Confirmatory tests of basic radicals :

Precipitates	Confirmatory Tests
Group I	
AgCl	Dissolves in NH_4OH, white ppt. of AgCl is again obtained on adding dil. HNO_3. Yellow ppt. of AgI is formed on adding KI.
$PbCl_2$	Dissolves in hot water, gives yellow ppt. of $PbCrO_4$ with K_2CrO_4 and yellow ppt. of PbI_2 with KI.
Hg_2Cl_2	Turns black with NH_4OH. Black residue {Hg + $Hg(NH_2)Cl$} dissolves in aquaregia forming mercuric chloride ($HgCl_2$). On addition of stannous chloride solution to $HgCl_2$ white ppt. (Hg_2Cl_2) is formed which turns grey (Hg).
Group II A	Precipitates do not dissolve in yellow ammonium sulphide.
HgS	Dissolves in aquaregia, grey ppt. of Hg is obtained with $SnCl_2$ or Cu turnings.
PbS	Dissolves in dil. HNO_3, white ppt. of $PbSO_4$ is obtained on adding dil. H_2SO_4.
Bi_2S_3	Dissolves in dil. HCl, white ppt. of BiOCl is obtained on adding excess of water. Black ppt. of Bi is obtained on adding Na_2SnO_2 solution.
CuS	Blue coloured solution is obtained on adding dil. HNO_3 and excess of NH_4OH which gives chocolate brown ppt. of $Cu_2[Fe(CN)_6]$ with $K_4[Fe(CN)_6]$.
CdS	Colourless solution is obtained on adding dil. HNO_3 and excess of NH_4OH, which gives yellow ppt. of CdS again on adding H_2S.
Group II B	Precipitates dissolve in yellow ammonium sulphide.
As_2S_3	Insoluble sulphide, As_2S_5 is obtained by treating with conc. HCl, which gives yellow ppt. of ammonium arsenomolybdate on adding conc. HNO_3 and heating with ammonium molybdate.
SnS_2 or SnS	Filtrate of sulphide in conc. HCl is reduced to $SnCl_2$ by treating with Fe or Zn which on adding $HgCl_2$ solution initially gives white ppt. of Hg_2Cl_2 and finally turns to grey Hg.
Sb_2S_3	Filtrate of sulphide in conc. HCl gives white ppt. of SbOCl on adding excess of water and orange ppt. of Sb_2S_3 on passing H_2S gas.
Group III	
$Fe(OH)_3$	Dissolves in dil. HCl, gives prussian blue solution or ppt. of $Fe_4[Fe(CN)_6]_3$ on adding $K_4[Fe(CN)_6]$ and blood red coloured $Fe(CNS)_3$ on adding KCNS.
$Cr(OH)_3$	The solution obtained on heating precipitate with NaOH and Br_2 water contains Na_2CrO_4 which gives yellow ppt. of $PbCrO_4$ on treating with acidified lead acetate solution.
$Al(OH)_3$	Dissolves in NaOH and is again precipitated out on boiling with NH_4Cl.
Group IV	Soluble in conc. HCl.
ZnS	Solution ($ZnCl_2$) is treated with NaOH, a white ppt. of $Zn(OH)_2$ appears which dissolves in excess of NaOH and on passing H_2S, white ppt. of ZnS is obtained.
MnS	Precipitate of MnO_2 is obtained on heating the solution with NaOH and Br_2 water. $HMnO_4$ imparts pink colour to the supernatant liquid on treating the ppt. with excess of HNO_3 and red lead (Pb_3O_4).
Group IV	Insoluble in conc. HCl
CoS	Dissolves in aqua-regia. Yellow ppt. of potassium cobaltinitrite $K_3[Co(NO_2)_6]$ is obtained on adding CH_3COOH (in excess) and KNO_2.
NiS	Dissolves in aqua-regia. Red ppt. of Ni-dmg complex is obtained on adding NH_4OH in excess and dimethyl glyoxime.

TITRATION

One of the important methods in quantitative analysis is volumetric analysis, a commonly used laboratory technique. It is used to determine the unknown concentration of a sample by measuring its volume.

Acid Base Titration

- It is a method used to determine the strength of an acid or alkali and this type of titration is based on the neutralisation reaction.

$$\underset{\text{(Acid)}}{AH} + \underset{\text{(Base)}}{BOH} \longrightarrow \underset{\text{(Salt)}}{AB} + H_2O$$

Indicator

- An indicator is a chemical substance that undergoes a colour change at the end point. The end point of an acid-base titration can be determined using acid-base indicators. Acid base indicators are either weak organic acids or weak organic bases. The colour change of an indicator depends on the pH of the medium. The un-ionized form of an indicator has one colour, but its ionized form has a different colour.

  For example, consider the indicator phenol-phthalein, whose ionization can be written as :

$$\underset{\text{Colourless}}{HPh} + H_2O \longrightarrow H_3O^+ + \underset{\text{Pink}}{Ph^-}$$

- **Some common examples of acid-base indicators :**

Indicators	pH Range	Acid	Base
Phenolphthalein	8.0 - 10.0	Colourless	Pink
Methyl orange	3.1 - 4.4	Red	Orange
Methyl red	4.4 - 6.2	Red	Yellow
Phenol red	6.4 - 8.0	Yellow	Red
Thymol blue	1.2 - 2.8	Red	Yellow
Thymol blue	8.0 - 9.6	Yellow	Blue
Methyl yellow	2.9 - 4.0	Red	Yellow

Titrimetric Calculations

- **Strength of a solution :** It is the amount of solute in grams present per litre of the solution.
  - Strength (g/L) = Normality × Eq. wt.
  - Strength (g/L) = Molarity × Mol. mass
- **Normality equation :** $\underset{\text{(Solution 1)}}{N_1V_1} = \underset{\text{(Solution 2)}}{N_2V_2}$
- **Molarity equation :** $\underset{\text{(Solution 1)}}{M_1V_1n_1} = \underset{\text{(Solution 2)}}{M_2V_2n_2}$

  [$\because N = M \times n$, where n = valency factor]

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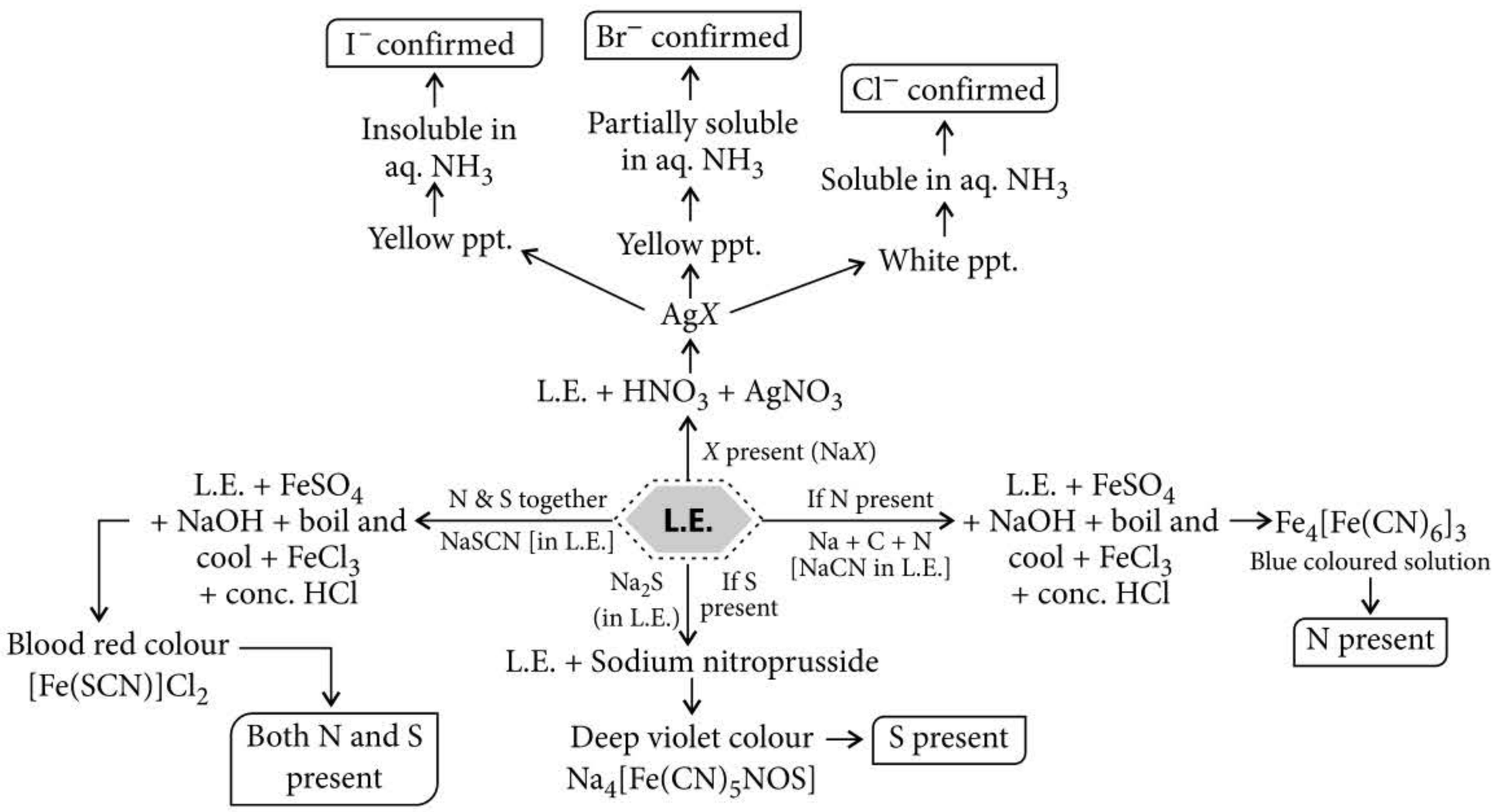
Group V	Soluble in acetic acid.
$BaCO_3$	Yellow ppt. of $BaCrO_4$ is obtained on adding K_2CrO_4 to solution.
$SrCO_3$	White ppt. of $SrSO_4$ is obtained on adding $(NH_4)_2SO_4$ to solution.
$CaCO_3$	White ppt. of CaC_2O_4 is obtained on adding $(NH_4)_2C_2O_4$ to solution.
Group VI	
Mg^{2+}	White ppt. of $Mg(NH_4)PO_4$ is formed on adding Na_2HPO_4 and NH_4OH to solution.
Zero	
NH_4^+	Salt evolves NH_3 gas on heating with NaOH which gives dense white fumes of NH_4Cl with HCl and a brown ppt. of $H_2N{\cdot}HgO{\cdot}HgI$ on adding Nessler's reagent, K_2HgI_4.

DETECTION OF N, S, Cl IN ORGANIC COMPOUNDS

Lassaigne's Test

- It is a general test for the detection of halogen, nitrogen and sulphur in organic compounds. These elements are covalently bonded to the organic compounds. In order to detect them, these have to be converted into their ionic forms. This is done by fusing the organic compound with sodium metal. The ionic compounds formed during the fusion are extracted in aqueous solution and can be detected by simple chemical tests.
- **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 filtred. Filtrate is known as Lassaigne's extract (L.E.).



- When sodium fusion is carried out with excess of sodium, thiocyanate decomposes to cyanide and sulphide ions which give their usual tests. Thus, we do not get blood red colour with ferric chloride even though N and S both are present.

$$Na + C + N + S \longrightarrow \underset{\text{Sodium thiocyanate}}{NaCNS}$$

$$NaCNS + 2Na \longrightarrow NaCN + Na_2S$$

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

(vii) Use of table is necessary, use of calculators is not allowed.

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1. What is an adsorption isotherm?

2. Write down the electronic configuration of gadolinium (Gd). (At. number : Gd = 64)

3. Write the structure of the compound :
4-*tert*-butyl-3-iodoheptane

4. What happens when ferrimagnetic Fe_3O_4 is heated at 850 K and why?

5. Write the equation involved in the acetylation of salicylic acid.

6. $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?

OR

Discuss the nature of bonding in metal carbonyls.

7. Knowing the electron gain enthalpy values for $O \rightarrow O^-$ and $O \rightarrow O^{2-}$ as –141 and 702 kJ mol^{-1} respectively, how can you account for the formation of large number of oxides having O^{2-} species and not O^-?

8. Calculate the mass of ascorbic acid (vitamin C, $C_6H_8O_6$) to be dissolved in 75 g acetic acid to lower its freezing point by 1.5°C. (K_f = 3.9 K kg mol^{-1})

9. A first order reaction has a specific reaction rate of 10^{-3} sec^{-1}. How much time will it take for 10 g of the reactant to reduce to 2.5 g? (Given : log 2 = 0.301, log 4 = 0.6021, log 6 = 0.778)