14

PRACTICAL CHEMISTRY

PRINCIPLES RELATED TO PRACTICAL CHEMISTRY (ACIDIC & BASIC RADICALS)

QUALITATIVE INORGANIC ANALYSIS

INTRODUCTION

Qualitative inorganic analysis deals with the identification of radicals (cations and anions) in an inorganic salt or in a mixture of salts. 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 basic radical and the negatively charged part of the salt (anion) which has been derived from an acid is termed acidic radical. For example, the salt copper sulphate is obtained by the action of a base (copper hydroxide) and an acid (sulphuric acid). Thus, it has copper ion (Cu^{2+}) as a basic radical and sulphate ion (SO_4^{2-}) as the acidic radical.

$$\underset{\text{Base}}{Cu(OH)_2} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow \underset{\text{Salt}}{CuSO_4} + H_2O$$

$$\underset{\text{Basic radical}}{Cu^{2+}} \qquad \underset{\text{Acidic radical}}{SO_4^{2-}}$$

A mixture may have two or more salt; thus qualitative inorganic analysis consists in identifying the presence of various cations and anions in it.

IDENTIFICATION OF ACIDIC RADICALS

Most of these salts are acted upon by dilute H_2SO_4 or dilute HCl and concentrated H_2SO_4 In each case, a gas is liberated which is characteristic of the particular acidic radical. There are some acidic radicals which are not decomposed either by dilute H_2SO_4 or concentrated H_2SO_4. Hence, for the identification of the acidic radicals, the following scheme is followed.

Group I : This group consists of radicals which are detected by dilute H_2SO_4 or dilute HCl. These are :
(i) carbonate, (ii) sulphite (iii) sulphide (iv) nitrite and
(v) acetate.

Group II : This group consists of radicals which are detected by concentrated H_2SO_4 These are :
(i) chloride (ii) bromide (iii) iodide (iv) nitrate and (v) oxalate

Group III : The radicals which do not give any characteristic gas with dilute and concentrated H_2SO_4. These are
(i) sulphate (ii) phosphate, (iii) borate and (iv) fluoride.

GROUP I

Take 0.2 g of the substance in a test tube and add 2 ml of dilute HCl or dilute H_2SO_4. Observe the reaction in cold, warm gently the contents and infer as follows.

S.N.	Observation	Inference	Confirmatory Tests
1.	Brisk effervescence in cold with evolution of colourless and odourless gas	CO_3^{2-} (Carbonate)	Pass the gas in a tests tube containing small quantity of lime water. It turns milky.
2.	A colourless gas with suffocating odour having smell of burning sulphur.	SO_3^{2-} (sulphite)	Moisten a piece of filter paper with acidified potassium dichromate and put it on the mouth of the test tube. It turns green.
3.	A colourless gas with smell of rotten eggs.	S^{2-} (sulphide)	Moisten a piece of filter paper with lead acetate solution and place it on the mouth of the test tube it turns black.
4.	A light brown gas	NO_2^- (nitrite)	(a) Pass the evolved gas through ferrous sulphate solution, it turns brown (b) Mix the given salt or mixture with a little of KI and add dilute H_2SO_4 Evolution of violet vapours (c) Place the piece of filter paper on the mouth of test tube moistened with solution of starch, potassium iodide and acetic acid it turns blue.
5.	Colourless vapours with smell of vinegar	CH_3COO^- (Acetate)	(a) To the aqueous solution of substance add neutral $FeCl_3$ solution blood red colour. (b) Rub the moistened salt or mixture with dry oxalic acid smell of vinegar.

Reactions :

(i) **Carbonate:** The carbonates are decomposed with dilute HCl or dilute H_2SO_4 with the evolution of carbon dioxide gas. When this gas is passed through lime water, the lime water turns milky with the formation of calcium carbonate

$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$

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

However, if the CO_2 gas is passed in excess, the milky solution becomes colourless due to the formation of soluble calcium bicarbonate.

$$\underset{\text{White ppt.}}{CaCO_3} + H_2O + CO_2 \longrightarrow \underset{\text{soluble}}{Ca(HCO_3)_2}$$

Note:

(a) Carbonates of bismuth and barium are not easily decomposed by dilute H_2SO_4 Dilute HCl should be used.

(b) Sulphur dioxide evolved from sulphites also turns lime water milky. In the test of carbonates, the evolved gas must be colourless and odourless (SO_2 is a pungent gas)

$$Ca(OH) + SO_2 \longrightarrow \underset{\text{White ppt.}}{CaSO_3} + H_2O$$

(c) $PbCO_3$ reacts with HCl or H_2SO_4 to give, in the initial stage, some effervescence but the reaction slows down due to formation of a protective insoluble layer of $PbCl_2$ or $PbSO_4$ on the surface of remaining salt or mixture.

(ii) **Sulphite:** A sulphite with dilute H_2SO_4 gives out sulphur dioxide gas which possesses suffocating smell of burning sulphur. When acidified potassium dichromate paper is exposed to the gas it attains green colour due to the formation of chromic sulphate.

$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2$

$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

(iii) **Sulphide:** Dilute H_2SO_4 decomposes a sulphide salt to form H_2S gas which smells like rotten eggs.

$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$

On exposure to this gas, the lead acetate paper turns black due to the formation of lead sulphide.

$Pb(CH_3COO)_2 + H_2S \longrightarrow PbS$ (Black ppt) $+ 2CH_3COOH$.

Note : Sulphides of lead, cadmium, nickel, cobalt, antimony and stannic are not decomposed with dilute H_2SO_4. Conc. HCl should be used for their test. In such cases, however, brisk evolution of H_2S takes place even by use of dilute H_2SO_4, if a pinch of zinc dust is added

$Zn + H_2SO_4 \longrightarrow ZnSO_4 + 2H$

$HgS + 2H \longrightarrow Hg + H_2S$

(iv) **Nitrite:** When a nitrite is treated with dilute H_2SO_4, it yields a colourless nitric oxide gas which in contact with oxygen of the air becomes brown due to the formation of nitrogen dioxide.

$2NaNO_2 + H_2SO_4 \longrightarrow NaSO_4 + 2HNO_2$ (Nitrous acid)

$3HNO_2 \longrightarrow H_2O + 2NO + HNO_3$

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

(a) On passing the gas in dilute $FeSO_4$ solution brown coloured complex salt is formed

$$FeSO_4.7H_2O + NO \longrightarrow \underset{\text{Brown colour}}{[Fe(H_2O)_5NO]SO_4} + 2H_2O$$

(b) When a mixture of iodide and nitrite is acted upon by dilute H_2SO_4, the iodide is decomposed giving violet vapours of iodine.

$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$

$2KI + H_2SO_4 \longrightarrow K_2SO_4 + 2HI$

$$2HNO_2 + 2HI \longrightarrow 2H_2O + \underset{\text{Violet vapours}}{I_2} + 2NO$$

(c) Starch-iodide paper is turned blue due to the liberation of iodine from iodide by nitrous acid which gives blue colour with starch.

$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$

$2KI + 2CH_3COOH + 2HNO_2$
$\longrightarrow 2CH_3COOK + 2NO + 2H_2O + I_2$

I_2 + Starch $\longrightarrow$ Blue colour

(v) **Acetate:** Acetates when heated with dilute H_2SO_4 decompose to give acetic acid vapours which possess characteristic smell of vinegar.

$2CH_3COONa + H_2SO_4 \longrightarrow 2CH_3COOH + Na_2SO_4$

(a) All acetates are soluble in water. On addition of neutral $FeCl_3$ solution to the solution of an acetate, blood red colouration develops due to the formation of ferric acetate.

$$FeCl_3 + 3CH_3COONa \longrightarrow \underset{\text{Blood red colour}}{(CH_3COO)_3Fe} + 3NaCl$$

Note:

(i) The ferric chloride solution supplied in the laboratory is always acidic containing HCl. It is made neutral by the addition of dilute solution of NH_4OH drop by drop with constant stirring till the precipitate formed does not dissolve. At this stage filter the solution. The filtrate is called neutral ferric chloride solution.

(ii) Before testing acetate in the aqueous solution of a salt or a mixture, it must be made sure that the solution does not contain the following ions which also combine with Fe^{3+} ions. (i) CO_3^{2-} (ii) SO_3^{2-} (iii) PO_4^{3-} (iv) I^-
These ions can be removed by addition of $AgNO_3$ solution and only after the removal of these ions, the test of acetate should be performed by neutral ferric chloride solution.

(b) Acetates are also decomposed with oxalic acid and give off acetic acid.

$2CH_3COONa + H_2C_2O_4 \longrightarrow Na_2C_2O_4 + 2CH_3COOH$

GROUP II

Take 0.2g of the substance and add 2 mL of concentrated H_2SO_4 warm gently, observe the changes and draw inference as follows :

Note : With concentrated H_2SO_4 carbonates, sulphites, sulphides, nitrites and acetates also behave in the same way as with dilute H_2SO_4.

Reactions :

(I) Chloride : Colourless pungent fumes of hydrogen chloride are evolved on heating the sodium chloride with conc. H_2SO_4. $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

(a) Yellowish-green gas of chlorine with suffocating odour is evolved when the solid chloride mixed with manganese dioxide is heated with conc. H_2SO_4.

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

(b) The gas evolved by heating chloride with sulphuric acid forms white fumes of ammonium chloride with NH_4OH

$NH_4OH + HCl \longrightarrow NH_4Cl \text{ (White fumes)} + H_2O$

(c) The gas evolved by heating chloride with H_2SO_4 forms a curdy precipitate of silver chloride with silver nitrate solution.

$AgNO_3 + HCl \longrightarrow \underset{\text{ppt}}{AgCl} + HNO_3$

The curdy precipitate dissolves in ammonium hydroxide by forming a complex salt.

$AgCl + 2NH_4OH \longrightarrow Ag(NH_3)_2Cl + 2H_2O$

when the solution having the silver complex is acidified with dilute nitric acid, a precipitate of silver chloride is again formed.

$Ag(NH_3)_2Cl + 2HNO_3 \longrightarrow AgCl + 2NH_4NO_3$

(d) Chromyl chloride test: When solid chloride is heated with conc. H_2SO_4 in presence of $K_2Cr_2O_7$, deep red vapours of chromyl chloride are evolved.

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

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

$CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 \text{ (Chromyl chloride)} + H_2O$

When these vapours are passed through NaOH solution, the solution becomes yellow due to the formation of sodium chromate.

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

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

$Na_2CrO_4 + Pb(CH_3COO)_2 \longrightarrow \underset{\text{Yellow ppt}}{PbCrO_4} + 2CH_3COONa$

Note :

(i) This test is not given by the chlorides of mercury, tin, silver, lead and antimony. In such cases this test may be performed by taking the residue obtained after evaporation of sodium carbonate extract.

(ii) The chromyl chloride test is always to be performed in a dry test tube; otherwise the chromyl chloride vapours will be hydrolysed in the test tube.

$CrO_2Cl_2 + 2H_2O \longrightarrow H_2CrO_4 + 2HCl$

(iii) The test is said to be positive when all the three observations viz, orange-yellow (red) vapours of chromyl chloride, yellow solution of sodium chromate, yellow precipitate of lead chromate, are correct.

(iv) Sometimes, a white precipitate is obtained after the addition of lead acetate solution even in absence of chloride. This may be due to strong heating of the mixture with conc. H_2SO_4 when H_2SO_4 vapours are absorbed in NaOH solution or due to incomplete neutralisation of NaOH solution which reacts with lead acetate to form lead hydroxide.

(v) Bromides and iodides do not give this test.

(II) Bromide : Reddish-brown fumes of bromine are formed when the sodium bromide is heated with conc. H_2SO_4.

$NaBr + H_2SO_4 \longrightarrow 2NaHSO_4 + HBr$

$2HBr + H_2SO_4 \longrightarrow Br_2 + 2H_2O + SO_2$

More reddish-brown fumes of bromine are evolved when MnO_2 is added.

$2NaBr + 2H_2SO_4 \longrightarrow 2NaHSO_4 + 2HBr$

$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + [O]$

$2HBr + [O] \longrightarrow H_2O + Br_2$

$2NaBr + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + Br_2$

(a) The aqueous solution of bromide gives pale yellow precipitate of silver bromide which dissolves in excess of NH_4OH forming a soluble complex. [AgBr is sparingly soluble in NH_4OH solution]

$NaBr + AgNO_3 \longrightarrow \underset{\text{Pale yellow ppt}}{AgBr} + NaNO_3$

$AgBr + 2NH_4OH \longrightarrow Ag(NH_3)_2Br + 2H_2O$

(b) When the fresh salt or mixture is treated with dilute H_2SO_4,$CHCl_3$ or CCl_4 and chlorine water, chlorine replaces bromine and the liberated bromine dissolves in $CHCl_3$ or CCl_4 layer giving it brown colour

$2KBr + Cl_2 \longrightarrow 2KCl + Br_2$

$Br_2 + \text{chloroform} \longrightarrow \text{Brown layer}$

Note: Excess of chlorine water should not be used Under this condition the layer attains either pale yellow colour due to formation of bromine monochloride or it becomes colourless due to formation of hypobromous acid.

$Br_2 + Cl_2 \longrightarrow 2BrCl \text{ (Bromine monochloride)}$

$Br_2 + 2H_2O + Cl_2 \longrightarrow \underset{\text{Hypobromous acid}}{2HBrO} + 2HCl$

(III) Iodide : Violet vapours of iodine are evolved on heating iodide with concentrated H_2SO_4.

$2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$

$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + 2H_2O$

More violet vapours are evolved when MnO_2 is added.

$2KI + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$

$MnO_2 + H_2SO_4 \longrightarrow MnSO_4 + H_2O + [O]$

$2HI + [O] \longrightarrow H_2O + I_2$

$2KI + MnO_2 + 3H_2SO_4 \longrightarrow 2KHSO_4 + MnSO_4 + 2H_2O + I_2$

(a) Violet vapours with starch produce blue colour.

$I_2 + \text{Starch} \longrightarrow \text{Blue colour}$

(b) Aqueous solution of the iodine gives yellow precipitate of AgI with silver nitrate solution which does not dissolve in NH_4OH.

$$NaI + AgNO_3 \longrightarrow AgI\ (\text{Yellow ppt.}) + NaNO_3$$

(c) When the given substance is treated with dilute H_2SO_4, $CHCl_3$ or CCl_4 and chlorine water, chlorine replaces iodine which dissolves in $CHCl_3$ or CCl_4 layer giving it violet colour. $2KI + Cl_2 \longrightarrow 2KCl + I_2$

$$I_2 + CHCl_3 \longrightarrow \text{Violet layer}$$

Note: Excess of chlorine water should be avoided as the layer becomes colourless with the conversion of iodine into iodic acid

$$[Cl_2 + H_2O \longrightarrow 2HCl + O] \times 5$$
$$I_2 + H_2O + 5[O] \longrightarrow 2HIO_3$$
$$I_2 + 5Cl_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$$

(IV) Nitrate: Light brown fumes of nitrogen dioxide gas are evolved on heating the nitrate with concentrated H_2SO_4

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$
$$4HNO_3 \longrightarrow 2H_2O + 4NO_2 + O_2$$

These fumes intensify when copper turnings are added

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

Ring Test : When the aqueous solution of the substance is treated with freshly prepared solution of ferrous sulphate and conc. H_2SO_4 a brown ring is formed on account of the formation of a complex at the junction of two liquids.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$
$$6FeSO_4 + 2HNO_3 + 3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$
$$\underset{\text{Ferrous sulphate}}{[Fe(H_2O)_6]SO_4.H_2O} + NO \longrightarrow \underset{\text{Brown ring}}{[Fe(H_2O)_5NO]SO_4} + 2H_2O$$

Note:

(a) Ring test is not reliable in presence of nitrite, bromide and iodide.

(b) The nitrates can be tested by boiling nitrate with Zn or Al in presence of concentrated NaOH solution when ammonia is evolved which can be detected by the characteristic odour.

$$Zn + 2NaOH \longrightarrow Na_2ZnO_2 + 2H$$
$$Al + NaOH + H_2O \longrightarrow NaAlO_2 + 3H$$
$$NaNO_3 + 8H \longrightarrow NaOH + 2H_2O + NH_3$$

(V) Oxalate: When oxalate is heated with conc. H_2SO_4, a mixture of CO and CO_2 is given off the CO burns with blue flame.

$$Na_2C_2O_4 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2C_2O_4$$
$$H_2C_2O_4 + [H_2SO_4] \longrightarrow CO + CO_2 + H_2O + [H_2SO_4]$$

GROUP III

Some anions are identified by their characteristic chemical reactions. These radicals are sulphate, borate, phosphate and fluoride.

(I) Sulphate : Dissolve a little amount of the substance (salt or mixture) in dil. HCl and add barium chloride solution and formed white precipitate of $BaSO_4$. A white precipitate insoluble in cone. HNO_3 is formed.

Reactions : White precipitate of barium sulphate is obtained when soluble sulphate is treated with barium chloride solution.

$$Na_2SO_4 + BaCl_2 \longrightarrow 2NaCl + BaSO_4\ (\text{White ppt})$$

The white precipitate is insoluble in conc. HNO_3. Certain chlorides e.g., NaCl and $BaCl_2$ when present in large quantities, may form a white precipitate which dissolves on dilution with water. Silver and lead, if present, may be precipitated as silver chlorides and lead chloride by the addition of barium chloride. To avoid it, barium nitrate may be used in place of barium chloride.

(II) Borate: To a small quantity of the substance (salt or mixture), add a few mL of ethyl alcohol and conc. H_2SO_4. Stir the contents with a glass rod. Heat the test tube and bring the mouth of the test tube near the flame. The formation of green edged flame indicates the presence of borate.

Reactions :

When borate is heated with ethyl alcohol and H_2SO_4, ethyl borate vapours come out which burn with green edged flame.

$$2Na_3BO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2H_3BO_3$$
$$H_3BO_3 + 3C_2H_5OH \longrightarrow \underset{\text{Ethyl borate}}{(C_2H_5)_3BO_3} + 3H_2O$$

(III) Phosphate: Take about 0.2 g of the substance in a test tube and add 2 mL cone. HNO_3. Heat and add 2 mL ammonium molybdate solution, Again heat. A canary yellow precipitate indicates the presence of phosphate.

Reactions :

The canary yellow precipitate is due to the formation of ammonium phosphomolybdate

$$Ca_3(PO_4)_2 + 6HNO_3 \longrightarrow 3Ca(NO_3)_2 + 2H_3PO_4$$
$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow$$
$$\underset{\text{(Canary yellow ppt)}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

(IV) Fluoride : Take a small amount of the substance in a dry test tube and add an equal amount of sand. Mix the contents and add conc. H_2SO_4. Heat the contents and place a glass rod moistened with water over the mouth of the test tube. A waxy white deposit on the rod is formed.

Reaction : The fluoride with cone. H_2SO_4 forms H_2F_2 (hydrofluoric acid) which attacks silica forming silicon tetrafluoride, SiF_4. The vapours of SiF_4 are hydrolysed by H_2O into gelatinous silicic acid which is deposited on the rod.

$$2NaF + H_2SO_4 \longrightarrow Na_2SO_4 + H_2F_2$$
$$SiO_2 + 2H_2F_2 \longrightarrow SiF_4 + 2H_2O$$
$$3SiF_4 + 4H_2O \longrightarrow \underset{\text{Silicic acid (white)}}{H_4SiO_4} + 2H_2SiF_6$$

(a) The test should be performed in perfectly dry test tube, otherwise waxy white deposit will not be formed on the rod.

(b) $HgCl_2$ and NH_4Cl also produce a deposit under these conditions, but this deposit is crystalline in nature.

IDENTIFICATION OF BASIC RADICALS

For systematic analysis, the basic radicals have been classified into groups. Each group has a reagent which shows the presence of the basic radical belonging to that particular group. It is necessary that the radical is completely removed in the respective group by using excess of group reagent, otherwise its presence creates difficulty in higher group.

Group	Group reagent	Basic radical	Composition and colour of the precipitate
1.	Dilute HCl	Ag^+ Pb^{2+} Hg_2^{2+}	AgCl : white $PbCl_2$: white Hg_2Cl_2 : white Chloride insoluble in cold dilute HCl
2.	H_2S in presence of dilute HCl	Hg^{2+} Pb^{2+} Bi^{3+} Cu^{2+} Cd^{2+} IIA As^{3+} Sb^{3+} Sn^{2+} Sn^{4+} IIB	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 dilute 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 are are insoluble 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 are are insoluble in NH_4OH
5.	$(NH_4)_2CO_3$ in presence of NH_4OH	Ba^{2+} Sr^{2+} Ca^{2+}	$BaCO_3$: white $SrCO_3$: white $CaCO_3$: white Carbonates are insoluble
6.	Na_2HPO_4	Mg^{2+}	$Mg(NH_4)PO_4$: white
7.	NaOH	NH_4^+	Ammonia gas is evolved

GROUP I

Radicals : Pb^{2+}, Ag^+, Hg_2^{2+} (ous)

Group reagent : Dil. HCl

Procedure: Take cold dilute original solution and add few drops of dilute HCl. If white precipitate appears, add more of dilute HCl. If white precipitate appears, add more of dilute HCl as to complete precipitation, of basic radicals of first group. Filter, keep the filtrate for subsequent groups. Wash the precipitate with cold water. Transfer precipitate in a test tube and add about 10 mL of water boil. If the precipitate dissolves, Pb^{2+} is present and if is does not dissolve, It may have Ag^+ or Hg_2^{2+}. If the precipitate does not dissolve, filter it.

When the precipitate dissolves In hot water	**Solid residue (Insoluble In hot water), add hot NH_4OH**	
Divide the filtrate In four parts (i) First part-cool under tap water-white crystalline ppt. of $PbCl_2$. (ii) Second part + K_2CrO_2 soln $\rightarrow$ yellow ppt. of $PbCrO_4$ (iii) Third part + KI solution $\rightarrow$ yellow ppt. of PbI_2 (iv) Fourth part + dilute H_2SO_4 $\rightarrow$ white ppt of $PbSO_4$, soluble in ammonium acetate Pb^{2+} confirmed	Black precipitate is obtained. Dissolve the black ppt in aqua-regia evaporate off most of the acids, dilute with water and divide into two parts. Part I : Add stannous chloride solution. A white precipitate appears which turns grey. Part II : Add copper turnings. A grey deposit is formed on copper Hg^{2+} confirmed	Solid residue dissolves. Divide the solution into two parts. First part + dil. $HNO_3 \rightarrow$ A white ppt appear Second Part + KI Soln $\rightarrow$ A yellow ppt. Ag^+ confirmed

GROUP II

Radicals : Hg^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+} Group II A

As^{3+}, Sb^{3+}, Sn^{2+}, Sn^{4+}, Group II B

Group reagent : H_2S gas in presence of dil. HCl

Procedure : Warm a part of the filtrate of first group or original solution containing dilute HCl (if first group is absent) and pass H_2S gas. If a precipitate (black or brown or yellow or orange) appears, pass H_2S through whole of the solution. Filter, dilute the filtrate, warm and again pass H_2S. Filter repeat this process till the precipitation is complete. Keep the filtrate for subsequent groups.

Wash the precipitate with hot water. Take small part of the precipitate in a test tube and add about 5mL of yellow ammonium sulphide solution, warm upto 60°C with shaking. If the precipitate does not dissolves, Group II A radical may be present.

If the precipitate dissolves group IIB radical may be present.

Insoluble In yellow ammonium sulphide II A Group		**Soluble In yellow ammonium sulphide II B Group**	
HgS	Black	AS_2S_3	Yellow
PbS	Black	Sb_2S_3	Orange
Bi_2S_3	Black	SnS	Brown
CuS	Black	SnS_2	Yellow
CdS	Yellow		

Note :

(i) Before passing H_2S, the acidic concentration of the solution should be properly adjusted. If the solution is too acidic, lead and cadmium will not be precipitated. On the other hand if too little HCl is used, zinc will also precipitated. The proper hydrogen ion concentration is 0.25 N to 0.5 N with respect to HCl.

(ii) The original solution must be free from any oxidising agent otherwise H_2S gets oxidised with precipitation of free sulphur. This is done by heating the mixture with concentrated HCl for sufficient time during preparation of original solution. This treatment will also remove sulphite, nitrite from the mixture which can oxidise H_2S.

(iii) Hydrogen sulphide should be passed slowly in hot solution to get granular and easily filterable precipitate.

GROUP IIA

Procedure : Take the precipitate (if insoluble in yellow ammonium sulphide) in a test tube and add 5 mL of dilute HNO_3, Boil for few minutes. If insoluble, filter it.

Insoluble (black) HgS. Dissolve it in aqua-regia and divide into two parts Part I : Add $SnCl_2$ solution $\rightarrow$ a white ppt. Which changes into greyish coloured ppt. Part II : Cu turnings $\rightarrow$ greyish deposit on copper turnings. **Hg^{2+} (IC) confirmed**	Soluble-It may have Pb^{2+}, Cu^{2+}, Bi^{3+} or Cd^{2+} Divide the solution into two parts : First Part : Add dilute H_2SO_4 and alcohol. The appearance of white precipitate confirms the presence of lead. In case no precipitate, use second part of filtrate. Second part of filtrate + excess of NH_4OH solution white precipitate (then filter) or blue coloured solution or colourless solution.		
	White precipitate	Blue coloured solution	Colourless solution
	Dissolve the ppt. in dilute HCl and divide into three parts :	Acidify the solution with acetic acid and add $K_4[Fe(CN)_6]$ Soln. $\longrightarrow$ A .	Pass H_2S through soln. $\rightarrow$ Appearance of yellow ppt

	Part I : Add solution stannite solution → black ppt. **Part II :** Dilute with water → white ppt: **Part III :** Add a little 10% thiourea soln → yellow colouration Bi^{3+} present	chocolate coloured ppt. **Cu^{2+} present**	**Cd^{2+} present**

Note:

(i) Sodium stannite is prepared by taking 1 mL of stannous chloride and adding to it drop by drop NaOH till the precipitate formed dissolves.

$$SnCl_2 + 2NaOH \longrightarrow \underset{\text{ppt}}{Sn(OH)_2} + 2NaCl$$

$$Sn(OH)_2 + 2NaOH \longrightarrow \underset{\substack{\text{Sodium stannite}\\ \text{(soluble)}}}{Na_2SnO_2} + 2H_2O$$

(ii) Yellow ammonium sulphide is used only for one radical, i.e, Sn^{2+} which is not soluble in ordinary in ammonium sulphide. Yellow ammonium sulphide consists excess of sulphur and is formulated as $(NH_4)_2S_x$, commonly as $(NH_4)_2S_2$, This converts SnS first into SnS_2 which then dissolves forming thio complex. In case Sn^{2+} is absent, ordinary ammonium sulphide can be used in place of yellow ammonium sulphide.

GROUP II B

Procedure : Take the remaining precipitate (if the precipitate is soluble in yellow ammonium sulphide) and add 1 mL of concentrated HCl and boil. If the precipitate is insoluble, filter and test for, arsenic and in case dissolves, test for antimony and tin.

Insoluble In conc. HCl	**Soluble In conc. HCl**	
Dissolve the yellow ppt. In conc. HNO_3. Add ammonium molybdate and again heat → yellow ppt. **As^{3+} confirmed**	Dilute the solution with water. Divide the solution in two parts	
	First part : Add NH_4OH and pass H_2S → orange ppt. **Sb^{3+} confirmed**	Second part : Add iron fillings and heat for 10 minutes Filter into a solution of mercuric chloride → A white ppt. turning grey. Sn^{2+} confirmed

GROUP III

Radicals : Fe^{3+}, $A1^{3+}$, Cr^{3+},

Group reagent : $NH_4OH + NH_4Cl$

Procedure : Boil off H_2S from the filtrate of II group or take original solution, if first and second group radicals are absent. Add few drops of concentrated HNO_3 and boil the solution. Add 10 g solid ammonium chloride and ammonium hydroxide slowly till the solution smells of ammonia. If the precipitate appears, filter. The filtrate should be kept for subsequent groups.

Reddish brown ppt. $Fe(OH)_3$	**Green precipitate $Cr(OH)_3$,**	**White precipitate $Al(OH)_3$**
Dissolve the ppt. in dilute HCl and divide into two parts : Part I + $K_4Fe(CN)_6$ soln. → Prussian blue solution or ppt. Part II + KCNS soln. → Red colouration. **Fe^{3+} confirmed**	ppt. + NaOH + Br_2 water → Yellow solution acidify the yellow solution with acetic acid and add lead acetate solution → Yellow ppt. **Cr^{3+} confirmed**	Dissolve the ppt. In dil. HCl. Add NaOH solution → White ppt. Appears which then dissolves in excess of NaOH. Treat this solution with solid ammonium chloride → Gelatinous white precipitate. **Al^{3+} confirmed**

Note :

(i) H_2S must be completely removed, otherwise the sulphides of the IV group will be precipitated here.

(ii) A very small amount of HNO_3 should be used, otherwise manganese from divalent state (Mn^{2+}) is oxidised to trivalent state (Mn^{3+}) which may get precipitated as $Mn(OH)_3$.

(iii) Precipitation should be done in hot condition and large excess of NH_4OH should not be used. Ammonium chloride should always be added before the addition of ammonium hydroxide.

GROUP IV

Radicals : Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}

Group reagent: H_2S gas in presence of NH_4Cl and NH_4OH

Procedure: Take the filtrate of third group, concentrate it by heating. Add ammonium hydroxide and again heat the solution. Pass H_2S gas. If the precipitate appears pass H_2S gas for sufficient time and then filter. Keep the filtrate for subsequent groups.

Black precipitate NiS or CoS	**MnS precipitate**	**White precipitate ZnS**
Wash the ppt. With hot water and dissolve it in aqua-regia and evaporate to dryness. Extract the residue with water or dilute HCl. divide it into two parts. Part I + dimethyl glyoxime + $NH_4OH \rightarrow$ Orange ppt. Part II + $NaHCO_3$ + Br_2 water $\rightarrow$ Black ppt. **Ni^{2+} confirmed**	Dissolve in HCl (dil.) Add NaOH to the clear solution and then Br_2 water Boil and filter. The ppt. is treated with conc. HNO_3 and PbO_2 or Pb_3O_4 (red lead) The contents are heated. Keep the test tube for sometime Purple coloured solution. **Mn^{2+} confirmed**	Dissolve the ppt. in dilute HCl and add NaOH drop by drop. The precipitate formed dissolves in NaOH Pass H_2S gas through this solution $\rightarrow$ Appearance of white ppt. **Zn^{2+} confirmed**

GROUP V

Radicals : Ba^{2+} , Sr^{2+} , Ca^{2+}

Group reagent: $(NH_4)_2CO_3$ in presence of NH_4OH

Procedure: Take the filtrate of fourth group. Boil off H_2S gas and concentrate to about 1/2 of its volume. Add a little solid NH_4Cl and NH_4OH. NH_4OH followed by $(NH_4)_2CO_3$ solution. Appearance of white precipitate shows the presence of V group. Filter and keep the filtrate for VI group. The white precipitate may be either of $BaCO_3$ or $CaCO_3$. Dissolve the precipitate in minimum quantity of acetic acid. Divide the solution into three parts.

1st part + K_2CrO_4 soln $\rightarrow$ Yellow precipitate **Ba^{2+} present**	If Ba^{2+} is absent, use 2nd part. Add $(NH_4)_2SO_4 \rightarrow$ solution White precipitate Sr^{2+} present	If Ba^{2+} and Sr^{2+} both are absent use 3rd part. Add $(NH_4)_2C_2O_4 \rightarrow$ White precipitate Ca^{2+} present

GROUP VI

Radicals : Mg^{2+}

Group reagent: Na_2HPO_4 in presence of NH_4OH

Procedure: Take the filtrate of V group and add a little NH_4OH and then Na_2HPO_4 solution. Scratch the walls of the test tube by a glass rod and allow to stand. Appearance of white precipitate confirms the presence of Mg^{2+}.

Test of NH_4^+: Take the mixture in a test tube and add 2-3 ml. NaOH solution and heat. If the smell of NH_3 is observed, it confirms the presence of NH_4^+ radical. The confirmation can further be done by the following test.

(i) Bring a rod dipped in HCl near the mouth of test tube ; white dense fumes are formed.

(ii) Take aqueous solution of mixture and add Nessler's reagent. Appearance of brown colour or precipitate confirms the presence of NH_4^+ radical.

CHEMICAL REACTIONS INVOLVED IN THE TESTS OF BASIC RADICALS

GROUP I

When dil. HCl is added to original solution, insoluble chlorides of lead, silver and mercurous are precipitated.

$$Pb(NO_3)_2 + HCl \longrightarrow PbCl_2 + 2HNO_3$$
$$AgNO_3 + HCl \longrightarrow AgCl + HNO_3$$
$$Hg_2(NO_3)_2 + 2HCl \longrightarrow Hg_2Cl_2 + 2HNO_3$$

Pb^{2+} (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.

$$PbCl_2 + K_2CrO_4 \longrightarrow \underset{\text{Yellow ppt.}}{PbCrO_2} + 2KCl$$
$$PbCrO_4 + 4NaOH \longrightarrow Na_2PbO_2 + Na_2CrO_4 + 2H_2O$$

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

$$PbCl_2 + 2KI \longrightarrow \underset{\text{Yellow ppt.}}{PbI_2} + 2KCl$$

(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.

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

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

$$Ag(NH_3)_2Cl + 2HNO_3 \longrightarrow \underset{\text{white ppt.}}{AgCl} + 2NH_4NO_3$$

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

$$Ag(NH_3)_2Cl + KI \longrightarrow \underset{\text{Yellow ppt.}}{AgI} + KCl + 2NH_3$$

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 coloured precipitate with stannous chloride.

$$2HgCl_2 + SnCl_2 \longrightarrow \underset{\text{white ppt.}}{Hg_2Cl_2} + SnCl_4$$
$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\text{Grey ppt.}}{2Hg} + SnCl_4$$

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

$$HgCl_2 + Cu \longrightarrow \underset{\text{Grey ppt.}}{Hg} + CuCl_2$$

GROUP II

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

$$Ag_2S_3 + 2(NH_4)_2S_2 \longrightarrow 2(NH_4)_2S + As_2S_5$$
$$Sb_2S_3 + 2(NH_4)_2S_2 \longrightarrow 2(NH_4)_2S + Sb_2S_5$$
$$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2S + SnS_2$$

$$\left.\begin{array}{l} As_2S_5 + 3(NH_4)_2S \longrightarrow \underset{\text{Ammonium thioarsenate}}{2(NH_4)_3AsS_2} \\ Sb_2S_5 + 3(NH_4)_2S \longrightarrow \underset{\text{Ammonium thloantimonate}}{2(NH_4)_3SbS_4} \\ SnS_2 + (NH_4)_2S \longrightarrow \underset{\text{Ammonium thioantimonate}}{(NH_4)_2SbS_3} \end{array}\right| \text{Soluble}$$

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 II A are soluble.

$$3PbS + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO + 3S + 4H_2O$$
$$Bi_2S_2 + 8HNO_3 \longrightarrow 2Bi(NO_3)_3 + 2NO + 3S + 4H_2O$$
$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$$
$$3CdS + 8HNO_3 \longrightarrow 3Cb(NO_3)_2 + 2NO + 3S + 4H_2O$$

Hg^{2+} (mercuric)

HgS is dissolved in aqua-regia.

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

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 turning 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.

$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow \underset{\text{White ppt}}{PbSO_4} + 2HNO_3$$

In absence of lead, the remaining solution is made alkaline by the addition of excess of NH_4OH. Bismuth forms a white precipitate of $Bi(OH)_3$, copper forms a deep blue coloured solution while cadmium forms a colourless soluble complex.

$$Bi(NO_3)_2 + 3NH_4OH \longrightarrow \underset{\text{white ppt.}}{Bi(OH)_3} + 3NH_4NO_3$$
$$Cu(NO_3)_2 + 4NH_4OH \longrightarrow \underset{\begin{array}{c}\text{Tetrammine cupric nitrate}\\ \text{(deep blue solution)}\end{array}}{[Cu(NH_3)_4](NO_3)_2} + 4H_2O$$
$$Cd(NO_3)_2 + 4NH_4OH \longrightarrow \underset{\begin{array}{c}\text{Tetrammine cadmium nitrate}\\ \text{(colourless solution)}\end{array}}{[Cd(NH_4)_4](NO_3)_2} + 4H_2O$$

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.

$$BiCl_3 + H_2O \longrightarrow \underset{\begin{array}{c}\text{Bismuth oxychloride}\\ \text{(white ppt.)}\end{array}}{BiOCl} + 2HCl$$

Part II : The solution of $BiCl_3$ is treated with sodium stannite solution when a black precipitate of metallic bismuth is formed.

$$2BiCl_3 + \underset{\text{Sod. Stannite}}{3Na_2SnO_2} + 6NaOH \longrightarrow \underset{\text{Sod. Stannite}}{3Na_2SnO_3} + 2Bi + 6NaCl + 3H_2O$$

Cu^{2+} (copper) :

Blue coloured solution is acidified with acetic acid. When potassium ferrocyanide is added, a chocolate coloured precipitate is formed

$$Cu(NH_3)_4(NO_3)_2 + 4CH_3COOH \rightarrow Cu(NO_3)_2 + 4CH_3COONH_4$$
$$2Cu(NO_3)_2 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{chocolate ppt.}}{Cu_2[Fe(CN)_6} + 4KNO_3$$

Cd^{2+} (cadmium) :

H_2S is passed through colourless solution. The appearance of yellow precipitate confirms the presence of cadmium.

$$Cd(NH_3)_4(NO_3)_2 + H_4S \longrightarrow \underset{\text{yellow ppt}}{CdS} + 2NH_4NO_3 + 2NH_3$$

GROUP II B

In case the precipitate dissolves in yellow ammonium sulphide, the test of the radicals arsenic, antimony and tin are performed. The sulphide is treated with concentrated hydrochloric acid. Antimony and tin sulphides dissolves 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

$$H_3AsO_4 + 12(NH_4)MoO_4 + 21HNO_3 \longrightarrow (NH_4)_3AsO_4.\,12MoO_3 + 21NH_4NO_3 + 12H_2O$$

yellow ppt.

Sn^{2+} or Sn^{4+} (tin) :

Solution of sulphide in concentrated HCl is reduced with Iron fillings or granulated zinc.

$$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$$

white ppt.

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

Grey

Sb^{3+} (antimony) :

Filtrate of sulphide in concentrated 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.

$$CrCl_3 + 3NH_4OH \longrightarrow Cr(OH)_3 + 3NH_4Cl$$

Green ppt.

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

Brownish red ppt.

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

Part 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.

$$2Cr(OH)_3 + 3KNO_3 + 2Na_2CO_3 \longrightarrow 2Na_2CrO_4 + 3KNO_2 + 2CO_2 + 3H_2O$$

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

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

$$2Cr(OH)_3 + 4NaOH + 3[O] \longrightarrow 2Na_2CrO_4 + 5H_2O$$

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.

$$Al(OH)_3 + NaOH \longrightarrow NaAlO_2 + 2H_2O$$

Soluble

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 cone. 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.

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

On passing H_2S, white precipitate of zinc sulphide is formed.

$$Na_2ZnO_2 + H_2S \longrightarrow ZnS + 2NaOH$$

White ppt.

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 dioxide gets precipitated.

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

$$Mn(OH)_2 + O \longrightarrow MnO_2 + H_2O$$

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.

$2MnO_2 + 4HNO_3 \longrightarrow 2Mn(NO_3)_2 + 2H_2O + O_2$

$2Mn(NO_3)_2 + 5Pb_3O_4 + 26HNO_3 \longrightarrow$

$2HMnO_4 + 15Pb(NO_3)_2 + 12H_2O$

Permaganic acid (pink)

Note : The above test fails in presence of HCl.

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

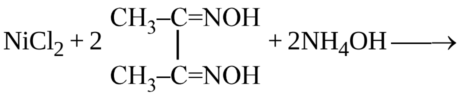
The black precipitate is dissolved in aqua-regia.

$3NiS + 6HCl + 2HNO_3 \longrightarrow 3NiCl_2 + 2NO + 3S + 4H_2O$

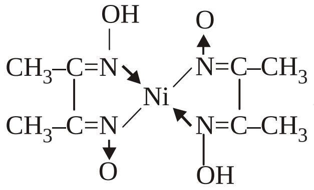
$3CoS + 6HCl + 2HNO_3 \longrightarrow 3CoCl_2 + NO + 3S + 4H_2O$

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

Part I : Add NH_4OH (excess) and dimethyl glyoxime. A rosy red precipitate appears, if nickel is present.



$$NiCl_2 + 2\begin{array}{l}CH_3–C{=}NOH\\ \quad\ \ |\\ CH_3–C{=}NOH\end{array} + 2NH_4OH \longrightarrow$$



$+ 2NH_4Cl + 2H_2O$

Part II : Add CH_3COOH in excess and KNO_2. The appearance of yellow precipitate 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 confirms the presence of cobalt. If no apple green colour is observed, the solution is heated when black precipitate is formed, which shows the presence of nickel.

$CoCl_2 + 2NaHCO_3 \longrightarrow Co(HCO_3)_2 + 2NaCl$

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

$Br_2 + H_2O \longrightarrow 2HBr + [O]$

$2Na_4Co(CO_3)_3 + H_2O + [O] \longrightarrow 2Na_3Co(CO_3)_3 + 2NaOH$

Sod. cobalt carbonate

(green colouration)

$NiCl_2 + 2NaHCO_3 \longrightarrow NiCO_3 + 2NaCl + H_2O + CO_2$

$2NiCO_3 + [O] \longrightarrow Ni_2O_3 + 2CO_2$

Black

Group V :

Ammonium carbonate precipitates V group radicals in the form of carbonates, These 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^{+} (strontium)

Strontium sulphate is insoluble and precipitated by the addition of ammonium sulphate solution

$Sr(CH_3COO)_2 + (NH_4)_2SO_4 \longrightarrow SrSO_4 + 3CH_3COONH_4$

white ppt

Ca^{2+} (calcium)

Calcium oxalate is insoluble and precipitated by the addition of ammonium oxalate.

$Ca(CH_3COO)_2 + (NH_4)_2C_2O_4 \longrightarrow CaC_2O_4 + 2CH_3COONH_4$

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.

$MgCl_2 + Na_2HPO_4 + NH_4OH$

$\longrightarrow Mg(NH_4)PO_4 + 2NaCl + H_2O$

Magnesium ammonium

phosphate (white ppt.)

NH_4^+ (ammonium)

The substance (salt or mixture) when heated with NaOH solution evolves ammonia

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

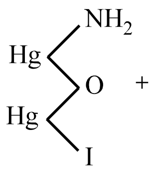
When a rod dipped in HCl is brought on the mouth of the test tube, white fumes of ammonium chloride are formed.

$NH_3 + HCl \longrightarrow NH_4Cl$

white fumes

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

$2K_2HgI_4 + NH_4Cl + 4KOH \longrightarrow$



$+ 7KI + KCl + 3H_2O$

Iodide of Millon's base (Brown ppt.)

Example 1 :

Chocolate brown precipitate is formed with –

(A) Cu^{2+} ions and $[Fe(CN)_6]^{3-}$

(B) Cu^{2+} ions and $[Fe(CN)_6]^{4-}$

(C) Fe^{2+} ions and $[Fe(CN)_6]^{4-}$

(D) Fe^{2+} ions and dimethylglyoxime

Sol. **(B).** (A) $Cu_3[Fe(CN)_6]_2 \downarrow$ (green)

(B) $Cu_2[Fe(CN)_6] \downarrow$ (chocolate brown)

(C) $Fe_4[Fe(CN)_6]_3 \downarrow$ (Prussian blue)

(D) Red solution of iron (II) dimethylglyoxime

Example 2 :

Which of the following gives a precipitate with $Pb(NO_3)_2$ but not with $Ba(NO_3)_2$?

(A) Sodium chloride
(B) Sodium acetate
(C) Sodium nitrate
(D) Disodium hydrogen phosphate

Sol. (A).

(A) $Pb^{2+} + 2Cl^- \rightarrow PbCl_2 \downarrow$ (white)
$Ba^{2+} + 2Cl^- \rightarrow BaCl_2 \downarrow$ (water soluble)
(B) $(CH_3COO)_2$ Pb & $(CH_3COO)_2$ Ba both are water soluble salts.
(C) Nitrates are mostly soluble in water.
(D) $3Pb^{2+} + 2HPO_4^{2-} \rightarrow Pb_3(PO_4)_2 \downarrow$ (white) + $2H^+$
$Ba^{2+} + HPO_4^{2-} \rightarrow BaHPO_4 \downarrow$ (white)

Example 3 :

Colour of cobalt chloride solution is –

(A) pink
(B) black
(C) colourless
(D) green

Sol. (A). Anhydrous Co (II) salts are blue in colour while hydrated Co (II) salts are pink/red.

Example 4 :

A red colouration or precipitate is not obtained when –

(A) Fe^{3+} reacts with potassium thiocyanate
(B) Fe^{2+} reacts with dimethylglyoxime.
(C) Hg^{2+} reacts with potassium iodide.
(D) None of these

Sol. (D). (A) $Fe^{3+} + 3SCN^- \rightarrow Fe(SCN)_3$ (red solution)
(B) Red solution of iron (II) dimethylglyoxime
(C) $Hg^{2+} + 2I^- \rightarrow HgI_2 \downarrow$ (red)

TRY IT YOURSELF-1

Q.1 Which of the following would give yellow turbidity with dilute HCl ?

(A) S^{2-}
(B) $S_2O_3^{2-}$
(C) CO_3^{2-}
(D) NO_2^-

Q.2 Salt A water soluble gives pink colour with phenolphthalene and salt B will not give pink colour with phenopthlene but both salt give colourless or odourless gas (X) on heating, gas (X) gives white turbidity with Baryta water which disappear on passing excess of gas (X). Salt A and B are

(A) CO_3^{2-}
(B) HCO_3^-
(C) HSO_3^-
(D) SO_3^{2-}

Q.3 Unknown solution of salt A $\xrightarrow{K_3[Fe(CN)_6]}$ green ppt is obtained. Which one of the following radicals will be confirmed

(A) Ni^{2+}
(B) Cu^{2+}
(C) $S_2O_3^{2-}$
(D) SO_3^{2-}

Q.4 Colour of nickel chloride solution is –

(A) pink
(B) black
(C) colourless
(D) green

Q.5 The acidic solution of a salt produced a deep blue colour with starch iodide solution. The salt may be –

(A) chloride
(B) nitrite
(C) acetate
(D) bromide

Q.6 When a mixture of solid NaCl, solid $K_2Cr_2O_7$ is heated with conc. H_2SO_4, orange red vapours are obtained. These are of the compound

(A) chromous chloride
(B) chromyl chloride
(C) chromic chloride
(D) chromic sulphate

Q.7 In Nessler's reagent, the ion present is –

(A) HgI^{2-}
(B) HgI_4^{2-}
(C) Hg^+
(D) Hg^{2+}

Q.8 Which of the following is not a preliminary test used to detect ions –

(A) borax bead test
(B) flame test
(C) brown ring test
(D) cobalt nitrate test

Q.9 The compound formed in the borax bead test of Cu^{2+} ion in oxidising flame is –

(A) Cu
(B) $CuBO_2$
(C) $Cu(BO_2)_2$
(D) None of these

Q.10 The alkaline earth metal that gives apple-green colour to bunsen flame when introduced in it in the form of its chloride is –

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

Q.11 Using dil. HCl, which of the following radical cannot be confirmed –

(A) S^{2-}
(B) $S_2O_3^{2-}$
(C) CO_3^{2-}
(D) NO_2^-

Q.12

$$\underset{\text{(Mix of two cation)}}{A} + HClO_4 \longrightarrow \underset{\text{white ppt.}}{B} + \underset{\text{filtrate}}{C}$$

$$\xrightarrow{NaOH} D \xrightarrow{K_2HgI_4/OH^-} \text{Brown ppt.}$$

The cations present in A

(A) K^+ & Na^+
(B) K^+ & NH_4^+
(C) NH_4^+ & Fe^{2+}
(D) Mg^{2+} & Na^+

Q.13 Sodium carbonate bead test is performed for salt powder A and if colour of bead become yellow then salt have –

(A) Cr
(B) Mn
(C) Fe
(D) None of these

Q.14 On addition of Na_2HPO_4 solution to which of the following reagent leads to the formation of yellow ppt.

(A) $AlCl_3$
(B) $ZnCl_2$
(C) $AgNO_3$
(D) $Pb(OAc)_2$

ANSWERS

(1) (B) **(2)** (AB) **(3)** (B)
(4) (D) **(5)** (B) **(6)** (B)
(7) (B) **(8)** (C) **(9)** (C)
(10) (A) **(11)** (C) **(12)** (B)
(13) (A) **(14)** (C)

PURIFICATION OF ORGANIC COMPOUNDS

Introduction : For characterization and determination of the structural formulae of an organic compound it is essential that it should be in the purest form . Methods usually adopted for the purification of organic compounds are

* Crystallization * Fractional crystallization
* Sublimation * Simple distillation
* Fractional distillation * Distillation under reduced pressure
* Steam distillation * Differential extraction
* Chromatography

Crystallization : The method is based on the difference in the solubility of the organic compound and the impurities present in it. A saturated solution of the impure compound in a suitable solvent is prepared. Of course the temperature has to be increased for more dissolution of the organic compound. Subsequently the solution is filtered and cooled, pure crystals get separated.

Solvent chosen must have the following properties :

***** Dissolve more substance.
***** Not react chemically with the compound to be purified
***** Not dissolve the impurities at all or dissolve to a limited extent so that they remain in the mother liquor

Solvents : Water, ethanol, dioxane, acetone, benzene, chloroform, petroleum ether etc.

Examples :

Compound and impurity	**Solvent chosen**
Benzoic acid + naphthalene	Water
Sugar + sand	Water
Sugar + Common salt	Ethanol
Iodoform + impurity	Ethanol

Fractional Crystallization : Separation of different compounds of a mixture by repeated crystallization is called fractional crystallization. A hot saturated solution containing two substances is cooled, the component with lower solubility crystalizes first and these crystals can then be separated out by filtration. The more soluble component crystallizes out on further cooling.

Example : [$KClO_3$ + KCl] mixture can be separated by fractional crystallisation. $KClO_3$ crystallized first being less soluble. After the separation of $KClO_3$, KCl will be crystallized subsequently being more soluble.

Sublimation :

$$\text{Solid} \quad \underset{\text{Cooling}}{\overset{\text{heating}}{\rightleftharpoons}} \quad \text{Vapour}$$

In the sublimation process, solid directly transforms into vapour state on heating and the vapours on cooling transform into solid state. This method is used for the purification of solids which sublime from the non–volatile impurities.

Example : Camphor, naphthalene, ammonium chloride, salicyclic acid, iodine, $AlCl_3$, $HgCl_2$ etc. are purified by sublimation.

Simple Distillation : Distillation implies conversion of liquid into vapour state by heating followed by condensation of the vapours by cooling. The method is suited for liquids which are stable at their boiling point.

Example : Ethanol, benzene, chloroform, carbon tetrachloride, toluene, xylene, nitrobenzene, chlorobenzene etc.

A mixture of two liquids can be separated if their boiling points differ by a wide range.

(i) Mixture of hexane (b.p. 342 K) and toluene (b.p. 384 K)
(ii) Mixture of benzene (b.p. 353 K) and aniline (b.p. 457 K)

Fractional Distillation :

Fractional distillation is a suitable process for separating two or more miscible liquids which have boiling points quite close to each other.

Example : (i) Mixture of acetone (b.p. 330K) and methyl alcohol (b.p. 338K)

(ii) Separation of petroleum into gasoline, kerosene oil, diesel oil etc. Distillation assembly is provided with fractionating column. The fractionating column is a long tube provided with obstructions to the passage of the vapours moving upwards and liquids moving downwards.

Fractionating column increase the cooling surface. Different types of fractionating columns are given in figure.

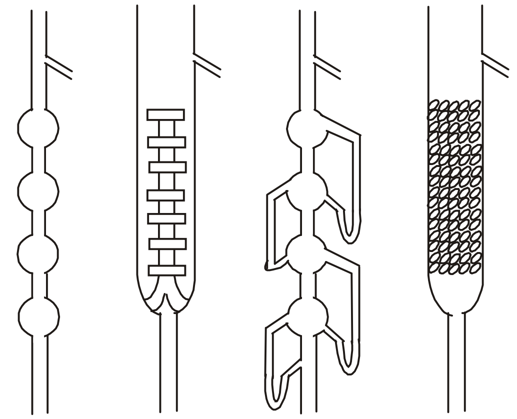
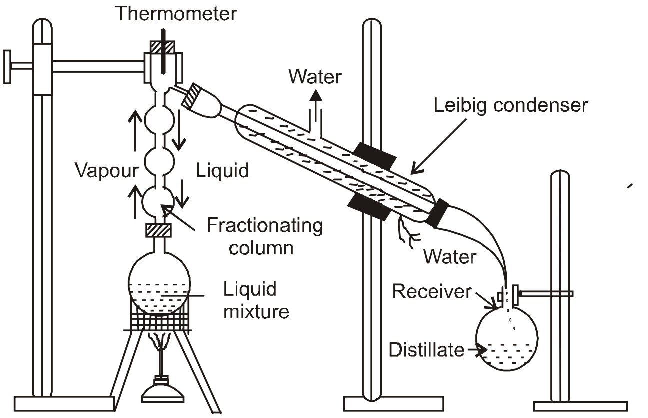


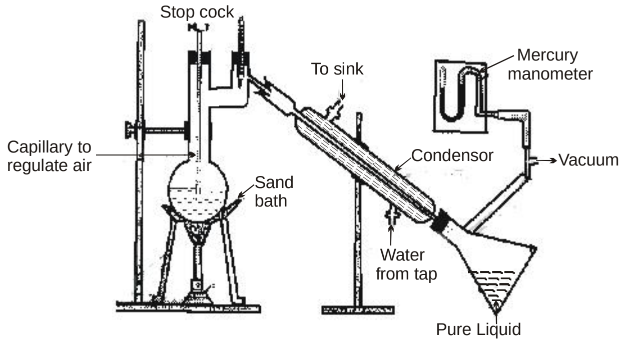
Figure : Different types of fractional columns

On heating the liquid in the distillation flask, vapours of more volatile liquid rise up in the fractionating column and condense while passing through the condenser [cooled by circulating water] and is collected in the receiver. The vapours of less volatile liquid simultaneously rise in the column but due to several obstructions they get condensed in the column itself and flow back to the distillation flask. Obviously the receiver contains the fraction rich in more volatile liquid. On repeating the process separation of mixture of two liquids can be accomplished.



Distillation under reduced pressure (vacuum distillation) Vacuum distillation is used for the distillation of those liquids which decompose before their boiling point in reached. Under reduced pressure the liquid will be boiled at lower temperature (without decomposition) and so its distillation can be carried out.

Example : Fatty acids, glycerol etc.



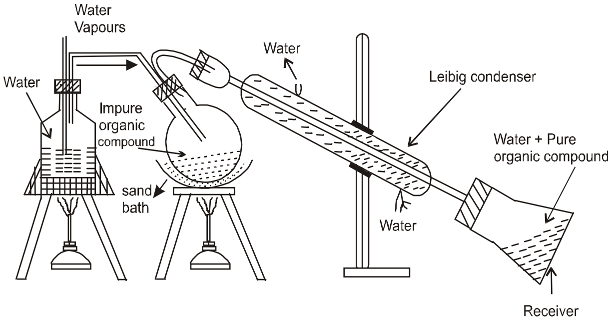
Distillation under reduced pressure

Steam Distillation : Steam distillation is used to purify the substances (liquids or solids)

* Which are volatile in steam.

* Immiscible with water.

* Contaminated with non–volatile impurities

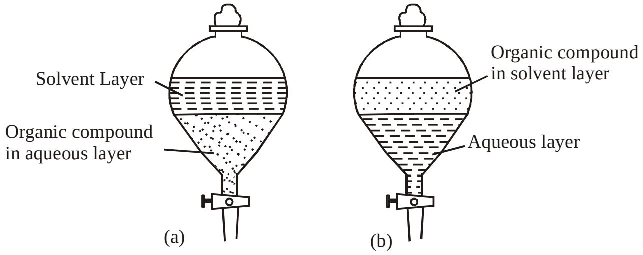


Steam distillation

Example : (i) Purification of aniline

(ii) Separation of ortho and para nitrophenol.

Differential Extraction : In order to recover organic compounds from their aqueous solution differential extraction method is prominently used. An aqueous solution of organic compound is taken in the separating funnel and is shaken with organic solvent which is immiscible with water but in which the organic compound is highly soluble. Organic compound is dissolved in the organic solvent which is extracted by the separating funnel. Organic compound is then recovered by evaporating the solvent in a water bath. The process is repeated to make further recovery of organic compound.



Separation with separating funnel

Note : It should however be noted that with a given amount of the solvent, if more number of extractions are carried out with small amount of the solvent greater will be amount of the extracted substance.

Solvents : the solvents Usually used in the extraction process are benzene, ether, chloroform, dioxane, acetone etc.

Example : To remove benzoic acid from aqueous solution of benzoic acid, benzene is used as the extracting solvent.

Chromatography : Chromatography is the most versatile analytical technique used for the separation, purification, isolation and identification of the constituents present in a mixture (coloured or colourless). It was discovered by Tswett (1906) for the separation of plant pigments.

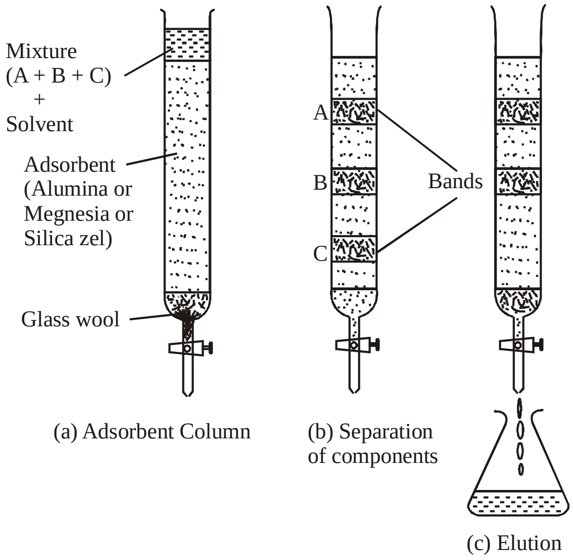
Chromatography may be defined as the technique of separating the components of a mixture in which separation is affected by movement of individual components through a stationary phase (fixed) under the influence of mobile phase. Different types of important chromatography are give in the table :

Chromatography	Stationary Phase	Mobile Phase
Adsorption chromatography	Solid	Liquid
Partition chromatography	Liquid	Liquid

Adsorption or column chromatography : Sample containing various constituents is dissolved in a suitable solvent and the solution is allowed to percolate through a column (glass tube or burette containing silica gel.) The solution moves down slowly and the various constituents of the mixture gets adsorbed to different extent over the adsorbent. The constituent which is adsorbed most strongly will be retained at top. The constituent which is adsorbed less strongly will be retained at the lower level. The constituent which is adsorbed still less will be retained at the still lower level and so on. Supposing there are three organic compounds A, B and C present in the mixture. The decreasing order of their adsorbing tendency is : A > B > C

Obviously A will be adsorbed near the top of the column while C having least adsorbing tendency will be adsorbed in the last. The column will appear as coloured bands or zones of various constituents. Further by the process of elution i.e. by percolating suitable solvents through the column. The least adsorbed constituent is eluted first by the solvent while the strongly adsorbed constituent will be eluted afterwards by a solvent. The pure compound is recovered by evaporation of the solvent.

Example : Chlorophyll from plants, pigments or dyes etc.



(a) Adsorbent Column

(b) Separation of components

(c) Elution

Column chromatography

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The qualitative analysis of an organic compound involves the detection of all the elements present in it.

Detection of Carbon and Hydrogen :A small amount of dry and powdered substance is mixed with about double amount of pure and dry copper oxide. The mixture is heated in a dried hard glass tube delivery tube and fitted with a carrying a bulb in the horizontal length The bulb of delivery tube contains anhydrous copper sulphate (white). When the mixture is heated, if the carbon present in the compound is oxidised to carbon dioxide which turns lime water milky and if the hydrogen present in the organic compound is oxidised to water which turns anhydrous copper sulphate in the bulb to blue.

$$C + 2CuO \xrightarrow{\text{Heat}} CO_2 + 2Cu$$

(O.C.)

$$\underset{\text{lime water}}{CO_2 + Ca(OH)_2} \longrightarrow \underset{\text{milky}}{CaCO_3} + H_2O$$

$$2H + CuO \xrightarrow{\text{Heat}} H_2O + Cu$$

(O.C.)

$$\underset{\substack{\text{anhydrous}\\\text{copper sulphate}\\\text{(white)}}}{CuSO_4} + 5H_2O \longrightarrow \underset{\substack{\text{hydrated copper}\\\text{sulphate}\\\text{(blue)}}}{CuSO_4 . 5H_2O}$$

This method is known as copper oxide test.

Detection of Nitrogen : Nitrogen in an organic compound is detected by the following tests :

(a) Soda lime test. A pinch of an organic compound is heated strongly with soda lime (NaOH + CaO) in a test tube. If ammonia gas evolves, it indicates nitrogen.

$$\underset{\text{acetamide}}{CH_3CONH_2} + NaOH \xrightarrow{CaO} CH_3COONa + NH_3\uparrow$$

Limitation : This method has a limitation. A large number of organic compounds such as nitro and diazo compounds do not liberate ammonia on heating with sodalime.

(b) Lassaigne's method : A small piece of a dry sodium is heated gently in an ignition tube till it melts to a shining globule. The filtered liquid is known as sodium extract or Lassaigne's extract.

The Lassaigne's extract is usually alkaline. If not, it may be made alkaline by adding a few drops of a dilute solution of sodium hydroxide. To a part of sodium extract a small amount of a freshly prepared ferrous sulphate solution is added and the contents are warmed. A few drops of ferric chloride solution are added. The appearance of a bluish green or a blue colouration, confirms the presence of nitrogen in the organic compound.

The following chemical reactions occur during the test :

$$Na + C + N \longrightarrow NaCN$$

(O.C.)

$$FeSO_4 + 2NaCN \longrightarrow Fe(CN)_2 + Na_2SO_4$$

$$Fe(CN)_2 + 4NaCN \longrightarrow \underset{\text{sodium ferrocyanide}}{Na_4[Fe(CN)_6]}$$

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\substack{\text{ferric ferrocyanide}\\\text{(blue colour)}}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

Detection of Sulphur :

Lassaigne's Test : The sulphur in the compound reacts with sodium metal to form sodium sulphide.

$$2\,Na + S \longrightarrow \underset{\text{(O.C.)}}{Na_2S}$$

The Lassaigne's extract is divided into three parts and following tests are performed.

(i) Sodium nitroprusside test. To one portion of the extract few drops of sodium nitroprusside are added. The appearance of violet colouration indicates sulphur.

$$Na_2S + \underset{\text{sod. nitroprusside}}{Na_2[Fe(CN)_5NO]} \longrightarrow \underset{\text{violet colouration}}{Na_4[Fe(CN)_5NO.S]}$$

(ii) Lead acetate test : The second part of the Lassaigne's extract is acidified with acetic acid and then lead acetate solution is added. Formation of black precipitate confirm the presence of sulphur.

$$\underset{\text{lead acetate}}{Na_2S + Pb(CH_3COO)_2} \longrightarrow \underset{\text{black}}{PbS\downarrow} + 2CH_3COONa$$

(iii) Silver nitrate test : The third part of Lassaigne's extract is acidified with acetic acid and then $AgNO_3$ solution is added. Formation of black ppt. confirms the presence of sulphur.–

$$Na_2S + 2AgNO_3 \longrightarrow \underset{\text{Black}}{Ag_2S\downarrow} + 2NaNO_3$$

Detection of Halogens :

Beilstein test : A stout copper wire is heated in non–luminous flame till it ceases to impart green colour to the flame.

The heated end of the wire is dipped into the O.C. and again taken to flame. Appearance of green or bluish green colour of the flame indicates the presence of halogens.

Note : Urea, thiourea etc. also give this test due to the formation of volatile $Cu(CN)_2$

Lassaigne's test : Sodium extract is prepared. During fusion, sodium will combine with the halogen (from the organic compound) to form sodium halide.

$$Na + \underset{\text{(O.C.)}}{X} \xrightarrow{\text{Fusion}} NaX(X = Cl, Br, I)$$

Now, we add $AgNO_3$ solution.

(i) If white precipitate appears then chlorine is confirmed.

$$NaCl + AgNO_3 \longrightarrow \underset{\text{white ppt.}}{AgCl\downarrow} + NaNO_3$$

(ii) If light yellow precipitate appears then bromine is confirmed.

$$NaBr + AgNO_3 \longrightarrow \underset{\text{light yellow ppt.}}{AgBr\downarrow} + NaNO_3$$

(iii) If dark yellow precipitate, appears then iodine is confirmed.

$$NaI + AgNO_3 \longrightarrow \underset{\text{dark yellow ppt.}}{AgI\downarrow} + NaNO_3$$

Special test for bromine and iodine. (NaBr & NaI come from Lassaigne's extract.

Acidified lassaigne's extract + Chlorine water $\longrightarrow Br_2$ or I_2 evolved

$$2NaBr + Cl_2 \longrightarrow 2NaCl + Br_2 \text{ (turns } CS_2 \text{ layer orange)}$$
$$2NaI + Cl_2 \longrightarrow 2NaCI + I_2 \text{ (turns } CS_2 \text{ layer violet)}$$

Detection of Phosphorus : Organic compound (O.C.) is fused with sodium peroxide (Na_2O_2) or fusion mixture ($Na_2CO_3 + KNO_3$) and the mass is extracted with water. The extract is boiled with conc. HNO_3 and then ammonium molybdate solution is added. The appearance of yellow precipitate or colouration (due to formation of Ammonium phosphomolybdate). Shows the presence of Phosphorus.

$$2P + 5\,Na_2O_2 + 4H_2O \longrightarrow 2Na_2HPO_4 + 6NaOH$$
$$Na_2HPO_4 + HNO_3 \xrightarrow{(NH_4)_2M_0O_4} \underset{\text{yellow}}{(NH_4)_3PO_4.12\,M_0O_3}$$

QUANTITATIVE ANALYSIS

It involves the estimation of following elements

[C and H] [N] [X] [S] [P] [O]

Estimation of C and H [Liebig's method]

A known weight of O.C. is heated with cupric oxide in an atmosphere of air or oxygen (free from CO_2). C and H of O.C. are oxidised to CO_2 and H_2O respectively. The former is collected over KOH and latter is absorbed by $CaCl_2$. From the amounts of CO_2 and H_2O vapours the percentage of C and H can be calculated.

$$\underset{\text{(O.C.)}}{C} + 2CuO \longrightarrow CO_2 + 2Cu;$$
$$\underset{\text{(O.C.)}}{2H} + CuO \longrightarrow H_2O + Cu$$

$$\%\text{ of C} = \frac{12}{44} \times \frac{\text{mass of } CO_2 \text{ formed}}{\text{mass of organic compound taken}} \times 100$$

$$\%\text{ of H} = \frac{2}{18} \times \frac{\text{mass of } H_2O \text{ formed}}{\text{mass of organic compound taken}} \times 100$$

Estimation of N : There are two methods for the estimation of nitrogen.

(a) Duma's Method (b) Kjeldahls Method

(a) Duma's Method : A known weight of O.C. is heated with cupric oxide in an atmosphere of CO_2. C and H are oxidised to CO_2 and H_2O respectively. N is converted to N_2. It is anticipated that some oxides of nitrogen may also be formed. It is reduced to N_2 by passing over heated copper gauze.

$$\underset{\text{(O.C.)}}{C} + 2CuO \longrightarrow CO_2 + 2Cu$$
$$\underset{\text{(O.C.)}}{2H} + CuO \longrightarrow H_2O + Cu$$
$$\underset{\text{(O.C.)}}{2N} + CuO \longrightarrow N_2 + \text{oxide of nitrogen}$$
$$\text{Oxide of nitrogen} + Cu \longrightarrow CuO + N_2$$

The gaseous nitrogen is collected over conc. KOH solution (all other gases are absorbed except nitrogen) and its volume is measured at room temperature and atmospheric pressure. The volume of the nitrogen gas so obtained is converted in to NTP and its mass is calculated.

% of nitrogen

$$= \frac{28}{22400} \times \frac{\text{Volume of } N_2 \text{ at NTP}}{\text{Mass of organic compound taken}} \times 100$$

Volume of N_2 at NTP can be calculated as :

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ (NTP)}$$

$$V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{(P-a) \times V_1 \times 273}{760 \times (273 + t)}$$

Where : V_1 = Volume of N_2 at room temperature
a = Aqueous tension at t°C (mm of Hg)
t°C = Room temperature
V_2 = Volume of nitrogen at NTP
P = Atmospheric pressure

(b) **Kjeldahl's Method :** A known weight of O.C. is heated strongly with conc. $H_2SO_4[CuSO_4$ catalyst]. As a result the nitrogen in the compound is converted quantitatively into ammonium sulphate. The solution is then treated with excess of NaOH. The ammonia gas evolved is passed into excess volume of HCl or H_2SO_4 solution of known strength. The acid left back is treated with standard alkali. From the acid consumed by ammonia. percentage of nitrogen can be calculated.

$$\underset{\text{(O.C.)}}{C + H + N} \xrightarrow[\Delta]{\text{conc. } H_2SO_4} (NH_4)_2SO_4 + CO_2 + H_2O$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2\,SO_4$$

% of nitrogen

$$= \frac{1.4 \times \text{Normality of the acid} \times \text{Volume of used acid}}{\text{Mass of organic compound taken}}$$

$$= \frac{1.4 \times N \times V}{W}$$

Estimation of X (Halogen) (Carius method)

The O.C. containing halogen is oxidised with fuming nitric acid in presence of $AgNO_3$. The halogens are converted in to silver halides The silver halides are washed and separated and dried. The percentage of halogen can be calculate.

$$\underset{\text{(O.C.)}}{X} \xrightarrow[AgNO_3]{F.HNO_3} AgX$$

$$\text{\% of chlorine} = \frac{35.5 \times \text{Mass of AgCl} \times 100}{143.5 \times \text{Mass of organic compound taken}}$$

$$\text{\% of bromine} = \frac{80 \times \text{Mass of AgBr} \times 100}{188 \times \text{Mass of O.C. taken}}$$

$$\text{\% of iodine} = \frac{127 \times \text{Mass of AgI} \times 100}{235 \times \text{Mass of O.C. taken}}$$

Estimation of S : The O.C. containing sulphur is heated with fuming HNO_3 sulphur is oxidised to H_2SO_4. Precipitation of sulphate is carried out with barium chloride solution in the form of $BaSO_4$. The precipitate is separated washed and weighed.

$$\underset{\text{(O.C.)}}{S} \xrightarrow{F.HNO_3} H_2SO_4$$

$$H_2SO_4 + BaCl_2 \longrightarrow BaSO_4\downarrow + 2HCl$$

$$\text{\% of sulphur} = \frac{32 \times \text{Mass of } BaSO_4 \times 100}{233 \times \text{Mass of O.C. taken}}$$

Estimation of P : Phosphorus is estimated by Carius method. The O.C. is heated with $F.HNO_3$ which oxidises phosphorus to phosphoric acid. It is treated with solution of magnesia mixture ($MgSO_4 + NH_4Cl + NH_4OH$). A precipitate of $MgNH_4PO_4$ is obtained. On ignition it gives magnesium pyrophosphate $Mg_2P_2O_7$. Its weight is determined.

$$\underset{\text{(O.C.)}}{P} + F.HNO_3 \longrightarrow H_3PO_4$$

$$H_3PO_4 + \text{Magnesia mixture} \longrightarrow \underset{\substack{\text{Magnesium ammonium}\\ \text{phosphate}}}{MgNH_4PO_4}$$

$$2MgNH_4PO_4 \xrightarrow{\Delta} \underset{\substack{\text{Magnesium}\\ \text{pyrophosphate}}}{Mg_2P_2O_7\downarrow} + 2NH_3 + H_2O$$

$$\text{\% of phosphorus} = \frac{62 \times \text{Mass of } Mg_2P_2O_7 \times 100}{222 \times \text{Mass of O.C. taken}}$$

Estimation of O : It is calculated by difference. It is estimated by adding the percentage of all other elements and subtracting this sum from 100.

Example 5 :

In Lassaigne's test when both N and S are present, blood red colour obtained is due to the formation of –

(A) Ferric ferrocyanide (B) Ferric sulphocyanide
(C) Ferric cyanide (D) None

Sol. **(B).** $3NaCNS + FeCl_3 \rightarrow \underset{\text{(Red)}}{Fe(CNS)_3} + 3NaCl$

Example 6 :

In sodium fusion test of organic compounds, the nitrogen of an organic compound is converted to –

(A) Sodamide (B) Sodium cyanide
(C) Sodium nitrite (D) Sodium nitrate

Sol. **(B).** $Na + C + N \xrightarrow{\text{Fusion}} NaCN$

Example 7 :

0.2475g of an organic compound gave on combustion 0.4950g of carbon dioxide and 0.2025g of water. The percentage of carbon and hydrogen are –

(A) 54.54. 9.09 (B) 52.54, 8.09
(C) 120, 5.8 (D) None

Sol. **(A).** Wt. of organic compound = 0.2475g
Wt. of CO_2 produced = 0.4950g
Wt. of H_2O produced = 0.2025g

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{\text{Wt. of } CO_2}{\text{Wt. of compound}} \times 100$$

$$= \frac{12}{44} \times \frac{0.4950}{0.2475} \times 100 = 54.54$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{\text{Wt. of } H_2O}{\text{Wt. of compound}} \times 100$$

$$= \frac{2}{18} \times \frac{0.2025}{0.2475} \times 100 = 9.09$$

Example 8 :

A bottle containing two immiscible liquids is given to you. They may be separated by using –

(A) Fractionating column (B) Separating funnel
(C) Vacuum distillation (D) Steam distillation

Sol. **(B).** Being immiscible liquids, they form different layers.

DETERMINATION OF MOLECULAR MASS

There are two methods for determination of molecular mass –

(i) Silver Salt Method (for organic acids)
(ii) Chloroplatinate salt method (for organic bases)

(i) Silver Salt Method : A known mass of the acid is dissolved in water followed by the subsequent addition of silver nitrate solution till the ppt of silver salt is complete. The ppt is separated, dried, weighed and ignited till decomposition is complete. The residue of pure silver left behind is weighed.

$$\text{Organic acid} \xrightarrow{AgNO_3} \text{Silver salt} \xrightarrow{\text{combustion}} Ag$$

Let the mass of silver salt formed = W gm
Mass of silver left behind = w gm

$$\frac{\text{Mass of silver salt}}{\text{Mass of silver left behind}} = \frac{\text{Equivalent mass of silver salt}}{\text{Equivalent mass of silver}}$$

$$\frac{W}{w} = \frac{E}{108} \; ; \; E = \frac{W}{w} \times 10^8$$

Hence , Equivalent mass of organic acid = Equivalent mass of silver salt – Equivalent mass of silver + Equivalent mass of hydrogen = E – 108 + 1 = E – 107

Molecular mass of organic acid
= Equivalent mass of acid x Basicity of acid

(ii) Chloroplatinate salt method : This chemical method is used to find the molecular mass of organic bases. A known mass of organic base is allowed to react with chloroplatinic acid ($H_2 Pt Cl_6$) to form insoluble chloroplatinate salt.

The ppt of chloroplatinate salt is separated, dried, weighed and is subsequently ignited till decomposition is complete. The residue left is platinum which is again weighed. The molecular mass is then calculated by knowing the mass of chloro platinate salt and that of platinum left. If B represents the molecule of mono acid organic base, then the formula of chloro platinate salt is $B_2H_2 Pt Cl_6$.

B

$$\text{organic base} \xrightarrow{H_2 Pt Cl_6} \underset{\text{(chloroplatinate salt)}}{B_2H_2 Pt Cl_6} \xrightarrow{\text{Ignite}} Pt$$

Mass of chlorplatinate salt = W g
Mass of platinum residue left = w g
If eq. weight of organic base = E

Thus molecular mass of chloroplatinate salt
$= 2E + (2 + 195 + 35.5 \text{ x } 6) = 2E + 410$

1 mole of chloroplatinate salt (2E + 410) on heating gives one atom of platinum (195).

$$\frac{\text{Mass of chloro platinate}}{\text{Mass of platinum residue}}$$

$$= \frac{\text{Molar mass of chloroplatinate salt}}{\text{Atomic weight of platinum}}$$

$$\frac{W}{w} = \frac{2E + 410}{195}$$

$$2E = \left(\frac{W}{w} \text{x} 195\right) - 410 \; ; \; E = \frac{1}{2}\left[\left(\frac{W}{w} \text{x} 195\right) - 410\right]$$

Molar mass of organic base = equivalent weight of base
× acidity of the base

PRACTICAL ORGANIC CHEMISTRY

1. Unsaturation : Alkenes & alkynes:

(a) Bayers test : Cold dil alk. $KMnO_4$ decolourisation test
Purple colour → Colourless + MnO_2 (Brown ppt)

(b) Br_2 water decolourisation test
Violet colourless of Br_2 → Colourless

2. Terminal alkynes: Confirmed by ppt of Acetylide ion with $NaNH_2$ or $AgNO_3$ or $Cu_2Cl_2NH_4OH$.

3. Alkyl halides :

(a) If they are capable of carbocation formation then they will give ppt with $AgNO_3$.

(b) Beilstein's test : A green colour is imported to the flame if small amount of organic compound is taken on copper wire.

4. Alcohol :

(a) Cerric ammonium nitrate → Give red colour
(b) Boil with acetic acid & conc. H_2SO_4 → fruity smell
(c) 2-alkanol & ethanol also give Iodoform test → Yellow ppt. of CH_3I on reaction with $I_2 + O^{\ominus}H$.

5. Aldehyde & Ketones:

2,4-Dinitrophenyl hydrazize (or) Braddy's reagent give yellow, orange or red color with ald. & Ketones (2, 4-DNP).

6. Aldehydes:

(a) Tollen's test → Silver mirror
(b) Fehling's test {except benzaldehyde} → Red colour
(c) Benedicts test → Red colour

(d) **Schiff's Test :** Given compound is dissolved in alcohol and then 1-2ml of Schiff's reagent is added. Appearance of pink, red or magenta colour confirms the presence of aldehyde group while ketones are without effect.

(e) Gly ppt with $HgCl_2$

7. **Ketones:**

(a) Methyl Ketones give haloform test.

(b) α-hydroxy Ketones give Tollen's & Fehling test's too.

8. **Carboxylic acids:**

(a) Brisk effervescence with aq. $NaHCO_3$ solution.

(b) HCOOH alone gives silver mirror test with Tollen's reagent.

(c) Blue litmus → red

(d) Give fruity smell on reaction with alcohols.

9. **Phenols :**

(a) Violet colouration with neural $FeCl_3$

(b) White ppt with Br_2 water

(c) Brisk effervescence with aq. $NaHCO_3$ is observed in case of Nitro phenols.

(d) **Litmus Test :** A drop of the given liquid or a crystal (if solid) is placed on a moist blue litmus paper. If the colour changes to red, phenolic group may be present.

(e) **Liebermann's Test :** When a few drops of phenol is heated with a few crystals of sodium nitrite and 1ml concentrated sulphuric acid, a green or blue colouration develops.

10. **Primary amines:**

(a) Carbylamine reaction → Isonitriles have very distinctive foul odors

(b) Hoffmann mustard oil reaction → Oily liquid with mustard like smell.

11. Aromatic 1° amine → diazo test

12. Amide boil with NaOH → NH_3

13. Nitrobenzene → Mulliken Baker test → Treat it with $ZnNH_4Cl$ then boil with Tollen's reagent → Silver mirror will appear.

14. **Proteins:**

(a) **Biuret test:** Also used for urea → Alkaline solution of protein treated with a drop of aq $CuSO_4$ when bluish violet colour is obtained.

(b) **Ninhydrin test :** Protein treated with a puridine solution of ninhydrin give colour ranging from deep blue to violet pink.

DIFFERENTATION TEST

1. **1°, 2° & 3° alcohols**

(a) Luca's test : Lucas reagent is conc. HCl +$ZnCl_2$

(b) Victor Meyer's test (RBC test)

(i) 1° Alcohol → Blood red colour

(ii) 2° Alcohol → Blue

(iii) 3°Alcohol → Colourless

2. **1°, 2° & 3° amines:**

Hinsberg's reagent

(i) 1°Amine yield a clear solution from which upon acidification an insoluble material separated.

(ii) 2° Amine yield an insoluble compound which is unaffected by acid.

(iii) 3°Amine yield insoluble compound.

SEPARATION TEST

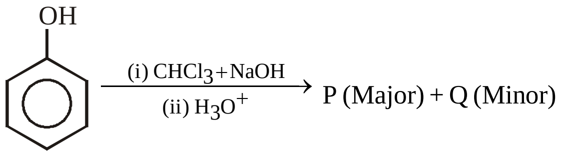
(i) **Aldehyde and Ketones from other liquid hydrocarbons and other neutral liquid compound (e.g. ethanal and ethanol):** The mixture is shaken with a solution of $NaHCO_3$, the carbonyl compound forms a solid bisulphite compound which is filtered off and decomposed with dil. acid in order to recover the aldehyde or ketone.

(ii) **Separation based on Differences in the volatilities of the component in aqueous solution Diethylamine and butan-1-ol :** They can be separated by adding sufficient dilute H_2SO_4 to neutralised the base ; steam distillation will remove the alcohol. The amine can be recovered by adding NaOH to the residue and repeating the distillation.

(iii) **Diethy Ketone and Acetic Acid :** The mixture is treated with sufficient dilute NaOH solution to transform the acid into sodium acetate and distilling the aqueous mixture. The ketone will pass over in the steam and the non volatile stable salt will remain in the flask. Acidification with dilute H_2SO_4 liberates acetic acid which can be isolated by steam distillation or by extraction.

Example 9 :

Consider the reaction :

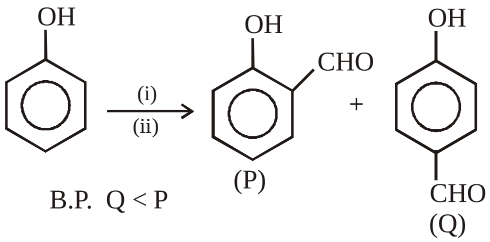


Mixture of P and Q can be best separated by –

(A) Steam distillation (B) Vacuum distillation

(C) Fractional distillation (D) Crystallisation

Sol. (C).



Example 10 :

Select reagent which is used in laboratory to differentiate 1°, 2° and 3° amines from each other.

(A) NaOH, I_2 (B) $PhSO_2Cl$
(C) $CHCl_3$, KOH (D) CS_2, $HgCl_2$.

Sol. (B). Hinsberg reagent $PhSO_2Cl$ is used to differentiate 1°, 2° and 3° amines.

SOME EXPERIMENTS

(1) Heat of solution of $CuSO_4$

Requirements :- Dewar's vacuum flask ring stirrer of glass tubing, watch glass and a 50 ml. beaker.

Chemicals : $CuSO_4$ (solid)

Procedure :

(A) Determination of water equivalent (w) of the vacuum flask.Take a Dewar's flask of about 300-500 ml capacity and fit in a cork on its mouth. Add a known mass of water in the flask. Wait for some time and note down its temperature T_1. Also take the known mass of hot water whose temperature is T_2 (T_2 should be higher than T_1 by at least 20^o). Add this hot water into the cold water taken in the flask. Stir the mixture and note the final temperature T_3.

Observations :

Suppose mass of cold water taken = 50 g
Temperature of cold water = $T_1{}^oC$
Let the mass of hot water taken =50g (Say)
Temperature of hot water = $T_2{}^oC$
Resultant temperature of the mixture = $T_3{}^oC$

Calculations : Heat given by hot water = Heat taken by cold water + Heat taken by the flask, stirrer etc.

or $50\,(T_2 - T_3) = 50\,(T_3 - T_1) + W\,(T_3 - T_1)$

Where W is the heat capacity of the flask stirrer etc.

(B) Adjust the temperature of distilled Heat water to room temperature (t_1°C) by slightly warming or cooling, as required. Take100 ml. of this water in the flask.

(C) Take any one of the compounds mentioned above at room temperature (t_1°C). Accurately weight about 1 g of the solid and add it to the distilled water taken in the flask all at once stirring vigourously so as to dissolve the substance in minimum time. Note the higher or lowest temperature (t_2°C) reached during the process of solution.

The amount of heat evolved or absorbed in dissolving 1 g of the solid given as $Q = (W + 100)\,(t_2 - t_1)$
Where W = water equivalent of the flask.
Let the molecular mass of the substance be M g mol^{-1}, then the heat of solution $\Delta H = -M \times Q$ Calories.

(2) Enthalpy of neutralization of strong acid and strong base:-

Requisiter:- Polythene bottle, thermometer stirrer, water bath, two beaker's

Chemicals : 100 ml of 0.5 N HCl and 100 ml of 0.5 N NaOH

Procedure:

(i) The above chemicals are taken into 2 different beakers.

(ii) Both the beakers are kept in water bath till the solution attain the same temperature.

(iii) HCl solution is transferred into polythene bottle. Immediately NaOH solution is added into the polythene bottle. Stirring is done to mix HCl and NaOH. The higest temperature attained is noted.

Calculations : Suppose the initial temperature of the acid and the base = $t_1{}^oC$.

Final temperature of the solution after mixing = $t_2{}^oC$

$\therefore$ Rise in temperature = $(t_2 - t_1)\ {}^oC$
Total mass of the solution = 100+100= 200 g
$\therefore$ Heat produced = Mass × Sp. heat × rise in temp.
$= 200 \times 4.184 \times (t_2 - t_1)J = x$ KJ (say.)

This is the heat produced by neutralisation of 100 ml of 0.5 NHCl.

$\therefore$ Heat produced by neutralisation of 1000 ml. or 1L of 1N HCl. (Containing 1 gm equivalent of HCl)

$$= \frac{x}{100} \times 1000 \times \frac{1}{0.5}\text{ Joules}$$

(3) Preparation of lyophilic and lyophobic sols :

(i) Aresenius sulphide sol. Boil 1-2 g of pure arsenius oxide with about 500 cm^3 of distilled water for about 10-15 minutes. After prolonged boiling cool the solution to room temperature and filter the undissolved As_2O_3, if any. Dilute this solution to 500 cm^3 with distilled water and pass a low current of H_2S (freed from HCl by passing through a tube containing soda lime, and then through 3-4 wash bottles containing distilled water) into the solution until it is saturated. Then pass a stream of pure hydrogen washed through 3-4 wahs bottles containing distilled water, so as to remove the excess of H_2S. Filter the solution to remove the coarse precipitate of AS_2S_3, if necessary.

(ii) Antimony sulphide sol. Prepare about 250 cm^3 of 1% solution of tartar emitic in distilled water and take it in a dropping funnel. Place about 250 cm^3 of distilled water in a flask and pass in it a stream of H_2S. The gas must be freed from HCl by passing through a soda lime tube and then through 3-4 wash bottles containing distilled water. Add the tartar emitic solution drop by drop into water through which H_2S is bubbled. Under these conditions, antimony sulphide formed due to double decomposition is not precipitated but remains in the dispersed state with particle size in the colloidal range. A deep orange coloured colloidal solution of Sb_2S_3 will thus be obtained. Free the sol from the excess of H_2S by passing a stream of pure hydrogen through it. Then dialyse the sol in order to remove the electrolytic impurities.

(4) Kinetic Study of reaction of iodide ion with H_2O_2 at room temperature :

Requirements : Gas burette, 5 and 10 cm^3 pipettes, stop clock thermostat or water trough as thermostat, 1.5% H_2O_2, 0.1 M KI and 0.1 M KCl.

Procedure :

(i) Place 5 cm^3 of 1.5 % H_2O_2 (if100 cm^3 gas burette is used) in a small conical flask as reaction vessel and add to it some glass beads.

(ii) Set the gas measuring apparatus and adjust the water reservoir so that the water level stands at 0.1cm^3 of the gas burette.

(iii) Remove the stopper of the reaction vessel, add to it 5cm^3 of KI solution using a pipette, shake well and stopper the vessel.

(iv) Without disconnecting the reaction vessel from the gas burette, heat it in a boiling water bath for a few minutes so as to complete the decomposition of H_2O_2. When the gas ceases to evolve, cool the reaction vessel back to the temperature of the experiment. Adjust the pressure in the pressure in the gas burette to atmoshpheric one and record the final volume V_∞ of oxygen.

(v) Repeat the experiment with 5 cm^3 of 1 : 1 mixture of 0.1M KI and 0.1 MKCl (ionic strength is kept constant).

(vi) In order to determine the energy of activation, repeat the experiment at higher temperatures, 35 and 40°C.

(vii) The initial concentration of H_2O_2 is proportional to V_∞ and the concentration at any time t to $(V_\infty - V_t)$. Thus, a plot of log the $(V_\infty - V_t)$ against t (abscissa) will be linerar graph, the slope of which will be $-\frac{K}{2.303}$.

Hence calculate K. Then using following equation calculate the energy of activation.

$$\log\frac{k_2}{k_1} = \frac{E}{19.147}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

TRY IT YOURSELF-2

Q.1 The fragrance of flowers is due to the presence of some steam volatile organic compounds called essential oils. These are generally insoluble in water at room temperature but are miscible with water vapour in vapour phase. A suitable method for the extraction of these oils from the flowers is:
(A) Distillation
(B) Crystallisation
(C) Distillation under reduced pressure
(D) Steam distillation

Q.2 In Kjeldahl's method, $CuSO_4$ acts as –
(A) Oxidising agent
(B) Catalytic agent
(C) Reducing agent
(D) Hydrolysing agent

Q.3 During hearing of a court case, the judge suspected that some changes in the documents had been carried out. He asked the forensic department to check the ink used at two different places. According to you which technique can give the best results?
(A) Column chromatography
(B) Solvent extraction
(C) Distillation
(D) Thin layer chromatography

Q.4 Carbon and Hydrogen are estimated by –
(A) Liebig's method (B) Duma's method
(C) Carius method (D) Kjeldahl's method

Q.5 The principle involved in paper chromatography is
(A) Adsorption (B) Partition
(C) Solubility (D) Volatility

Q.6 In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of :
(A) $Na_4[Fe(CN)_6]$ (B) $Fe_4[Fe(CN)_6]_3$
(C) $Fe_2[Fe(CN)_6]$ (D) $Fe_3[Fe(CN)_6]_4$

Q.7 If 0.32gm of an organic compound containing sulphur produces 0.233g of $BaSO_4$ then the percentage of sulphur in its –
(A) 10 (B) 15
(C) 20 (D) 25

Q.8 The best and latest technique for isolation, purification and separation of organic compounds is :
(A) Crystallisation (B) Distillation
(C) Sublimation (D) Chromatography

Q.9 Duma's method involves the determination of content of nitrogen in the organic compound in the form of –
(A) Gaseous NH_3 (B) Gaseous N_2
(C) NaCN (D) $(NH_4)_2SO_4$

Q.10 Nitrogen in an organic compound can be estimated by
(A) Kjeldahl's method only (B) Duma's method only
(C) Both method (D) None of these

Q.11 0.420g of an organic substances was Kjeldahilsed. The ammonia evolved on distilling the Kjeldahilsed extract neutralised 37.5ml of N/10 H_2SO_4. What is the percentage of nitrogen in the compound?
(A) 12.5 (B) 14.5
(C) 10.5 (D) 18.5

ANSWERS

(1) (D) **(2)** (B) **(3)** (D)
(4) (A) **(5)** (B) **(6)** (B)
(7) (A) **(8)** (D) **(9)** (B)
(10) (C) **(11)** (A)

USEFUL TIPS

1. **Flame Test:** Carefully clean a platinum wire by dipping it into dilute nitric acid and heating it in the Bunsen flame. Repeat until the flame is colourless. Dip the heated wire into the substance being tested (either solid or solution), and then hold it in the hot outer part of the Bunsen flame.

Characteristic flame colour

(1) Pb → Yellow, green
(2) Cu salt, BO_3^{-3} → blue or green
(3) Li → red
(4) Na → golden yellow
(5) K → violet
(6) Rb → violet red
(7) Cs → violet blue
(8) Ca → brick red
(9) Sr → crimson red
(10) Ba → apple green

2. **PHYSICAL APPEARANCE OF INORGANIC SALT**

S. NO.	INORGANIC SALT	COLOUR
1.	Cu^{+2}	Blue
2.	Cr^{+3}, Cr^{+6}	Dark green
3.	Fe^{+3}	Green
4.	Fe^{2+}	Yellow or Brown
5.	Mn^{+2}	Light Pink
6.	Co^{+2}	Pink
7.	Ni^{+2}	Green or Blue
8.	HgO, HgI_2, Pb_3O_4	Red
9.	Pb, Hg and Ba Salts	Comparatively heavy

3. **Bicarbonates and Carbonates:**
   (i) Generally carbonates on heating give metal oxide and CO_2
   (ii) Except Li_2CO_3, all alkalimetal carbonates are thermally stable.
   (iii) Silver and mercury carbonates on heating precipitates metal, CO_2 and O_2

4. **Nitrates**
   (i) Generally nitrates on heating give metal oxide, NO_2 and O_2
   (ii) Except $LiNO_3$, all alkali metal nitrates decomposed into metal nitrite and O_2.
   (iii) Silver and mercury nitrates on heating precipitates metal, NO_2 and O_2

5. **Sulphates**
   (i) Sulphates of Ba, Pb, Na etc. are quite stable and loose water of crystallization on heating.
   (ii) On strong heating sulphates give metal oxide and SO_3 (some times into SO_2 and O_2)
   (iii) Ferrous sulphate on heating gives ferric oxide, SO_2 and SO_3 both

6. **Phosphates :**
   Phosphoric acid (H_3PO_4) forms three series of phosphates i.e. 1° phosphate ($H_2PO_4^-$); 2 ° phosphate (HPO_4^{--}); and 3° phosphate (PO_4^{---})
   1° phosphate on heating give metaphosphate and H_2O
   2° phosphate on heating give pyrophosphate and H_2O
   3° phosphate are thermally stable

7. **General Solubility Rules: (Solubility in water)**
   (i) All nitrates, nitrites bicarbonates, acetates, thiosulphate, chlorates are soluble. $KClO_3$ and $KClO_4$ are sparingly soluble.
   (ii) All chlorides, bromides and iodides are soluble, except those of lead, mercurous and silver ions. Lead chloride is only slightly soluble in cold water but more soluble in hot water. Antimony and bismuth salts hydrolyse in the absence of acids to the insoluble oxychlorides SbOCl and BiOCl.
   (iii) All carbonates and phosphates are insoluble, except those of Na^+, K^+ and NH_4^+ and Ag^+ are moderately soluble.
   (iv) All carbonates and phosphates are insoluble, except those of Na^+, K^+ and NH_4^+.
   (iv) All hydroxides, oxides and sulphides except those of Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+} and Sr^{2+} are insoluble.

ADDITIONAL EXAMPLES

Example 1 :

An aqueous solution of gas (X) shows the following reactions:
(i) It turns red litmus blue.
(ii) When added in excess to a copper sulphate solution, a deep blue colour is obtained.
(iii) On addition of $FeCl_3$ solution, a brown precipitate, soluble in dilute HNO_3 is obtained. Identify (X) and give equations for the reactions at step (ii) and (iii).

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

$$NH_3 + H_2O \longrightarrow NH_4OH$$

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

(Tetramine cupricsulphate
Deep blue complex)

Ferric chloride gives brown precipitate of $Fe(OH)_3$.

$$FeCl_3 + 3NH_4OH \longrightarrow \underset{\text{(Brown precipitate)}}{Fe(OH)_3} + 3NH_4Cl$$

Brown precipitate is soluble in HNO_3.

$$Fe(OH)_3 + 3HNO_3 \longrightarrow \underset{\text{(Soluble complex)}}{Fe(NO_3)_3 + 3H_2O}$$

Example 2 :

A certain compound (X) is used in laboratory for analysis, its aqueous solution gives the following reactions :

(i) On adding copper sulphate, a brown precipitate is obtained which turns white on addition of excess of $Na_2S_2O_3$ solution.

(ii) On addition of Ag^+ ion solution a yellow curdy precipitate is obtained which is insoluble in ammonium hydroxide.

Identify (X) and give equations for the reactions at step (i) and (ii).

Sol. Yellow curdy precipitate with Ag+ confirms the presence of I^- ion in the compound. The precipitate is insoluble in NH_4OH.

$$Ag^+ + I^- \longrightarrow AgI$$

Compound (X) gives brown precipitate with $CuSO_4$ which becomes white when $Na_2S_2O_3$ is added. Thus, compound (X) should be KI. Reactions involved may be given as :

$$CuSO_4 + \underset{(x)}{2KI} \longrightarrow CuI_2 + K_2SO_4$$

$$2CuI_2 \longrightarrow \underset{\text{Brown}}{Cu_2I_2} + I_2$$

$$2Na_2S_2O_3 + I_2 \longrightarrow \underset{\text{Sodium tetrathionate (White)}}{Na_2S_4O_6} + 2NaI$$

Example 3 :

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

Sol. Alkaline gas (C) with NaOH indicate that solid should be ammonium salt. heating the salt, a colourless gas (D) non-reactive is formed. The gas (D) may be nitrogen. The compound may thus be NH_4NO_2. Reactions involved may be given as :

(i) $NH_4NO_2 \xrightarrow{HCl} NH_4Cl + HNO_2$

$$2HNO_2 \longrightarrow H_2O + 2NO + [O]$$

$$2NO + 2[O] \longrightarrow \underset{\text{(B) Brown gas}}{2NO_2}$$

(ii) $\underset{(A)}{NH_4NO_2} + NaOH \longrightarrow NaNO_2 + H_2O + \underset{(C)}{NH_3}\uparrow$

(iii) $\underset{(A)}{NH_4NO_2} \longrightarrow \underset{(D)}{N_2}\uparrow + 2H_2O\uparrow$

Example 4 :

An aqueous solution of gas (X) gives the following reactions :

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

(ii) On boiling it with H_2O_2, cooling it and then adding an aqueous solution of $BaCl_2$ a precipitate insoluble in dil. HCl is obtained.

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

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

Sol. The reactions given in (i), (ii) and (iii) may be explained if we consider the gas (X) to be SO_2,

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

$$H_2O + SO_2 + [O] \longrightarrow H_2SO_4$$

(ii) $H_2O_2 + SO_2 \longrightarrow H_2SO_4$

$$H_2SO_4 + BaCl_2 \longrightarrow \underset{\text{(White ppt.)}}{BaSO_4} + 2HCl$$

(iii) $2H_2S + SO_2 \longrightarrow 2H_2O + \underset{\text{(Colloidal sulphur White turbidity)}}{3S}$

Example 5 :

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

(ii) (A) on treatment with an excess of NH_4SCN gives a red coloured compound (B) and on treatment with a solution of $K_4(Fe(CN)_6]$ gives a blue coloured compound (C).

(iii) (A) on heating with excess of $K_2Cr_2O_7$ in presence of concentrated H_2SO_4 evolves deep red vapours of (D).

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

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

Sol. (i) $\underset{(A)}{FeCl_3} + 3H_2O \longrightarrow Fe(OH)_3 + 3HCl$

Solution becomes acidic due to hydrolysis. $FeCl_3$ sub limes at 300°C

(ii) $FeCl_3 + 3NH_4SCN \longrightarrow \underset{\text{(B) Blood red}}{Fe(CNS)_3} + 3NH_4Cl$

$$4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{(C) Prussian blue}}{Fe_4[Fe(CN)_6]_3}$$

(iii) $4FeCl_3 + 9H_2SO_4 + 3K_2Cr_2O_7 \longrightarrow$
$6CrO_2Cl_2 + 2Fe_2(SO_4)_3 + 3K_2SO_4 + 9H_2O$
(D)
Chromyl chloride

(iv) $CrO_2Cl_2 + 4NaOH \longrightarrow 2NaCl + Na_2CrO_4 + 2H_2O$
$NaCrO_4 + (CH_3COO)_2Pb \longrightarrow PbCrO_4 + 2CH_3COONa$
(E) Yellow ppt.

Example 6 :

Identify A, B, C and D in the following sequence of reactions

(i) $A + NaOH \xrightarrow{Heat} NaCl + NH_3 + H_2O$
(ii) $NH_3 + CO_2 + H_2O \longrightarrow B$
(iii) $B + NaCl \longrightarrow C + NH_4Cl$
(iv) $C \xrightarrow{\Delta} Na_2CO_3 + H_2O + D$

Sol. Since the reaction (i) involves NH_3 as one of the products, (A) will be NH_4Cl. In reaction (ii), (B) will be NH_4HCO_3. In reaction (iii) (C) will be $NaHCO_3$ and finally in reaction (iv) (D) will be CO_2.

(i) $\underset{(A)}{NH_4Cl} + NaOH \xrightarrow{\Delta} NH_3 + NaCl + H_2O$
(ii) $NH_3 + CO_2 + H_2O \longrightarrow \underset{(B)}{NH_4HCO_3}$
(iii) $\underset{(B)}{NH_4HCO_3} \longrightarrow \underset{(C)}{NaHCO_3} + NH_4Cl$
(iv) $\underset{(C)}{2NaHCO_3} \xrightarrow{\Delta} Na_2CO_3 + H_2O + \underset{(D)}{CO_2}$

Example 7 :

Can NaOH be used of NH_4OH in group III ?

Sol. No, NaOH being a very strong electrolyte, its ionization cannot be suppressed. Moreover, it dissolves precipitates of $A1^{3+}$ by forming AlO_2^- complex.

Example 8 :

NH_4OH is added before the addition of $(NH_4)_2CO_3$ solution in group V, why ?

Sol. Ba, Sr, and Ca bicarbonates are soluble in water thus do not get precipitated in the form of bicarbonates. NH_4OH reacts with any of such bicarbonate.

$$NH_4HCO_3 + NH_4OH \longrightarrow (NH_4)_2CO_3 + H_2O$$

Example 9 :

0.41 g of silver salt of a dibasic organic acid left 0.216 g residue of silver on ignition. Calculate the molecular mass of the acid. (equivalent weight of silver = 108)

Sol. Mass of the silver salt taken = 0.41 g
Mass of silver left behind = 0.216 g

$$\frac{\text{Mass of silver salt}}{\text{Mass of silver residue}} = \frac{\text{Equivalent mass of silver salt}}{\text{Equivalent mass of silver}}$$

Equivalent mass of silver salt $= \frac{0.41 \times 108}{0.216} = 205$

Equivalent mass of acid $= 205 - 108 + 1 = 98$

Molar mass of acid = Equivalent mass of acid × basicity of acid

$= 98 \times 2 = 196$

Example 10 :

0.532 g of the platinic chloride of a monoacid organic base left 0.195 g of platinum as residue on ignition . Calculate the equivalent & molecular mass of the base.
(At mass of Pt = 195)

Sol. $$\frac{\text{mass of chloroplatinate salt}}{\text{mass of Pt residue}} = \frac{\text{molar mass of chloroplatinate salt}}{\text{atomic weight of platinum}}$$

$$\frac{0.532}{0.195} = \frac{2E + 410}{195}$$

$$2E = \left(\frac{0.532 \times 195}{0.195}\right) - 410$$

$$E = \frac{1}{2}\left[\left(\frac{0.532 \times 195}{0.195}\right) - 410\right]$$

Equivalent weight of base $= \frac{122}{2} = 61$

The acidity of organic base is one thus molecular mass is equal to equivalent mass.

Example 11 :

An organic compound of carbon, hydrogen and nitrogen having mass ratio is 9 : 1 : 3.5 and molecular weight is 108. What is empirical and molecular formula of the compound.

Element	Mass ratio	Atomic mass	Atomic ratio	Simplest ratio
C	9	12	$\frac{9}{12} = 0.75$	$\frac{0.75}{0.25} = 3.00$
H	1	1	$\frac{1}{1} = 1.0$	$\frac{01.00}{0.25} = 4.00$
N	3.5	14	$\frac{3.5}{14} = 0.25$	$\frac{0.25}{0.25} = 1$

Empirical formula of compound = C_3H_4N
Empirical formula mass = $(3 \times 12) + (4 \times 1) + 14 = 54$
Molecular mass of compound = 108

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{108}{54} = 2$$

y Molecular formula of compound = $(C_3H_4N)_2 = C_6H_8N_2$

Example 12 :

Which of the following pair(s) of ions would be expected to form precipitate when dilute solutions are mixed ?

(A) NH_4^+, $[Co(NO_2)_6]^{3-}$ (B) NH_4^+, CO_3^{2-}
(C) Fe^{3+}, OH^- (D) Ba^{2+}, SO_4^{2-}

Sol. **(ACD).**

(A) $NH_4^+ + [Co(NO_2)_6]^{3-} \rightarrow (NH_4)_3\,[Co(NO_2)_6] \downarrow$ (yellow)
(B) Ammonium & alkali metal carbonates are water soluble.
(C) $Fe^{3+} + OH^- \rightarrow Fe(OH)_3 \downarrow$ (reddish-brown)
(D) $Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4 \downarrow$ (white)

Example 13 :

0.395g of an organic compound by Carius method for the estimation of sulphur gave 0.582g of $BaSO_4$. The percentage of sulphur in the compound is –

(A) 20.24 (B) 35
(C) 40 (D) 45

Sol. **(A).** Mass $BaSO_4 = 0.582g$

We know that, $\underset{233}{BaSO_4} \equiv \underset{32}{S}$

233g of $BaSO_4$ contains sulphur = 32g

$$0.582g \text{ of } BaSO_4 \text{ contains sulphur} = \frac{32}{233} \times 0.582$$

$$\text{Percentage of sulphur} = \frac{\text{Wt. of sulphur}}{\text{Wt. of compound}} \times 100$$

$$= \frac{32 \times 0.582}{233 \times 0.395} \times 100 = 20.24\%$$

Example 14 :

Why does potassium dichromate paper turns green in the test of sulphite ?

Sol. SO_2 gas evolved as a result of attack of dil. H_2SO_4 on sulphites reduces orange Cr (VI) to green Cr (III)

Example 15 :

Why should only freshly prepared $FeSO_4$ solution be used for the ring test ?

Sol. $FeSO_4$ solution on standing oxidised to ferric sulphate which do not form brown colour complex with NO gas.

Example 16 :

Why is $AgNO_3$ solution stored in dark coloured bottles

Sol. To prevent its decomposition by sunlight.

Example 17 :

Why is it essential to boil off H_2S gas before precipitation of Group III ?

Sol. If H_2S would not be boil off, Group IV radical will also get precipitate along with Group III radicals.

Example 18 :

What is function of adding nitric acid before precipitation of Group III.

Sol. It is added to oxidise ferrous salts to ferric salts. It also helps in removal of H_2S gas.

Example 19 :

The gas liberated on heating a mixture of two salts with NaOH, gives a reddish brown precipitate with an alkaline solution of K_2HgI_4. The aqueous solution of mixture on treatment with $BaCl_2$ gives a white precipitate with is sparingly soluble in conc. HCl. On heating the mixture with $K_2Cr_2O_7$ and conc. H_2SO_4, red vapours (A) are produced. The aqueous solution of mixture gives a deep blue colouration (B) with potassium ferricyanide. Identify the radicals in given mixture and write the balanced equation for formation of (A) and (B).

Sol. (i) Gas given by heating mixture with NaOH gives brown ppt. with Nessler's reagent K_2HgI_4. It shows that the salt is a ammonium salt.

(ii) $BaCl_2$ solution gives white precipitate sparingly soluble in HCl. It shows the presence of SO_4^{2-} ion in the mixture.

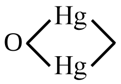
(iii) Blue colour with $K_3Fe(CN)_6$ indicates the presence of Fe^{2+} ion.

(iv) $\text{Mixture} + K_2Cr_2O_7 \xrightarrow[\Delta]{H_2SO_4} \underset{(A)}{\text{Red vapours } (CrO_2Cl_2)}$

It shows that the mixture contains Cl^- ion. Reactions involved may be given as

(i) $NH_4Cl + NaOH \xrightarrow{\Delta} NaCl + NH_3\uparrow + H_2O$

$K_2HgI_4 + NaOH + NH_3 \longrightarrow$


$NH_2I + KI + H_2O + NaI$

(Brown ppt.)

(ii) $FeSO_4 + BaCl_2 \longrightarrow BaSO_4 + FeCl_2$
(White ppt)

(iii) $3FeSO_4 + 2K_3Fe(CN)_6 \longrightarrow 3K_2SO_4 + Fe_3[Fe(CN)_6]_2$
Ferrous ferricyanide
(Blue)

(iv) $4NH_4Cl + K_2Cr_2O_7 + 3H_2SO_4$
$\longrightarrow 2CrO_2Cl_2 + K_2SO_4 + 3H_2O + 2(NH_4)_2SO_4$
Chromyl chloride

Example 20 :

The pair(s) of ions where BOTH the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is(are)

(A) Ba^{2+}, Zn^{2+} (B) Bi^{3+}, Fe^{3+}
(C) Cu^{2+}, Pb^{2+} (D) Hg^{2+}, Bi^{3+}

Sol. **(CD).** Precipitate is formed on passing H_2S in acidic medium i.e. ion must be of group II.
Cu^{2+} , Pb^{2+} , Hg^{2+} , Bi^{3+}

For Example 21-22

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7 ºC was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (–57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6 ºC was measured. (Consider heat capacity of all solutions as 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1})

Example 21 :

Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt. 2 is

(A) 1.0 (B) 10.0
(C) 24.5 (D) 51.4

Sol. **(A).** Let the heat capacity of insulated beaker be C.

Mass of aqueous content in expt. 1 = (100 + 100) × 1
= 200 g

Total heat capacity = (C + 200 × 4.2) J/K

Moles of acid, base neutralised in expt. 1 = 0.1 × 1 = 0.1

⇒ Heat released in expt. 1 = 0.1 × 57 = 5.7 KJ

⇒ $5.7 \times 1000 = (C + 200 \times 4.2) \times \Delta T$

$5.7 \times 1000 = (C + 200 + 4.2) \times 5.7$

⇒ $(C + 200 \times 4.2) = 1000$

In second experiment,

$n_{CH_3COOH} = 0.2,\ n_{NaOH} = 0.1$

Total mass of aqueous content = 200 g

⇒ Total heat capacity = (C + 200 × 4.2) = 1000

⇒ Heat released = 1000 × 5.6 = 5600 J.

Overall, only 0.1mol of CH_3COOH undergo neutralization.

⇒ $\Delta H_{neutralization}$ of $CH_3COOH = \dfrac{-5600}{0.1}$

= – 56000 J/mol = – 56 KJ/mol.

⇒ $\Delta H_{ionization}$ of CH_3COOH = 57 – 56 = 1 KJ/mol

Example 22 :

The pH of the solution after Expt. 2 is

(A) 2.8 (B) 4.7
(C) 5.0 (D) 7.0

Sol. **(B).** Final solution contain 0.1 mole of CH_3COOH and CH_3COONa each. Hence it is a buffer solution.

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$= 5 - \log 2 + \log\frac{0.1}{0.1} = 4.7$$

Example 23 :

0.2313 g of an organic substance gave 30ml of moist nitrogen measured at 15°C and 745 mm pressure. Calculate the percentage of nitrogen. (Aq. tension at 15°C is 12.7mm.)

Sol. Mass of substance = 0.2313 g

Volume of moist nitrogen (V) = 30ml

Temperature (T_1) = 273 + 15 = 288 K

Pressure (P_1) = 745 – 12.7 = 732.3 mm

Now, $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

where P_2 and T_2 denote normal pressure and temperature and V_2 is the corresponding volume.

Thus, $\dfrac{732.3 \times 30}{288} = \dfrac{760 \times V_2}{273}$

or $V_2 = \dfrac{732.3 \times 30}{288} = \dfrac{273}{760} = 27.4$ ml

Since, 22,400 ml of nitrogen at NTP weighs = 28g

∴ 1ml of nitrogen at NTP weighs = 28/22400 g

Thus, 27.4 ml of nitrogen at NTP weighs

$$= \left(\frac{28}{22400} \times 27.4\right) g$$

Hence, percentage of nitrogen

$$= \frac{28}{22400} \times 27.4 \times \frac{1}{0.2313} \times 100 = 14.8$$

QUESTION BANK

EXERCISE - 1

Q.1 Insulin contains 3.4% sulphur. The minimum molecular weight of insulin is
(A) 350
(B) 470
(C) 560
(D) 940

Q.2 Which element is estimated by Carius method
(A) Carbon
(B) Hydrogen
(C) Halogen
(D) Nitrogen

Q.3 On complete combustion 1.4 g hydrocarbon gave 1.8g water. Empirical formula of the hydrocarbon is
(A) CH
(B) CH_2
(C) CH_3
(D) CH_4

Q.4 0.24 g of an organic compound gave 0.22 g CO_2 on complete combustion. If it contains 1.66 % hydrogen, then the percentage of C and O will be
(A) 12.5 and 36.6
(B) 25 and 75
(C) 25 and 36.6
(D) 25 and 80

Q.5 Molecular weight of an organic acid is given by
(A) Equivalent weight × basicity
(B) $\frac{\text{Equivalent weight}}{\text{Basicity}}$
(C) $\frac{\text{Basicity}}{\text{Equivalent weight}}$
(D) Equivalent weight × valency

Q.6 If two compounds have the same empirical formula but different molecular formulae they must have
(A) Different percentage composition
(B) Different molecular weight
(C) Same viscosity
(D) Same vapour density

Q.7 A compound has 50% carbon, 50% oxygen and approximate molecular weight is 290. Its molecular formula is
(A) CO
(B) C_4O_3
(C) $C_{12}O_9$
(D) C_3O_3

Q.8 64 gm of an organic compound contains 24 gm of carbon, 8 gm of hydrogen and the rest oxygen. The empirical formula of the compound is
(A) CH_2O
(B) C_2H_4O
(C) CH_4O
(D) $C_2H_8O_2$

Q.9 The vapour density of the methyl ester of an organic monocarboxylic acid is 37. What is the molecular weight of the acid
(A) 46
(B) 60
(C) 70
(D) 74

Q.10 Which of the following relations gives the value of n =
(A) $\frac{\text{Moleculer Mass}}{\text{Atomic Mass}}$
(B) $\frac{\text{Molecular Mass}}{\text{Empirical Mass}}$
(C) $\frac{\text{Empirical Mass}}{\text{Molecular Mass}}$
(D) None of these

Q.11 In kjeldahl's method, $CuSO_4$ acts as
(A) Oxidising agent
(B) Reducing agent
(C) Hydrolysing agent
(D) Catalytic agent

Q.12 Which of the following is the best scientific method to test the presence of water in a liquid
(A) Use of anhydrous copper sulphate
(B) Use of litmus paper
(C) Taste
(D) Smell

Q.13 An organic compound has been found to possess the Empirical formula CH_2O and molecular weight 90. The molecular formula of it is (C= 12, H = 1 and O = 16)
(A) $C_3H_6O_3$
(B) CH_2O
(C) $C_3H_6O_2$
(D) C_2H_2O

Q.14 An organic compound containing carbon hydrogen and oxygen contains 52.20% carbon and 13.04% hydrogen. Vapour density of the compound is 23. Its molecular formula will be
(A) C_2H_6O
(B) C_3H_8O
(C) C_4H_8O
(D) $C_5H_{10}O$

Q.15 The latest technique for the purification of organic compounds is
(A) Fractional distillation
(B) Chromatography
(C) Vacuum distillation
(D) Crystallisation

Q.16 The presence of halogen, in an organic compounds, is detected by
(A) Iodoform test
(B) Silver nitrate test
(C) Beilstein's test
(D) Millon's test

Q.17 Quantitative measurement of nitrogen in an organic compounds is done by the method
(A) Berthelot method
(B) Belstein method
(C) Lassaigne test
(D) Kjheldahl's method

Q.18 The best method for the separation of naphthalene and benzoic acid from their mixture is
(A) Chromatography
(B) Crystallisation
(C) Distillation
(D) Sublimation

Q.19 Which of the following pair of the species has the same percentage of carbon
(A) CH_3COOH and C_2H_5OH
(B) $C_6H_{12}O_6$ and $C_{12}H_{22}O_{11}$
(C) $HCOOCH_3$ and $C_{12}H_{22}O_{11}$
(D) CH_3COOH and $C_6H_{12}O_6$

Q.20 A mixture of camphor and benzoic acid can be separated by
(A) Chemical method (B) Sublimation
(C) Fractional distillation (D) Extraction with a solvent

Q.21 The metal that does not give the borax-bead test is
(A) Chromium (B) Nickel
(C) Lead (D) Manganese

Q.22 The metal that does not give the borax bead test is
(A) Cr (B) Ni
(C) Na (D) Mn

Q.23 Blue borax bead is obtained with
(A) Zn (B) Cobalt
(C) Chromium (D) Fe

Q.24 Which of the following gives black precipitate when H_2S gas is passed through its solution
(A) Acidic $AgNO_3$ (B) $Mg(NO_3)_2$
(C) Ammonical $BaCl_2$ (D) Copper nitrate

Q.25 A substance on treatment with dil H_2SO_4 liberates a colourless gas which produces (i) turbidity with baryta water and (ii) turns acidified dichromate solution green. The reaction indicates the presence of
(A) CO_3^{2-} (B) S^{2-}
(C) SO_3^{2-} (D) NO_2^-

Q.26 Chromyl chloride test is performed for the confirmation of the presence of the following in a mixture
(A) Sulphate (B) Chromium
(C) Chloride (D) Chromium and chloride

Q.27 The gas which is absorbed by ferrous sulphate solution giving blackish brown colour is
(A) NO (B) CO
(C) N_2 (D) NH_2

Q.28 Which of the following give white precipitate when HCl is added to its aqueous solution
(A) Hg^+ (B) Mg^{++}
(C) Zn^{++} (D) Cd^{++}

Q.29 Of the following sulphides which one is insoluble in dilute acids but soluble in alkalies
(A) PbS (B) CdS
(C) FeS (D) Sb_2S_3

Q.30 $Pb(CH_3COO)_2$ gives....colour with H_2S
(A) Orange (B) Red
(C) Black (D) White

Q.31 Fe^{2+} ion can be distinguished by Fe^{3+} ion by
(A) NH_4SCN (B) $AgNO_3$
(C) $BaCl_2$ (D) None of these

Q.32 AgCl dissolves in ammonia solution giving
(A) Ag^+, NH_4^+ and Cl^- (B) $Ag(NH_3)^+$ and Cl^-
(C) $Ag_2(NH_3)^+$ and Cl^- (D) $Ag(NH_3)_2^+$ and Cl^-

Q.33 What product is formed by mixing the solution of $K_4[Fe(CN)_6]$ with the solution of $FeCl_3$
(A) Ferro-ferricyanide (B) Ferric-ferrocyanide
(C) Ferri-ferricyanide (D) None of these

Q.34 When H_2S gas is passed into a certain solution, it reacts to form a white precipitate. The solution referred to contains ions of
(A) Lead (B) Zinc
(C) Copper (D) Nickel

Q.35 A precipitate of .... would be obtained on adding HCl to a solution of (Sb_2S_3) in yellow ammonium sulphide
(A) Sb_2S_3 (B) Sb_2S_5
(C) SbS (D) SbS_2

Q.36 Which compound does not dissolve in hot dilute HNO_3
(A) HgS (B) PbS
(C) CuS (D) CdS

Q.37 The ion that can be precipitated by HCl as well as H_2S is
(A) Pb^{2+} (B) Fe^{3+}
(C) Zn^{2+} (D) Cu^{2+}

Q.38 The following four solutions are kept in separate beakers and copper metal is put in each of them. Which solution will become blue after some time
(A) $AgNO_3$ solution (B) $Zn(NO_3)_2$ solution
(C) $Ba(NO_3)_2$ solution (D) $NaNO_3$ solution

Q.39 Cu^{2+} ions will be reduced to Cu^+ ions by the addition of an aqueous solution of
(A) KF (B) KCl
(C) KI (D) KOH

Q.40 On passing H_2S black ppt. of II group is obtained. The mixture may not contain
(A) Pb^{++} (B) Cd^{++}
(C) Hg^{++} (D) Cu^{++}

Q.41 $AgNO_3$ gives yellow ppt with -
(A) KIO_3 (B) KI
(C) CHI_3 (D) CH_2I_2

Q.42 Which can be used in place of NH_4Cl in III group precipitation -
(A) $NH_4 NO_3$ (B) $(NH_4)_2CrO_4$
(C) $(NH_4)_2SO_4$ (D) NaCl

Q.43 Which on mixing gives deep brown colour -
(A) $N_2O + O_2$ (B) $NO + O_2$
(C) $N_2O_3 + O_2$ (D) None

Q.44 Redish brown (chocolate) ppt are formed with-
(A) Cu^{2+} and $[Fe(CN)_6]^{2-}$ (B) Ba^{2+} and SO_4^{2-}
(C) Pb^{2+} and I^- (D) none

Q.45 On passing H_2S in II group, sometimes a white turbidity is formed. This is due to -
(A) colloidal sulphur (B) SnS_2
(C) Bi_2S_3 (D) ZnS

Q.46 For the tests of halides, the soda extract is acidified with -
(A) dil. H_2SO_4 (B) dil. HNO_3
(C) dil. HCl (D) any of the three

Q.47 The colour developed when sodium sulphide is added to sodium nitroprusside is -
(A) violet (B) yellow
(C) red (D) black

Q.48 All ammonium salts liberate ammonia when-
(A) heated
(B) heated with caustic soda
(C) heated with H_2SO_4
(D) heated with $NaNO_2$

Q.49 If 'a' is the initial conc. of a substance which reacts according to zero order kinetic and k is rate constant, the time for the reaction to go to completion is -
(A) a/k (B) 2/ka
(C) k/a (D) 2k/a

Q.50 The term-dc/dt in a rate equation referes to-
(A) the conc. of a reactant
(B) the decrease in conc. of the reactant with time
(C) the velocity constant of reaction
(D) none

Q.51 When H_2S is passed through an ammonical salt solution X, a white precipitate is obtained. Then X can be a -
(A) Co^{2+} solution (B) Mn^{2+} solution
(C) Ni^{2+} solution (D) Zn^{2+} solution

Q.52 In third group, bromine water is used to test-
(A) Fe^{3+} ions (B) Cr^{3+} ions
(C) Al^{3+} ions (D) All of these

Q.53 In IV group analysis NH_4OH is added before passing H_2S gas because -
(A) The sulphides of IV group are insoluble in NH_4OH
(B) The sulphides of other metals are soluble in NH_4OH
(C) The concentration of S^{2-} ions is increased
(D) The sulphides of second group are soluble in NH_4OH

Q.54 An aq. solution containing Hg_2^{2+}; Hg^{2+}, Pb^{2+} and Cd^{2+} ions is mixed with dil. HCl. Which will be precipitated -
(A) Hg_2Cl_2 (B) $PbCl_2$
(C) Both (A) and (B) (D) None of these

Q.55 Disodium hydrogen phoshate is used to test-
(A) Mg^{2+} (B) Na^+
(C) Ca^{2+} (D) All

Q.56 In inorganic salt solution on treatment with HCl gives a white precipitate of which metal ions -
(A) Hg_2^{2+} (B) Hg^{2+}
(C) Zn^{2+} (D) Cd^{2+}

Q.57 An inorganic salt solution gives a yellow preceipte with silver nitrate. The precipitate dissolves in dilute nitric acid as well as in ammonium hydroxide. The solution contains -
(A) Bromide (B) Iodide
(C) Phosphate (D) Chromate

Q.58 Which of the following salts will turn water coloured when fumes evolved on treatment with conc. H_2SO_4 are passed in water -
(A) Nitrate (B) Bromide
(C) Both (D) None

Q.59 A salt which gives CO_2 with hot conc. H_2SO_4 and also decolourizes acidified $KMnO_4$ on warming is -
(A) HCO_3^- (B) CO_3^{2-}
(C) Oxalate (D) Acetate

Q.60 Sodium extract is heated with conc. HNO_3
(A) silver halides are insoluble in HNO_3
(B) Na_2S and NaCN are decomposed by HNO_3
(C) Ag_2S is soluble in HNO_3
(D) AgCN is soluble in HNO_3

Q.61 In the brown ring test for the nitrate ion, $[Fe(H_2O)_5NO]^{+2}$ imparts the colour due to -
(A) $\pi \rightarrow \sigma^*$ Transition
(B) Charge transfer transition
(C) d-d transition
(D) $\pi^* \rightarrow \sigma^*$ transition

Q.62 Na_2CO_3 cannot be used in place of $(NH_4)_2$ CO_3 for the precipitation of V group, because -
(A) Na^+ interferes in the detection of V group
(B) conc.of CO_3^{2-} is very low
(C) Na will react with acid radicals
(D) Mg will be precipitated

Q.63 Which gives blood red colour with ammonium thiocyanate
(A) Fe^{3+} (B) Fe^{2+}
(C) Cu^{2+} (D) Cd^{2+}

Q.64 Which combines with Fe^{2+} to form brown complex -
(A) N_2O (B) NO
(C) N_2O_3 (D) N_2O_5

Q.65 In III group precipitation NH_4Cl is added before adding NH_4OH due to -
(A) decreasing conc. of OH^-
(B) prevent interference of PO_4^{3-}
(C) increase in conc. of Cl^-
(D) increase in conc. of OH^- ions

ASSERTION & REASON QUESTIONS

Each questions contain STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 4 choices (A), (B), (C) and (D) out of which ONLY ONE is correct.
(A) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement -1
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement- 2 is False
(D) Statement-1 is False, Statement -2 is True

Q.66 **Statement-1 :** Order of reaction for the decomposition of H_2O_2 is one.
Statement-2 : This reaction is catalysed by nitrate ion.

Q.67 **Statement-1:** Colour of chromyl chloride vapour is deep red.
Statement - 2 : these vapours are formed in the chromyl chloride test which is used for the detection of chloride.

Q.68 **Statement - 1 :** In the titration of strong acid and weak base suitable indicator is methyl orange.

Statement - 2 : pH range of methyl oragne indicator is 5.6 – 7.4.

Q.69 **Statement - 1 :** When methyl ketones are treated with hypohalides, they produce trihalogen methane.

Statement - 2 : This reaction is called haloform reaction.

Passage (Q.70-Q.74)

A metal sulphide (A) gives (B) gas with rotten egg smell and (C) a colourless sulphates, when treated with dil. H_2SO_4.(B) reacts with $K_2Cr_2O_7/H^+$ to form (D) a white grey element. (D) burns in oxygen to yield (E) a colourless gas. If (B) is added in (E), it gives (D) and colourless liquid, which turns anhydrous $CuSO_4$ blue. (C) gives a precipitate with $NH_{3(aq.)}$ or NaOH which dissolves in excess of NaOH.

Q.70 A is :
(A) CuS (B) ZnS
(C) Cu_2S (D) None of these

Q.71 B is :
(A) SO_2 (B) SO_3
(C) H_2S (D) CS_2

Q.72 C is :
(A) $CuSO_4$ (B) $BaSO_4$
(C) $ZnSO_4$ (D) Na_2ZnO_2

Q.73 D is :
(A) Zn (B) Cu
(C) S (D) B

Q.74 E is :
(A) H_2S (B) SO_3
(C) SO_2 (D) None of these

Passage (Q.75-Q.77)

There are four bottles which contains :

Copper (II) sulphate	Lead nitrate
Hydrochloric acid	Sodium carbonate

By mixing samples of the contents of the bottles in pairs, a chemist made the following observations :

Bottle (1) + Bottle (2) white precipitate
Bottle (1) + Bottle (4) white precipitate
Bottle (2) + Bottle (4) no visible reaction
Bottle (1) + Bottle (3) white precipitate
Bottle (2) + Bottle (3) colourles gas evolved
Bottle (3) + Bottle (4) green blue precipitate

Q.75 Bottle (1) contains :
(A) $Pb(NO_3)_2$ (B) HCl
(C) Na_2CO_3 (D) $CuSO_4$

Q.76 Bottle (2) contains :
(A) $Pb(NO_3)_2$ (B) HCl
(C) Na_2CO_3 (D) $CuSO_4$

Q.77 Bottle (3) contains :
(A) $Pb(NO_3)_2$ (B) HCl
(C) Na_2CO_3 (D) $CuSO_4$

Q.78 Match the Column –

Column I	**Column II**
(A) White crystalline ppt	(p) Sb_2S_3
(B) Reddish brown ppt	(q) $Cr(OH)_3$
(C) Orange ppt	(r) $PbCl_2$
(D) Yellow ppt.	(s) $Fe(OH)_3$
(E) Green ppt.	(t) $K_3[Co(NO_2)_6]$

EXERCISE - 2

PREVIOUS YEARS JEE MAIN / AIPMT / NEET QUESTIONS

Q.1 $HgCl_2$ on passing H_2S gives -
(A) HgS (B) Hg_2S
(C) Hg + HgS (D) HgS + H_2S

Q.2 How do we differentiate between Fe^{3+} and Cr^{3+} in qualitative analysis gp. III :
(A) By taking excess of NH_4OH
(B) By increasing NH_4^+ ion concentration
(C) By decreasing OH^- ion concentration
(D) Both (B) and (C)

Q.3 In a compound C, H and N atoms are present in 9 : 1 : 35 by weight. Molecular weight of compound is 108. Molecular formula of compound is:
(A) $C_2H_6N_2$ (B) C_3H_4N
(C) $C_6H_8N_2$ (D) $C_9H_{12}N_3$

Q.4 Which statement is correct :
(A) Fe^{3+} ions give deep green precipitate with $K_4[Fe(CN)_6]$ solution.
(B) On heating K^+, Ca^{2+} and HCO_3^- ions, we get a precipitate of $K_2[Ca(CO_3)_2]$.
(C) Manganess salts give a violet borax bead test in the reducing flame.
(D) From a mixed precipitate of AgCl and AgI ammonia solution dissolves only AgCl.

Q.5 The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is:
(A) $Fe_4[Fe(CN)_6]_3$ (B) $Na_3[Fe(CN)_6]$
(C) $Fe(CN)_3$ (D) $Na_4[Fe(CN)_5NOS]$

Q.6 The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 M sulphuric acid. The excess of acid required 20mL of 0.5 M sodium hydroxide solution for complete neutralization. The organic compound is:
(A) urea (B) benzamide
(C) acetamide (D) thiourea

Q.7 A solution containing 2.675 g of $CoCl_3$. 6 NH_3 (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl.
(Molar mass = 143.5 g mol^{-1}).
The formula of the complex is (At. Mass of Ag = 108 u)

(A) $[Co(NH_3)_6]Cl_3$ (B) $[CoCl_2(NH_3)_4]Cl$
(C) $[CoCl_3(NH_3)_3]$ (D) $[CoCl(NH_3)_5]Cl_2$

Q.8 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralization. The percentage of nitrogen in the compound is –
(A) 59.0 (B) 47.4
(C) 23.7 (D) 29.5

Q.9 The compound A on heating gives a colourless gas and a residue that is dissolved in water to obtain B. Excess of CO_2 is bubbled through aqueous solution of B, C is formed which is recovered in the solid form. Solid C on gentle heating gives back A. The compound A is :
(A) $CaCO_3$ (B) Na_2CO_3
(C) K_2CO_3 (D) $CaSO_4.2H_2O$

Q.10 The Lassaigne's extract is boiled with conc. HNO_3 while testing for halogens. By doing so it.
(A) Increase the concentration of NO_3^- ions
(B) Decomposes Na_2S and NaCN, if formed
(C) Helps in the precipitation of AgCl
(D) Increases the solubility product of AgCl

Q.11 CH_3CHO and $C_6H_5CH_2CHO$ can be distinguished chemically by :
(A) Benedict test (B) Iodoform test
(C) Tollen's reagent test (D) Fehling solution test

Q.12 Roasting of sulphides gives the gas X as a by product.This is colourless gas with choking smell of burnt sulphur and causes great damage to respiratory organs as a result of acid rain. It aqueous solution is acidic, acts as reducing agent and its acid has never been isolated. The gas X is –
(A) SO_3 (B) H_2S
(C) SO_2 (D) CO_2

Q.13 For the estimation of nitrogen, 1.4 g of organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of M/10 sulphuric acid. The unreacted acid required 20 ml of M/10 sodium hydroxide for complete neutralization. The percentage of nitrogen in the compound is –
(A) 3% (B) 5%
(C) 6% (D) 10%

Q.14 In the Kjeldahl's method for estimation of nitrogen present in a soil sample, ammonia evolved from 0.75 g of sample neutralized 10 mL of 1 M H_2SO_4. The percentage of nitrogen in the soil is –
(A) 37.33 (B) 45.33
(C) 35.33 (4) 43.33

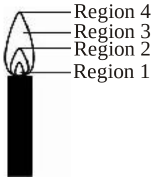
Q.15 Which of the following compounds is not colored yellow?
(A) $K_3[Co(NO_2)_6]$ (B) $(NH_4)_3[As(Mo_3O_{10})_4]$
(C) $BaCrO_4$ (D) $Zn_2[Fe(CN)_6]$

Q.16 In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is (At mass Ag = 108; Br = 80)
(A) 36 (B) 48
(C) 60 (D) 24

Q.17 In Duma's method for estimation of nitrogen 0.25g of an organic compound gave 40mL of nitrogen collected at 300K temperature and 725 mm pressure. If the aqueous tension at 300 K is 25 mm, the percentage of nitrogen in the compound is :
(A) 18.20 (B) 16.76
(C) 15.76 (D) 17.36

Q.18 Cobalt (III) chloride forms several octahedral complexes with ammonia. Which of the following will not give test for chloride ions with silver nitrate at 25°C ?
(A) $CoCl_3 \cdot 4NH_3$ (B) $CoCl_3 \cdot 5NH_3$
(C) $CoCl_3 \cdot 6NH_3$ (D) $CoCl_3 \cdot 3NH_3$

Q.19 The hottest region of Bunsen flame shown in the figure is



(A) region 2 (B) region 3
(C) region 4 (D) region 1

Q.20 The distillation technique most suited for separating glycerol from spent-lye in the soap industry is:
(A) Fractional distillation
(B) Steam distillation
(C) Distillation under reduced pressure
(D) Simple distillation

Q.21 Sodium salt of an organic acid 'X' produces effervescence with conc. H_2SO_4. 'X' reacts with the acidified aqueous $CaCl_2$ solution to give a white precipitate which decolourises acidic solution of $KMnO_4$. 'X' is :
(A) $Na_2C_2O_4$ (B) C_6H_5COONa
(C) HCOONa (D) CH_3COONa

Q.22 A metal on combustion in excess air forms X, X upon hydrolysis with water yields H_2O_2 and O_2 along with another product. The metal is :
(A) Rb (B) Na
(C) Mg (D) Li

Q.23 The strength of an aqueous NaOH solution is most accurately determined by titrating :
(Note : consider that an appropriate indicator is used)

(A) Aq. NaOH in a volumetric flask and concentrated H_2SO_4 in a conical flask.
(B) Aq. NaOH in a pipette and aqueous oxalic acid in a burette.
(C) Aq. NaOH in a burette and concentrated H_2SO_4 in a conical flask.
(D) Aq. NaOH in a burette and aqueous oxalic acid in a conical flask.

ANSWER KEY

EXERCISE - 1

Q	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
A	D	C	B	B	A	B	C	C	D	B	D	A	A	A	B	C	D	B	D	A
Q	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**	**40**
A	C	C	B	A	C	C	A	A	D	C	A	D	B	B	B	A	A	A	C	B
Q	**41**	**42**	**43**	**44**	**45**	**46**	**47**	**48**	**49**	**50**	**51**	**52**	**53**	**54**	**55**	**56**	**57**	**58**	**59**	**60**
A	B	A	B	A	A	B	A	B	A	B	D	B	C	C	A	A	A	B	C	B
Q	**61**	**62**	**63**	**64**	**65**	**66**	**67**	**68**	**69**	**70**	**71**	**72**	**73**	**74**	**75**	**76**	**77**	**78**		
A	B	D	A	B	A	C	A	C	A	B	C	C	C	C	A	B	C	r,s,p,t,q		

EXERCISE 2

Q	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**
A	A	D	C	D	A	A	A	C	A	B	B	C	D	A	D	D	B	D	A	C	A	A	D

PRACTICAL CHEMISTRY

TRY IT YOURSELF-1

(1) **(B).** $S_2O_3^{2-} + 2HCl \xrightarrow{\Delta} \underset{\substack{\text{Suffocating smell}\\ \text{of burning sulphur}}}{SO_2\uparrow} + 2Cl^- + \underset{\substack{\text{yellow turbidity}\\ \text{or white turbidity}}}{S\downarrow} + H_2O$

(2) **(AB).** Salt A + HPh → Pink colour

CO_3^{2-}

Salt B + Hph → Hot pink colour

$HCO_3^{\ominus}$

$$CO_3^{2-} | HCO_3^{\ominus} \xrightarrow{\Delta} CO_2\uparrow [X]$$

$$[X] + Ba(OH)_2 \rightarrow \underset{\text{white turbidity}}{BaCO_3} \xrightarrow{\text{excess } CO_2} \underset{\text{soluble}}{Ba(HCO_3)_2}$$

(3) **(B).** $Cu^{2+} + K_3[Fe(CN)_6] \rightarrow Cu_3[Fe(CN)_6]$ (green ppt)

(4) **(D).** $NiCl_2$ solution is green in colour.

(5) **(B).** $NO_2^- + KI \rightarrow I_2$

Starch + KI_3 → Starch-Iodine complex (blue colour)

(6) **(B).** NaCl + Solid $K_2Cr_2O_7$ + Conc. H_2SO_4

→ CrO_2Cl_2 (Red/Orange vapour) + $Na_2SO_4 + H_2O$

(7) **(B).** Basic solution of K_2HgI_4 is called nessler's reagent.

(8) **(C).** Brown ring test is confirmation test of nitrate & nitrite ions.

(9) **(C).** $Na_2B_4O_7 \xrightarrow{\Delta} 2NaBO_2 + B_2O_3$

(10) **(A).** Ba^{+2} absorbs red colour light & reflect green colour.

(11) **(C).** $S^{2-} + 2HCl \xrightarrow{\Delta} H_2S\uparrow + 2Cl^-$

Rotten egg smell} ⇒ Specific smell

$$S_2O_3^{2-} + 2HCl \xrightarrow{\Delta} \underset{\substack{\text{Suffocating smell}\\ \text{of burning sulphur}}}{SO_2\uparrow} + 2Cl^- + \underset{\substack{\text{yellow turbidity}\\ \text{or white turbidity}}}{S\downarrow} + H_2O$$

$$CO_3^{2-} + 2HCl \xrightarrow[\text{or cold}]{\Delta} CO_2\uparrow + H_2O + 2Cl^-$$

Odourless gas evolves with brisk effervescences HCO_3^- also behave similarly.

$$NO_2^- + HCl \xrightarrow{\Delta} HNO_2 + Cl^-$$

$$\rightarrow NO\uparrow \text{(colourless)} \xrightarrow[\text{air}]{\text{atmosphere}} NO_2\uparrow$$

(Brown colour gas)

(12) **(B).** $\underset{\substack{\text{Mixture of two}\\ \text{cations (A)}}}{(K^+ + NH_4^+)} \xrightarrow{HClO_4} \underset{\substack{\text{White}\\ \text{(B)}}}{KClO_4\downarrow} + \underset{\text{(C)}}{NH_4^+}$

$$\xrightarrow[\Delta]{NaOH} \underset{\text{(D)}}{NH_3\uparrow} \xrightarrow[KOH]{K_2[HgI_4]} \underset{\text{(Brown ppt.)}}{HgO\cdot Hg(NH_2)I\downarrow}$$

(13) **(A).** $Cr_2O_3 + 2Na_2CO_3 + \frac{3}{2}O_2$

$$\xrightarrow{\text{O.F.}} 2Na_2CrO_4 + 2CO_2\uparrow$$

(Yellow opaque bead)

(14) **(C).** Only $AgNO_3$ produces yellow ppt of Ag_3PO_4 rest from white ppt. of respective metal tertiary phosphates.

TRY IT YOURSELF-2

(1) (D)

(2) **(B).** $CuSO_4$ catalyses the reaction.

(3) (D)

(4) **(A).** Liebig's method is used for estimation of carbon and hydrogen.

(5) (B)

(6) **(B).** In the Lassaigne's test for nitrogen in an organic compound, the sodium fusion extract is boiled with iron (II) sulphate and then acidified with sulphuric acid. In the process, sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanoferrate (II). Then, on heating with sulphuric acid, some iron (II) gets oxidised to form iron (III) hexacyanoferrate (II), which is Prussian blue in colour. The chemical equations involved in the reaction can be represented as

$6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{x\,H_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3.xH_2O}$$

Hence, the Prussian blue colour is due to the formation of $Fe_4[Fe(CN)_6]_3$

(7) **(A).** $\% \text{ of S} = \frac{32}{233} \times \frac{\text{Mass of S}}{\text{Mass of compound}} \times 100$

a = mass of BaSO4, W = Mass of organic compound=W

$BaSO_4 = S$

$$\frac{32 \times 0.233}{233} \times \frac{100}{0.32} = 10\%$$

(8) **(D).** Chromatography

(9) **(B).** All compound convert into N_2 and oxides of N_2.

(10) **(C).** Both method's is used to estimate quantity of N.

(11) **(A).** Wt. of the substance taken = 0.420g

Vol. of acid neutralised by ammonia = 35.7ml (given)

Normality of the acid = N/10 (given)

Percentage of nitrogen

$$= \frac{1.4 \times \text{Normality of acid} \times \text{vol. of acid used}}{\text{Wt. of the substance}}$$

$$= \frac{1.4 \times \frac{1}{10} \times 37.5}{0.42} = 12.5$$

SOLUTIONS EXERCISE-1

(1) **(D).** Minimum mass of sulphur = wt. of its one atom = 32

$\because$ 3.4 gms of sulphur present in 100 gms.

$\therefore$ 32 gms of sulphur present in $= \dfrac{100 \times 32}{3.4} = 940$

(2) **(C).** Halogen is estimated by carius method.

(3) **(B).** $\because$ 1.8gm water obtained from 1.4gm hydrocarbon

$\therefore$ 18gm water obtained from $- \dfrac{1.4}{1.8} \times 18 = 14$ gm.

Empirical formula Mass = 14

$\therefore$ Empirical formula = CH_2.

(4) **(B).** $\% \text{ of C} = \dfrac{12}{44} \times \dfrac{\text{Mass of } CO_2}{\text{Mass of substance}} \times 100$

$$= \frac{12 \times 0.22}{44 \times 0.24} \times 100 = 25$$

(5) **(A).** Mol. mass of an acid = Equivalent wt. × basicity.

(6) **(B).** If molecular formula is different than molecular weight is also different.

(7) **(C).**

Elements	Simple ratio
C = 50	50/12 = 4
O = 50	50/16 = 3

Empirical formula = C_4O_3

Empirical formula mass = 96

$$n = \frac{290}{96} = 3$$

Molecular formula = $(C_4O_3)_3 = C_{12}O_9$.

(8) **(C).**

Elements	No. of moles	Simple ratio
C (24 gm)	24/12 = 2	1
H (8 gm)	8/1 = 8	4
O (32 gm)	32/16 = 2	1

Empirical formula = CH_4O

(9) **(D).** Molecular mass = 2 × V.D. = 2 × 37 = 74.

(10) **(B).** $n = \dfrac{\text{Molecular mass}}{\text{Emperical mass}}$

(11) **(D).** Kjeldahl's method depends upon the fact that most of the organic compounds containing nitrogen are quantitatively decomposed to give $(NH_4)_2SO_4$ when heated strongly with conc. H_2SO_4. In this method $CuSO_4$ acts as catalytic agent.

(12) **(A).** Anhydrous $CuSO_4$ is used to test presence of water in any liquid because it changes its colour white to blue.

(13) **(A).** Molecular weight of $C_3H_6O_3$ is 90.

(14) **(A).** Molecular weight = V.D. × 2 = 23 × 2 = 46

Molecular weight of $C_2H_6O = 46$

(15) **(B).** Chromatography is the latest technique for the purification of organic compounds. Chromatography are of various type viz. Column chromatography, gas chromatography, paper chromatography etc.

(16) **(C).** Halogens are detected by Beilstein's test. In this test, a copper wire is dipped in original solution and heated in a bunsen burner flame. Green colour is imparted to the flame, due to the formation of a volatile copper halide. This proves the presence of halogen.

(17) **(D).** Kjeldahl's and Duma's methods are used for the quantitative estimation of nitrogen in an organic compound. In the Kjeldahl method, the nitrogen element of organic compound is changed to the ammonia.

(18) **(B).** Mixture of benzoic acid and naphthalene can be separated from hot water in which benzoic acid dissolves but naphthalene does not.

(19) **(D).** CH_3COOH and $C_6H_{12}O_6$ both have same percentage of carbon i.e. 40%.

(20) **(A).** Chemical method using $NaHCO_3$ solution.

(21) **(C).** Borax bead test is generally given by transition elements.

(22) **(C).** Metals which form basic compounds and have coloured salts give the borax bead test.

(23) **(B).** $CoO + B_2O_3 \xrightarrow{\text{Heat}} \underset{\text{Copper metabrate (blue)}}{Co(BO_2)_2}$

(24) **(A).** $2AgNO_3 + H_2S \rightarrow \underset{\text{Black ppt.}}{Ag_2S} + 2HNO_3$

(25) **(C).** $Na_2SO_3 + 2HCl(\text{dil.}) \rightarrow 2NaCl + H_2O + SO_2$,

$K_2Cr_2O_2 + H_2SO_4 + 3SO_4 \rightarrow K_2SO_4 + \underset{\text{(Green)}}{Cr_2(SO_4)_3} + H_2O$

(26) **(C).** It is a test for chloride ion.

(27) **(A).** $3FeSO_4 + NO_2 + 3H_2SO_4 \rightarrow$

$$Fe_2(SO_4)_3 + \underset{\text{(Black brown)}}{FeSO_4.NO} + H_2O$$

(28) **(A).** $2Hg + 2HCl \rightarrow \underset{\text{white ppt.}}{Hg_2Cl_2} + H_2 \uparrow$

(29) **(D).** It is an acidic salt

(30) **(C).** $(CH_3COO)_2Pb + H_2S \rightarrow 2CH_3COOH + \underset{\text{black ppt.}}{PbS \downarrow}$

(31) **(A).** $(NH_4)SCN$ is a red colour substance.

(32) **(D).** $AgCl + 2NH_3 \rightarrow \underset{\text{complex}}{[Ag(NH_3)_2]Cl}$

$$\rightleftharpoons [Ag(NH_3)_2]^+ + Cl^-$$

(33) **(B).** $Fe^{3+} + K_4[Fe(CN)_6] \rightarrow \underset{\text{Prussian blue}}{K\left[Fe[Fe(CN)_6]\right]} + 3K^+$

(34) **(B).** ZnS is white.

(35) **(B).** $Sb_2S_3 + 2(NH_4)_2S_2 \rightarrow 2(NH_4)_2S + Sb_2S_5$

(36) **(A).** $HgS + HNO_3 \rightarrow$ No reaction

(37) **(A).** Pb^{2+} as it's precipitated as chloride and sulphide in I^{st} and II^{nd} group respectively

(38) **(A).** $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$

(39) **(C).** $2CuSO_4 + 4KI \rightarrow \underset{\text{Cuprous iodide}}{2CuI} + 2K_2SO_4 + I_2$.

(40) **(B).** $Cd^{++} + H_2S \rightarrow \underset{\text{Yellow ppt}}{CdS} + H_2O$

SOLUTIONS EXERCISE-2

(1) **(A).** $HgCl_2$ on passing H_2S gives HgS.

(2) **(D).** To differentiate between Fe^{3+} and Cr^{3+} in qualitative analysis gp. III :

(i) By increasing NH_4^+ ion concentration

(ii) By decreasing OH^- ion concentration

(3) **(C).** Molar mass = 108 gm/mole

$$\text{Weight of carbon} = \frac{9}{13.5}\times 108 = 72\text{gm}$$

$$\therefore \text{ No. of carbon atom} = \frac{72}{12} = 6$$

$$\text{Weight of hydrogen} = \frac{1}{13.5}\times 108 = 8\text{gm}$$

$$\therefore \text{ No. of hydrogen atom} = \frac{8}{1} = 8$$

$$\text{Weight of nitrogen} = \frac{3.5}{13.5}\times 108 = 28\text{gm}$$

$$\therefore \text{ No. of nitrogen atom} = \frac{28}{14} = 2$$

Therefore, molecular formula is $C_6H_8N_2$

(4) **(D).** From a mixed precipitate of AgCl and AgI ammonia solution dissolves only AgCl

(5) **(A).** $Na + C + N \longrightarrow NaCN$

$2NaOH + FeSO_4 \longrightarrow Na_2SO_4 + Fe(OH)_2$

$6NaCN + Fe(OH)_2 \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$

$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\text{Blue}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$

(6) **(A).** $N_1V_1 = N_2V_2$

$0.2 \times V_1 = 0.5 \times 20$

$V_1 = 50\text{ ml}$

Acid required to neturalize the ammonia = 100 – 50 = 50ml

$$\text{Percent of N} = 1.4 \times \frac{\text{Volume of acid} \times \text{Noarmality}}{\text{Weight of compound}}$$

$$= \frac{1.4 \times 50 \times 0.2}{0.30} = 46.67\%$$

$$\text{N in } CH_3CONH_2 = \frac{14\times 100}{59} = 23.73\%$$

$$\text{N in } C_6H_6CONH_2 = \frac{14\times 100}{122} = 11.48\%$$

$$\text{N in } NH_2CONH_2 = \frac{28\times 100}{60} = 46.67\%$$

$$\text{N in } NH_2CSNH_2 = \frac{28\times 100}{76} = 36.84\%$$

So, compound is urea.

(7) **(A).** $CoCl_3.\,6NH_3 \rightarrow x\,Cl^- \xrightarrow{AgNO_3} x\,AgCl\downarrow$

$n(AgCl) = x\,n\,(CoCl_3.\,6NH_3)$

$$\frac{4.78}{143.5} = x\,\frac{2.675}{267.5}$$

$\therefore x = 3$

$\therefore$ The complex is $[Co(NH_3)_6]Cl_3$

(8) **(C).** Moles of HCl reacting with ammonia = (moles of HCl absorbed) – (moles of NaOH solution required)

= $(20 \times 0.1 \times 10^{-3}) - (15 \times 0.1 \times 10^{-3})$ = moles of NH_3 evolved = moles of nitrogen in organic compound

$\therefore$ wt. of nitrogen in org. comp

$= 0.5 \times 10^{-3} \times 14 = 7 \times 10^{-3}$ g

$$\%\text{ wt} = \frac{7\times 10^{-3}}{29.5\times 10^{-3}} = 23.7\%$$

(9) **(A).** The reactions can be summarised as follows

$A \xrightarrow{\Delta}$ colourless gas + residue

$\text{Residue} + H_2O \longrightarrow B \xrightarrow{\text{excess } CO_2} C \xrightarrow{\Delta} A$

This is possible only when A is $CaCO_3$. The reactions are as follows :

$$\underset{(A)}{CaCO_3} \xrightarrow{\Delta} \underset{\text{Colourless gas}}{CO_2} + \underset{\text{residue}}{CaO}$$

$$CaO + H_2O \longrightarrow \underset{(B)}{Ca(OH)_2}$$

$$\xrightarrow[\text{(excess)}]{CO_2} \underset{(C)}{Ca(HCO_3)_2} \xrightarrow{\Delta} \underset{(A)}{CaCO_3}$$

(10) **(B).** Na_2S and NaCN, if present in the extract, will be decomposed to H_2S and HCN by HNO_3.

$NaCN + HNO_3 \rightarrow NaNO_3 + HCN$

$Na_2S + 2HNO_3 \rightarrow 2NaNO_3 + H_2S$

These will escape from the solution and will not interfere with the test for halogens.

(11) **(B).** $CH_3-CH{=}O$ gives Iodoform test but $C_6H_5CH_2CH{=}O$ does not give Iodoform test.

(12) **(C).**

(13) **(D).** $\%\text{ of N} = \dfrac{1.4 \times \text{milliequivalent of acid consumed}}{\text{Mass of organic compound}}$

Meq of acid consumed

$$= \left(60 \times \frac{1}{10} \times 2\right) - \left(20 \times \frac{1}{10} \times 1\right) = 10$$

$$\%\text{ of N} = \frac{1.4\times 10}{1.4} = 10\%$$

(14) **(A).** $\%N = \dfrac{1.4 \times N \times V}{w} = \dfrac{1.4 \times 10 \times 2}{0.75} = 37.33\%$

(15) **(D).** $(NH_4)_3[As(Mo_3O_{10})_4]$, $BaCrO_4$ and $K_3[Co(NO_2)_6]$ are yellow colored compounds but $Zn_2[Fe(CN)_6]$ is not yellow colored compound.

(16) **(D).** $$\%\text{ of Br} = \frac{\text{Weight of AgBr}}{\text{Mol. mass of AgBr}} \times \frac{\text{Mol. mass of Br}}{\text{Weight of O.C.}} \times 100$$

$$= \frac{141}{188} \times \frac{80}{250} \times 100 = 24\%$$

(17) **(B).** Mass of organic comp. = 0.25 g
$V_1 = 40$ ml, $T_1 = 300$ K, $P_1 = 725 - 25 = 700$ mm of Hg

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

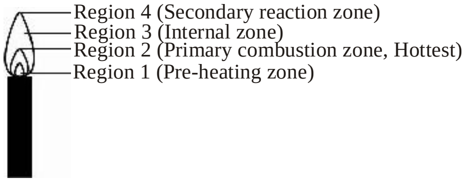
$$V_2 = \frac{700 \times 40 \times 273}{300 \times 760} = 33.52 \text{ ml}$$

$$\%\text{ of N} = \frac{28 \times V \times 100}{22400 \times \text{mass of org. comp.}}$$

$$= \frac{28 \times 33.52 \times 100}{22400 \times 0.25} = 16.76$$

(18) **(D).** $CoCl_3 \cdot 3NH_3$ is $[Co(NH_3)_3Cl_3]$ so it will not ionize and does not give Cl^- ion test.

(19) **(A).**



(20) **(C).** Steam distillation is preferred for separation of substances which are steam volatile and are immiscible with water.
Fractional distillation is used if the difference in boiling points of two liquids is not much. This technique is used to separate different fractions of crude oil in petroleum industry.
Distillation under reduced pressure is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Glycerol can be separated from spent-lye in soap industry by using this technique
Simple distillation ⇒ This technique is used to separate volatile liquids from nonvolatile impurities or liquids having sufficient difference in their boiling points.

(21) **(A).** $$\underset{(X)}{Na_2C_2O_4} + \underset{(conc.)}{H_2SO_4} \rightarrow Na_2SO_4 + H_2O + CO_2\uparrow + CO\uparrow$$

$$CaCl_2 + Na_2C_2O_4 \rightarrow \underset{\text{(white ppt)}}{CaC_2O_4} + 2NaCl$$

$$C_2O_4^{2-} + MnO_4^- \xrightarrow{H^+} CO_2 + Mn^{2+}$$

(22) **(A).** $Rb + O_2(\text{excess}) \rightarrow RbO_2$
$2RbO_2 + 2H_2O \rightarrow 2RbOH + H_2O_2 + O_2$

(23) **(D).**