

Practical Inorganic Chemistry

Volumetric Analysis :-

- It is a technique used to find the volume of one solution which will exactly react with a definite volume of another solution.
- Important terms used in volumetric analysis.
- Titrant is the solution of known strength (usually taken in the burette).
- Titre is the substance whose concentration is to be determined by titration.
- Equivalence point or end point is the point at which the chemical rxn involved in the titration is just complete.
- Indicator is the substance which indicates the endpoint of titration (by change of colour)
- Strength of a solution is the amount of solute in grams present per litre of the solution. Strength = Eq. wt. × Normality
- Equivalent weight.

$$\text{Equivalent weight} = \frac{\text{Molecular mass of acid/base/salt/substance}}{\text{Acidity/basicity/total +ve or -ve valency/no. of e's gained or lost.}}$$

What is titration?

An: The process of adding one solution (titrant) from the burette to another in the conical flask (titre) in order to complete the chemical rxn involved is known as Titration.

■ Equivalent weight of some acids/bases/ Salts :-

Acid	Equiv. wt.
HCl	$36.5/1 = 36.5$
H ₂ SO ₄	$98/2 = 49$
HNO ₃	$63/1 = 63$
(COOH) ₂	$90/2 = 45$
(COOH) ₂ 2H ₂ O Hydrated oxalic acid	$126/2 = 63$

Base

NaOH	$40/1 = 40$
KOH	$56/1 = 56$
Ca(OH) ₂	$74/2 = 37$
Ba(OH) ₂ (anhydrous)	$171/2 = 85.5$
NH ₄ OH	$35/1 = 35$

Salt

Na ₂ CO ₃	$106/2 = 53$
NaHCO ₃	$84/1 = 84$
K ₂ CO ₃	$138/2 = 69$
KHCO ₃	$100/1 = 100$

In permanganate titrations, we observe the upper meniscus. Why?

① The soln of KMnO₄ is coloured & hence the upper meniscus is observed taken since it is clearly visible.

② To prevent corrupt reading
some drops of water may come
why we don't wash the titration flask before use?

■ Equivalent weight of some oxidising/reducing agents

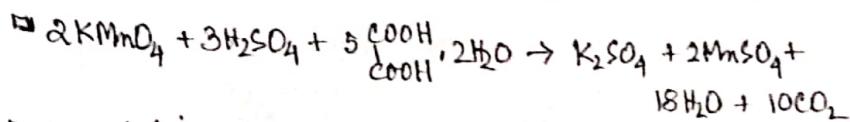
substance	Molecular mass	Balanced ionic equation	No. of electrons gained/lost per mol (n)	Equiv.Wt. = $\frac{\text{Mol.mass}}{n}$
KMnO ₄	158	$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	5	$\frac{158}{5} = 31.6$
K ₂ Cr ₂ O ₇	294	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	6	$\frac{294}{6} = 49$
Anhydri. FeSO ₄	152	$\text{Fe}^{2+} - e^- \rightarrow \text{Fe}^{3+}$	1	$\frac{152}{1} = 152$
Hydrated FeSO ₄ .7H ₂ O	278	$\text{Fe}^{2+} - e^- \rightarrow \text{Fe}^{3+}$	1	$\frac{278}{1} = 278$
Mehrl's salt FeSO ₄ .(NH ₄) ₂ SO ₄ . 6H ₂ O	392	$\text{Fe}^{2+} - e^- \rightarrow \text{Fe}^{3+}$	1	$\frac{392}{1} = 392$
Oxalic acid (anhydri.) H ₂ C ₂ O ₄	90	$\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2e^-$	2	$\frac{90}{2} = 45$
Oxalic acid hydrated H ₂ C ₂ O ₄ .2H ₂ O	126	$\text{C}_2\text{O}_4^{2-} - 2e^- \rightarrow 2\text{CO}_2$	2	$\frac{126}{2} = 63$
Ferrous oxalate (anhydri.) FeC ₂ O ₄	144	$\text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} - 3e^- \rightarrow \text{Fe}^{3+} + 2\text{CO}_2$	3	$\frac{144}{3} = 48$
Ferrous oxalate (hydrated) FeC ₂ O ₄ .2H ₂ O	188	$\text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} - 3e^- \rightarrow \text{Fe}^{3+} + 2\text{CO}_2$	3	$\frac{188}{3} = 60$
Ammonium oxalate (NH ₄) ₂ C ₂ O ₄	124	$\text{C}_2\text{O}_4^{2-} - 2e^- \rightarrow 2\text{CO}_2$	2	$\frac{124}{2} = 62$
Sodium oxalate (Na ₂ C ₂ O ₄)	134	$\text{C}_2\text{O}_4^{2-} - 2e^- \rightarrow 2\text{CO}_2$	2	$\frac{134}{2} = 67$

■ Primary standard solution can be prepared directly by dissolving a known weight of the substance & making a known volume of the solution, eg:- Oxalic acid, Sodium carbonate, etc.

■ Secondary standard solutions can't be prepared directly by weighing, eg., KMnO₄ or hygroscopic substances like NaOH, KOH, or whose concentrations are known only approximately like HCl, H₂SO₄, etc.

Acid (taken in the burette)	Alkali (taken in the titration flask)	Indicator	End point
Strong acid ($\text{HCl}, \text{H}_2\text{SO}_4, \text{HNO}_3$)	Strong alkali (NaOH, KOH)	Phenolphthalein or methyl orange	Pink to colourless or yellow/orange to red.
Weak acid (oxalic, acetic acid)	Strong alkali (NaOH, KOH)	Phenolphthalein	Pink to colourless
Strong acid ($\text{HCl}, \text{H}_2\text{SO}_4, \text{HNO}_3$)	Weak alkali ($\text{Na}_2\text{CO}_3, \text{NaHCO}_3, \text{K}_2\text{CO}_3, \text{KHCO}_3$)	Methyl orange	Yellow/orange to red.

■ Titration of Oxalic acid vs KMnO_4

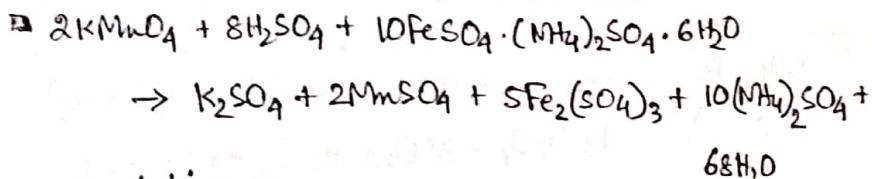


■ Calculations :-

$$\frac{M_{\text{KMnO}_4} \times V_{\text{KMnO}_4}}{M_{\text{Oxalic acid}} \times V_{\text{Oxalic acid}}} = \frac{2}{5}$$

$$\bullet \% \text{ purity of a given salt} = \frac{\text{Strength of pure sample}}{\text{Strength of given sample}} \times 100$$

■ Titration of Mohr's salt vs KMnO_4



■ Calculations :-

$$\frac{M_{\text{KMnO}_4} \times V_{\text{KMnO}_4}}{M_{\text{Mohr's salt}} \times V_{\text{Mohr's salt}}} = \frac{1}{5}$$

Qualitative Analysis

■ It deals with the identification of various constituents (cations & anions) present in a given substance.

Preliminary tests

■ It involves identification of salt by their colour or characteristic smell.

Preliminary test	Observation	Inference
colour	<ul style="list-style-type: none"> Blue or bluish green Green Light green Yellow or brown Pink Light pink, earthy colour or flesh colour White 	Cu^{2+} Ni^{2+} Fe^{2+} Fe^{3+} Co^{2+} Mn^{2+} Shows absence of above

Preliminary Test	Observation	Inference
Smell	<ul style="list-style-type: none"> • Ammoniacal • Vinegar like smell • Rotten egg like smell 	NH_4^+ CH_3COO^- S^{2-}

- Identification of acidic radicals (anions)
- Acid radicals are divided into three groups.

- Group I : Salt + dilute HCl or dilute H_2SO_4

	Observation	Gas	Radical	Reaction
a)	Brisk effervescence, turns lime water milky	CO_2	carbonate (CO_3^{2-})	$\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ (salt) $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ Lime water (milky) $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}(\text{HCO}_3)_2$ (soluble)
b)	Rotten egg like smell, turns lead acetate paper black	H_2S	Sulphide (S^{2-})	$\text{Na}_2\text{S} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{S}$ (salt) $\text{Pb}(\text{CH}_3\text{COO})_2 + \text{H}_2\text{S} \rightarrow \text{PbS} \downarrow + 2\text{CH}_3\text{COOH}$ Black $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \rightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NO}]$ sodium Nitroprusside violet colour
c)	Pungent smell, turns acidified $\text{K}_2\text{Cr}_2\text{O}_7$ paper or solution green	SO_2	Sulphite (SO_3^{2-})	$\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{SO}_2 \uparrow$ $\text{K}_2\text{Cr}_2\text{O}_7 + 3\text{SO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{OH})_3 + \text{H}_2\text{O}$ green
d)	reddish brown gas, turns starch iodide paper blue	NO_2	Nitrite (NO_2^-)	$2\text{NaNO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HNO}_2$ Nitrous acid $3\text{HNO}_2 \rightarrow \text{H}_2\text{O} + 2\text{NO} + \text{HNO}_3$ $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \uparrow$ Brown colour.

- Group II : salt + conc. H_2SO_4

	Observation	Gas	Radical	Reaction
a)	colourless gas with a pungent smell, white fumes with aqueous ammonia (NH_4OH), white ppt with AgNO_3 solution	HCl	chloride (Cl^-)	$2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ $\text{NH}_4\text{OH} + \text{HCl} \rightarrow \text{NH}_4\text{Cl} + \text{H}_2\text{O}$ (white fumes) $\text{HCl} + \text{AgNO}_3 \rightarrow \text{AgCl} \downarrow + \text{HNO}_3$ $\text{AgCl} + 2\text{NH}_4\text{OH} \rightarrow [\text{Ag}(\text{NH}_3)_2]^{+} \text{Cl}^{-} + 2\text{H}_2\text{O}$ (white soluble)

QUALITATIVE ANALYSIS (ACID RADICALS) >

- Dilute H_2SO_4 or dilute HCl or concn H_2SO_4 can detect.
 - CO_3^{2-} , SO_3^{2-} , S^{2-} , NO_2^- , $S_2O_3^{2-}$ and CH_3COO^- .
- Conc. H_2SO_4 can detect : Cl^- , Br^- , I^- , NO_3^- , $C_2O_4^{2-}$
- Special tests : SO_4^{2-} , PO_4^{3-} , BO_3^{3-} , MnO_4^- , CrO_4^{2-} , $Cr_2O_7^{2-}$
- CO_3^{2-}
 - Lime water test. $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$
 - White precipitate with $BaCl_2$, $CaCl_2$ and $AgNO_3$.
 - $CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$
soluble
- SO_3^{2-}
 - Lime water test. The released gas turns dichromate paper from orange to green.
 - White precipitate with $BaCl_2$, $Ca(OH)_2$.
 - $Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2 \uparrow$
 - $K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$
 - $Na_2SO_3 + BaCl_2 \rightarrow BaSO_3 \downarrow + 2NaCl$
 - $BaSO_3 + 2HCl \rightarrow BaCl_2 + H_2O + SO_2 \uparrow$
white ppt
soluble
 - $Na_2S + H_2SO_4 \rightarrow Na_2SO_4 + H_2S \uparrow$
- S^{2-}
 - Gives rotten egg smell with dilute acid
 - The released gas turns lead acetate paper black and cadmium acetate paper yellow.
 - Gives violet colour with sodium nitroprusside solution. $(CH_3COO)_2Pb + H_2S \rightarrow PbS \downarrow + 2CH_3COOH$
 - Methylene blue test.
- NO_2^-
 - Brown fumes are released with dil. acid.
 - With dilute H_2SO_4 gives brown ring test.
 - With KI solution, it can release I_2 that forms blue colour complex with starch.
- SO_3^{2-}
 - With dilute acid gives white precipitate of 'S'.
 - With $FeCl_3$ forms short-lasting violet colour due to $[Fe(S_2O_3)]^{4-}$.
 - Gives white precipitate with $BaCl_2$, $Pb(CH_3COO)_2$, $AgNO_3$.
- CH_3COO^-
 - with dil. acid gives vinegar smell.
 - Gives deep red colour with $FeCl_3$.
 - $2CH_3COONa + H_2SO_4 \xrightarrow{\text{salt}} 2CH_3COOH + Na_2SO_4$
 - $3CH_3COONa + FeCl_3 \xrightarrow{\text{blood red}} (CH_3COO)_3Fe + 3NaCl$
 - $2CH_3COONa + COOH \xrightarrow{\text{COOH}} COONA + 2CH_3COOH$
 $COONA$ vinegar smell
- Cl^-
 - Gives chromyl chloride test ($PbCl_2$, $AgCl$, $StCl_3$, $SnCl_2$, etc. fail due to their covalent nature). Solid salt when heated with $K_2Cr_2O_7$ powder and conc. H_2SO_4 releases CrO_2Cl_2 vapour (orange coloured).

- White precipitate with AgNO_3 that dissolves in NH_3 solution.

o $\text{Br}^{(-)}$

- When shaken with Cl_2 water and CHCl_3 , orange colour is observed in the chloroform layer.

- With conc. H_2SO_4 gives brown fumes that intensifies with addition of MnO_2 .

o $\text{I}^{(-)}$

- In CHCl_3 layer test develops violet colour.

- With AgNO_3 gives yellow precipitate.

- With $\text{Pb}(\text{C}_2\text{H}_5\text{COO})_2$ gives yellow precipitate soluble in hot water.

- With conc. H_2SO_4 gives violet fumes.

o $\text{F}^{(-)}$

- Salt, sand and few drops of conc. H_2SO_4 when heated releases a gas that develops a white deposit on a glass rod moistened with water.

o $\text{NO}_3^{(-)}$

- With concentrated H_2SO_4 releases brown fumes that intensify on addition of Cu-turnings.

- With conc. H_2SO_4 and freshly prepared FeSO_4 solution develops browning due to the formation of $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}] \text{SO}_4$.

o SO_4^{2-}

- White precipitate with BaCl_2 solution. The precipitate doesn't dissolve in mineral acid. $\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow \text{BaSO}_4 \downarrow + 2\text{NaCl}$

(white ppt
insoluble in conc. HNO_3)

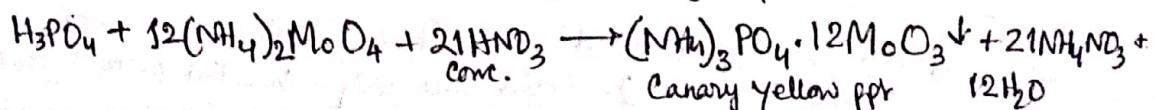
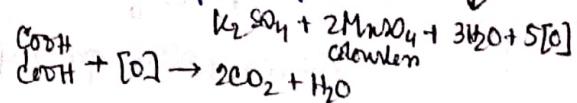
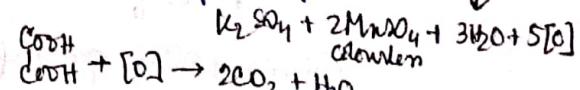
o BO_3^{2-}

- Salt is mixed with 1 ml. conc. H_2SO_4 and 1 ml. ethyl alcohol and heated. The mouth of the test tube when shown to the flame gives green colour.

o $\text{C}_2\text{O}_4^{2-}$ obs. & Rxn $\text{Na}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{C}_2\text{O}_4$ Confirmative test
 $\text{H}_2\text{C}_2\text{O}_4 + [\text{H}_2\text{SO}_4] \xrightarrow{\text{burns with blue flame turns milky}} \text{CO} + \text{CO}_2 + \text{H}_2\text{O} + [\text{H}_2\text{SO}_4]$ $\text{Na}_2\text{C}_2\text{O}_4 + \text{CaCl}_2 \rightarrow \text{CaC}_2\text{O}_4 \downarrow + 2\text{NaCl}$
- conc. H_2SO_4 decomposes the salt to form CO & CO_2 . $\text{CaC}_2\text{O}_4 + \text{dil. H}_2\text{SO}_4 \xrightarrow{\text{white ppt}} \text{H}_2\text{C}_2\text{O}_4 + \text{CaSO}_4$
- AgNO_3 solution and CaCl_2 solution gives white precipitate. 2KMnO_4 (few drops) + $3\text{H}_2\text{SO}_4$ Purple

o PO_4^{3-}

- About 3 ml. of conc. HNO_3 is added to the salt mixture followed by excess of ammonium molybdate solution to get a canary yellow precipitate. $\text{Ca}_3(\text{PO}_4)_2 + 6\text{HNO}_3 \rightarrow 3\text{Ca}(\text{NO}_3)_2 + 2\text{H}_3\text{PO}_4$



Group II:

Observation	Gas	Radical	Rxn
b) Reddish brown vapours, turns starch paper yellow, a pale yellow ppt. with AgNO_3 partially soluble in NH_4OH	Br_2	Bromide (Br^-)	$\text{AgNO}_3 + \text{HBr} \rightarrow \text{AgBr} \downarrow + \text{HNO}_3$ (Pale yellow) $\text{AgBr} + 2\text{NH}_4\text{OH} \rightarrow [\text{Ag}(\text{NH}_3)_2]\text{Br}$ [Soluble silver ammonium bromide complex] + $2\text{H}_2\text{O}$
c) Deep violet vapours, yellow ppt with AgNO_3 insoluble in NH_4OH	I_2	Iodide (I^-)	$\text{AgNO}_3 + \text{HI} \rightarrow \text{AgI} \downarrow + \text{HNO}_3$ (Yellow)
d) Light brown fumes, intensified on adding Cu turnings.	NO_2	Nitrate (NO_3^-)	$\text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HNO}_3$ $4\text{HNO}_3 \rightarrow 2\text{H}_2\text{O} + 4\text{NO}_2 + \text{O}_2$ $\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$

Group III : These radicals can't be detected by either dil. H_2SO_4 or conc. H_2SO_4 .
For detection of the acidic radicals we need some specific tests.

Observation	Radical	Rxn
A white ppt. formed with BaCl_2 , insoluble in conc. HNO_3 .	Sulphate	$\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow \text{BaSO}_4 \downarrow + 2\text{NaCl}$
A yellow ppt with HNO_2 and ammonium molybdate solution.	Phosphate (PO_4^{3-})	$\text{Ca}_3(\text{PO}_4)_2 + 6\text{HNO}_3 \rightarrow 3\text{Ca}(\text{NO}_3)_2 + 2\text{H}_3\text{PO}_4$ $\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 \rightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ canary yellow + $21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O}$
Green edged flame on igniting the vapours evolved by heating the salt with ethyl alcohol and conc. H_2SO_4 .	Borate (BO_3^{3-})	$2\text{Na}_3\text{BO}_3 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{Na}_2\text{SO}_4 + 2\text{H}_3\text{BO}_3$ $\text{H}_3\text{BO}_3 + 3\text{C}_2\text{H}_5\text{OH} \rightarrow (\text{C}_2\text{H}_5)_3\text{BO}_3 + 3\text{H}_2\text{O}$

Oxalate

Group II:

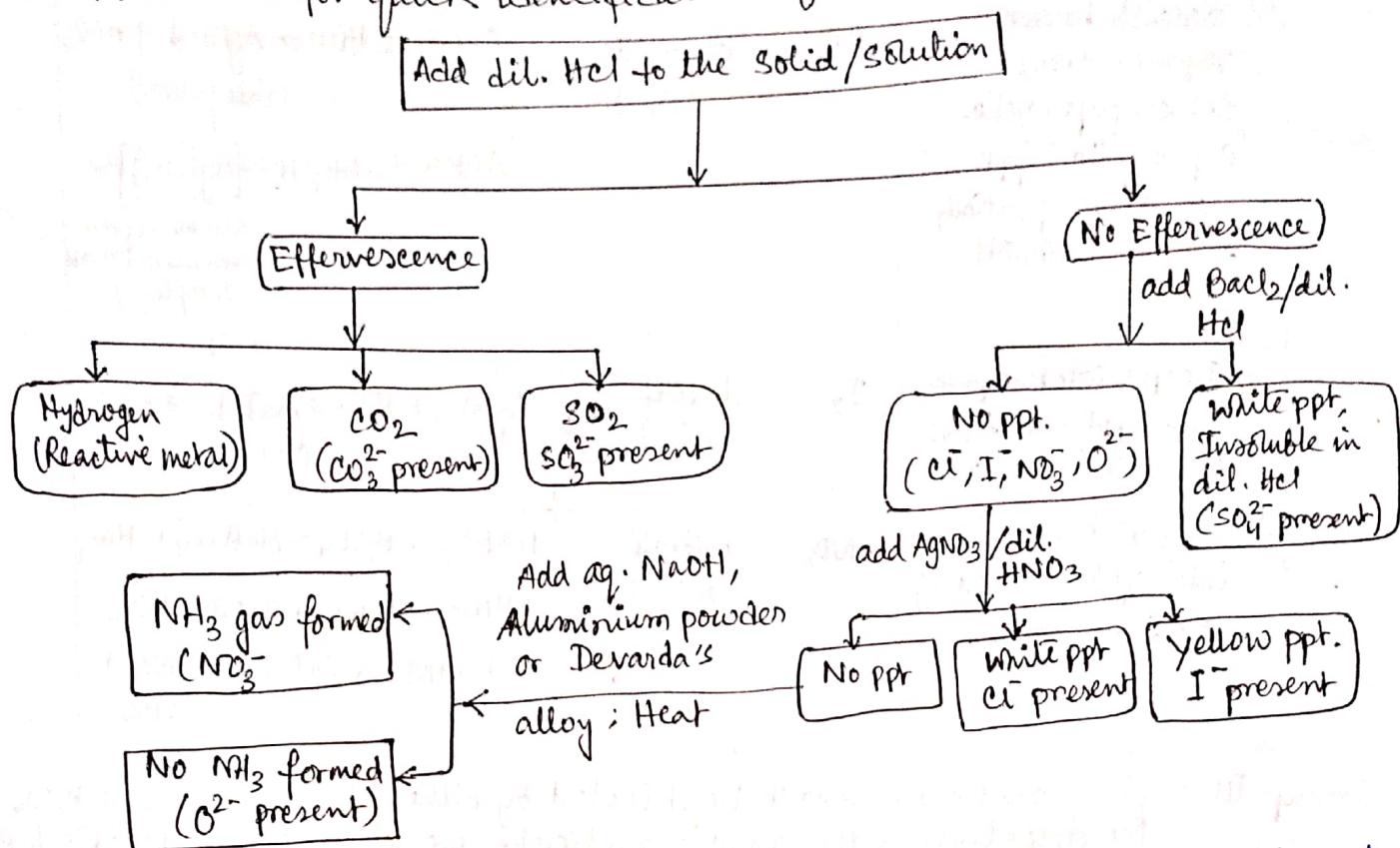
Observation	Gas	Radical	Rxn
b) Reddish brown vapours, turns starch paper yellow, a pale yellow ppt. with AgNO_3 partially soluble in NH_4OH	Br_2	Bromide (Br^-)	$\text{AgNO}_3 + \text{HBr} \rightarrow \text{AgBr} \downarrow + \text{HNO}_3$ (Pale yellow) $\text{AgBr} + 2\text{NH}_4\text{OH} \rightarrow [\text{Ag}(\text{NH}_3)_2]\text{Br}$ (Soluble silver ammonium bromide complex) $+ 2\text{H}_2\text{O}$
c) Deep violet vapours, yellow ppt with AgNO_3 insoluble in NH_4OH	I_2	Iodide (I^-)	$\text{AgNO}_3 + \text{HI} \rightarrow \text{AgI} \downarrow + \text{HNO}_3$ (Yellow)
d) Light brown fumes, intensified on adding Cu turnings.	NO_2	Nitrate (NO_3^-)	$\text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HNO}_3$ $4\text{HNO}_3 \rightarrow 2\text{H}_2\text{O} + 4\text{NO}_2 + \text{O}_2$ $\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$

Group III : These radicals can't be detected by either dil. H_2SO_4 or conc. H_2SO_4 . For detection of the acidic radicals we need some specific tests.

Observation	Radical	Rxn
A white ppt. formed with BaCl_2 , insoluble in conc. HNO_3 .	Sulphate	$\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow \text{BaSO}_4 \downarrow + 2\text{NaCl}$
A yellow ppt with HNO_2 and ammonium molybdate solution.	Phosphate (PO_4^{3-})	$\text{Ca}_3(\text{PO}_4)_2 + 6\text{HNO}_3 \rightarrow 3\text{Ca}(\text{NO}_3)_2 + 2\text{H}_3\text{PO}_4$ $\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 \rightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ (Canary yellow) $+ 21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O}$
Green edged flame on igniting the vapours evolved by heating the salt with ethyl alcohol and conc. H_2SO_4 .	Borate (BO_3^{3-})	$2\text{Na}_3\text{BO}_3 + 3\text{H}_2\text{SO}_4 \rightarrow 3\text{Na}_2\text{SO}_4 + 2\text{H}_3\text{BO}_3$ $\text{H}_3\text{BO}_3 + 3\text{C}_2\text{H}_5\text{OH} \rightarrow (\text{C}_2\text{H}_5)_3\text{BO}_3 + 3\text{H}_2\text{O}$.

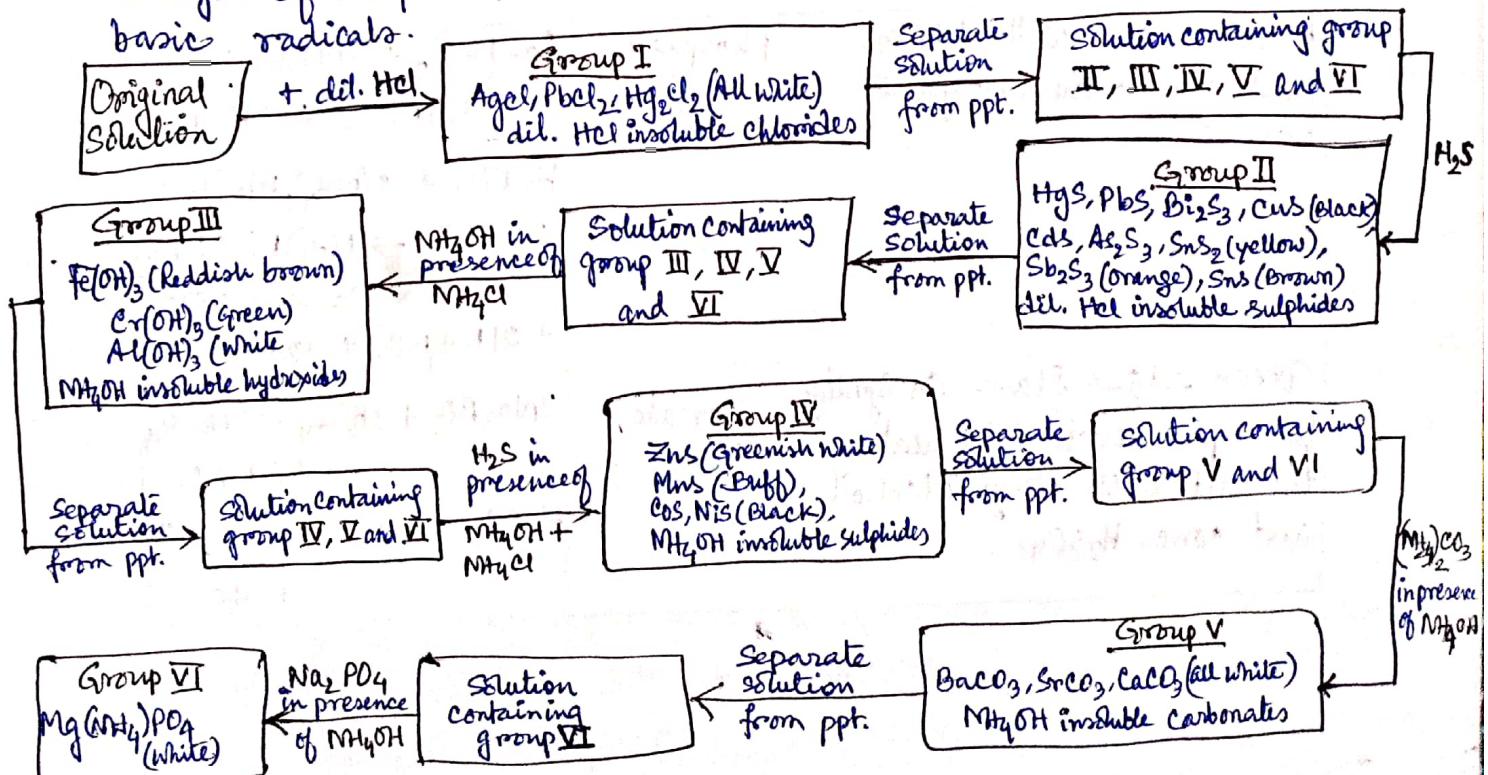
Oxalate

Flow chart for quick identification of anions



- Identification of basic radicals (cations) : Wet analysis of basic radicals involves three steps.
- Preparation of the original solution.
 - Separation of basic radicals into different groups

- Analysis of the precipitates obtained in different groups & confirmation of the basic radicals.



Identification of Acidic Radicals

Group I: The radicals which are analysed by dil. H_2SO_4 or dil. HCl these are
 1. Carbonate (CO_3^{2-}) 2. Sulphate (SO_4^{2-}) 3. Sulphide (S^{2-})
 4. Nitrite (NO_2^-) 5. Acetate (CH_3COO^-)

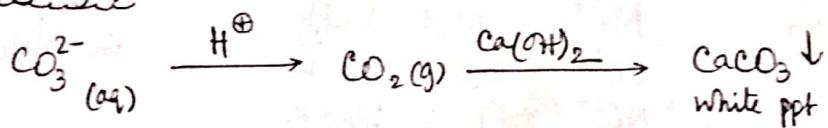
Group II: The radicals which are analysed by conc. H_2SO_4 there are
 1. Chloride (Cl^-) 2. Bromide (Br^-) 3. Iodide (I^-) 4. Nitrate (NO_3^-)
 & 5. Oxalate ($C_2O_4^{2-}$)

Group III: The radicals which can't be analysed by dil. or conc. H_2SO_4 ,
 these are 1. Sulphate (SO_4^{2-}), 2. phosphate (PO_4^{3-}), 3. Borate (BO_3^{3-})
 4. Fluoride (F^-)

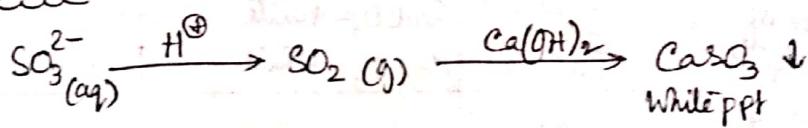
In Brief

Group I: Add dil. HCl or H_2SO_4 to a small amount of substance
 & warm gently, observe.

1. Carbonate (CO_3^{2-})

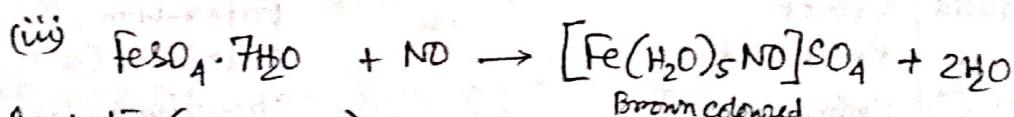
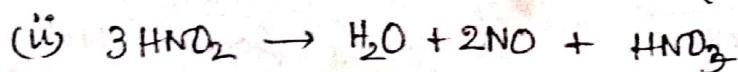
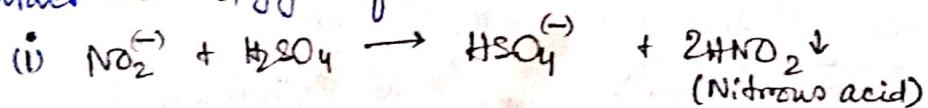


2. Sulphate (SO_4^{2-})

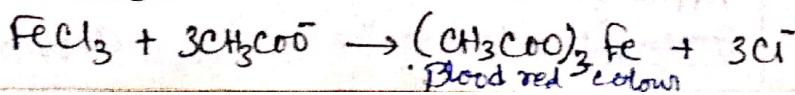


3. Sulphide (S^{2-}) The sulphides also turn sodium nitroprusside solution violet (use Na_2CO_3 extract for this test) $Na_2S + Na_2[FeNO(CN)_5] \rightarrow Na_4[Fe(CN)_5NOS]$ violet.

4. Nitrite (NO_2^-): The nitrites yield a colourless nitric oxide gas which in contact with oxygen of the air becomes brown due to formation of NO_2 .



5. Acetate (CH_3COO^-)



Group	Group reagent	Basic radical	Composition & Colours of the precipitate	
1.	Dil HCl	Ag^+ Pb^{2+} Hg^{2+}	AgCl - white PbCl_2 - white Hg_2Cl_2 - white	chlorides insoluble in cold dil. HCl
2.	H_2S in presence of dil. HCl	Hg^{2+} Pb^{2+} Bi^{3+} Cu^{2+} Cd^{2+} As^{3+} Sb^{3+} Sn^{2+} Sn^{4+}	HgS - black PbS - black Bi_2S_3 - black CuS - black CdS - yellow As_2S_3 - yellow Sb_2S_3 - orange SnS - brown SnS_2 - yellow	Sulphides, insoluble in dil. HCl
3.	NH_4OH in presence of NH_4Cl	Fe^{3+} Cr^{3+} Al^{3+}	Fe(OH)_3 - reddish brown Cr(OH)_3 - green Al(OH)_3 - white	Hydroxides in NH_4OH
4.	H_2S in presence of NH_4OH	Zn^{2+} Mn^{2+} Co^{2+} Ni^{2+}	ZnS - greenish white MnS - buff CoS - black NiS - black	Sulphides, insoluble in NH_4OH .
5.	$(\text{NH}_4)_2\text{CO}_3$ in presence of NH_4OH	Ba^{2+} Sr^{2+} Ca^{2+}	BaCO_3 - white SrCO_3 - white CaCO_3 - white	Carbonates, in NH_4OH
6.	$\text{Na}_2\text{HPO}_4 + \text{NH}_4\text{OH}$	Mg^{2+}	$\text{Mg}(\text{NH}_4)\text{PO}_4$ - white	
0.	NaOH	Na^+	Ammonia gas is evolved	

Qualitative Salt Analysis

► Dry Tests: Following tests are performed in dry state:

1. Flame test
2. Borax bead test
3. Microcosmic salt bead test
4. Cobalt nitrate charcoal test.

► Flame test

Salt with 1 or 2 drops of conc. HCl is introduced in the nonluminous (oxidising part) flame of the Bunsen burner using Pt wire.

► Colour of flame

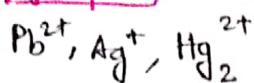
- Golden yellow
- Violet
- Brick red
- Crimson red
- Apple green
- Green with a blue centre

► Inference

- Sodium, Na^+
- Potassium, K^+
- Calcium, Ca^{2+}
- Strontium, Sr^{2+}
- Barium, Ba^{2+} or Mo^{2+}
- Copper, Cu^{2+} or BrO_3^{-} , Ti^{3+}

QUALITATIVE ANALYSIS OF BASIC RADICALS

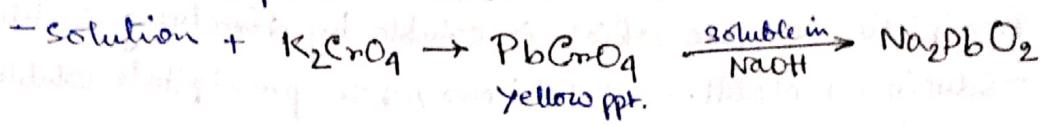
Group - I



— white precipitate are obtained in dil. HCl.

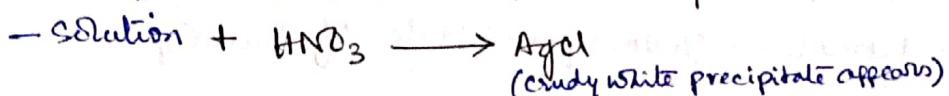
Tests:

— Pb^{2+} : Precipitate is soluble in hot water.



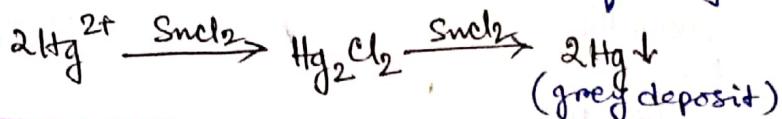
Ag^+ :

— Precipitate is soluble in dilute NH_4OH .



Hg_2^{2+} :

— Precipitate dissolves in aqua regia, where it is converted into Hg^{2+} .



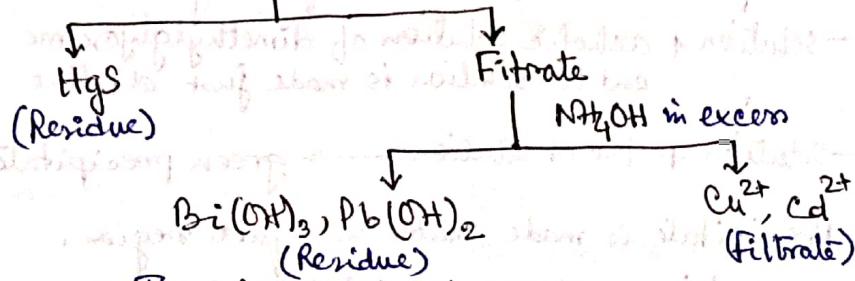
Group - II A

$\text{Hg}^{2+}, \text{Bi}^{3+}, \text{Cu}^{2+}, \text{Cd}^{2+}$: (Precipitate appears on passing H_2S gas in dilute HCl)

Group-II A

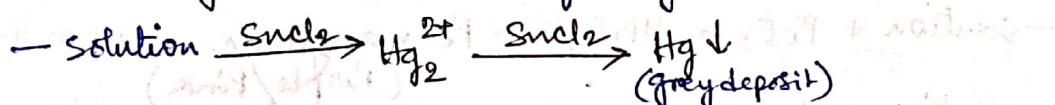
Precipitate

1:1 mixture of nitric acid and water



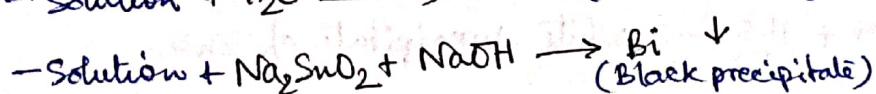
Hg^{2+} :

Residue HgS is dissolved in aqua regia.

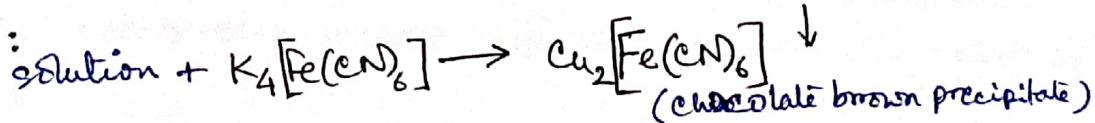


Bi^{3+} :

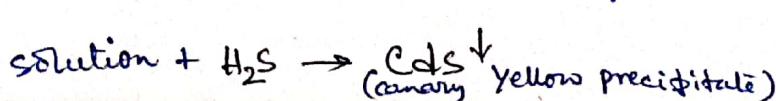
Bi(OH)_3 is made soluble in minimum amount of HCl.



Cu^{2+} :



Cd^{2+} :



■ Group-III A

Fe^{3+} , Al^{3+} , Cr^{3+} (Precipitate in NH_4OH and NH_4Cl)

- Fe^{3+} : Precipitate is dissolved in dilute HCl
 - Solution + NH_4SCN \rightarrow Red colour
 - Solution + $\text{K}_4[\text{Fe}(\text{CN})_6]$ \rightarrow Prussian blue

- Al^{3+} : Precipitate is made which is soluble by dissolving in dilute HCl.
 - Solution + NaOH \rightarrow Gelatinous white precipitate soluble in excess NaOH .

- Cr^{3+} : Cr(OH)_3 is precipitate that is made soluble using Br_2 water and NaOH .
 - Solution + BaCl_2 \rightarrow Yellow precipitate of BaCrO_4 .

■ Group-III B

Zn^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} : (Precipitate in NH_4OH and H_2S)

Group-III B
Precipitate

| dil. HCl

CoS, NiS
(Black residue)

Mn(OH)_2
(Precipitate)

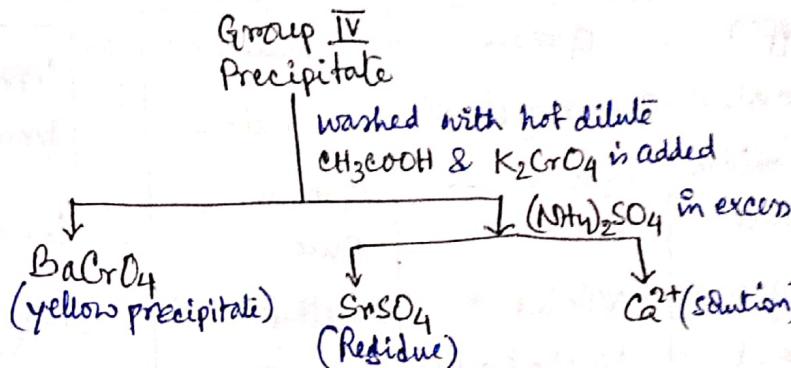
| NaOH (excess)

Na_2ZnO_2 (Filtrate)

- Ni^{2+} : Precipitate is dissolved in aqua regia
 - solution + acoholic solution of dimethylglyoxime and the solution is made just alkaline \rightarrow Nickel dimethyl glyoxime (rosy red precipitate)
 - solution + KCN solution \rightarrow green precipitate.
- Co^{2+} : Precipitate is made soluble in aqua regia.
 - solution + KHC_2O_4 (solution) + Br_2 water \rightarrow green colour.
- Mn^{2+} : Precipitate is treated with conc. HNO_3 boiled & cooled.
 - solution + PbO_2 + HNO_3 \rightarrow Permanganic acid. (Purple/Pink)
 - solution + NaBiO_3 + HNO_3 \rightarrow Permanganic acid.
- Zn^{2+} :
 - solution + H_2S \rightarrow White precipitate of ZnS .

■ **Group IV**

$\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$: Precipitates in presence of $\text{NH}_4\text{OH}, \text{NH}_4\text{Cl} \& (\text{NH}_4)_2\text{CO}_3$

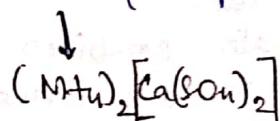


- Ba^{2+} : The residue is treated with concn HCl.



- Sr^{2+} : The residue can be subjected to flame test.

- Ca^{2+} : Solution + $(\text{NH}_4)_2\text{SO}_4 \rightarrow \text{CaSO}_4$ (white precipitate)



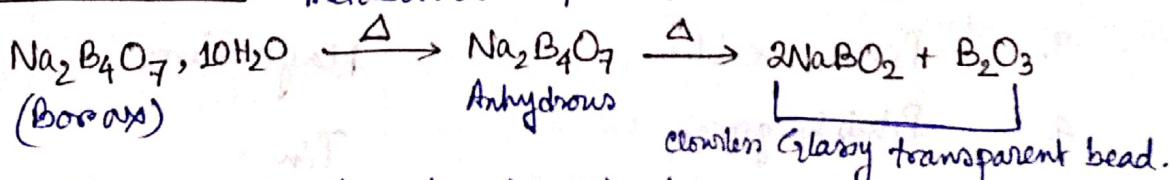
Dissolves in excess of the reagent.

■ **Group-V**

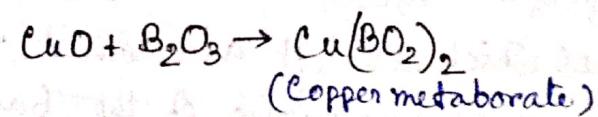
- $\overset{(+)}{\text{NH}_4}$: Solution + Nessler's reagent $\rightarrow [\text{Hg}-\text{O}-\text{Hg}]\text{NH}_2\text{I} = \begin{array}{c} \text{Hg} \\ | \\ \text{O} \\ || \\ \text{Hg} \end{array} \text{NH}_2\text{I}$
brown precipitate
of iodides of Milan's base

- K^+ : Solution + sodium cobaltinitrato $\rightarrow (\text{K}_2\text{Na}[\text{Co}(\text{NO}_2)_6])$
(yellow precipitate)

- **Borax bead test**: Coloured salts are heated on the glassy bead, coloured metaborates are formed.



On heating coloured salt on the glassy bead of metaborate is formed in the oxidising flame: e.g. $\text{CuSO}_4 \rightarrow \text{CuO} + \text{SO}_2$



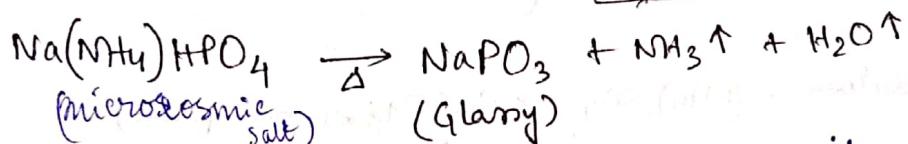
The metaborates possess different characteristic colour of oxidising flame:

→

Metal	Oxidizing - flame	
	Hot	Cold
Copper	Green	Blue
Iron	Brown-yellow	Pale-yellow
Chromium	Green	Green
Cobalt	Blue	Blue
Manganese	Violet	Amethyst red
Nickel	Violet or Red brown	Brown

Metal	Reducing flame	
	Hot	Cold
Copper	Colorless	Brown Red
Iron	Bottle green	Bottle green
Chromium	Green	Green
Manganese	Colorless	Colorless
Cobalt	Blue	Blue
Nickel	Grey	Grey

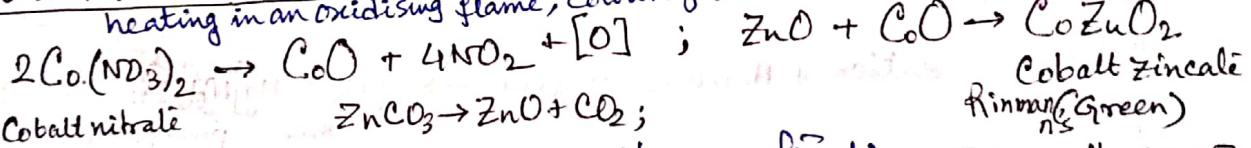
Microcosmic salt bead test :-



Sodium metaphosphate combines with metallic oxides to form orthophosphates which are usually coloured.

Cobalt Nitrate. Charcoal test

If the residue in charcoal cavity test is white, it is moistened with a drop of cobalt nitrate & on colour of the residue changes.



The colour produced in charcoal cavity is noticed: $ZnSO_4 + Na_2CO_3 \rightarrow ZnCO_3 + Na_2SO_4$

Observation

Inference

Aluminium

1. Blue mass

~~Zinc~~

2. Green residue

Magnesium

3. Pink residue

Tina

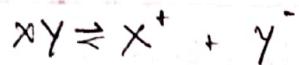
4. Blush green

- charcoal cavity Test (Reduction Test): salt is heated with fusion mixture (Na_2CO_3 and K_2CO_3) in a charcoal cavity in reducing flame to form metallic oxides which are left as coloured residues. The colour of the residue being characteristic of the basic radical present.

Principles behind precipitation occurring in various groups

Common-Ion Effect :

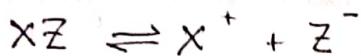
Considering the ionisation of a weak electrolyte XY ,



$$K = \frac{[X^+][Y^-]}{[XY]}$$

If another electrolyte,

XZ is added to the above solution.



This results increase in concentration of X^+ ions. In order to keep K as a constant the concentration of XY must evidently increase. In other words, the equilibrium will shift backwards. The ionisation of a weak electrolyte or sparingly soluble salt is suppressed by the addition of another electrolyte containing a common-ion. This is known as — common-ion effect.

Solubility Product :

For a salt A_xB_y ; equilibrium constant

$$K = [A^{y+}][B^{x-}] \Rightarrow K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

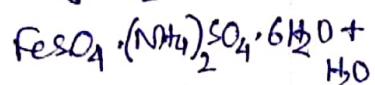
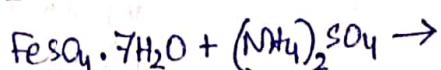
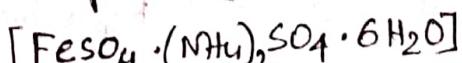
If S be the solubility of A_xB_y then

$$K_{sp} = x^x y^y S^{(x+y)}$$

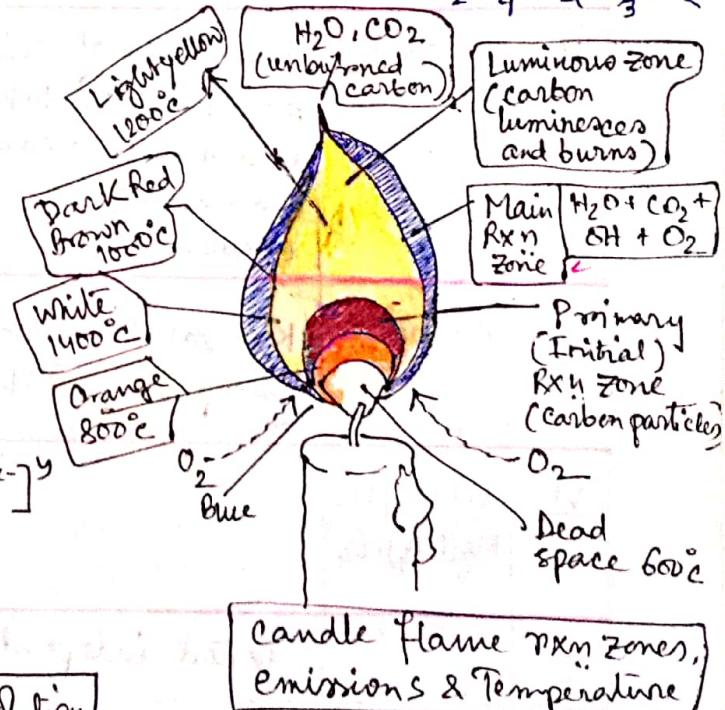
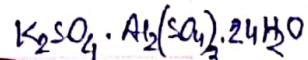
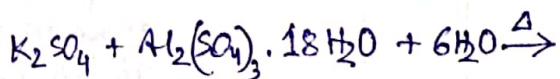
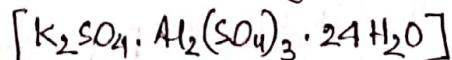
Condition	Precipitation	Nature of solution
$K > K_{sp}$	✓	Supersaturated
$K < K_{sp}$	✗	Unsaturated
$K = K_{sp}$	✗	Saturated (at equilibrium)

Preparation of some inorganic compounds.

Ferrous ammonium sulphate (Mohr's salt)



Potash alum (Phit Kari)



Group	Precipitate as	Explanation
I	Chlorides	K _{sp} values of chlorides are low, hence precipitated. Others have higher K _{sp} values hence not precipitated.
II	Sulphides	K _{sp} values of sulphides are low hence precipitated by low [S ²⁻] ion. HCl (with common H ⁺ ion) decreases the ionization of H ₂ S which gives low [S ²⁻]. Hence group II is precipitated. Others with higher K _{sp} values are not precipitated.
III	Hydroxides	K _{sp} values of Al(OH) ₃ , etc. are low. NH ₄ Cl (with common NH ₄ ⁺ ion) decreases the ionization of NH ₃ O ⁺ giving low [OH ⁻]. Hence, group III is precipitated.
IV	Sulphides	K _{sp} values of sulphides of group IV are high, hence precipitation takes place in higher [S ²⁻]. Basic medium increases the ionization of H ₂ S, thus increasing [S ²⁻], hence precipitation of group IV occurs.
V	Carbonates	K _{sp} values of carbonates are less than that of group VI (Mg ²⁺) hence precipitates before Mg ²⁺ .
VI	White ppt. Mg(NH ₄)PO ₄	
0		Tested independently from original solution

PRACTICAL ORGANIC CHEMISTRY

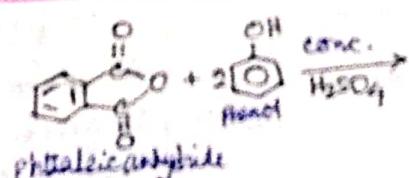
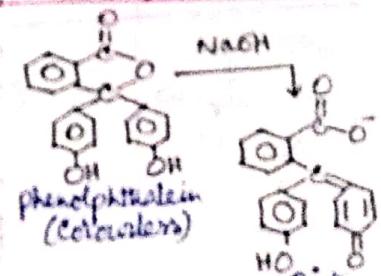
- **Detection of extra elements** :- The elements other than C, H and O are called extra elements.

Lassaigne's test

- Principle :- The elements are usually tested in the form of ions. Since organic compounds are covalent in nature, they don't ionize. Therefore to convert elements present in organic compounds into ions, the organic compound is fused with Sodium metal.
- Preparation of Lassaigne's extract** :- The organic compd. is fused with a small piece of Na metal which is plunged in distilled water, boiled and filtered. The filtrate is called Lassaigne's filtrate or sodium extract.

Element	Sodium extract	Confirmatory test
Nitrogen	$\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$	($\text{NaCN} + \text{Fe}_2\text{O}_4 + \text{NaOH} \rightarrow \text{FeCl}_3 + \text{cone. HCl}$) boil and cool \rightarrow Blue or green colour $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$
Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$	(i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \rightarrow$ A deep violet colour of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ (ii) $\text{Na}_2\text{S} + \text{CH}_3\text{COOH} + (\text{CH}_3\text{COO})_2\text{Pb} \rightarrow$ A black ppt.
Halogen	$\text{Na} + \text{X} \xrightarrow{\Delta} \text{NaX}$	$\text{NaX} + \text{HNO}_3 + \text{AgNO}_3$ (i) White ppt. soluble in aq. NH_3 confirms Cl. (ii) Yellow ppt. partially soluble in aq. NH_3 confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 confirms I.
Nitrogen and Sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaCNS}$	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.

Detection of functional groups :-

	Test	Reaction	Confirmation
(A) Detection of unsaturation			
(i) Baeyer's or KMnO ₄ test	$2\text{KMnO}_4 + \text{H}_2\text{O} \rightarrow 2\text{KOH} + 2\text{MnO}_2 + 3[\text{O}]$ $\text{C=C} + \text{H}_2\text{O} + [\text{O}] \rightarrow \text{C}-\text{C}$ OH OH	Disappearance of pink colour of KMnO ₄	
(ii) Br ₂ -CCl ₄ test	$\text{C=C} + \text{Br}_2 \xrightarrow{\text{ccly}} \text{C-Br}$ Red brown Br	Disappearance of brown colour	
(B) Detection of alcoholic group			
(i) Ester test	$\text{RCOOH} + \text{R}'\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{RCOOR}'$ (Ester)	Fruity smell of ester indicates -OH group	
(ii) Ceric ammonium nitrate test	$2\text{ROH} + (\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6] \rightarrow [(\text{ROH})_2\text{Ce}(\text{NO}_3)_4] + 2\text{NH}_4^+$ Pink or red	Appearance of pink or red colour.	
(C) Detection of phenolic group			
(i) FeCl ₃ test	$\text{FeCl}_3 + 6\text{O} \rightarrow [\text{Fe}(\text{OC}_6\text{H}_5)_6]^{3-}$ + 3H ⁺ + 3HCl	Appearance of violet colouration.	
(ii) Azodye test	$\text{O} \text{---} \text{NH}_2 + \text{NANO}_2 + \text{HCl} \rightarrow \text{O} \text{---} \text{N}=\text{O}$ $\text{O} \text{---} \text{NH}_2^+ + \text{O} \text{---} \text{N}=\text{O}^- \text{ pH } 7-10$ p-hydroxyacetobenzen ($\text{O} \text{---} \text{NH} \text{---} \text{OCH}_2\text{C}_6\text{H}_4\text{OH}$)	Formation of orange or red dye.	
(iii) Phthalein test or fluorescein			
(iv) Liebermann's nitroso rxn	$\text{C}_6\text{H}_5\text{OH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{NANO}_2} \text{HO}-\text{C}_6\text{H}_4-\text{N}=\text{O} \xrightleftharpoons{\text{Tautomerises}} \text{O}=\text{C}_6\text{H}_4-\text{N}=\text{O} \text{---} \text{green}$ $\text{Phenol} \xrightarrow[\text{H}_2\text{SO}_4]{\text{H}_2\text{NCONHNHCO}_2} \text{Indophenol (red)} \xrightarrow{\text{NaOH}} \text{O}=\text{C}_6\text{H}_4-\text{N}=\text{O} \text{---} \text{OH} \text{---} \text{Blue}$		

(D) Detection of carbonyl group

Aldehydic group

(i)	Tollen's test	$\text{RCHO} + 2[\text{Ag}(\text{NH}_3)_2]^{\text{OH}} \rightarrow \text{RCOONH}_4 + 3\text{NH}_3 + \text{H}_2\text{O} + 2\text{Ag}(\text{s})$ silver mirror	Formation of silver mirror along the sides of the test tube.
(ii)	Fehling's test	$\text{RCHO} + 2\text{Cu}^{2+} + 3\text{OH}^- \xrightarrow{\text{heat}} 2\text{Cu}^{\downarrow} + \text{RCOO}^{-} + 2\text{H}_2\text{O}$	A red ppt. is formed only by aliphatic aldehydes.
(iii)	Schiff's test	$\text{RCHO} + \text{P}-\text{rosaniline hydrochloride (colorless)}$	Appearance of pink colour.
(iv)	Benedict's test	$\text{RCHO} + 2\text{Cu}(\text{OH})_2 + \text{NaOH} \rightarrow \text{RCOONa} + \text{Cu}_2\text{O} \downarrow + 3\text{H}_2\text{O}$	Appearance of red ppt.

Ketonic group

(i)	Iodoform test	$\text{RCOCH}_3 + 3\text{I}_2 + 4\text{NaOH} \rightarrow 3\text{NaI} + \text{CHI}_3 + \text{RCOONa} + 3\text{H}_2\text{O}$	Formation of yellow ppt of CHI_3 (for methyl ketones only).
(ii)	Sodium nitroprusside test	$\text{RCOR} + \text{Sodium nitroprusside solution} + \text{NaOH}$	Appearance of wine-red colour.

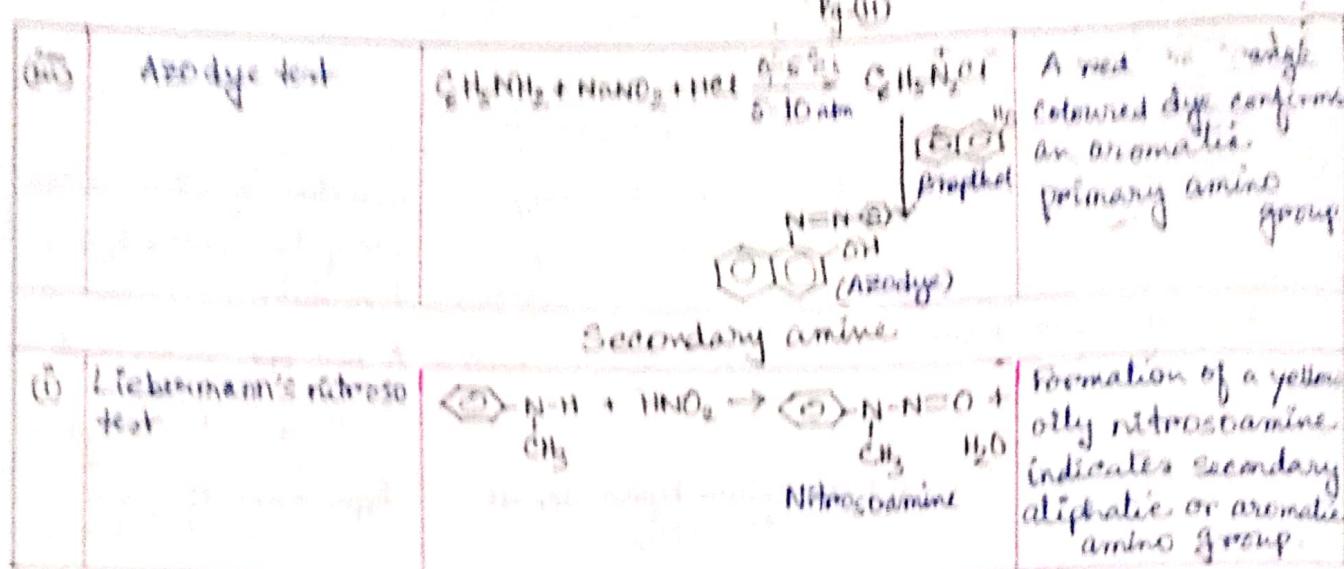
(E) Detection of Carboxylic group

(i)	Litmus test	Blue litmus paper turns red.	-COOH group may be present.
(ii)	NaHCO_3 test	$\text{RCOOH} + \text{NaHCO}_3 \rightarrow \text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2 \uparrow$	Burst effervescence of CO_2 indicates -COOH group.
(iii)	Ester test	$\text{RCOOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{conc.}} \text{RCOOC}_2\text{H}_5 + \text{H}_2\text{O}$	Fruity smell of esters formed
(iv)	FeCl_3 test	$3\text{RCOOH} + 3\text{NH}_4\text{OH} + \text{FeCl}_3 \rightarrow (\text{RCOO})_3\text{Fe} + 3\text{NH}_4\text{Cl} + 3\text{H}_2\text{O}$ $(\text{RCOO})_3\text{Fe} \xrightarrow{\text{H}_2\text{O}} \text{Fe(OH)}(\text{OCOR})_2 + \text{RCOOH}$ Basic iron salt	Red \rightarrow acetic acid, formic acid. No colour change \rightarrow oxalic acid. Violet \rightarrow salicylic acid. Buff \rightarrow benzoic acid

(F) Detection of amino group

Primarily amines

(i)	Nitrous acid test	$\text{R-NH}_2 + \text{HNO}_2 \rightarrow \text{RNH}_3^+ + \text{N}_2 \uparrow + \text{H}_2\text{O}$	N_2 effervescence indicates 1° amino group
(ii)	Carbylamine test	$\text{R-NH}_2 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\Delta} \text{R-N}\equiv\text{C} + 3\text{KCl}$ (isocyanide + 3H ₂ O)	Offensive smell of isocyanide e.g. indicates 1° aliphatic or aromatic amino group



Distinctions

Test	Phenol	Alcohol
Blue litmus test	turns red	x
Felty test	gives violet colouration	x
AZO dye test	forms orange-red colour dye	x
Bry-Water test	gives white ppt.	x

Test	Phenol	Carboxylic acid	Test	Aldehyde	Ketone
NaHCO ₃ test	*	gives brisk effervescence	Tollen's test	gives shiny silver mirror	*
Fehling's solution test			Schiff's reagent test	gives red ppt	*
Reduction with LiAlH ₄			Peroxyacid (Caro's acid, peroxylactic acid)	reduced to 1° alcohol	reduced to 2° alcohol
p-nitroacetanilide				acid is formed	ether is formed

Preparation of some Organic compounds

- Acetanilide

$$\text{C}_6\text{H}_5\text{NH}_2 + \text{CH}_3\text{COOC}_2\text{H}_5 \xrightarrow{\text{CH}_3\text{COOH}} \text{C}_6\text{H}_5\text{NHCOCH}_3 + \text{CH}_3\text{COOH}$$

Acetanilide

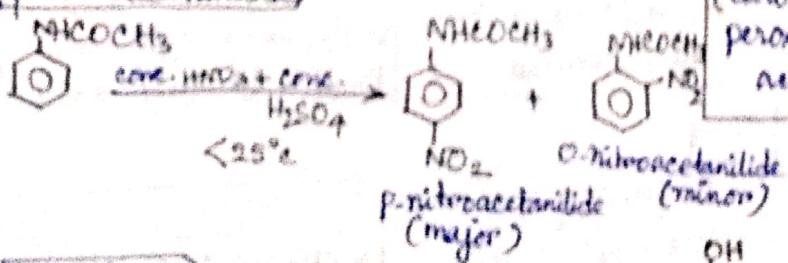
$$\text{C}_6\text{H}_5\text{NH}_2 + \text{CH}_3\text{COCl} \xrightarrow{\text{pyridine}} \text{C}_6\text{H}_5\text{NHCOCH}_3 + \text{HCl}$$

Acetanilide

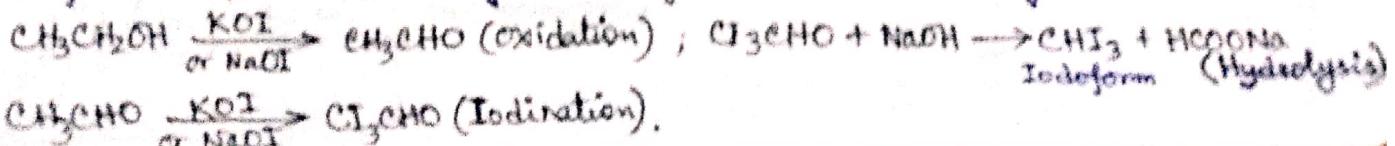
- p-nitroacetanilide

$$\text{C}_6\text{H}_5\text{NHCOCH}_3 + \text{conc. HNO}_2 + \text{conc. H}_2\text{SO}_4 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{HNO}_2 + \text{H}_2\text{O}$$

p-nitroacetanilide

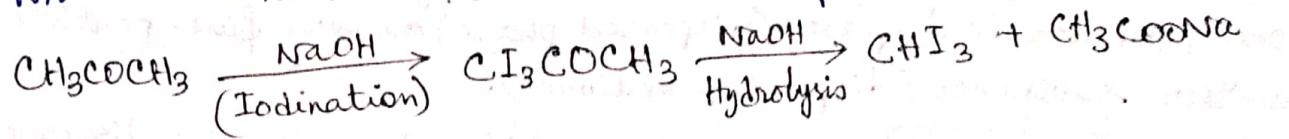


Iodoform: Compounds containing $\text{CH}_3\text{CH}-$ group or $\text{C}_2\text{HCO}-$ group can form iodoform on rxn with sodium hypiodide eg., ethanol, acetaldehyde, acetone etc.

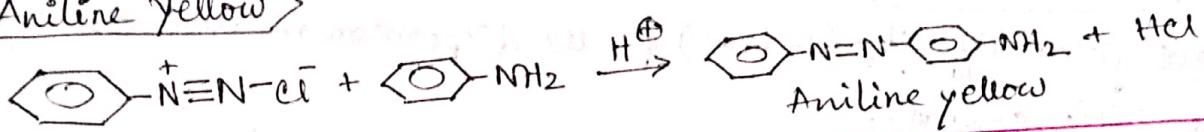


$$\text{C}_6\text{H}_5\text{CHO} \xrightarrow[\text{or NaCl}]{\text{KI}} \text{C}_6\text{H}_5\text{CHI} \text{ (Iodination).}$$

with acetone no initial oxidation takes place.



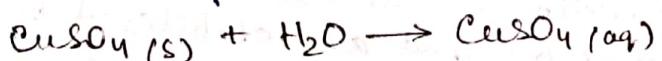
■ **Aniline yellow**



Chemical principles involved in the physical chemistry experiments

■ To find enthalpy of solution of CuSO_4

- Enthalpy of solution is the amount of heat change involved during the dissolution of 1 mole of a solute in such a large excess of solvent so that no further heat changes occur on dilution.



- Dissolution of CuSO_4 in water is exothermic the enthalpy of solution of $\text{CuSO}_4(s)$ is calculated from the highest temperature attained during its dissolution.

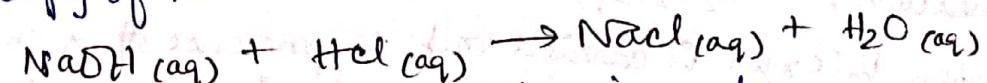
- Calculations:** If dissolution of w gm of CuSO_4 in 200 gm solvent (water) causes $\Delta t^\circ\text{C}$ change in temperature, then
heat evolved during the process (q) = mass \times specific heat \times change in temperature.

$$q = 200 \times 4.2 \times \Delta t \text{ Joule}$$

$$\text{Enthalpy of solution of } \text{CuSO}_4 \text{ in water} = \frac{-q \times 159.5 \times 10^{-3}}{w} \text{ KJ}$$

■ To find enthalpy of neutralisation of strong acid and strong base

- Enthalpy change accompanying neutralisation of one gram equivalent of a base by an acid in dilute solutions at a given temperature is known as the enthalpy of neutralisation.



This rxn is exothermic in nature.

- Calculation:** Heat evolved during neutralisation of 100 ml of 0.5 N HCl. $q = 200 \times \Delta t \times 4.2 \text{ J}$. Thus enthalpy of neutralisation of 1000 ml of 1 N HCl and NaOH = $\frac{-q}{0.5 \times 100} \text{ KJ}$

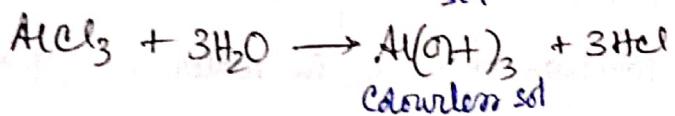
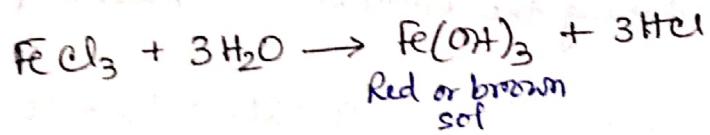
Preparation of sols :- A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance (dispersion medium).

- **Lyophilic colloids** :- The colloidal solutions in which the dispersed phase have great affinity (or love) for the dispersion medium are called lyophilic colloids.

- **Preparation of Lyophilic sols** :- These sols are prepared by shaking the lyophilic material with the dispersion medium, e.g., Colloidal sols of gelatin, gum, starch, egg albumin, etc.

- **Lyophobic colloids** :- The colloidal solution in which the particles of the dispersed phase have no affinity (or love) for the dispersion medium are called lyophobic colloids. Such solutions are formed with difficulty and are unstable and are stabilised by the addition of a small amount of electrolytes, also called stabilizers. In case the dispersion medium is water, the lyophobic colloids are called hydrophobic colloids.

- **Preparation of Lyophobic colloids** :- Colloidal sols of ferric hydroxide and aluminium hydroxide can be prepared by hydrolysis of FeCl_3 & AlCl_3 with distilled water. HCl produced, is removed with dialysis.



■ Kinetic study of rxn of iodide ion with hydrogen peroxide at room temperature.

- Hydrogen peroxide oxidises iodide ion (from KI) to iodine in acidic medium.

$$\text{H}_2\text{O}_2(\text{aq}) + 2\text{I}^{\ominus}(\text{aq}) + 2\text{H}^{\oplus}(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{H}_2\text{O(l)}$$
- When this rxn is carried out in presence of a small amount of sodium thiosulphate and starch, the iodine produced first reacts with sodium thiosulphate as follows :

$$2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{S}_4\text{O}_6^{2-}(\text{aq}) + 2\text{I}^{\ominus}(\text{aq})$$
- When thiosulphate ions get completely consumed, the liberated iodine reacts with starch solution to give blue coloured complex.

$$\text{I}_2(\text{aq}) + \text{Starch}(\text{aq}) \rightarrow \text{Blue complex.}$$

As the concentration of thiosulphate ion is kept constant, the different time taken (t_c) for the appearance of blue colour with change in concentration of either reactant indicates the relative rate of rxn.

Initial rate $\propto \frac{1}{t_c}$

- o The rate of rxn decreases with decrease in concentration of KI.
- o The graph of $1/t_c$ vs. volume of KI solution is a straight line.
- o Rate of reaction \propto concentration of KI.
- Normality equation : Let N_1 and V_1 are the volume and normality of one solution which completely neutralises V_2 volume of another solution having normality N_2 , then according to the law of equivalence

$$N_1 V_1 = N_2 V_2$$

- Dilution formula : The change in concentration of a solution on dilution can be calculated by $\frac{N_1 V_1}{(text{before dilution})} = \frac{N_2 V_2}{(after dilution)}$
- Normality = Molarity $\times n$
Where n = valency factor, Thus $N_1 V_1 = N_2 V_2$ can be written as
 $M_1 V_1 n_1 = M_2 V_2 n_2$ or $\frac{M_1 V_1}{M_2 V_2} = \frac{n_2}{n_1}$

- Calculation of Strength of an unknown solution

Strength in g/L = Normality \times equiv. weight
calculating number of molecules of water of crystallisation (x) present in the hydrated substance.

$$x = \frac{\text{Mol. wt. of hydrated substance} - \text{mol. weight of anhydrous substance}}{18}$$

- What is basic principle of Volumetric Analysis?

The concentration of a solution is determined by allowing a known volume of the solution to react quantitatively with another solution of a known concentration.

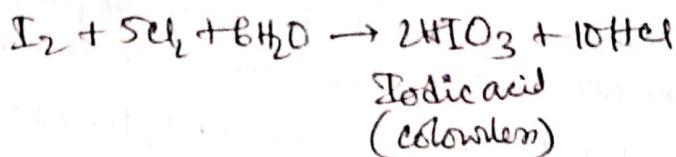
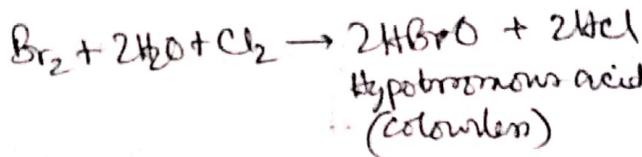
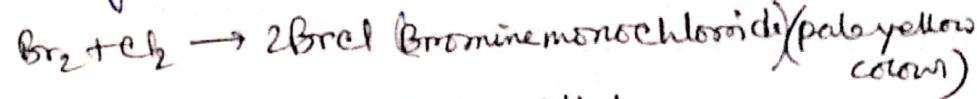
- Which type of titration is KMnO₄ vs Mohr's Salt or KMnO₄ vs Oxalic acid ?

Ans: Redox Titration, KMnO₄ works as self indicator here.

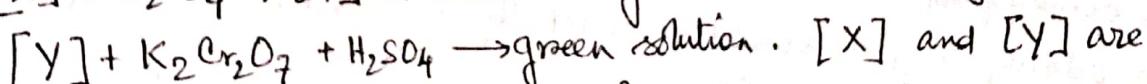
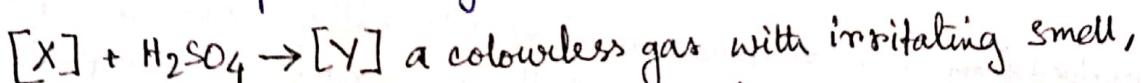
Key point :-

- **Ferric ammonium test** :-
 - Many aromatic amines which are easily oxidisable also give this test.
 - Some phenols also give green or brown ppt.
- **Ferric chloride test** :- Also given by enols i.e. $[-\overset{\text{OH}}{\underset{\text{C}}{\text{C}}}=\text{C}-]$
- **Sodium bisulphite test** :-
 - Aliphatic aldehydes and methyl Ketones which are not sterically hindered such as Acetaldehyde, acetone, ethyl methyl Ketone give this test.
 - Among aromatic aldehydes and Ketones, only benzaldehyde gives this test but acetophenone, benzophenone don't give this test.
- **Iodoform test** : Only methyl ketones (Ketones containing $-\text{COCH}_3$ group) give this test.
- **NaHCO₃ test** : Some phenols such as 2,4-dinitrophenol and 2,4,6-trinitrophenol (picric acid) also respond to this test.
- For the identification of β -naphthol using dye test, it is necessary to use :-
 - a) dichloromethane solution of β -naphthol
 - b) acidic solution of β -naphthol
 - c) neutral solution of β -naphthol
 - d) alkaline solution of β -naphthol(JEE Advanced 2014)
- Which of the following reagents may be used to distinguish between phenol and benzoic acid ?
 - a) Aqueous NaOH
 - b) Tollen's reagent
 - c) Molisch's reagent
 - d) Neutral FeCl₃(AIEEE 2011)

- Brunn ring test is not reliable in the presence of NO_2^- , Br^- , I^- ions.
- While performing confirmatory test for $\text{C}_2\text{O}_4^{2-}$ ion, in presence of F^- ion a white ppt. of CaF_2 is also formed by the addition of CaCl_2 solution but CaF_2 doesn't dissolve in dil. H_2SO_4 & doesn't discharge the colour of KMnO_4 .
- While performing layer test for Br^\ominus & I^\ominus ions, excess of Cl_2 water should be avoided.

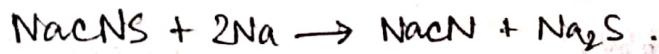


- Test for F^\ominus ion should be performed in perfectly dry test tube, otherwise waxy white deposit will not be formed on the rod.
- HgCl_2 and NH_4Cl also produce a deposit under these conditions but this deposit is crystalline in nature.



- (a) $\text{SO}_3^{2-}, \text{SO}_2$ (b) $\text{Cl}^\ominus, \text{HCl}$ (c) $\text{S}^{2-}, \text{H}_2\text{S}$ (d) $\text{CO}_3^{2-}, \text{CO}_2$ (IIT-JEE 2003)

- When sodium fusion is carried out with excess of Na, ~~etc~~ thiocyanate decomposes to cyanide and Sulphide ions which give their usual tests. Thus we don't get blood red colour with ferric chloride even though N and S both are present. $\text{Na} + \text{C} + \text{N} + \text{S} \rightleftharpoons \text{NaCN} \text{S} \text{ [sodium thiocyanate]}$

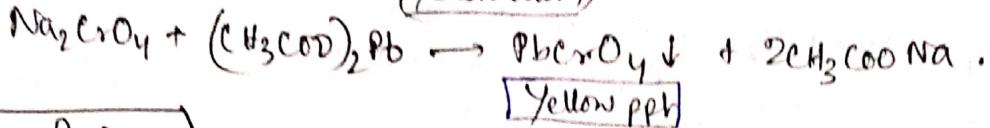
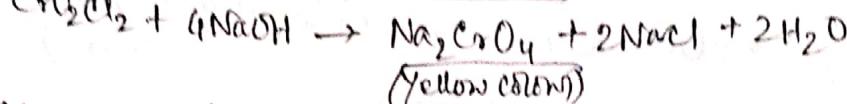
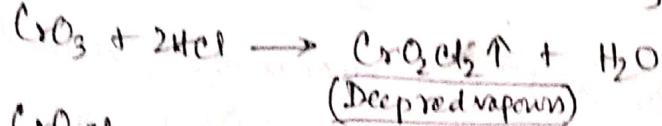
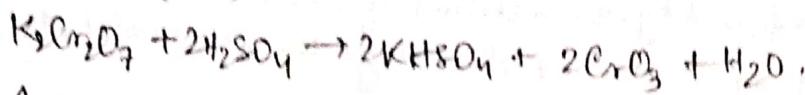
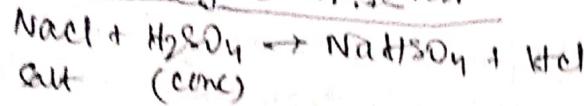


- Lassaigne's test fails in case of compounds which contain nitrogen but no carbon e.g., hydrazine (NH_2NH_2) and hydroxylamine (NH_2OH).

The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is

- (a) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (b) $\text{Na}_3[\text{Fe}(\text{CN})_6]$ (c) $\text{Fe}(\text{CN})_3$
 (d) $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$ (AIEEE 2004)

Chromyl Chloride Test



Key Points

Flame test shouldn't be performed in the presence of As, Sb, Bi, Sn, Pb as these radicals form alloy with platinum and hence the wire is spoiled.

- The yellow colouration due to sodium masks that of potassium. In such cases, view the flame through cobalt glass, the yellow sodium colour is absorbed and the potassium flame appears crimson.
- Cobalt nitrate test should be performed with 2-3 drops of cobalt nitrate solution otherwise black cobalt oxide is formed which will mask the colour of the residue.
- SO_2 gas evolved from SO_3^{2-} ion, also turns limewater milky. Thus for test of CO_3^{2-} ion odour of gas should be carefully observed as SO_2 is a pungent gas while CO_2 is odourless gas.
- $\text{PbS}, \text{CdS}, \text{NiS}, \text{CoS}, \text{Sb}_2\text{S}_3$ & SnS aren't decomposed by dil. H_2SO_4 therefore a pinch of Zn dust is added along with it conc. HCl should also be used.
- Carbonates of Bi & Ba are not easily decomposed by dil. H_2SO_4 . dil. HCl should be used.
- With conc. H_2SO_4 group I radicals (i.e., $\text{CO}_3^{2-}, \text{S}^{2-}, \text{SO}_3^{2-}, \text{NO}_2^-$, CH_3COO^-) behave in the same way as with dil. H_2SO_4 .
- Before testing CH_3COO^- ion with neutral FeCl_3 solution, make sure that the solution is free from $\text{CO}_3^{2-}, \text{SO}_3^{2-}, \text{PO}_4^{3-}$ and I^- ions as they combine with Fe^{3+} ions.
- Chromyl chloride Test
 - ① Dry test tube should be used to prevent the hydrolysis of chromyl chloride vapours. $\text{CrO}_2\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{CrO}_4 + 2\text{HCl}$
 - ② In case of chlorides of Hg, Sn, Ag, Pb & Sb this test is performed by taking residue obtained after evaporation of sodium carbonate extract.

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

- ① Write down the formula of Mohr salt? What kind of salt is it?
- ② Where does the colour of KMnO_4 go when it comes in contact with mohr salt / oxalic acid?
- $\text{MnO}_4^- \xrightarrow{\text{H}^+} \text{Mn}^{2+}$
 (more covalent character increases)
 in +7 oxidation state
 Since charge transfer is stopped, hence no colour).
- ③ What is standard solution? how many types of standard solutions are there?
- Ans: Standard solution is a solution whose concentration is precisely known. They are used to determine the concentration of other solution in titration. It is of 2 types 1^o solution, 2^o standard solution.
- ④ Why do we titrate mohr's salt and not FeSO_4 versus KMnO_4 ?
- Ans: because FeSO_4 gets easily oxidised in air as compared to Mohr salt.
- ⑤ KMnO_4 solution bottle develops a brown colour on glass why?
- Ans: It is due to the formation of MnO_4^- ion.
- ⑥ Why is dilute Sulphuric acid added while preparing a standard solution of Mohr's salt? Ans: it is added to prevent hydrolysis of ferrous salt. Due to common ion effect SO_4^{2-} from H_2SO_4 prevent the ionisation of Fe^{2+} .
- ⑦ Why potassium permanganate is used in acidic medium but not in alkaline medium? Ans: because in alkaline medium it forms ppt of MnO_2 which is brown in colour.
- ⑧ Can we use HCl or HNO_3 in KMnO_4 titration instead of dil- H_2SO_4 ?
- Ans: no because HCl is oxidised to Cl_2 and HNO_3 act itself as oxidising agent.
- ⑨ What happens if HCl is not added before passing H_2S in group II?
- Ans: it may precipitate group 4 ions.
- ⑩ Na_2CO_3 can't be used in place of $(\text{NH}_4)_2\text{CO}_3$ in group IV. Explain why?
- Ans: Na_2CO_3 is highly insoluble electrolyte, which may produce very high concentration of CO_3^{2-} ions as a result ionic product of MgCO_3 may increased its K_{sp} and may get precipitated along with the radicals of V group.

- (11) What is chromyl chloride test? \rightarrow it is used as confirmatory test for Cl^- ion.
 $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{chromyl chloride} + \text{NaOH}$
 (12) Why do Bromides and iodides not respond to chromyl chloride test? $\text{Na}_2\text{Cr}_2\text{O}_7$
Ans Because chromyl bromide and its compounds aren't formed instead of these Bromine and Iodine are evolved.

- (13) Why acetic acid is added before adding lead acetate solution?
Ans to prevent the hydrolysis of lead acetate which would yield white ppt of lead hydroxide. \Rightarrow common ion effect.
- (14) Why don't we use concn HCl in preparing a paste of the salt for flame test?
Ans In order to convert metal salt \rightarrow metal chlorides which are more volatile than other salts.
- (15) Why Platinum metal is preferred over metals for flame test?
Ans This is because Pt doesn't react with acids and doesn't itself impart any characteristic colour to the flame.
- (16) Why can't we use glass rod instead of Pt wire for performing flame test?
Ans This is because glass contains Na_2SiO_3 (sodium silicate) which imparts its own golden yellow colour to the flame.
- (17) Ammonium ion has been kept in group(zero) why?
Ans This is because it is the only nonmetallic cation & doesn't resemble any other cation & so it is tested first.

From Salt analysis (i) Why zero group is detected first?

Ans Group zero includes NH_4^+ . During the systematic analysis of cations, ammonium hydroxide and ammonium chloride are added at various stages. Therefore NH_4^+ ion is detected in the beginning of the cation analysis using the given solid mixture. Hence NH_4^+ radical constitutes a separate group called zero group.

- (ii) Pb^{2+} is present in both group I and group II. Why?
Ans It is because Pb^{2+} can form ppt with both dil. HCl as well as with H_2S gas.
- Ex. $\text{Pb}(\text{NO}_3)_2 + 2\text{HCl} \rightarrow \text{PbCl}_2 \downarrow + 2\text{HNO}_3$; $\text{Pb}(\text{NO}_3)_2 + \text{H}_2\text{S} \rightarrow \text{PbS} \downarrow + 2\text{HNO}_3$
- (iii) Why we add HNO_3 (concn) before proceeding for Group III test?
Ans HNO_3 oxidizes $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$
- (iv) Why solution of Oxalic acid is heated at $60^\circ - 70^\circ\text{C}$ before titrating it with KMnO_4 ?
Ans The formation of Mn^{2+} is slow in cold condition, so to increase it, oxalic acid is heated & it also liberates CO_2 so that rxn goes to completion.