrow{\Delta} Br_2 + 2H_2O + MnBr_2$
(v) $NaBr + AgNO_3 \xrightarrow{\text{pale yellow ppt.}} AgBr \downarrow + NaNO_3$

Layer Test : $S.E. + Cl_2$ $+ CHCl_3 \xrightarrow{\text{shake}}$ yellowish orange colour in $CHCl_3$ layer (CS_2 or CCl_4 can be taken instead of $CHCl_3$);

partially soluble

$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2$$
orange yellow
(soluble in CHCl 3)

 $AgBr + aq. 2NH_3 \longrightarrow [Ag(NH_3)_2]Br$

In case of I^- , violet colour of I_2 in $CHCl_3$ layer, $2NaI + Cl_2 \longrightarrow 2NaCl + I_2$ (violet)

Iodide: (vii)
$$KI + \text{conc. } H_2SO_4 \xrightarrow{\Delta} KHSO_4 + HI$$
;
 $2HI + H_2SO_4 \xrightarrow{} I_2 + 2H_2O + SO_2$

Nitrate:
$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

$$4HNO_3 \longrightarrow 4NO_2 + O_2 2H_2O$$
; brown fumes

$$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

(viii) **Ring test**: To water extract (all NO_3^- are water soluble) add freshly prepared $FeSO_4$ solution and then conc. H_2SO_4 carefully by the side of the test-

tube. A dark brown ring of $[Fe(H_2O)_5 NO]^{2+} SO_4^{2-}$ at the interface between the two liquids is formed.

$$2NaNO_3 + H_2SO_4 \longrightarrow 2NaHSO_4 + 2HNO_3$$
;
 $2HNO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + 2NO + 4H_2O$

 $[Fe(H_2O)_6]SO_4 + NO \longrightarrow [Fe(H_2O)_5 NO]^{2+} SO_4^{2-} + H_2O$

$$Na_2C_2O_4 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO + CO_2$$

 ${\it CO}$ burns with blue flame and ${\it CO}_2$ turns lime water milky.

(ix)
$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \longrightarrow 10 CO_2 + 2Mn^{2+} + 8H_2O$$
(violet) colourless

$$\begin{array}{ccc} \text{(x)} & \textit{CaCl}_2 + \textit{NaC}_2O_4 & \longrightarrow \textit{CaC}_2O_4 & \downarrow + 2\textit{NaCl} & \textit{CaC}_2O_2 \\ & & \text{white ppt.} \end{array}$$

decolourises acidified KMnO₄.

Specific test in solution

(i) **Sulphate**: S.E. add dil. (to decompose CO_3^{2-} until reaction ceases). Add $BaCl_2$ solution. White ppt. insoluble in conc. HNO_3 , $BaCl_2 + NaSO_4 \longrightarrow BaSO_4 \downarrow + 2NaCl_{white ppt.}$

(ii) **Borate**: Ignite the mixture containing borate, conc. H_2SO_4 . And ethanol in a china-dish with a burning splinter –green edged flame of ethyl borate.

$$2Na_3BO_3 + 3H_2SO_4 \rightarrow 2H_3BO_3 + 3Na_2SO_4$$
;

$$H_3BO_3 + 3C_2H_5OH \xrightarrow{\Delta} (C_2H_5O)_3B + 3H_2O$$

ethanol burns with green flame (volatile)

In presence of Cu^{2+} , perform this test in a test tube since Cu^{2+} salts are not volatile.

(iii) $S.E. + HNO_3 +$ ammonium molybdate solution. Heat, yellow crystalline ppt. confirms

$$Na_3PO_4 + 12(NH_4)_2MoO_4 + 24HNO_3 \xrightarrow{\Delta}$$

 $(NH_4)_3PO_4 \cdot 12MoO_3 + 21NH_4NO_3 + 3NaNO_3 + 12H_2O_3$
yellowppt.

Arsenic also gives this test. Hence presence of phosphate should also be checked after group II.

(iv) **Fluoride**: Sand +salt (F^-) +conc. H_2SO_4 ; heat and bring a water wetted rod in contact with vapours at the mouth of the test tube. A white deposit on the rod shows the presence to F^-

$$NaF + H_2SO_4 \xrightarrow{\Delta} NaHSO_4 + HF$$

 $SiO_2 + 4HF \xrightarrow{\Delta} SiF_4 + 2H_2O$
 $3SiF_4 4H_2O \xrightarrow{\Delta} 2H_2SiF_6 + H_4SiO_4$
white

(3) Wet tests for basic radicals: Analysis of Basic Radicals

Table : 21.0

Table : 21.9						
Group	Basic radicals	Group reagent	Ppt. as	Explanation		
I	$Ag^{+}, Hg_{2}^{2+}(I), Pb^{2+}$	dil <i>HCl</i>	Chloride	K_{SP} values of chlorides are low,		
			$(AgCl, Hg_2Cl_2, PbCl_2)$	hence precipitated. Others have		
				higher K_{SP} values hence not		
				precipitated.		
II	$Cu^{2+}, Cd^{2+}, Pb^{2+},$	H_2S gas in	Sulphides	K_{SP} values of sulphides are low		
	Hg^{2+} (II), Bi^{3+} , As^{3+} ,	presence of dil.	$(CuS, As_2S_3 \text{ etc.})$	hence precipitated by low $[S^{2-}]$		
	Sb^{3+}, Sn^{2+}	HCl		ion. HCl (with common H^+ ion)		
				decreases ionization of H_2S		
				which gives low $[S^{2-}]$. Hence II		
				group is precipitated. Others		
				with higher K_{SP} values not		
				precipitated.		
III	$Al^{3+}, Cr^{3+}, Fe^{3+}$	NH ₄ OH in	Hydroxide, Al(OH) ₃	K_{SP} values of $Al(OH)_3$ etc. are		
		presence of	etc.	low. NH_4Cl (with common NH_4^+		
	NH_4Cl			ion) decreases ionization of		
				NH_4OH giving low $[OH^-]$. Hence		
				group III is precipitated.		

IV	$Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}$	H_2S in	Sulphides (ZnS	K_{SP} values of sulphides of
		ammonical	etc.)	group IV are high hence
		medium		precipitation takes place in
				higher $[S^{2-}]$. Basic medium
				increases ionization of H_2S
				increasing [S ²⁻] hence
				precipitation of group IV.
V	$Ca^{2+}, Ba^{2+}, Sr^{2+}$	$(NH_4)_2 CO_3 + NH_4 Cl$	Carbonates (CaCO ₃	K_{SP} values of carbonate are less
			etc.)	than that of group VI (Mg^{2+})
				hence precipitation before
				Mg^{2+} .
VI	$Mg^{2+}, (Na^+, K^+)$ also	$NH_4OH + Na_2HPO_4$	White ppt.	-
	included)	(only for Mg^{2+})	$(MgHPO_4)$	
0	NH ₄ +	-	-	Tested independently from original
(Zero)				solution.

Chemical reactions involved in the tests of basic radicals

Group I: When dil. HCl is added to original solution, insoluble chlorides of lead, silver mercurous mercury are precipitated.

$$Pb(NH_3)_2 + 2HCl \longrightarrow PbCl_2 + 2HNO_3$$
;

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

$$Hg(NO_3)_2 + 2HCl \longrightarrow HgCl_2 + 2HNO_3$$

Pb²⁺ (lead)

- (i) $PbCl_2$ is soluble in hot water and on cooling white crystals are again formed.
- (ii) The solution of $PbCl_2$ gives a yellow precipitate with potassium chromate solution which is insoluble in acetic acid but soluble in sodium hydroxide.

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

$$PbCrO_4 + 4 NaOH \longrightarrow Na_2 PbO_2 + Na_2 CrO_4 + 2H_2O$$

(iii) The solution of $PbCl_2$ forms a yellow precipitate with potassium iodide solution.

$$PbCl_2 + 2KI \longrightarrow PbI_2 + 2KCl$$
Yellow ppt.

(iv) White precipitate of lead sulphate is formed with dilute H_2SO_4 . The precipitate is soluble in ammonium acetate, $PbCl_2 + H_2SO_4 \longrightarrow PbSO_4 + 2HCl$;

$$PbSO_4 + 2CH_3COONH_4 \longrightarrow Pb(CH_3COO)_2 + (NH_4)_2SO_4$$

Ag⁺(silver)

(i) AgCl dissolves in ammonium hydroxide,

$$AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O$$
Diammine silver (I)
chloride

(ii) On adding dilute HNO_3 to the above solution, white precipitate is again obtained

$$Ag(NH_3)_2 Cl + 2HNO_3 \longrightarrow AgCl + 2NH_4 NO_3$$

White ppt.

(iii) On adding *KI* to the complex solution, yellow precipitate is obtained.

$$Ag(NH_3)_2Cl + KI \longrightarrow AgI + KCl + 2NH_3$$

Hg_2^{2+} (mercurous)

- (i) Hg_2Cl_2 turns black with NH_4OH , $Hg_2Cl_2 + 2NH_4OH \longrightarrow \underbrace{Hg + Hg(NH_2)Cl}_{\text{Black}} + NH_4Cl + 2H_2O$
- (ii) The black residue dissolves in aqua-regia forming mercuric chloride.

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

$$2Hg(NH_2)Cl + 6Cl \longrightarrow 2HgCl_2 + 4HCl + N_2$$

$$Hg + 2Cl \longrightarrow HgCl_2$$

(iii) The solution of $HgCl_2$ forms white or slate-coloured precipitate with stannous chloride.

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$
Grey ppt.

(iv) The solution of HgCl_2 with copper turning forms a grey deposit.

$$HgCl_2 + Cu \longrightarrow Hg + CuCl_2$$
Grey ppt.

Group II: When hydrogen sulphide is passed in acidified solution, the radicals of second group are precipitated as sulphides. The precipitate is treated with yellow ammonium sulphide. The sulphides of IIB are first oxidised to higher sulphides which then dissolve to form thio-compounds.

$$Ag_{2}S_{3} + 2(NH_{4})_{2}S_{2} \longrightarrow 2(NH_{4})_{2}S + As_{2}S_{5}$$

$$Sb_{2}S_{3} + 2(NH_{4})_{2}S_{2} \longrightarrow 2(NH_{4})_{2}S + Sb_{2}S_{5}$$

$$SnS + (NH_{4})_{2}S_{2} \longrightarrow (NH_{4})_{2}S + SnS_{2}$$

$$As_{2}S_{5} + 3(NH_{4})S \longrightarrow 2(NH_{4})_{3}AsS_{4}$$
Ammonium thioarsena te
$$Sb_{2}S_{5} + 3(NH_{4})_{2}S \longrightarrow 2(NH_{4})_{2}SbS_{4}$$
Ammonium thioantimo nate
$$SnS_{2} + (NH_{4})_{2}S \longrightarrow (NH_{4})_{2}SnS_{3}$$
Ammonium thiosanna te

All the three are soluble.

In case, the precipitate does not dissolve in yellow ammonium sulphide, it may be either HgS or PbS or Bi_2S_3 or CuS or CdS. The precipitate is heated with dilute HNO_3 . Except HgS, all other sulphides of IIA are soluble.

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

 $Bi_2S_3 + 8HNO_3 \rightarrow 2Bi(NO_3)_3 + 2NO + 3S + 4H_2O$
 $3CuS + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$
 $3CdS + 8HNO_3 \rightarrow 3Cd(NO_3)_2 + 2NO + 3S + 4H_2O$

Hg²⁺ (mercuric)

HgS is dissolved in aqua-regia,

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

The solution is divided into two parts:

Part I: Stannous chloride solution reduces $HgCl_2$ first into white Hg_2Cl_2 and then to grey metallic mercury.

Part II: Copper displaces Hg from $HgCl_2$ which gets coated on copper turnings as a shining deposit.

Pb^{2+} (lead)

In case the sulphide dissolves in dilute HNO_3 , a small part of the solution is taken. Dilute H_2SO_4 is added. If lead is present, a white precipitate of lead sulphate appears, $Pb(NO_3)_2 + H_2SO_4 \rightarrow PbSO_4 + 2HNO_3$

In absence of lead, the remaining solution is made alkaline by the addition of excess of NH_4OH . Bismuth forms a white precipitat of $Bi(OH)_3$, copper forms a

deep blue coloured solution while cadmium forms a colourless soluble complex,

$$Bi(NO_3)_3 + 3NH_4OH \longrightarrow Bi(OH)_3 + 3NH_4NO_3$$

White ppt.

$$Cu(NO_3)_2 + 4NH_4OH \longrightarrow [Cu(NH_3)_4](NO_3)_2 + 4H_2O;$$

Tetrammin e cupric nitrate
(deep blue solution)

$$Cd(NO_3)_2 + 4NH_4OH \longrightarrow [Cd(NH_3)_4](NO_3)_2 + 4H_2O$$
Tetrammin e cadmium nitrate
(colourles s solution)

 Bi^{3+} (bismuth): The precipitate dissolves in dilute HCl, $Bi(OH)_3 + 3HCl \longrightarrow BiCl_3 + 3H_2O$

Part I: Addition of excess of water to $BiCl_3$ solution gives a white precipitate due to hydrolysis.

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

Bismuth Oxychlorid e (White ppt.)

Part II: The solution of $BiCl_3$ is treated with sodium stannite when a black precipitate of metallic bismuth is formed, $2BiCl_3 + 3Na_2SnO_2 + 6NaOH \longrightarrow$

$$3Na_2SnO_3 + 2Bi + 6NaCl + 3H_2O$$

Sod. stannate

 Cu^{2+} (copper): Blue coloured solution is acidified with acetic acid. When potassium ferrocyanide is added a chocolate coloured precipitate is formed,

$$Cu(NH_3)_4(NO_3)_2 + 4CH_3COOH \longrightarrow$$

$$Cu(NO_3)_2 + 4CH_4COONH_4$$

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

Chocolate ppt.

Cd²⁺ (cadmium):
$$H_2S$$
 is passed through

 ${\it Cd^{2+}}$ (cadmium) : H_2S is passed through colourless solution. The appearance of yellow precipitate confirms the presence of cadmium,

$$Cd\:(NH_{\:3})_4(NO_{\:3})_2 + H_2S \xrightarrow{\hspace*{1cm}} CdS \: + 2NH_{\:4}NO_{\:3} + NH_{\:3}$$
 Yellow ppt.

Group IIB: In case the precipitate dissolves in yellow ammonium sulphide, the tests of the radicals arsenic, antimony and tin are performed. The sulphide is treated with concentrated hydrochloric acid. Antimony and tin sulphide dissolve while arsenic sulphide remains insoluble.

 As^{3+} (arsenic): The insoluble sulphide is treated with concentrated nitric acid which is then heated with ammonium molybdate. Yellow precipitate of ammonium arsenomolybdate is formed.

$$As_2S_5 + 10HNO_3 \longrightarrow 2H_3AsO_4 + 10NO_2 + 2H_2O + 5S$$
Arsenic acid

$$H_3 AsO_4 + 12(NH_4)_2 MoO_4 + 21HNO_3 \longrightarrow$$

$$(NH_4)_3$$
 As O_4 . $12MoO_3 + 21NH_4NO_3 + 12H_2O_3$

 Sn^{2+} or Sn^{4+} (tin): Solution of sulphide in concentrated HCl is reduced with iron fillings or granulated zinc.

$$SnS_2 + 4HCl \longrightarrow SnCl_4 2H_2S$$
White ppt.

$$SnCl_4 + Fe \longrightarrow SnCl_2 + FeCl_4$$
Grey

 $HgCl_2$ solution is added to above solution which gives first a white precipitate that turns to grey.

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

White ppt.

$$Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4$$
 Grey

 ${\it Sb}^{2+}$ (antimony) : Filtrate of sulphide in concentrated ${\it HCl}$ is divided into two parts.

 $Part\ I:$ On dilution with excess of water, a white precipitate of antimony oxychloride is obtained.

$$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$$
White ppt.

Part $II: H_2S$ is circulated. Orange precipitate is formed, $2SbCl_3 + 3H_2S \longrightarrow Sb_2S_3 + 6HCl$ Orange ppt.

Group III : Hydroxides are precipitated on addition of excess of ammonium hydroxide in presence of ammonium chloride.

$$AlCl_3 + 3NH_4OH \longrightarrow Al(OH)_3 + 3NH_4Cl$$
Gelatinous ppt.

$$CrCl_3 + 3NH_4OH \xrightarrow{} Cr(OH)_3 + 3NH_4Cl$$
Green ppt.

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

 Fe^{3+} (iron): The brownish red precipitate dissolves in dilute HCl. The solution is divided into two parts.

Part $I: K_4[Fe(CN)_6]$ solution is added which forms deep blue solution or precipitate.

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

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

 ${\it Part}$ ${\it II}$: Addition of potassium thiocyanate solution gives a blood red colouration.

$$FeCl_3 + 3KCNS \longrightarrow Fe(CNS)_3 + 3KCl$$
Blood red colour

 Cr^{3+} (chromium): The green precipitate is fused with fusion mixture $(Na_2CO_3 + KNO_3)$. The fused product

is extracted with water or the precipitate is heated with NaOH and bromine water.

$$2Cr(OH)_3 + 3KNO + 2Na_2CO_3 \longrightarrow$$

$$2Na_2CrO_4 + 3KNO_2 + 2CO_2 + 3H_2O_3 + 2CO_4 + 3KNO_3 + 2CO_3 + 3H_3O_3 + 2CO_3 + 2CO_3 + 3H_3O_3 + 2CO_3 + 2CO_$$

or
$$2NaOH + Br_2 \longrightarrow NaBrO_4 + NaBr + H_2O$$

$$NaBrO \longrightarrow NaBr + [O]$$

$$2Cr(OH)_3 + 4NaOH + 3[O] \longrightarrow 2NaCrO_4 + 5H_2O$$

The solution thus obtained contains sodium chromate. The solution is acidified with acetic acid and treated with lead acetate solution. A yellow precipitate appears.

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

Yellow ppt.

 Al^{3+} (aluminium): The gelatinous precipitate dissolves in NaOH, $Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$

The solution is boiled with ammonium chloride when $Al(OH)_3$ is again formed.

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

Group IV: On passing H_2S through the filtrate of the third group, sulphides of fourth group are precipitated. NiS and CoS are black and insoluble in concentrated HCl while MnS (buff coloured), ZnS (colourless) are soluble in conc. HCl.

 Zn^{2+} (zinc): The sulphide dissolves in HCl. $ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S$

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

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

White ppt.

$$Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$$
(Soluble)

On passing H_2S , white precipitate of zinc sulphide is formed

$$Na_2ZnO_2 + H_2S \longrightarrow ZnS$$
_{White ppt.} $+ 2NaOH$

 Mn^{2+} (manganese) : Manganese sulphide dissolves in HCl $MnS + 2HCl \longrightarrow MnCl_2 + H_2S$

On heating the solution with NaOH and Br_2 -water, manganese dissolve gets precipitated.

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

$$Mn(OH)_2 + O \longrightarrow MnO_2H_2O$$

The precipitate is treated with excess of nitric acid and PbO_2 or Pb_3O_4 (red lead). The contents are heated. The formation of permanganic acid imparts pink colour to the supernatant liquid.

The above test fails in presence of HCl.

Ni^{2+} (nickel) and Co^{2+} (cobalt)

The black precipitate is dissolved in aqua- regia.

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

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

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

 ${\it Part}~{\it I}$: Add ${\it NH}_4{\it OH}$ (excess) and dimethyl glyoxime. A rosy red precipitate appears, if nickel is present,

$$CH_{3} - C = NOH$$

$$NiCl_{2} + 2 \qquad | \qquad +2NH_{4}OH \longrightarrow$$

$$CH_{3} - C = NOH$$

$$OH \qquad O$$

$$| \qquad \uparrow$$

$$CH_{3} - C = N \qquad N = C - CH_{3}$$

$$| \qquad N = C - CH_{3}$$

$$| \qquad CH_{3} - C = N \qquad N = C - CH_{3}$$

$$| \qquad OH$$

 $Part\ II: Add\ CH_3COOH\$ in excess and $KNO_2.$ The appearance of yellow precipite confirms the presence of cobalt.

$$KNO_2 + CH_3COOH \longrightarrow CH_3COOK + HNO_2$$
 $CoCl_2 + 2KNO_2 \longrightarrow Co(NO_2)_2 + 2KCl$
 $Co(NO_2)_2 + 2HNO_2 \longrightarrow Co(NO_2)_3 + NO + H_2O$
 $Co(NO_2)_3 + 3KNO_2 \longrightarrow K_3[Co(NO_2)_6]$

Part III: Solution containing either nickel or cobalt is treated with $NaHCO_3$ and bromine water. Appearance of apple green colour is observed, the solution is heated when black precipited is formed, which shows the presence of nickel, $CoCl_2 + 2NaHCO_3 \longrightarrow Co(HCO_3)_2 + 2NaCl$

$$Co(HCO_3)_2 + 4NaHCO_3 \longrightarrow Na_4Co(CO_3)_3 + 3H_2O + 3CO_2$$

$$\begin{array}{l} Br_2 + H_2O \longrightarrow 2HBr + O \\ 2Na_4Co(CO_3)_3 + H_2O + O \longrightarrow 2Na_3Co(CO_3)_3 + 2NaOH \\ \text{sod. cobalti carbonate} \\ \text{(Green colouration)} \\ \\ NiCl_2 + 2NaHCO_3 \longrightarrow NiCO_3 + 2NaCl + H_2O + CO_2 \\ \\ 2NiCO_3 + [O] \longrightarrow Ni_2O_3 + 2CO_2 \\ \text{(Black)} \end{array}$$

Group V: Ammonium carbonate precipitates V group radicals in the form of carbonates are soluble in acetic acid.

$$BaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ba + CO_2 + H_2O$$

 $SrCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Sr + CO_2 + H_2O$
 $CaCO_3 + 2CH_3COOH \longrightarrow (CH_3COO)_2Ca + CO_2 + H_2O$

 Ba^{2+} (barium): Barium chromate is insoluble and precipitated by the addition of potassium chromate solution,

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

 Sr^{2+} (Strontium) : Strontium sulphate is insoluble and precipitated by the addition of ammonium sulphate solution,

$$Sr(CH_3COO)_2 + (NH_4)_2SO_4 \longrightarrow SrSO_4 + 2CH_3COONH_4$$

White ppt.

 $\it Ca^{2+}$ (calcium): Calcium oxalate is insoluble and precipitated by the addition of ammonium oxalate.

$$Ca(CH_3COO)_2 + (NH_4)_2 C_2 O_4 \longrightarrow CaC_2 O_4 + 2CH_3COONH_4$$

White ppt.

Group VI: In the filtrate of V group, some quantity of ammonium oxalate is added as to remove Ba, Ca and Sr completely from the solution. The clear solution is concentrated and made alkaline with NH_4OH . Disodium hydrogen phosphate is now added, a white precipitate is formed.

$$\begin{array}{c} \textit{MgCl}_2 + \textit{Na}_2\textit{HPO}_4 + \textit{NH}_4\textit{OH} \\ \\ \textit{Mg(NH}_4)\textit{PO}_4 + 2\textit{NaCl} + \textit{H}_2\textit{O} \\ \\ \text{Megnesium ammonium phosphate} \\ \text{(White ppt.)} \end{array}$$

Zero group NH_4^+ (ammonium): The substance (salt or mixture) when heated with NaOH solution evolves ammonia.

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

When a rod dipped in HCl is brought on the mouth of the test tube, white fumes of ammonium chloride are formed, $NH_3 + HCl \longrightarrow NH_4Cl$

To the aqueous solution of ammonium salt when Nessler's reagents is added, brown coloured precipitate is formed.

$$2K_{2}HgI_{4} + NH_{4}Cl + 4KOH \longrightarrow NH_{2}$$

$$Hg \longrightarrow O + 7KI + KCl + 3H_{2}O$$

$$I \text{ Iodide of Millon's base}$$
(Prown per l.)

Volumetric analysis

Volumetric analysis is a quantitative analysis. It involves the measurement of the volume of a known solution required to bring about the completion of the reaction with a measured volume of the unknown solution.

Titration: The process of addition of the known solution from the burette to the measured volume of solution of the substance to be estimated until the reaction between the two is just complete, is termed as titration. Thus, a titration involves two solutions;

- (i) *Unknown solution*: The solution consisting the substance to be estimated is termed unknown solution. The substance is termed titrate.
- (ii) **Standard solution:** The solution in which an accurately known amount of the reagent (titrant) has been dissolved in a known volume of the solution is termed standard solution. There are two types of reagents (titrants):
- (a) *Primary standards*: These can be accurately weighed and their solutions are not to be standardised before use. Oxalic acid $(H_2C_2O_4.2H_2O)$, potassium dichromate $(K_2Cr_2O_7)$, silver nitrate $(AgNO_3)$, copper sulphate $(CuSO_4.5H_2O)$, ferrous ammonium sulphate $[FeSO_4(NH_4)_2SO_4.6H_2O]$, sodium thiosulphate $(Na_2S_2O_3.5H_2O)$, etc., are the examples of primary standards.
- (b) Secondary standards: The solutions of these reagents are to be standardised before use as these cannot be weighed accurately. The examples are sodium hydroxide (NaOH), potassium hydroxide (KOH), hydrochloric acid (HCl), sulphuric acid (H_2SO_4), potassium permanganate (KMnO $_4$), iodine, etc.

Law of equivalence: It is applied in all volumetric estimations. According to it, the chemical substances react in the ratio of their chemical equivalent masses.

 $\frac{\text{Mass of substance } A}{\text{Mass of substance } B} = \frac{\text{Chemical equivalent mass of } A}{\text{Chemical equivalent mass of } B}$

or $\frac{\text{Mass of substance } A}{\text{Chemical equivalent mass of } A}$

 $= \frac{\text{Mass of substance } B}{\text{Chemical equivalent mass of } B}$

or gram equivalent of $A=\operatorname{gram}$ equivalent of B or milli-gram equivalent of $A=\operatorname{milli-gram}$ equivalent of B

The point at which the amounts of the two reactants are just equivalent is known as equivalence point or end point. An auxiliary substance which helps in the usual detection of the completion of the titration or equivalence point or end point is termed as indicator, *i.e.*, substances which undergo some easily detectable changes at the equivalence point are used as indicators.

Methods of expressing concentrations of solutions

The concentration of a solution can be expressed in various ways.

- (1) Percent by mass
- (2) Molarity
- (3) molality
- (4) Mole fraction
- (5) Normality

- (1) Acid base titrations or acidimetry and alkalimetry
- (2) Oxidation reduction titrations or redox titrations
 - (3) Precipitation titrations
 - (4) Complexometric titrations.
- (1) **Acid-base titrations**: When the strength of an acid is determined with the help of a standard solution of base, it is known as **acidimetry**. Similarly, when the strength of a base (alkali) is determined with the help of a standard solution of an acid, it is known as **alkalimetry**. Both these titrations involve neutralisation of an acid with an alkali. In these titrations H^+ ions of the acid combine with OH^- ions of the alkali to form unionised molecules of water.

$$HA + BOH \longrightarrow BA + H_2O$$
Acid Alkali $\longrightarrow BA + H_2O$
or $H^+ + A^- + B^+ + OH^- \longrightarrow B^+ + A^- + H_2O$
or $H^+ + OH^- \longrightarrow H_2O$

The end point in these titrations is determined by the use of organic dyes which are either weak acids or weak bases. These change their colours within a limited range of hydrogen ion concentrations, *i.e.*, pH of the solution. Phenolphthalein is a suitable indicator in the titrations of strong alkalies (free from carbonate) against strong acids or weak acids. Methyl orange is

used as an indicator in the titrations of strong acids against strong and weak alkalies. As no indicator gives correct results in the titrations of weak acids against weak bases, such titrations are performed by some other methods (physical methods).

- (2) **Oxidation reduction titrations:** The titrations based on oxidation-reduction reactions are called redox titrations. The chemical reactions proceed with transfer of electrons (simultaneous loss or gain of electrons) among the reacting ions in aqueous solutions. Sometimes these titrations are named after the reagent used, as:
- (i) **Permanganate titrations:** These are titrations in which potassium permanganate is used as an oxidising agent in acidic medium. The medium is maintained by the use of dilute sulphuric acid. Potassium permanganate acts as a self-indicator. The potential equation, when potassium permanganate acts as an oxidising agent, is:

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

or $MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$

Before the end point, the solution remains colourless (when KMnO_4 solution is taken in burette) but after the equivalence point only one extra drop of KMnO_4 solution imparts pink colour, i.e., appearance of pink colour indicates the end point. Potassium permanganate is used for the estimation of ferrous salts, oxalic acid, oxalates, hydrogen peroxide, etc. The solution of potassium permanganate is always first standardised before its use.

(ii) *Dichromate titrations*: These are titrations in which, potassium dichromate is used as an oxidising agent in acidic medium. The medium is maintained acidic by the use of dilute sulphuric acid. The potential equation is

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

or $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

The solution of potassium dichromate can be directly used for titrations. It is mainly used for the estimation of ferrous salts and iodides. In the titration of $K_2Cr_2O_7$ versus ferrous salt either an external indicator (potassium ferricyanide) or an internal indicator (diphenyl amine) can be used.

(iii) *Iodimetric and iodometric titrations*: The reduction of free iodine to iodide ions and oxidation of iodide ions to free iodine occurs in these titrations.

$$I_2 + 2e^- \longrightarrow 2I^-$$
 (reduction)
 $2I^- \longrightarrow I_2 + 2e^-$ (oxidation)

These are divided into two types:

(a) *Iodimetric titrations*: These are the titrations in which free iodine is used. As it is difficult to prepare

the solution of iodine (volatile and less soluble in water), it is dissolved in potassium iodide solution.

$$KI + I_2 \longrightarrow KI_3$$
Potassium tri-iodide

This solution is first standardised before use. With the standard solution of I_2 . Substances such as sulphite, thiosulphate, arsenite, etc., are estimated.

(b) *Iodometric titrations*: In iodometric titrations, an oxidising agent is allowed to react in neutral medium or in acidic medium, with excess of potassium iodide to liberate free iodine.

$$KI$$
 + oxidising agent $\longrightarrow I_2$

Free iodine is titrated against a standard reducing agent usually with sodium thiosulphate. Halogens, oxyhalogens, dichromates, cupric ion, peroxides, etc., can be estimated by this method.

$$\begin{split} I_2 + Na_2S_2O_3 & \longrightarrow 2NaI + Na_2S_4O_6 \\ 2CuSO_4 + 4KI & \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2 \\ K_2Cr_2O_7 + 6KI + 7H_2SO_4 & \longrightarrow \end{split}$$

$$Cr_2(SO_4)_3 + 4K_2SO_4 + 7H_2O + 3I_2$$

In iodimetric and iodometric titrations, starch solution is used as an indicator. Starch solution gives blue or violet colour with free iodine. At the end point the blue or violet colour disappears when iodine is completely changed to iodide.

(3) **Precipitation titrations:** The titrations which are based on the formation of insoluble precipitates, when the solutions of two reacting substances are brought in contact with each other, are called **precipitation titrations.** For example, when a solution of silver nitrate is added to a solution of sodium chloride or a solution of ammonium thiocyanate, a white precipitate of silver chloride or silver thiocyanate is formed.

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

 $AgNO_3 + NH_4CNS \longrightarrow AgCNS + NH_4NO_3$

Such titrations involving silver nitrate are called argentometric titrations.

(4) **Complexometric titrations :** A titration, in which an undissociated complex is formed at the equivalence point, is called **complexometric titration**. These titrations are superior to precipitation titrations as there is no error due to co-precipitation.

$$Hg^{2+} + 2SCN^{-} \longrightarrow Hg(SCN)_{2}$$

 $Ag^{+} + 2CN^{-} \longrightarrow [Ag(CN)_{2}]^{-}$

EDTA (ethylenediamine tetra-acetic acid) is a useful reagent which forms complexes with metals. In the form of disodium salt, it is used to estimate Ca^{2+}

and Mg^{2+} ions in presence of eriochrome black- T as an indicator.

Equivalent masses of acids and bases : Equivalent masses of some acids and bases are given in the following table

Table: 21.10

14010 : 21.10							
Acid	Basicity	Mol. Mass	Eq. Mass				
HCl	1	36.5	$\frac{36.5}{1}$ = 36.5				
HNO ₃	1	63	$\frac{63}{1}$ =63.0				
H_2SO_4	2	98	$\frac{98}{2}$ =49.0				
CH₃COOH	1	60	$\frac{60}{1}$ =60.0				
$H_2C_2O_4.2H_2O$	2	126	$\frac{126}{2}$ =63.0				
H_3PO_4	3	98	$\frac{98}{3}$ =32.7				
H_3PO_3	2	82	$\frac{82}{2}$ =41.0				
H ₃ PO ₂	1	66	$\frac{66}{1}$ =66.0				

Table : 21.11

Alkali	Acidity	Mol. Mass	Eq. Mass
NaOH	1	40	$\frac{40}{1} = 40$
КОН	1	56	$\frac{56}{1} = 56$
Ca(OH) ₂	2	74	$\frac{74}{2} = 37$
NH_4OH	1	35	$\frac{35}{1} = 35$

Calculations of Volumetric analysis

The following points should be kept in mind while making calculations of volumetric exercises.

(i) 1g equivalent mass of a substance reacts completely with 1g equivalent mass of any other substance. 1g equivalent mass of a substance means equivalent mass of the substance in grams. For example,

1g equivalent mass of NaOH = 40g of NaOH

1g equivalent mass of $H_2SO_4 = 49g$ of H_2SO_4

1g equivalent mass of KMnO_4 in acidic medium

=31.6 g of $KMnO_A$

1g equivalent mass of hydrated oxalic acid

= 63 g of hydrated oxalic acid

Note: Equivalent mass is a variable quantity and depends on the reaction in which the substance takes part. The nature of the reaction should be known before writing the gram equivalent mass of the substance. For example in the reactions.

$$2NaCl + 2H_2SO_4 \longrightarrow 2NaHSO_4 + 2HCl$$
(i)

$$2NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$$
(ii)

The value of g equivalent mass of H_2SO_4 in reaction (i) is $98\,g$ and in reaction (ii) $49\,g$.

(ii) Number of g equivalents

 $= \frac{\text{Mass of the substance in } g}{\text{Equivalent mass of the substance}}$

Number of g moles = $\frac{\text{Mass of the substance in } g}{\text{Molecular mass of the substance}}$

$$= \frac{\text{Volume in litres of the substance at N.T.P.}}{22.4} \text{ (only }$$

gases)

Number of milli-equivalent = $\frac{\text{Mass in } g \times 1000}{\text{Equivalent mass}}$

Number of milli-moles =
$$\frac{\text{Mass in } g \times 1000}{\text{Molecular mass}}$$

(iii) Molarity =
$$\frac{\text{No. of moles of the solute}}{\text{No. of litres of the solution}} = \frac{w}{m \times V}$$

Molarity \times molecular mass = strength of the solution (g/L) No. of moles of the solute = Molarity \times No. of litres of solution Mass of the solute in g(w) = molarity \times No. of litres of solution \times mol. mass of solute

Normality =
$$\frac{\text{No. of } g \text{ equivalent of the solute}}{\text{No. of litres of the solution}} = \frac{w}{E \times V}$$

Normality \times equivalent mass = strength of the solution (g/L)

No. of equivalents of the solute = Normality \times No. of litres of solution

Mass of the solute in $g(w) = \text{Normality} \times \text{No. of}$ litres of solution \times Eq. mass of the solute

$$\frac{\text{Molecular mass}}{\text{Equivalent mass}} = n = \frac{\text{Normality}}{\text{Molarity}}$$

Normality = $n \times$ Molarity

(iv) *Normality equation*: When solutions A and B react completely.

$$N_A V_A = N_B V_B$$

Normality of $A \times$ volume of A = Normality of $B \times$ volume of B

$$\text{or } \frac{\text{Strength } A}{\text{Eq. mass } A} \times V_A = \frac{\text{Strength } B}{\text{Eq. mass } B} \times V_B$$

 $\frac{\text{Wt. of metal hydroxide}}{\text{wt, of metal oxide}} = \frac{\text{Eq. wt. of metal hydroxide}}{\text{Eq. wt. of metal oxide}}$

$$= \frac{\text{Eq. wt of metal } + \text{Eq. wt of } OH}{\text{Eq. wt. of metal } + \text{Eq. wt of } O^{2-}}$$

(v) When the solution is diluted, the following formulae can be applied:

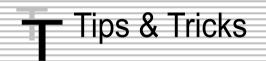
$$N_1V_1 = N_2V_2$$
 or $M_1V_1 = M_2V_2$ or $S_1V_1 = S_2V_2$

Before dilution = After dilution

(vi) If a number of acids are mixed, the combined normality of the mixture, $N_{\scriptscriptstyle X}$, is given

$$N_x V_x = N_1 V_1 + N_2 V_2 + N_3 V_3 + \dots$$

Where V_x is the total volume of the mixture, N_1 and V_1 are the normality and volume respectively of one acid, N_2 and V_2 of the second acid and so on.



- Glass rod should never be used in flame test as it gives a golden yellow colour due to sodium present in it. An asbestos fibre can be safely used in place of platinum wire.
- \angle The transparent bead in borax bead test is made of $NaBO_2 + B_2O_3$.
- Filter ash test is an alternative to cobalt nitrate test and gives better results.
- Both CO₂ and SO₂ turn lime water milky.

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

$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 \downarrow + H_2O$$
(Milkiness)

 \mathcal{E} Eq. wt. of $KMnO_4$ is different in acidic, alkaline and neutral medium *i.e.*, 31.6, 158 and 52.67 respectively.