NEET | JEE ESSENTIALS

Class XI

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Unit 9 — Principles Related to Practical Chemistry

Practical work in labs improves the scientific knowledge and understanding of students, as well as providing opportunities for working scientifically and developing hands on skills.
Much of forensic science, medicine, pharmaceutical research and many chemical manufacturing processes, rely on accurate techniques and observations.

QUANTITATIVE ESTIMATION

A quantitative analysis is one in which the amount or concentration of a particular species in a sample is determined accurately and precisely.

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.

Titration

- **Unknown Solution**: The solution consisting of substance to be estimated is termed as titrate or unknown solution.
- **Standard Solution**
  - **Primary Standard**: These can be accurately weighed and their solutions are not to be standardised before use *e.g.*, oxalic acid, potassium dichromate, etc.
  - **Secondary Standard**: The solutions of these reagents are to be standardised before use as these cannot be weighed accurately *e.g.*, sodium hydroxide, hydrochloric acid, etc.

Acid-base titration

- When the strength of an acid is determined with the help of a standard solution of base, it is known as acidimetry.
- When the strength of a base is determined with the help of a standard solution of an acid, it is known as alkalimetry.

These titrations involve neutralisation of an acid with an alkali.

$$\underset{\text{Acid}}{HA} + \underset{\text{Alkali}}{BOH} \longrightarrow \underset{\text{Salt}}{BA} + \underset{\text{Water}}{H_2O}$$

Indicator

A substance which helps in physical detection of completion of the titration is called indicator.

Indicators

External Indicators

These indicators are not added in the reaction mixture. They are used outside the system *e.g.*, potassium ferricyanide is used in titration of Mohr's salt against potassium dichromate.

Internal Indicators

These indicators are added in the reaction mixture *e.g.*, in acid-base titration, methyl orange, methyl red and phenolphthalein.

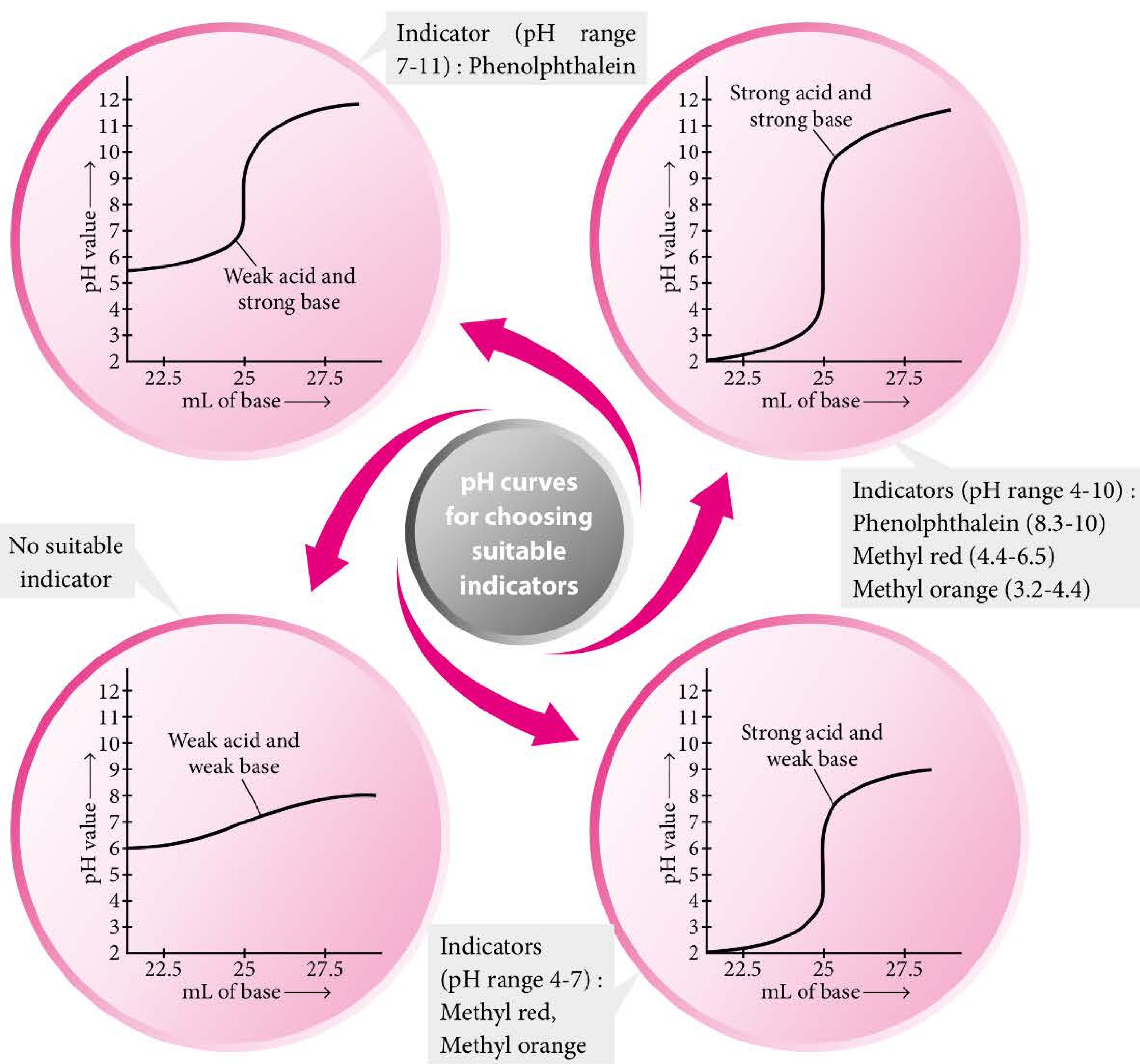
Self Indicators

These indicators themselves show colour change at the end of titration *e.g.*, in titration of oxalic acid against $KMnO_4$, $KMnO_4$ acts as self indicator.

How to choose a suitable indicator :

Indicator in a titration is selected on the basis of pH range at end point.

Indicator	pH-range	Colour of indicator	
		Acid	Alkaline
Phenolphthalein	8.3 – 10	Colourless	Pink
Methyl orange	3.2 – 4.4	Red	Yellow
Methyl red	4.4 – 6.5	Red	Yellow
Litmus	5.0 – 8.0	Red	Blue
Phenol red	6.8 – 8.4	Yellow	Red



Determination of Strength of NaOH

Principle : Strength of NaOH solution can be determined by titrating it against standard solution of oxalic acid.

$$\begin{matrix} COOH \\ | \\ COOH \end{matrix} + 2NaOH \rightarrow \begin{matrix} COONa \\ | \\ COONa \end{matrix} + 2H_2O$$

Indicator : Phenolphthalein

Preparation of standard solution :

Oxalic acid $\left(\begin{matrix} COOH \\ | \\ COOH \end{matrix} \cdot 2H_2O\right)$

Equivalent weight $= \frac{126}{2} = 63$

For preparing 250 mL solution of N/10 oxalic acid,

$$\text{weight required} = \frac{63 \times \frac{1}{10} \times 250}{1000} = 1.575 \text{ g}$$

Thus, for preparing N/10 oxalic acid, take 1.575 g of oxalic acid and make it upto 250 mL using distilled water.

Calculation :

$$\underset{\text{(Oxalic acid)}}{N_1V_1} = \underset{\text{(Caustic soda)}}{N_2V_2}$$

$$N_2 = \frac{N_1V_1}{V_2}$$

Strength of caustic soda = Normality × Equivalent weight = $(N_2 \times 40)$ g/L

Determination of Strength of HCl

Principle : When hydrochloric acid is titrated against Na_2CO_3 solution, strength of HCl can be determined.

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2\uparrow$$

Indicator : Methyl orange

Preparation of standard solution :

Eq. weight $= \frac{106}{2} = 53$

For preparing 250 mL solution of N/10 Na_2CO_3,

$$\text{weight required} = \frac{53 \times \frac{1}{10} \times 250}{1000} = 1.325 \text{ g}$$

Calculation :

$$\underset{(Na_2CO_3)}{N_1V_1} = \underset{(HCl)}{N_2V_2} \quad ; \quad N_2 = \frac{N_1V_1}{V_2}$$

Strength of given HCl = Normality × Eq. weight of HCl = $(N_2 \times 36.5)$ g/L

Qualitative Analysis

Qualitative analysis deals with the identification of various constituents present in a given material. For example, zinc blende contains zinc and sulphur in the form of Zn^{2+} and S^{2-} ions.

Preliminary Tests

Flame Test :

Salt with 1-2 drops of conc. HCl is introduced in the non-luminous (oxidising part) flame of the Bunsen burner using platinum wire.

- Greenish blue → Cu^{2+}
- Lilac → K^+
- Golden yellow → Na^+
- Brick red → Ca^{2+}
- Apple green → Ba^{2+}
- Crimson red → Sr^{2+}

Borax Bead Test :

- Borax is heated on a loop of Pt wire, colourless, glassy bead of sodium metaborate and boric anhydride is formed.

$$Na_2B_4O_7 \cdot 10H_2O \xrightarrow{\Delta} Na_2B_4O_7 \xrightarrow{\Delta} \underbrace{2NaBO_2 + B_2O_3}_{\text{Glassy bead}}$$

- Coloured salts are then heated on the glassy bead, coloured metaborate is formed in the oxidising flame.

Colour of bead in oxidising flame	Ion indicated
Green in hot, blue in cold	Copper
Pinkish violet in both hot and cold	Manganese
Yellowish brown in hot and pale yellow in cold	Iron
Brown in hot and pale brown in cold	Nickel

Acidic Radicals

Anions are acidic radicals

First group
CO_3^{2-}, S^{2-}, SO_3^{2-}
CH_3COO^-,
$S_2O_3^{2-}$, NO_2^-
Reagent used : dil. HCl

Second group
Br^-, Cl^-, I^-
NO_3^-, $C_2O_4^{2-}$
Reagent used : conc. H_2SO_4

Third group
SO_4^{2-}, PO_4^{3-}
Reagent used : dil.H_2SO_4/ conc. H_2SO_4

First Group :

Salt + dil. HCl

Effervescence or evolution of gas shows presence of group I acidic radicals

- Colourless gas with suffocating smell with yellow ppt. of sulphur $\xrightarrow{\text{Pass through } K_2Cr_2O_7}$ Blackish green solution $\rightarrow S_2O_3^{2-}$ confirmed
- Brown gas (NO_2) $\xrightarrow{\text{Starch iodide paper}}$ Blue $\rightarrow NO_2^-$ confirmed
- Colourless gas with vinegar smell (CH_3COO^- may be present) Salt solution + $FeCl_3$ (neutral) $\rightarrow$ $(CH_3COO)_3Fe$ (Blood red colour solution) $\rightarrow CH_3COO^-$ confirmed
- Colourless gas with suffocating smell (SO_2) $\xrightarrow{\text{Heat and pass through } K_2Cr_2O_7}$ Solution turns green due to $Cr_2(SO_4)_3 \rightarrow SO_3^{2-}$ confirmed
- Colourless gas with rotten egg smell (H_2S gas) $\xrightarrow{\text{Lead acetate}}$ PbS (Black ppt.) $\rightarrow S^{2-}$ confirmed
- Colourless, odourless gas (CO_2 gas) $\xrightarrow{\text{Lime water}}$ $CaCO_3$ (Milky) (CO_3^{2-} or HCO_3^- may be present)
- Confirmatory test for HCO_3^- & CO_3^{2-}

  Salt + water $\rightarrow$ boil and pass through lime water
  - Lime water does not turn milky $\downarrow$ HCO_3^- confirmed
  - Lime water turns milky $\downarrow$ CO_3^{2-} confirmed

Second Group : Salt + conc. H_2SO_4

Effervescence or evolution of gases indicates the presence of group II acidic radicals.

Gas	Radical	Observations and Reactions
HCl (Colourless gas, pungent smell)	Chloride (Cl^-)	$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$ (NaCl: Salt) $NH_4OH + HCl \rightarrow NH_4Cl\uparrow + H_2O$ (NH_4Cl: White dense fumes)
Br_2 (Brown fumes)	Bromide (Br^-)	$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$ (NaBr: Salt) $2HBr + H_2SO_4 \rightarrow Br_2\uparrow + 2H_2O + SO_2$ (Br_2: Brown)
I_2 (Deep violet gas)	Iodide (I^-)	$2KI + 2H_2SO_4 \rightarrow 2KHSO_4 + 2HI$ (KI: Salt) $2HI + H_2SO_4 \rightarrow I_2\uparrow + SO_2 + 2H_2O$ (I_2: Violet)
NO_2 (Light brown gas, pungent smell)	Nitrate (NO_3^-)	$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$ ($NaNO_3$: Salt) $4HNO_3 \rightarrow 2H_2O + 4NO_2\uparrow + O_2\uparrow$ (NO_2: Light brown fumes)
$CO + CO_2$ (Colourless, odourless gas)	Oxalate ($C_2O_4^{2-}$)	$Na_2C_2O_4 + H_2SO_4 \rightarrow Na_2SO_4 + H_2C_2O_4$ ($Na_2C_2O_4$: Salt) $H_2C_2O_4 + H_2SO_4 \rightarrow CO + CO_2 + H_2O$ (CO: Burns with blue flame; CO_2: Turns lime water milky)

INFO SHOTS

Determination of sulphate by conductometric titration!

Titrimetric methods are much faster, but a good indicator has not been found for sulphate titrations. However, because the relative concentrations of ions in solution change during titration sequence, monitoring conductivity during the progress of a titration produces a signal which can be used to indicate equivalence point. A conductometric titration protocol has been developed which is relatively rapid, inexpensive and can produce accurate results.

Confirmatory Tests for Group II

Confirmatory tests for acid radicals of group II

Nitrate (NO_3^-)

Brown ring test : On treating aqueous solution of salt with freshly prepared solution of ferrous sulphate and concentrated sulphuric acid, gives a brown ring at the junction of two liquids.

$\underset{\text{Salt}}{NaNO_3} + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$

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

$[Fe(H_2O)_6]SO_4 + NO \longrightarrow \underset{\text{Brown ring}}{[Fe(H_2O)_5NO]SO_4} + H_2O$

Oxalate ($C_2O_4^{2-}$)

On acidifying salt solution or sodium carbonate extract with acetic acid and on adding calcium chloride solution gives white precipitate.

$\underset{\text{Salt}}{Na_2C_2O_4} + CaCl_2 \longrightarrow \underset{\text{White ppt.}}{CaC_2O_4\downarrow} + 2NaCl$

Filter and dissolve the precipitate in dilute sulphuric acid and add few drops of potassium permanganate solution.

$CaC_2O_4 + H_2SO_4 \longrightarrow H_2C_2O_4 + CaSO_4$

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

$\begin{matrix} COOH \\ | \\ COOH \end{matrix} + [O] \longrightarrow 2CO_2 + H_2O$

Pink colour discharge of $KMnO_4$ confirming presence of oxalate ion.

Chloride (Cl^-)

Chromyl chloride test :

$\underset{\text{Salt}}{NaCl} + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

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

$CrO_3 + 2HCl \longrightarrow \underset{\substack{\text{Chromyl chloride} \\ \text{(Red vapours)}}}{CrO_2Cl_2\uparrow} + H_2O$

These vapours on passing through sodium hydroxide solution give yellow solution of sodium chromate.

$CrO_2Cl_2 + 4NaOH \longrightarrow \underset{\text{Yellow colour}}{Na_2CrO_4} + 2NaCl + 2H_2O$

The yellow solution on neutralising with acetic acid and on addition of lead acetate gives yellow precipitate of lead chromate.

$Na_2CrO_4 + (CH_3COO)_2Pb \longrightarrow \underset{\text{Yellow ppt.}}{PbCrO_4\downarrow} + 2CH_3COONa$

Iodide (I^-)

Layer test : On treating salt with dilute sulphuric acid, chloroform or carbon tetrachloride and chlorine water, gives violet coloured layer.

$\underset{\text{Salt}}{2NaI} + Cl_2 \longrightarrow 2NaCl + I_2$

I_2 + Chloroform $\longrightarrow$ Violet coloured layer

Starch paper test :

I_2 + Starch $\longrightarrow$ I_2-starch complex (Blue colour)

Bromide (Br^-)

Layer test : On treating salt with dilute sulphuric acid, chloroform or carbon tetrachloride and chlorine water gives brown coloured layer.

$\underset{\text{Salt}}{2NaBr} + Cl_2 \longrightarrow 2NaCl + Br_2$

Br_2 + Chloroform $\longrightarrow$ Brown coloured layer

Third Group : These anions are identified by their characteristic chemical reactions.

Salt $\xrightarrow[\text{dil. HCl}]{BaCl_2}$ $BaSO_4$ White ppt. (Insoluble in dil. HCl) $\downarrow$ SO_4^{2-} confirmed (Sulphate)

Salt $\xrightarrow[C_2H_5OH]{H_2SO_4}$ $(C_2H_5)_3BO_3$ Burns with green edged flame $\downarrow$ BO_3^{3-} confirmed (Borate)

Salt $\xrightarrow{\text{dil. } HNO_3 \text{ + ammonium molybdate}}$ $(NH_4)_3PO_4\cdot 12MoO_3$ (Canary yellow ppt.) $\rightarrow$ PO_4^{3-} confirmed (Phosphate)

Basic Radicals

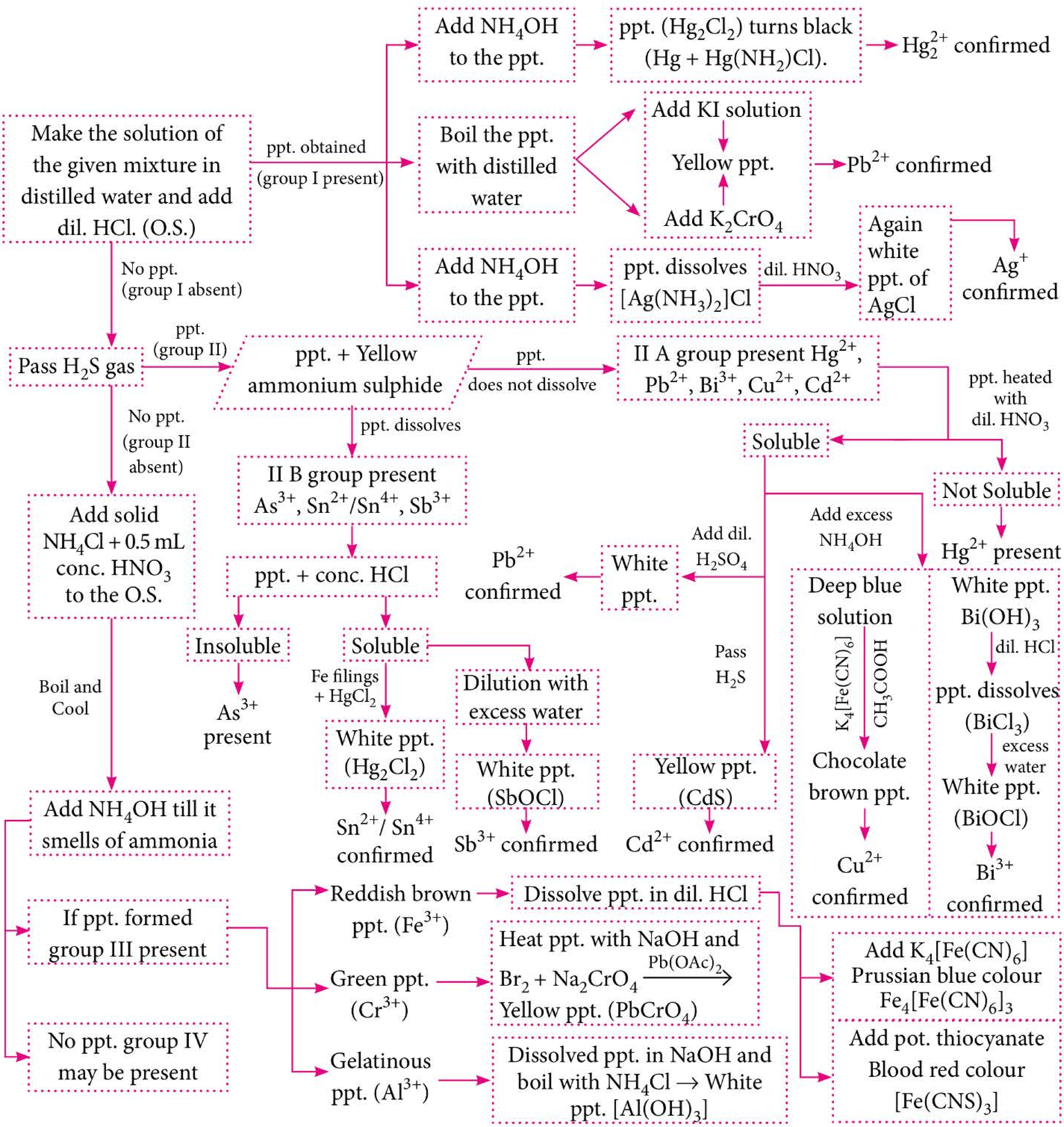
Cations are the basic radicals.

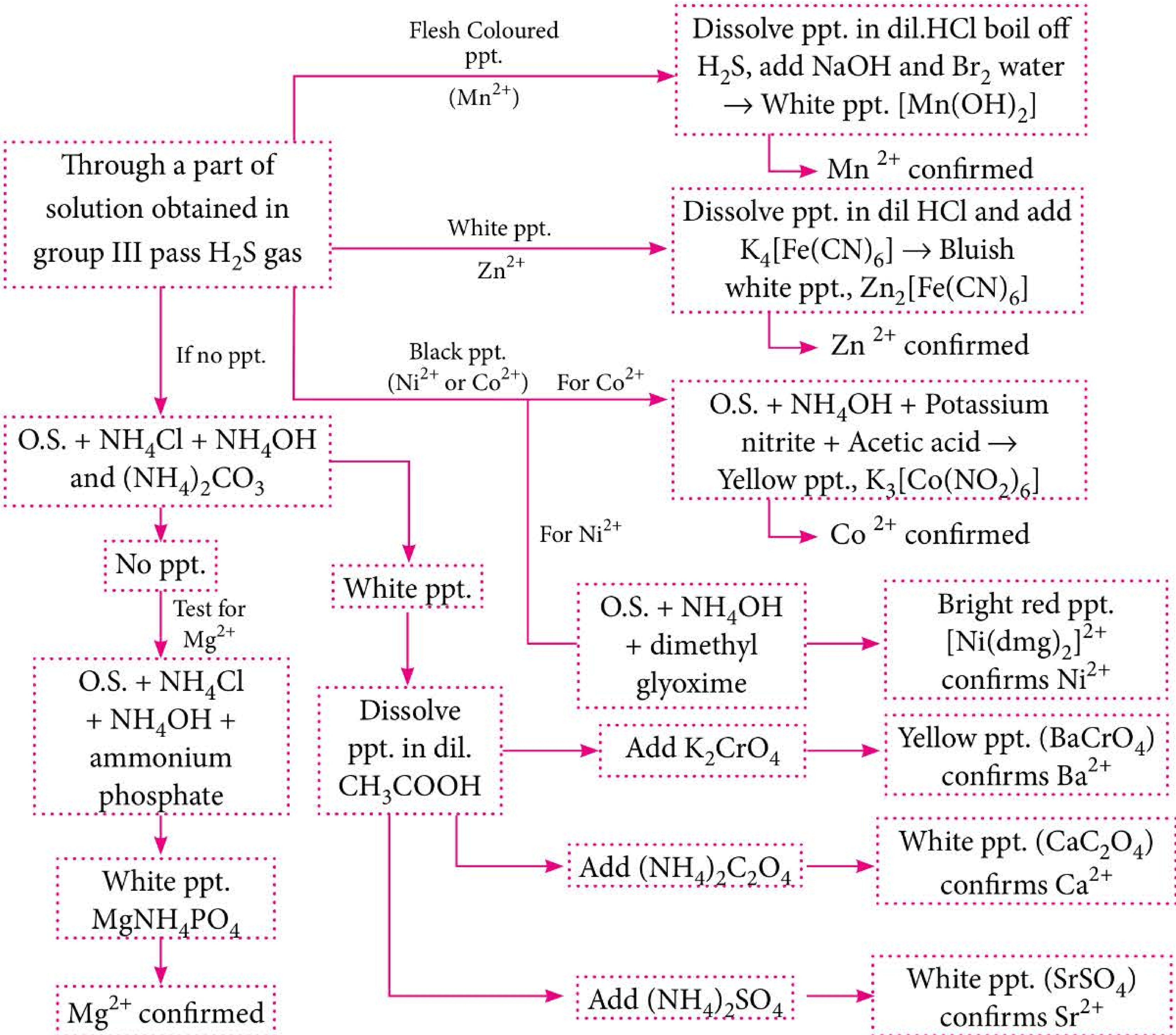
Group	Group reagent	Cations	Form of ppt.
I	dil. HCl	Pb^{2+}, Ag^+, Hg_2^{2+}	Chlorides
II	dil. HCl + H_2S gas	Pb^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, Sb^{3+}, As^{3+}, Sn^{2+}/Sn^{4+}	Sulphides

III	$NH_4Cl + NH_4OH$	Fe^{3+}, Al^{3+}, Cr^{3+}	Hydroxides
IV	$NH_4Cl + NH_4OH + H_2S$ gas	Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}	Sulphides
V	$(NH_4)_2CO_3 + NH_4OH + NH_4Cl$	Ca^{2+}, Sr^{2+}, Ba^{2+}	Carbonates
VI	$Na_2HPO_4 + NH_4OH$	Mg^{2+}	Phosphates

Analysis of Basic Radicals : Zero group $[NH_4^+]$: To the salt, add NaOH solution and heat. If ammonia gas evolves, NH_4^+ is present.

Pass the gas through Nessler's reagent → Brown ppt. → NH_4^+ confirmed.





Detection of N, S, Cl in organic compounds

Lassaigne's extract :

A small pellet of metallic sodium together with a little amount of the substance is heated to red hot in an ignition tube. It is then suddenly plunged into about 10 mL of distilled water in a China dish. The mixture is boiled well and filtered. Filtrate is known as Lassaigne's extract (L.E.).

Element	Detection	Confirmatory test	Reactions
Nitrogen	Lassaigne's extract (L.E.) $Na + C + N \xrightarrow{\Delta} \underset{(L.E.)}{NaCN}$	L.E. + $FeSO_4$ + NaOH, boil and cool + $FeCl_3$ + conc. HCl Gives blue or green colour.	$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$ $Fe(OH)_2 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$ $Na_4[Fe(CN)_6] + FeCl_3 \xrightarrow{HCl} \underset{\text{Prussian blue}}{NaFe[Fe(CN)_6]} + 3NaCl$ or $3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$

Sulphur	$2Na + S \xrightarrow{\Delta} \underset{\text{(L.E.)}}{Na_2S}$	(i) L.E. + sodium nitroprusside A deep violet colour. (ii) L.E. + CH_3COOH + $(CH_3COO)_2Pb$ Gives a black ppt.	(i) $\underset{\text{Sodium nitroprusside}}{Na_2S + Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{Deep violet}}{Na_4[Fe(CN)_5NOS]}$ (ii) $Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH} \underset{\text{Black ppt.}}{PbS\downarrow} + 2CH_3COONa$
Halogens	$Na + X \xrightarrow{\Delta} \underset{\text{(L.E.)}}{NaX}$ (X = Cl, Br, I)	L.E. + HNO_3 + $AgNO_3$ (i) White ppt. soluble in aq. NH_3 (or NH_4OH) confirms Cl. (ii) Pale yellow ppt. partially soluble in aq. NH_3 (or NH_4OH) confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 (or NH_4OH) confirms I.	$NaX + AgNO_3 \xrightarrow{HNO_3} \underset{\text{White ppt.}}{AgX\downarrow} + NaNO_3$ $AgCl + 2NH_4OH_{(aq.)} \longrightarrow \underset{\text{Soluble}}{[Ag(NH_3)_2]Cl} + 2H_2O$
Nitrogen and sulphur together	$Na + C + N + S \xrightarrow{\Delta} \underset{\text{(L.E.)}}{NaSCN}$ Sodium thiocyanate	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.	$3NaSCN + FeCl_3 \longrightarrow \underset{\text{Blood red colour}}{[Fe(SCN)_3]} + 3NaCl$

SPEED PRACTICE

1. An aqueous solution of 6.3 g oxalic acid dihydrate is made upto 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is
(a) 40 mL (b) 20 mL
(c) 10 mL (d) 4 mL

2. Which of the following compounds does not show Lassaigne's test for nitrogen?
(a) Urea (b) Hydrazine
(c) Phenylhydrazine (d) Azobenzene

3. The group reagent for the group V radicals is
(a) $(NH_4)_2CO_3$ (b) $(NH_4)_2SO_4$
(c) NH_4Cl (d) $(NH_4)_2C_2O_4$

4. In qualitative analysis, Cd^{2+} is under
(a) group IV (b) group III
(c) group II (d) group I.

5. A colourless salt gives violet colour in Bunsen flame, it may be
(a) Na_2CO_3 (b) Na_2CrO_4
(c) K_2CO_3 (d) $BaCO_3$.

6. A doctor by mistake administered $Ba(NO_3)_2$ solution to a patient for radiography investigations. Which of the following should be given as the best to prevent the absorption of soluble barium?
(a) Na_2CO_3 (b) NH_4Cl
(c) NaCl (d) Na_2SO_4

7. Which of the following compounds are partially soluble or insoluble in NH_4OH solution?
(1) $Fe(OH)_3$ (2) Ag_2CrO_4
(3) $Al(OH)_3$ (4) Ag_2CO_3
(5) $Ni(OH)_2$
(a) 1, 3 (b) 2, 3, 5 (c) 1, 3, 5 (d) 2, 3, 4