16

Principles Related to Practical Chemistry

IN THIS CHAPTER ....

- Qualitative Analysis of Organic Compounds
- Preparation of Inorganic Compounds
- Preparation of Organic Compounds
- Practical Inorganic Chemistry

Experimental (practical) chemistry involves the study of concerned material under specific experimental conditions. It can be divided into two branches : **synthetic chemistry** and **analytical chemistry**.

Qualitative Analysis of Organic Compounds

Two major steps involved in the characterisation of an organic compound are (i) Element detection (For it see chapter 12 purification and characterisation of organic compounds) (ii) Detection of functional group.

Detection of Functional Groups

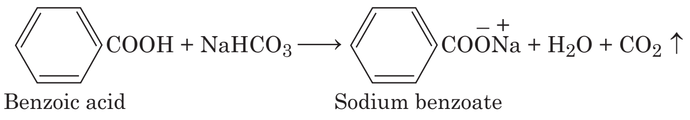
Element detection shows the presence or absence of different elements. On the basis of element present, the test of corresponding functional group is performed.

Tests for different functional groups are given below

Tests for Carboxylic (— COOH) Group

(i) **Litmus paper test** Dip blue litmus paper in the aqueous solution or suspension of the compound. It turns red.

(ii) **Sodium bicarbonate test** In a test tube, take a little quantity of the compound and then, add a saturated solution of sodium bicarbonate. Formation of brisk effervescence due to the formation of CO_2 shows the presence of —COOH group.



(iii) **Ester formation** Heat a small quantity of organic compound with ethyl alcohol and a little conc. H_2SO_4. Cool the solution and pour in a tube containing water. A fruity smell, due to formation of an ester, indicates the presence of carboxylic group.

$$\underset{\text{Carboxylic acid}}{R\text{—COOH}} + \underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} \underset{\substack{\text{Ester}\\\text{(fruity smell)}}}{RCOOC_2H_5} + H_2O$$

Tests for Alcoholic (—OH) Group

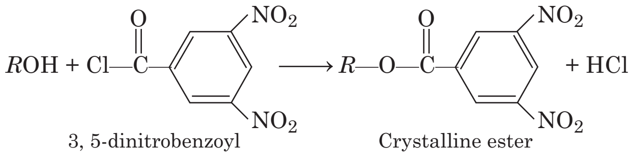
(i) **Sodium test** In a test tube, take some organic compound and add a thin piece of sodium metal to it. A brisk effervescence due to the formation of hydrogen gas takes place.

$$2ROH + 2Na \longrightarrow 2R\overset{-}{O}\overset{+}{Na} + H_2\uparrow$$

(ii) **Ester test** Heat the given compound with acetic acid in the presence of sulphuric acid. A fragrance of fruity smell indicates the formation of ester.

$$ROH + \underset{\text{Acetic acid}}{CH_3COOH} \xrightleftharpoons{\text{Conc. } H_2SO_4} \underset{\substack{\text{Ester}\\\text{(fruity smell)}}}{CH_3COOR} + H_2O$$

Alcohols give crystalline esters with 3,5-dinitrobenzoyl chloride. These esters have sharp melting points and can be used for testing a given alcohol.



3, 5-dinitrobenzoyl chloride

Crystalline ester

(iii) **Ceric ammonium nitrate test** To small amount of organic compound or its aqueous solution, add a few drops of ceric ammonium nitrate. A red colour indicates the presence of alcoholic hydroxy group.

$$\underset{\text{Alcohol}}{2ROH} + \underset{\substack{\text{Ceric ammonium}\\\text{nitrate}}}{(NH_4)_2Ce(NO_3)_6} \longrightarrow \underset{\text{Red colour}}{Ce(NO_3)_4\cdot(ROH)_2} + 2NH_4NO_3$$

This test is useful when the compound contains less than 10 C-atoms.

(iv) **Lucas test** This test is used to distinguish between primary, secondary and tertiary alcohols.

In this test, treat 2 mL of organic compound with approx. 8 mL of Lucas reagent (for preparing Lucas reagent dissolve 32 g of anhyd. $ZnCl_2$ in 20 mL of conc. HCl) and shake them properly following observations are seen

- Immediate formation of turbidity indicates the presence of **tertiary alcohol.**
- Formation of turbidity after 4-5 min shows the presence of **secondary alcohols.**
- If solution remains clear, then **primary alcohol** is present.

Tests for Phenolic (Ph—OH) Group

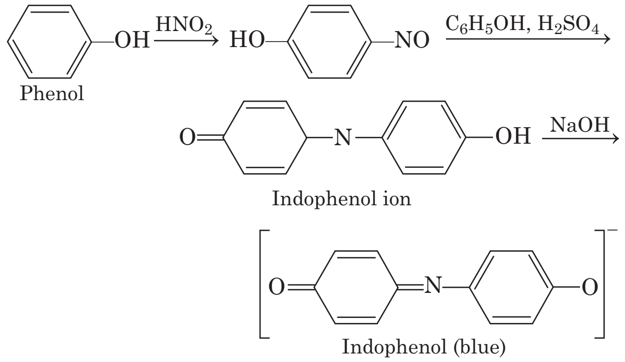
(i) **Ferric chloride test** Take few drops of ferric chloride solution and add 2-3 drops of the compound to it. Appearance green, blue or violet colour shows the presence of phenol.

$$\underset{\text{Phenol}}{6C_6H_5OH} + \underset{\substack{\text{Ferric}\\\text{chloride}}}{FeCl_3} \longrightarrow 3H^+ + \underset{\text{Violet}}{[Fe(OC_6H_5)_6]^{3-}} + 3HCl$$

This test is also given by enols.

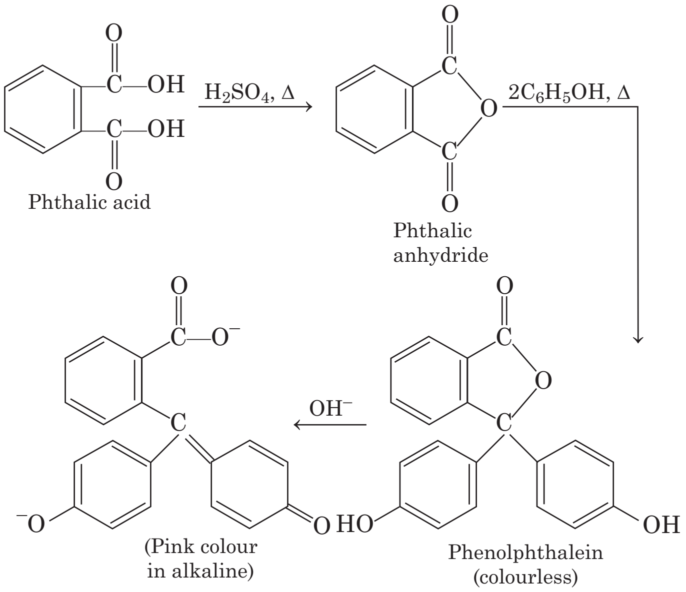
(ii) **Liebermann's nitroso reaction** Take little amount of compound and add 1mL of conc. H_2SO_4 to it. Shake and warm the test tube. Cool and then add crystals of sodium nitrite ($NaNO_2$).

A deep green to blue solution is formed which turns red on dilution. The red aqueous solution becomes again deep green or blue if made alkaline with NaOH. It shows the presence of phenol.



Note Nitrophenol do not respond to $FeCl_3$ test as well as Liebermann's nitroso reaction.

(iii) **Phthalein test** Phenol on heating with phthalic acid in presence of conc. H_2SO_4 gives colourless compound called phenolphthalein, which appear pink coloured compound in alkaline medium.



Phenolphthalein is used as an indicator in acid-base titrations. It is colourless in acidic medium and pink in basic medium.

Tests for Aldehyde (—CHO) Group

(i) **Tollen's reagent test** Take a little quantity of the compound in a test tube and add 2 mL of freshly prepared reagent. Shake, warm and allow the contents to stand for 2-3 minutes.

Formation of silver mirror or a grey ppt. indicates the presence of an aldehydic group.

$$2Ag(NH_3)_2OH + R\cdot CHO \longrightarrow \underset{\substack{\text{Silver mirror}\\ \text{or grey ppt.}}}{2Ag\downarrow} + RCO\overset{-}{O}\overset{+}{N}H_4 + 3NH_3\uparrow + H_2O$$

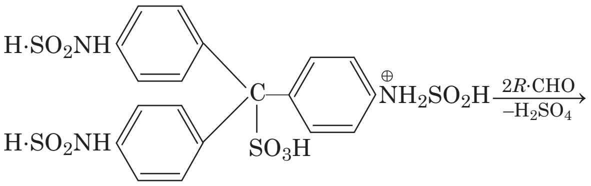
(ii) **Fehling's solution test** Take a mixture of equal amounts of Fehling's solution *A* and *B*, and add few drops of organic compound and boil the contents. Formation of a red ppt. shows the presence of an aldehyde.

$$\underset{\substack{\text{Cupric}\\ \text{oxide}}}{2CuO} + \underset{\text{Aldehyde}}{R\cdot CHO} \longrightarrow \underset{\text{Red ppt.}}{Cu_2O\downarrow} + RCOOH$$

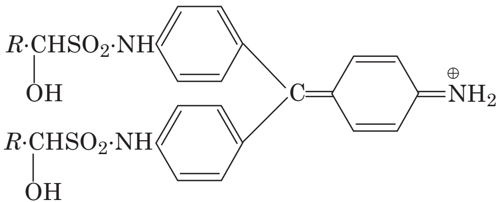
Note

- Both the above tests are also given by reducing sugars.
- Benzaldehyde does not reduce Fehling's solution (a distinction from other aldehydes). Benzaldehyde is confirmed by malachite green test.

(iii) **Schiff's reagent test** Add 5-6 drops of organic compound to 2 mL of the Schiff's reagent. Shake vigorously. After some time formation of a deep red or violet colour indicates the presence of an aldehydic group.



Schiff's reagent (colourless)



Violet colour

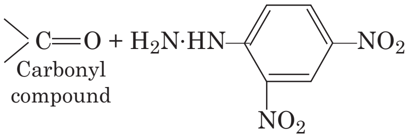
(iv) **Benedict's solution test** Boil the compound with 2-3 mL of Benedict's solution for few minutes. Appearance of a red-yellow ppt. confirms the presence of aliphatic aldehydes.

Note This test is usually given by only aliphatic aldehydes, thus used to differentiate between aliphatic and aromatic aldehydes.

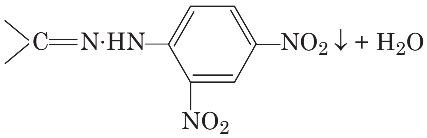
Tests for Ketone $\left(\begin{matrix}R\\R\end{matrix}\!\!>C{=}O\right)$ Group

(i) **2,4-dinitrophenyl hydrazine test** In a dry test tube, add few drops of the organic compound (if liquid) or its alcoholic solution (if solid) to about 2 mL of the reagent and one drop of conc. H_2SO_4. Shake vigorously, heat (if necessary) and allow to stand for about 5 minutes.

A yellow or orange ppt. separates out in case of a compound containing carbonyl group due to the formation of respective hydrazones.

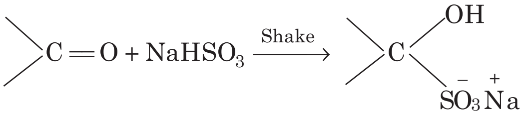


2, 4-dinitrophenyl hydrazine



Yellow or orange red coloured crystalline derivative of 2, 4-dinitrophenyl hydrazine of carbonyl compound

(ii) **Sodium bisulphite test** Add a very small quantity of organic compound to 1 mL of saturated solution of sodium bisulphite and shake vigorously. Formation of white ppt. shows the presence of carbonyl group.



$$>C=O + NaHSO_3 \xrightarrow{\text{Shake}} >C\begin{matrix}OH\\ \overset{-}{S}O_3\overset{+}{N}a\end{matrix}$$

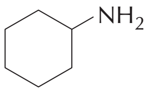
Sodium bisulphite derivative of carbonyl compound (white crystalline ppt.)

(iii) **Sodium nitroprusside test** Add 0.1 g of solid or 0.2 cc of liquid compound to 2 cc of sodium nitroprusside, $Na_2[Fe(CN)_5NO]$ solution. After that make the solution alkaline with 2-3 drops of sodium hydroxide. A red or purple colour indicates the presence of ketone (benzophenone does not give this test).

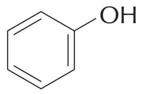
Example 1. *The organic compound that gives following qualitative analysis is* ***(JEE Main 2019)***

Test	Inference
(i) Dil. HCl	Insoluble
(ii) NaOH solution	Soluble
(iii) Br_2/water	Decolourisation

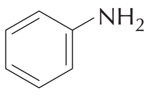
(a)



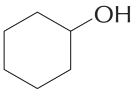
(b)



(c)

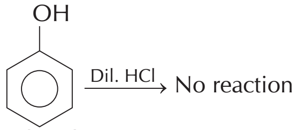


(d)



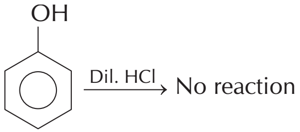
Sol. (*b*) Phenol (*Ar*OH) is insoluble in dil. HCl and readily soluble in NaOH solution. It reacts with Br_2/water to give 2, 4, 6-tribromophenol. It readily decolourises the yellow colour of Br_2 water. Reactions involved are as follows

(i)



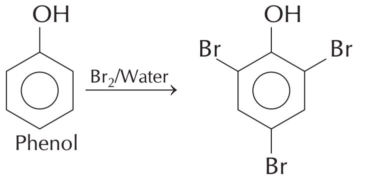
Phenol
(Acidic in nature)

(ii)



Phenol
(Acidic in nature)

(iii)



White ppt.
(2, 4, 6-tribromophenol)

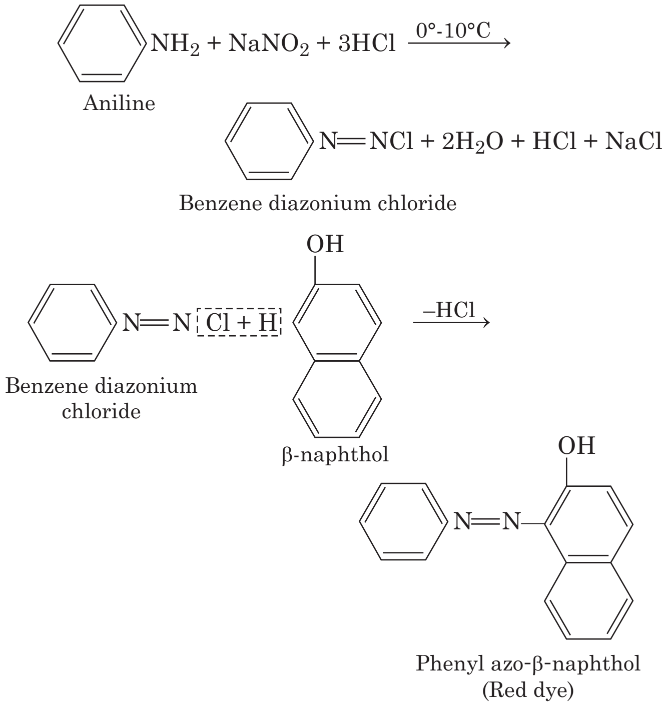
Tests for Primary Amine (—NH_2) Group

Tests for primary amine are

(i) **Carbylamine test** Boil a little quantity of the compound with 2 drops of chloroform and 2 mL of alcoholic caustic potash. An intolerable offensive odour of carbylamine indicates the presence of primary amine.

$$\underset{\text{Primary amine}}{R\text{—}NH_2} + CHCl_3 + (\text{alc.})\ 3KOH \longrightarrow \underset{\text{Carbylamine}}{R\cdot NC\uparrow} + 3KCl + 3H_2O$$

(ii) **Dye test** Dissolve about 0.2 g of the compound in dil. HCl and cool. Now, add 10% *aq*. $NaNO_2$ solution. Pour all this content into a beaker containing alkaline β-naphthol solution. Formation of a red or orange dye indicates the presence of aromatic primary amino group.



Phenyl azo-β-naphthol
(Red dye)

Tests to Distinguish between Primary, Secondary and Tertiary Amines

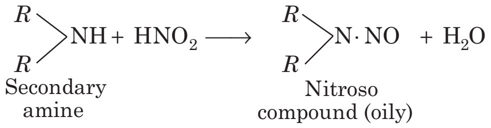
(i) **Nitrous acid test** Prepare a solution of nitrous acid by adding ice cold dil. HCl to a solution of 1% *aq*. $NaNO_2$. Add gradually this solution to 0.2 g of the organic compound in 10 mL dil. HCl.

Observations are as follows

- Formation of brisk effervescence shows the presence of **aliphatic primary amine.**

$$\underset{\text{Primary amine}}{R\text{—}NH_2} + HNO_2 \longrightarrow \underset{\text{Alcohol}}{ROH} + H_2O + \underset{\text{Nitrogen}}{N_2\uparrow}$$

- Formation of an oily dark coloured liquid indicates the presence of **secondary amine.**



$$\underset{\text{Secondary amine}}{R_2NH} + HNO_2 \longrightarrow \underset{\text{Nitroso compound (oily)}}{R_2N\cdot NO} + H_2O$$

- No reaction indicates the presence of **aliphatic tertiary amine** while production of green or brown colour indicates the presence of **aromatic tertiary amines.**

(ii) **Hinsberg's test** Take 0.2 g of the organic compound, add 1 mL of 5% NaOH and 3 mL pyridine.

Shake well and add few drops of benzene sulphonyl chloride (Hinsberg's reagent) with continuous shaking.

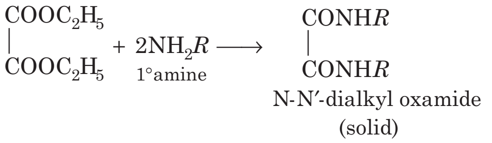
Observations are as follows

- Formation of yellow colour indicates the presence of **primary amine.**
- Formation of orange colour shows the presence of **secondary amine.**
- Formation of a red or purple colour shows the presence of **tertiary amines.**

(iii) **Hofmann's method** Take some organic compound in a test tube and add diethyl oxalate solution to it, shake well.

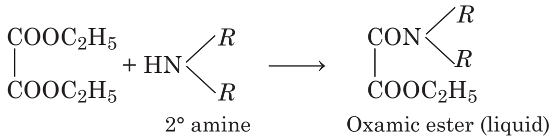
Observations are as follows

- Formation of solid product (N, N′-dialkyl oxamide) indicates the presence of 1° amine.



$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + \underset{1^\circ\text{amine}}{2NH_2R} \longrightarrow \underset{\text{N-N}'\text{-dialkyl oxamide (solid)}}{\begin{matrix} CONHR \\ | \\ CONHR \end{matrix}}$$

- Formation of liquid product (oxamic ester) indicates the presence of 2° amine.



$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + \underset{2^\circ\text{ amine}}{HNR_2} \longrightarrow \underset{\text{Oxamic ester (liquid)}}{\begin{matrix} CONR_2 \\ | \\ COOC_2H_5 \end{matrix}}$$

- 3° amine does not react with diethyl oxalate.

Preparation of Inorganic Compounds

(i) **Mohr's salt or Ferrous ammonium sulphate, $[FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O]$.** It is a double salt. When solutions of ferrous sulphate and ammonium sulphate are mixed together, evaporated and cooled, light green crystals of Mohr's salt are obtained.

$$(NH_4)_2SO_4 + FeSO_4 \cdot 7H_2O \longrightarrow \underset{\substack{\text{Mohr's salt} \\ \text{(light green)}}}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O} + H_2O$$

During the preparation of ferrous sulphate solution in boiling water, dilute H_2SO_4, (in small amount), is also added in boiling water to prevent the hydrolysis of ferrous sulphate, i.e. to prevent conversion of ferrous sulphate into ferrous hydroxide.

(ii) **Potash alum,** $KAl(SO_4)_2 \cdot 12H_2O$ It is also a double salt. Potash alum is prepared by dissolving K_2SO_4 and $Al_2(SO_4)_3$ in equimolar ratio in small amount of water containing some drops of conc. H_2SO_4. On cooling potash alum separates as colourless crystals.

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$$

Example 2. *Alum is found to contain hydrated monovalent cation* $[M(H_2O)]^+$, *trivalent cation* $[M'(H_2O)_6]^{3+}$ *and* SO_4^{2-} *in the ratio of*

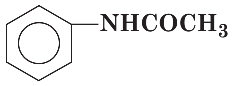
(a) 1:1:1 (b) 1:2:3 (c) 1:3:2 (d) 1:1:2

Sol. (*d*) General formula for potash alum is $KAl(SO_4)_2 \cdot 12H_2O$ (1 : 1 : 2).

K^+ = monovalent cation and Al^{3+} = trivalent cation

Preparation of Organic Compounds

Some preparation of organic compounds are discussed below

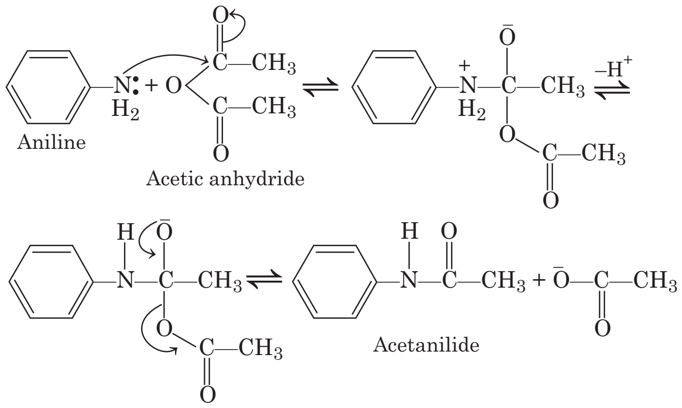
1. **Acetanilide,** 

It is prepared by direct acetylation of aniline by using the mixture of equal volumes of acetic anhydride and acetic acid. Amines containing —NH_2 or > NH groups respectively can be directly acetylated.

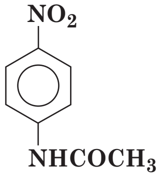
Their reactive hydrogen atoms get replaced by acetyl group (—$COCH_3$) to give acetyl derivatives of the type $RNH \cdot COCH_3$ and $R_2N \cdot COCH_3$ respectively which may be regarded as mono and di-alkyl substituted acetamide.

$$R—NH_2 + (CH_3CO)_2O \longrightarrow RNH \cdot COCH_3 + CH_3COOH$$

The **mechanism** of this reaction is as follows



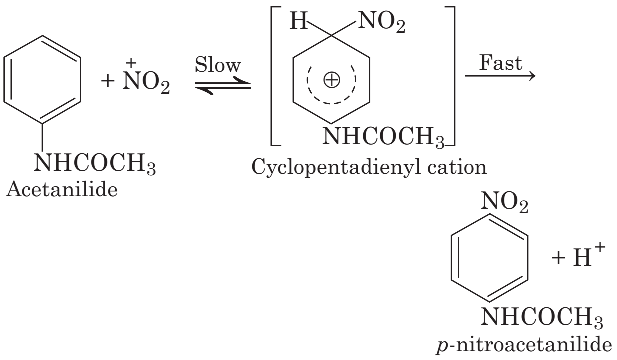
Small amount of zinc is added to the reaction mixture to prevent the oxidation of aniline and to reduce the coloured impurities present in aniline during the reaction.

2. ***p*-Nitro Acetanilide,** 

It is prepared by the nitration of acetanilide. It is dissolved in glacial acetic acid. Then, concentrated H_2SO_4 is added to it with vigorous stirring. Temperature of reaction mixture should be maintained below 10°C. Now add fuming HNO_3 drop by drop with regular stirring.

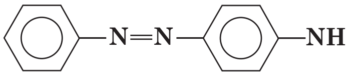
It gives *p*-nitro acetanilide along with a little amount of *o*-isomer. In this process, fuming HNO_3 in the presence of conc. H_2SO_4, gives nitronium ion (NO_2^+) which attack on acetanilide to form *p*-nitro acetanilide through the cyclopentadienyl cation (intermediate) formation.

$$HNO_3 + H_2SO_4 \longrightarrow \underset{\text{Nitronium ion}}{NO_2^+} + H_2O + HSO_4^-$$

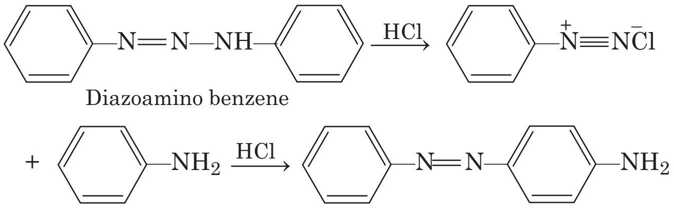


$$H^+ + HSO_4^- \longrightarrow H_2SO_4$$

3. **Aniline Yellow or** ***p*-Amino Azobenzene,**



It is an azo dye prepared from diazoamino benzene. When diazoaminobenzene is heated with aniline and a little amount of hydrochloride at about 40°C, for a short time, it gives *p*-amino azobenzene or aniline yellow in good yield.

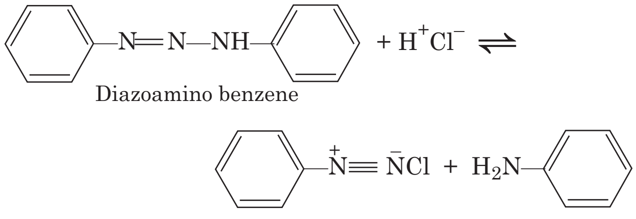


Diazoamino benzene

Aniline

p-amino azobenzene

The mechanism of the reaction is based on the equilibrium involving the diazoamino compound, phenyl diazonium chloride and aniline.



Diazoamino benzene

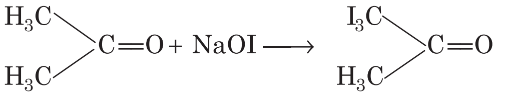
Phenyl diazonium chloride

Aniline

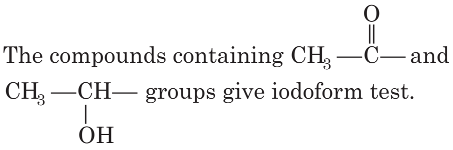
The reaction takes place between the two latter compounds under weakly acidic conditions.

4. **Iodoform, CHI_3** It is prepared from acetone. Acetone when treated with potassium iodide and sodium hypochlorite (NaOCl), gives iodoform.

$$NaOCl + KI \longrightarrow NaOI + KCl$$



$$\xrightarrow{NaOH} CH_3CO\overset{-}{O}\overset{+}{N}a + \underset{\text{Iodoform}}{CHI_3}\downarrow$$



Note The compounds containing $CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—$ and $CH_3—\underset{\underset{\displaystyle OH}{|}}{CH}—$ groups give iodoform test.

Practical Inorganic Chemistry

Inorganic chemistry practical chemistry are divided into two parts, i.e.

I. Quantitative analysis (volumetric analysis)
II. Qualitative analysis

I. Quantitative Analysis

(Volumetric Analysis)

It involves the calculations based on volume relationships for solutions.

Titrimetric Analysis or Titration

A titration is an experiment where the volume of reactant solution (titrant) needed to react exactly with some amount of another reactant is measured. This volume is called equivalence point.

A titration is performed by slowly adding a standard solution from a burette to a solution under examination until the reaction between the two is observed to be complete. The volume or mass of the reagent needed to complete the titration is determined from the difference between the initial and final readings.

The solution taken in the burette during titration is known as **titrant**. The other solution being titrated is called the **titrate**.

Standard Solutions

A volumetric method employs one or more standard solutions which are reagents of exactly known concentrations. A standard solution used for acid-base titration is usually a solution of strong acids or bases e.g. HCl, H_2SO_4, NaOH, KOH and $Ba(OH)_2$.

Bases, however, are not as good as acid for permanent standards because they absorb CO_2 whenever they come in contact with air. Therefore, the accuracy of a volumetric method is limited by the accuracy with which the concentration of the standard solution is known.

The ideal standard solution (of known concentration) must have the following characteristics

- It should be sufficiently stable so that it is necessary to determine its concentration only once.
- It must react rapidly with the analyte.

If concentration of a substance can be known simply by dissolving its known amount in a given volume of solution, then the substance is called **primary standard and the solution formed as primary standard solutions.**

e.g. Oxalic acid, potassium dichromate. In most cases, concentration can be determined by standardisation against primary standard solution. Such solutions are called **secondary standard solutions.** e.g. Ferrous sulphate, mineral acids (H_2SO_4, HNO_3), Their solutions are prepared by dissolving a known amount or volume but they have to be standardised using primary standard. Thus, all these are secondary standards.

Equivalence Point and End Point

The equivalence point in a titration is a theoretical point where the amount of added titrant is chemically equivalent to the amount of analyte (titrate) in the sample. It cannot be determined experimentally. We can only estimate its position by observing some physical change associated with the condition so equivalence. This is called end point of titration.

For example, equivalent point is reached when 1 mole of HCl is neutralised by 1 mole of NaOH. But we cannot detect this equivalent point. If one drop of suitable indicator such as phenolphthalein is added in HCl (analyte), then additional drop of NaOH (from burette) will give light pink colour. This is the **end point.**

Therefore, end point is the point of completion of the reaction indicated by suitable indicator. It has an additional drop of titrating reagent but for the reaction.

$$\mathrm{NaOH} + \mathrm{HCl} \longrightarrow \mathrm{NaCl} + \mathrm{H_2O}$$

$$N_1V_1 = N_2V_2$$

$$1 \text{ equivalent of NaOH} \equiv 1 \text{equivalent of HCl}$$

$$\equiv 1 \text{ mol of HCl}$$

$$2\mathrm{NaOH} + \mathrm{H_2SO_4} \longrightarrow \mathrm{Na_2SO_4} + 2\mathrm{H_2O}$$

$$1 \text{ equivalent of NaOH} \equiv 1 \text{ equivalent of } \mathrm{H_2SO_4}$$

$$\equiv 0.5 \text{ mol of } \mathrm{H_2SO_4}$$

Acid-Base Indicators

An indicator is a dye or substance which changes colour over a short pH range.

- Acid-base indicators are special types of substances which possess one colour in acid solution and different colour in alkaline medium.
- For acid-base titration, a weak acid or weak base is used as an indicator. Since, the concentration of acid or base is controlled by pH, the colour of an indicator solution is pH dependent.
- The Henderson-Hasselbalch equation shows that when $\mathrm{pH} = \mathrm{p}K_a$, the acid and base concentrations are equal. Thus, the colour will be a mixture of both the acid and base forms. Since, there is at least 20 times higher acid concentration than base, the acidic form and colour predominate at $\mathrm{pH} < \mathrm{p}K_a - 1.0$. Likewise, the basic form and colour predominate at $\mathrm{pH} > \mathrm{p}K_a + 1.0$. Some acid-base indicators are as follows

pH Transition Ranges and Colours of Some Common Indicators

	pH range	Colour in acid solution	Colour in alkaline solution
Thymol blue	1.2 - 2.8	Red	Yellow
Bromophenol blue	3.1 - 4.6	Yellow	Purple
Methyl orange	3.1 - 4.5	Red	Yellow
Methyl red	4.2 - 6.3	Red	Yellow
Bromothymol blue	6.0 - 7.5	Orange	Blue
Phenol red	6.4 - 8.2	Yellow	Red
Thymol blue (base)	8.1 - 9.6	Yellow	Blue
Phenolphthalein	8.0 - 9.8	Colourless	Pink
Thymophthalein	9.3 -10.5	Colourless	Blue
Alizarin yellow R	10.1 - 12.1	Yellow	Lilac

Titration Curve

By constructing a titration curve, we can easily explain how the end point of a titration can be detected. A titration curve is constructed by plotting the pH of the solution as a function of the volume of titrant added. The titrant is always a strong acid or a strong base.

Types of Titrations

Some important types of titrations are as discussed below

Acid-Base Titration

(or Neutralisation Method of Analysis)

The reaction between acid and base is called **neutralisation**. It is very fast and the equilibriun constant for a neutralisation reaction is so large that it nearly proceed to completion. It is a simple and convenient volumetric method.

The reaction is characterised by a rapid change in pH near the equivalence point, which is detected by the colour change of indicator that occur at the end point.

The analysis that can be done by neutralisation method may be grouped in two general classes

(i) Determination of acid or base or their anhydride in a sample by titrating with a standard solution of base or acid.

(ii) Determination of salts of weak acids or bases by titrating with a standard solution of a strong base or acid.

The titration of a very weak base with strong acid and a titration of a very weak acid with strong base cannot be performed because a sharp end point cannot be observed for them. Usually when acid is too weak to be titrated with a standard base, a salt of acid can be titrated with standard base solution.

For example, carbonic acid cannot be titrated by sodium hydroxide quantitatively, but sodium carbonate can be titrated by hydrochloric acid or sulphuric acid.

$$\mathrm{CO_3^{2-}} + 2\mathrm{H^+} \longrightarrow \mathrm{H_2O} + \mathrm{CO_2}$$

e.g. Na_2CO_3 (Strong Base) vs HCl (Strong Acid)

The titration of Na_2CO_3 *vs* HCl is a neutralisation titration (acidimetry and alkalimetry) which involve the neutralisation of an acid with a base. In this sodium carbonate is attacked by dil. HCl in the following way

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

Methyl orange is used as an indicator for end pont detection. In this titration, sodium carbonate is estimated by titrating it with a standard solution of HCl.

Indicators in Acid-Base Titrations

Acid-base titrations	Indicators
Strong acid *vs* strong base	Bromothymol blue, phenolphthalein methyl orange, thymophthalein
Strong acid *vs* weak base	Methyl orange, methyl red, bromocresol green
Weak acid *vs* strong base	Phenolphthalein, thymophthalein
Weak acid *vs* weak base	Phenol red

Redox Titrations

Reducing agents such as Fe, Fe^{2+}, H_2O_2, $CaOCl_2$, MnO_2 can be determined by suitable oxidising agents such as $KMnO_4$, $K_2Cr_2O_7$ in acidic or basic or neutral medium. These are called redox titrations. Such reactions are accompanied by the change in valency of ions.

Some examples of this titration are as follows

1. **Fe^{2+} is oxidised to Fe^{3+} by MnO_4^-** which in turn is reduced to Mn^{2+} in acidic medium.

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

In all cases, $N_1V_1 = N_2V_2$ but $M_1V_1 \neq M_2V_2$

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{Total change in oxidation number}} = \frac{\text{Molecular weight}}{\text{Number of electrons gained or lost}}$$

2. **Oxalic acid *vs* $KMnO_4$ titration** This is an example of redox titration in which a reducing agent (as oxalic acid) is estimated by titrating it with a standard solution of oxidising agent (as $KMnO_4$) Such reactions are accompanied by the change in valency of ions. In these titrations, oxidation and reduction takes place simultaneously, i.e. while one substance is being oxidised, the other one is being reduced.

$$\underset{\text{Oxidising agent}}{2KMnO_4} + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]\ ;\ \left(E_{KMnO_4} = \frac{M}{5}\right)$$

$$\underset{\text{Reducing agent}}{5\begin{array}{l}COOH\\ |\\ COOH\end{array}} + 5\,[O] \longrightarrow 5H_2O + 10CO_2\uparrow;\ \left(E_{H_2C_2O_4} = \frac{M}{2}\right)$$

- $KMnO_4$ acts as self indicator for end point detection.
- This titration is carried out in the presence of HCl or H_2SO_4 but not in the presence of conc. HNO_3 because it is a strong oxidising agent and hence interfere with oxidising action of $KMnO_4$.
- In $KMnO_4$ *vs* oxalic acid titration, the oxalic acid solution is heated with dilute H_2SO_4 upto 70-80°C.

3. **Mohr's salt, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ *vs* $KMnO_4$ titration** In this titration, the active constituent of ferrous ammonium sulphate (Mohr's salt) is ferrous sulphate, which is oxidised to ferric sulphate by acidified potassium permanganate as follows.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5\,[O];\ \left(E_{KMnO_4} = \frac{M}{5}\right)$$

$$\underline{[2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5}$$

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O\quad \left(E_{FeSO_4} = \frac{M}{1}\right)$$

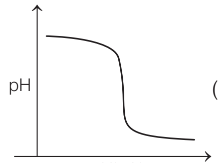
- $KMnO_4$ acts as self indicator for end point detection.
- This titration is carried out at room temperature because Mohr's salt is oxidised by air on heating.
- Sulphuric acid should be present in excess otherwise a brown precipitate due to the formation of MnO_2 will be formed.

Redox Titrations (Excluding Iodometric/Iodimetric Titrations)

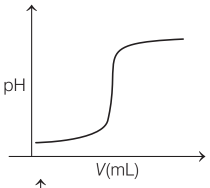
Estimation of	By titrating with	Reactions	Relation between O.A and R.A
Fe^{2+}	MnO_4^-	$Fe^{2+} \longrightarrow Fe^{3+} + e^-$ $MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$	$5\,Fe^{2+} \equiv MnO_4^-$ Eq.wt. $Fe^{2+} = \frac{M}{1}$; Eq.wt $MnO_4^- = \frac{M}{5}$
Fe^{2+}	$Cr_2O_7^{2-}$	$Fe^{2} \longrightarrow Fe^{3+} + e^-$ $Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7H_2O$	$6\,Fe^{2+} \equiv Cr_2O_7^{2-}$; Eq.wt. $Cr_2O_7^{2-} = M/6$
$C_2O_4^{2-}$	MnO_4^-	$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$ $MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$	$5\,C_2O_4^{2-} \equiv 2MnO_4^-$ E.wt. $C_2O_4^{2-} = M/2$; Eq.wt. $MnO_4^- = \frac{M}{5}$
H_2O_2	MnO_4^-	$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$	$5\,H_2O_2 = 2MnO_4^-$ Eq.wt $H_2O_2 = M/2$; Eq.w.t $MnO_4^- = \frac{M}{5}$
As_2O_3	MnO_4^-	$As_2O_3 + 5\,H_2O \longrightarrow 2AsO_4^{3-} + 10\,H^+ + 4\,e^-$	Eq.wt of $As_2O_3 = M/4$
AsO_3^{3-}	BrO_3^-	$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$ $BrO_3^- + 6\,H^+ + 6\,e^- \longrightarrow Br^- + 3\,H_2O$	Eq.wt. $AsO_3^{3-} = M/2$ Eq.wt. of $BrO_3^- = M/6$

Example 3. *In an acid-base titration,* 0.1 M HCl *solution was added to the* NaOH *solution of unknown strength. Which of the following correctly shows the change of pH of the titration mixture in this experiment ?* ***(JEE Main 2019)***

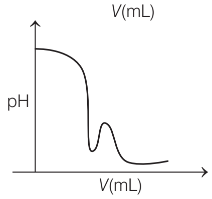
(A)



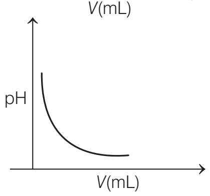
(B)



(C)

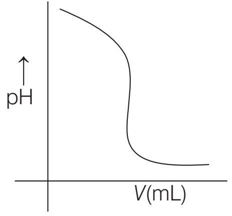


(D)



(a) (D) (b) (A) (c) (B) (d) (C)

Sol. (*b*) The graph that shows the correct change of pH of the titration mixture in the experiment is



In this case, both the titrants are completely ionised.

$$\mathrm{HCl + NaOH \rightleftharpoons \overset{+}{Na}\overset{-}{Cl} + H_2O}$$

As $\overset{\oplus}{\mathrm{H}}$ is added to a basic solution, $[\mathrm{OH}^{\ominus}]$ decreases and $[\mathrm{H}^+]$ increases. Therefore, pH goes on decreasing. As the equivalence point is reached, $[\mathrm{OH}^{\ominus}]$ is rapidly reduced. After this point $[\mathrm{OH}^{\ominus}]$ decreases rapidly and pH of the solution remains fairly constant. Thus, there is an inflexion point at the equivalence point.

The difference in the volume of NaOH solution between the end point and the equivalence point is not significant for most of the commonly used indicators as there is a large change in the pH value around the equivalence point. Most of them change their colour across this pH change.

II. Salt Analysis or Qualitative Analysis of Inorganic Mixture

Qualitative analysis of given inorganic mixture is done in the following steps

(i) **Dry tests** Dry tests involve following tests

- Physical observation
- Smell of compound
- Flame tests
- Cobalt nitrate test
- Effect of heating
- Solubility of salts
- Charcoal cavity test
- Borax bead test
- Microcosmic salt bead test
- Sodium carbonate bead test

(ii) **Wet tests** Dry tests tells us about the presence of possible radicals in the mixture but these are confirmed by wet tests.

Dry Test

These are preformed in the following manner

1. Physical Observation of Salt or Mixture

In physical examination, colour, smell and density of a given mixture are observed.

Observation	Inference
A. If colour of the substance is	
blue, its aqueous solution is also blue.	Cupric salt
green, its aqueous solution is also green.	Salts of nickel
dark green, its aqueous solution is also dark green but becomes light on dilution.	Salts of chromium
violet-pink, its aqueous solution is pink.	Salts of cobalt
light pink, its aqueous solution is colourless.	Salts of manganese
reddish brown	Fe_2O_3
red	HgO, HgI_2, Pb_3O_4, Cu_2O
orange red	Sb_2S_3
black	CuO, NiO, SnO, FeS, CuS, HgS, PbS, CoS, FeO, Co_3O_4, Ni_2O_3, Cu_2S, $CuBr_2$, NiS etc.
yellow	As_2S_3, CdS, Bi_2O_3, As_2S_5, PbI_2, AgI, chromates etc.
yellow-green, aqueous solution is light green or almost colourless.	Salts of Fe^{2+}
yellow-brown, aqueous solution is yellow	Salts of Fe^{3+}
colourless	Transition metals absent except some salts of Mn^{2+}
purple	Some Cr^{3+} salts and permanganates.
B. Odour of the substance	
Vinegar like smell	Acetates
Rotten egg like smell	Sulphides
Ammoniacal smell	Ammonia salts mainly $(NH_4)_2CO_3$ Some ammonium salts and sulphides do not give smell.
C. Density	
Mixture or salt is light	Salts of Zn, Bi, Al, Ba, Sr, Ca and Mg.
Mixture of salts is heavy	Salts of Hg and Pb.

2. Effect of Heating

Take the given substance in a clear, dry test tube and heat it first gently and then strongly. Observe the changes that takes place upon heating.

Observation	Inference
Substance melts	Salts of alkali metals, chlorides of Hg, Ag and Pb and salts having water of crystallisation.
Substance cracks	$Pb(NO_3)_2$, $Ba(NO_3)_2$, NaCl and KI
Substance swells	Alums, salts of phosphate and borate.
Substance sublimes on heating and the colour of sublimate is	
• White	$HgCl_2$, As_2O_3, Hg_2Cl_2, $AlCl_3$, Sb_2O_3, halides of NH_3

Observation	Inference
- Yellow	As_2S_3 and HgI_2
- Black	Sulphides of Hg, Sb, As
- Blue, yellow or violet vapours	Iodides
- Grey (having garlic odour)	As
Colour, of residue obtained after heating (Residue mainly contains metallic oxides	
- White and non-fusible	Oxides of Ca, Ba, Sr, Mg, Zn and Al.
- Red-brown	Fe_2O_3
- Yellow-brown when hot, on cooling it is brown	SnO_2
- Black and infusible	NiO, MnO_2 and CuO
- Dark orange red in heating state and sublimes	HgO
- White, infusible, becomes yellow on heating	ZnO
- Initially, it is blue or green but becomes white on heating	$CuSO_4 \cdot 5H_2O$
Observations of gases evolved	
(i) Colourless, odourless gas	
- O_2, which supports combustion.	Nitrates of Na and K
- CO_2, which turns lime water milky	Carbonates and oxalates.
(ii) Colourless, odorous gas	
- H_2S, smell of rotten eggs	Sulphides.
- HCl, Pungent smell and forms white fumes with NH_3	Hydrated chloride salts
- NH_3, turns red litmus to blue	Ammonium salts
- SO_2, smell of burning sulphur	Sulphite and thiosulphate.
(iii) Coloured, odorous gas	
- Cl_2, yellow-green pungent smelling gas.	Chloride
- I_2, violet gas	Iodides
- Br_2, red-brown gas	Bromides
- NO_2, brown gas	Nitrates or nitrites of heavy metals

3. Smell of Compound

Smell of compound also gives an idea about the radical present in the salt.

Smell	Inference
Ammoniacal smell	Ammonium salts
Vinegar like smell	Acetates
Chlorine like smell	Hypochlorites

4. Solubility of Salts

Type of the salts	Observation
Nitrates and nitrites	All metal salts are soluble in water
Acetates	All metal acetates are soluble in water
Chlorides	All common chlorides are soluble in water except AgCl, Hg_2Cl_2 and $PbCl_2$.
Bromides	All common bromides are soluble in water except AgBr, Hg_2Br_2, $PbBr_2$ and $HgBr_2$.
Iodides	All common iodides are soluble in water except AgI, Hg_2I_2, HgI_2, PbI_2.
Sulphides	All common sulphides are insoluble in water except sulphides of group I and group II metals and ammonium ion.
Carbonates	All common carbonates are insoluble in water except carbonates of group I and $(NH_4)_2CO_3$.
Sulphates	All common sulphates are soluble in water except $PbSO_4$, Hg_2SO_4, $BaSO_4$, $CaSO_4$ and Ag_2SO_4 which are sparingly soluble.
Phosphates	All common phosphates are insoluble in water except phosphates of group I and $(NH_4)_3PO_4$.
Hydroxides	All common metal hydroxides are insoluble in water except group I hydroxides and $Ba(OH)_2$, $Sr(OH)_2$ and $Ca(OH)_2$.

5. Flame Test

This test is based upon the fact that in a state of high ionisation of chloride some of the cations impart characteristic colour to the flame, as the cation absorbs energy from the flame and transmit the same as light of characteristic colour.

In this method, paste of the salt and conc. HCl is taken into the lower oxidising zone and colour imparted to the flame by salts is observed.

Salts particularly of group V (Ba^{2+}, Ca^{2+}, Sr^{2+}) are identified by colours of the flame.

Colour in Flame Test

Colour	Cation
Golden yellow	Na^+
Violet	K^+
Carmine red	Li^+
Brick red	Ca^{2+}
Apple-green	Ba^{2+}, Mo^{2+}
Green	Cu^{2+}, BO_3^{3-}, Tl^{3+}
Crimson red	Sr^{2+}
Blue	Cu^{2+}, As^{3+}, Sb^{3+}, Bi^{3+}

6. **Charcoal Cavity Test**

When a salt is fused with anhydrous Na_2CO_3 or oxidising mixture in a cavity on charcoal block in reducing flame, first metallic carbonates is formed followed by metallic oxides.

e.g. $M(\text{NO}_3)_2 + \text{Na}_2\text{CO}_3 \xrightarrow{\Delta} M\text{CO}_3 + 2\text{NaNO}_3$

$$M\text{CO}_3 \xrightarrow{\Delta} M\text{O} + \text{CO}_2\uparrow$$

These metallic oxides reduce to metals by the action of carbon present in reducing flame. On cooling, these metals form beads.

$$M\text{O} + \text{C} \longrightarrow M + \text{CO}\uparrow$$

Colour in charcoal cavity test with different ions are shown below.

Colour in Charcoal Cavity Test

Sample Bead	Crust	Inference
Greyish white soft bead which marks paper.	Brown which turns yellow on cooling	Pb^{2+}
Lustrous white bead	—	Ag^{+}
White-brown bead	Orange which turns yellow on cooling	Bi^{3+}
Garlic like smelly fumes without bead	—	As^{3+}
—	Red-brown precipitate, easily turns into vapour	Cd^{2+}
Smell of ammonia	Red	NH_4^{+}
—	Black precipitate	Fe^{3+}, Co^{2+}, Mn^{2+}

7. **Cobalt Nitrate Test**

In this test, 1-2 drops cobalt nitrate is added to infusible mass obtained in charcoal cavity and heat the mixture in oxidising flame. Infusible mass contains metallic oxides like CaO, Al_2O_3, MgO and ZnO.

Colours of some ions shown in cobalt nitrate test are as follows

Colour in Cobalt Nitrate Test

Colour of the residue	Inference
Green	Zn^{2+}
Pink-dirty residue	Mg^{2+}
Bluish green	Sn^{2+}
Blue	Al^{3+}, PO_4^{3-}, BO_3^{3-}

Cobalt nitrate should not be used in excess otherwise black coloured cobalt oxide (Co_3O_4), may be formed and it is difficult to identify other colours in presence of black colour.

8. **Borax Bead Test**

If borax, $Na_2B_4O_7 \cdot 10H_2O$ is heated on the platinum loop, a transparent colourless glass like bead of sodium metaborate ($NaBO_2$) and boric anhydride (B_2O_3) is formed.

$$\text{Na}_2\text{B}_4\text{O}_7 \xrightarrow{\Delta} 2\text{NaBO}_2 + \text{B}_2\text{O}_3$$

Characteristics coloured beads are produced with salts of Cu, Fe, Cr, Mn, Co and Ni. The colour of the bead depends upon the flame in which it has been heated.

$$\text{CuO} + \text{B}_2\text{O}_3 \longrightarrow \underset{\substack{\text{Copper (II) metaborate} \\ \text{(green when hot and} \\ \text{blue when cold)}}}{\text{Cu(BO}_2)_2} \quad \text{(Oxidising flame)}$$

$$2\text{Cu(BO}_2)_2 + \text{C} \longrightarrow 2\text{CuBO}_2 + \text{B}_2\text{O}_3 + \text{CO}\uparrow \quad \text{(Reducing flame)}$$

$$2\text{CuBO}_2 + \text{C} \longrightarrow \underset{\text{Red}}{2\text{Cu}\downarrow} + \text{B}_2\text{O}_3 + \text{CO}\uparrow$$

Colours of some ions shown is borax bead test.

Colour in Borax Bead Test

Oxidising flame		Reducing flame		Metal
Hot	**Cold**	**Hot**	**Cold**	
Green	Blue	Colourless	Opaque red-brown	Cu
Yellowish-brown	Yellow	Green	Green	Fe
Yellow	Green	Green	Green	Cr
Violet	Amethyst	Colourless	Colourless	Mn
Blue	Blue	Blue	Blue	Co
Violet	Reddish-brown	Grey	Grey	Ni
Yellow	Colourless	Brown	Brown	Mo
Rose-violet	Rose-violet	Red	Violet	Au
Yellow	Colourless	Yellow	Yellowish to brown	W
Yellow	Pale yellow	Green	Bottle Green	U
Yellow	Greenish yellow	Brownish	Emerald green	V
Yellow	Colourless	Grey3	Pale violet	Ti
Orange-red	Colourless	Colourless	Colourless	Ce

9. **Microcosmic Salt Bead Test**

A test similar to borax bead test is used for identification of coloured cations, if microcosmic salt $Na(NH_4)HPO_4 \cdot 4H_2O$ is used.

$$\text{Na(NH}_4)\text{HPO}_4 \xrightarrow{\Delta} \underset{\text{Transparent bead}}{\text{NaPO}_3} + \text{H}_2\text{O}\uparrow + \text{NH}_3\uparrow$$

$$\text{NaPO}_3 + \text{CoO} \longrightarrow \underset{\text{Blue bead}}{\text{NaCoPO}_4}$$

Colours of some ions shown in microcosmic bead test are as follows

Colour Obtained in Microcosmic Salt Bead Test

Oxidising flame	Reducing flame	Metal
Green when hot, blue when cold	Colourless when hot, red when cold	Cu
Yellow or red-brown when hot, yellow when cold	Yellow when hot, colourless to green when cold	Fe
Green, hot and cold	Green, hot and cold	Cr
Violet, hot and cold	Colourless, hot and cold	Mn
Blue, hot and cold	Blue, hot and cold	Co
Brown, hot and cold	Grey when cold	Ni
Yellow, hot and cold	Green when cold	V
Yellow when hot, yellow green when cold	Green hot and cold	U
Pale yellow when hot, colourless when cold	Green when hot, blue when cold	W
Colourless, hot and cold.	Yellow when hot, violet when cold	Ti

10. Sodium Carbonate Bead Test

The sodium carbonate bead is prepared by fusing small quantity of sodium carbonate on a platinum wire loop in the Bunsen flame, a white opaque bead is formed. If this is moistened, dipped into a little KNO_3 and then into a small quantity of the given salt and the whole is heated in the oxidising flame, a coloured bead is formed. For example.

$$MnO + Na_2CO_3 + O_2 \xrightarrow{\Delta} \underset{\substack{\text{Sodium manganate}\\ \text{(Green bead)}}}{Na_2MnO_4} + CO_2\uparrow$$

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 \xrightarrow{\Delta} \underset{\substack{\text{Sodium chromate}\\ \text{(Yellow bead)}}}{4Na_2CrO_4} + 4CO_2\uparrow$$

Wet Tests

- In wet analysis, the substance is first dissolved in water to bring it in solution form and is analysed for acid and basic radicals.
- In the analysis of inorganic salt mixture, first acid radicals are analysed and then basic radicals.

Analysis of Acid Radicals

Following sequence is adopted to analyse the acid radical

1. Analysis of First Group Anions (CO_3^{2-}, S^{2-}, NO_2^-)

Acidic radicals or anions of first group, when treated with dil. H_2SO_4, (Group reagent) evolve gases with characteristic colour and smell. On the basis of gases released, anions are identified.

I. **Test for** CO_3^{2-}

Experiment	Observation	Inference
Take mixture in a dry test tube and add dil. HCl or H_2SO_4. Warm gently	Brisk effervescence with the evolution of colourless and odourless gas (CO_2)	may be CO_3^{2-}
Pass the evolved gas into lime water [$Ca(OH)_2$]	Lime water turns milky	CO_3^{2-} confirmed
Pass excess lime water to the evolved gas	Milkiness disappears	CO_3^{2-} confirmed

Reactions Involved in the Test of Carbonate (CO_3^{2-})

- $Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + \underset{\substack{\text{Colourless,}\\ \text{odourless}\\ \text{gas}}}{CO_2\uparrow}$
- $Ca(OH)_2 + CO_2 \longrightarrow \underset{\substack{\text{Calcium carbonate}\\ \text{(milky)}}}{CaCO_3\downarrow} + H_2O$
- $CaCO_3 + H_2O + CO_2(\text{excess}) \longrightarrow \underset{\substack{\text{Calcium bicarbonate}\\ \text{(colourless)}}}{Ca(HCO_3)_2}$

II. **Tests for** S^{2-}

Experiment	Observation	Inference
Take mixture in a dry test tube and add dil. HCl or H_2SO_4 and warm gently	A colourless gas (H_2S) with smell of rotten eggs evolved	may be S^{2-}
Bring filter paper dipped in lead acetate over the mouth of test tube	Filter paper turns black due to formation of PbS	S^{2-} confirmed

Reactions Involved in the Test of Sulphide (S^{2-})

(i) $Na_2S + H_2SO_4 \longrightarrow H_2S + Na_2SO_4$

(ii) $(CH_3COO)_2Pb + H_2S \longrightarrow \underset{\text{Black}}{PbS\downarrow} + 2CH_3COOH$

III. **Tests for Nitrate** (NO_3^-)

Experiment	Observation	Inference
Take mixture in a dry test tube and add dil. HCl. Warm gently	Brown fumes (NO_2) with pungent odour are evolved	May be NO_2^-
Take filter paper dipped in (starch + KI) solution, on the mouth of test tube	Evolved gas turns filter paper blue	NO_2^- confirmed
Add 2-3 drops of KI and starch solution in the test tube	Deep blue or violet colour appears	NO_2^- confirmed

Reactions Involved in the Test of Nitrite (NO_2^-)

- $$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$$
  $$3HNO_2 \longrightarrow HNO_3 + 2NO\uparrow + H_2O$$
  $$2NO + O_2 \longrightarrow \underset{\text{(Brown)}}{2NO_2\uparrow}$$
- $$2KI + 2NO_2 \longrightarrow 2KNO_2 + I_2$$
  $$I_2 + \text{Starch} \longrightarrow \text{Blue colour}$$

2. **Analysis of Second Group Anions**

(Cl^-, Br^-, I^-, NO_3^-)

Acidic radicals or anions of second group give no response with dil. acids. However, with conc. acids (conc. H_2SO_4 group reagent), they evolve gases with characteristic colour and smell, thus can be identified by using conc. acids.

I. **Tests for Chloride** (Cl^-)

Experiment	Observation	Inference
Heat the mixture with 1-2 mL conc. H_2SO_4 in a dry test tube.	A colourless, pungent gas (HCl) is evolved.	May be Cl^-
Bring a glass rod dipped in NH_4OH near the mouth of test tube.	White dense fumes of NH_4Cl is evolved.	Cl^- confirmed
Heat the mixture with conc. H_2SO_4 and MnO_2 in a dry test tube.	Greenish-yellow (Cl_2) pungent gas is evolved.	Cl^- confirmed
Chromyl chloride test • Heat the mixture with solid $K_2Cr_2O_7$ and conc. H_2SO_4.	Orange-yellow vapours of chromyl-chloride (CrO_2Cl_2) are evolved.	Cl^- confirmed
• Collect evolved vapours in a test tube containing NaOH. Acidified it with acetic acid and add lead acetate solution.	A yellow ppt or solution of lead chromate is formed.	

Reactions Involved in the Test of Chloride (Cl^-)

- $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + \underset{\text{Pungent smelling gas}}{HCl\uparrow}$
- $HCl + NH_4OH \longrightarrow \underset{\text{White fumes}}{NH_4Cl\uparrow} + H_2O$
- $2NaCl + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + \underset{\text{Yellowish-green}}{Cl_2\uparrow}$
- **Chromyl chloride test**

$$4NaCl + K_2Cr_2O_7 + \underset{\text{(Conc.)}}{3H_2SO_4} \longrightarrow \underset{\substack{\text{Chromyl chloride}\\ \text{(orange yellow gas)}}}{2CrO_2Cl_2} + 2Na_2SO_4 + K_2SO_4 + 3H_2O$$

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

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

Note If a mixture contains chlorates, chromyl chloride test for chloride anion should not be performed because chlorates on reaction with H_2SO_4 form chlorine dioxide gas which dissolves in H_2SO_4 and form highly explosive orange yellow solution.

$$3KClO_3 + 3H_2SO_4 \longrightarrow 2ClO_2\uparrow + ClO_4^- + 3SO_4^{2-} + 4H^+ + 3K^+ + H_2O$$

II. **Test for Bromide** (Br^-)

Experiment	Observation	Inference
Heat the mixture with 1-2 mL conc. H_2SO_4 in a dry test tube.	A colourless, pungent gas (HBr) or sometimes brown fumes are evolved.	May be Br^-
Heat the mixture with MnO_2 and conc. H_2SO_4.	Red brown vapour of Br_2 evolved.	Br^- confirmed
To the solution of mixture in dil. HNO_3, add $AgNO_3$ solution.	A pale yellow ppt. of AgBr is formed (hardly soluble in NH_4OH).	Br^- confirmed

Reactions Involved in the Test of Bromide (Br^-)

- $NaBr + \underset{\text{Conc.}}{H_2SO_4} \longrightarrow NaHSO_4 + HBr\uparrow$

  $2HBr + H_2SO_4(\text{conc.}) \longrightarrow 2H_2O + SO_2\uparrow + \underset{\text{Reddish brown}}{Br_2\uparrow}$
- $2NaBr + MnO_2 + 3H_2SO_4 \longrightarrow 2NaHSO_4 + MnSO_4 + 2H_2O + \underset{\text{Reddish brown}}{Br_2\uparrow}$
- $NaBr + AgNO_3 \longrightarrow \underset{\text{Pale yellow}}{AgBr\downarrow} + NaNO_3$
- $AgBr + 2NH_4OH \longrightarrow \underset{\substack{\text{Diammine silver (I)}\\ \text{bromide}\\ \text{(hardly soluble)}}}{[Ag(NH_3)_2]Br} + 2H_2O$

III. **Test for Iodide** (I^-)

Experiment	Observation	Inference
Heat the mixture with 1-3 mL conc. H_2SO_4 in a dry test tube.	Dark violet fumes (I_2) are evolved.	May be I^- may
Heat the mixture with MnO_2 and conc. H_2SO_4.	Violet vapours in excess are evolved.	May be I^-
Bring a paper dipped in starch solution on the mouth of test tube.	Paper turns blue.	I^- confirmed
To the solution of mixture in dil. HNO_3, add $AgNO_3$ solution.	A yellow ppt. of AgI is formed (insoluble in NH_4OH).	I^- confirmed

Reactions Involved in the above Test of Iodide (I^-)

- $NaI + \underset{\text{Conc.}}{H_2SO_4} \longrightarrow HI + NaHSO_4$

  $H_2SO_4 + 2HI \longrightarrow \underset{\substack{\text{Violet}\\ \text{vapours}}}{I_2\uparrow} + SO_2 + 2H_2O$
- $2NaI + MnO_2 + 3H_2SO_4 \longrightarrow I_2\uparrow + 2NaHSO_4 + MnSO_4 + 2H_2O$
- $I_2 + \text{Starch} \longrightarrow \text{Blue colour}$
- $NaI + AgNO_3 \longrightarrow \underset{\text{Yellow}}{AgI\downarrow} + NaNO_3$
- $AgI + NH_4OH \longrightarrow \underset{\substack{\text{Yellow ppt.}\\ \text{insoluble}}}{[Ag(NH_3)_2]I} + H_2O$

IV. **Tests for Nitrate** (NO_3^-)

Experiment	Observation	Inference
Heat the mixture with 1-2 mL conc. H_2SO_4 in a dry test tube.	Pungent light brown gas (NO_2) is evolved.	May be NO_3^-
Heat the mixture with copper turnings and conc. H_2SO_4.	Deep brown fumes (NO_2) in excess are evolved.	May be NO_3^-
Perform ring test To the solution of mixture in dil. HCl, add freshly prepared solution of $FeSO_4$. Shake well gradually and add conc. H_2SO_4 by the sides of test tube.	A brown ring of $FeSO_4 \cdot NO$ is formed at the junction of two liquids.	NO_3^- confirmed

Reactions Involved in the above Test of Nitrate (NO_3^-)

- $NaNO_3 + \underset{\text{(Conc.)}}{H_2SO_4} \longrightarrow NaHSO_4 + HNO_3$

$$4HNO_3 \longrightarrow \underset{\text{Brown}}{4NO_2} \uparrow + O_2 \uparrow + 2H_2O$$

- $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO \uparrow + 4H_2O$

$$2NO + O_2 \longrightarrow 2NO_2 \uparrow$$

- **Ring test**

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

$$FeSO_4 + NO \longrightarrow \underset{\substack{\text{Ferrous nitroso sulphate} \\ \text{(brown ring)}}}{FeSO_4 \cdot NO}$$

3. Analysis of Third Group Anion (SO_4^{2-})

Third group radical is identified on the basis of precipitate obtained.

Tests for Sulphate (SO_4^{2-})

Radical or anion	Experiment	Observation	Inference
Sulphate (SO_4^{2-})	In the solution of mixture, add $BaCl_2$ solution.	A curdy white ppt. ($BaSO_4$) is formed (insoluble in all conc acids).	May be SO_4^{2-}
	In the solution of mixture, add lead acetate solution.	White ppt. of $PbSO_4$ is formed.	SO_4^{2-} confirmed

Reactions Involved in the above Test of Sulphate (SO_4^{2-})

- $Na_2SO_4 + BaCl_2 \longrightarrow \underset{\text{White}}{BaSO_4} \downarrow + 2NaCl$
- $(CH_3COO)_2Pb + Na_2SO_4 \longrightarrow \underset{\text{White}}{PbSO_4} \downarrow + 2CH_3COO\overset{-\ +}{Na}$

Analysis of Basic Radical (Cations)

Basic radicals have been classified into six groups on the basis of the solubility products of their salts with group reagent. The radicals have been grouped in the order of increasing solubility product.

Basic radicals are classified into following groups

Classification of Basic Radicals into Groups Based on K_{sp} Values

Group	Basic radicals	Group reagent	Precipitate as	Explanation
(I)	Ag^+, Hg_2^{2+}, Pb^{2+}	Dil. HCl	Chlorides ($AgCl$, Hg_2Cl_2, $PbCl_2$)	K_{sp} values of chlorides are low, hence precipitated. Other have higher K_{sp} values, hence not precipitated.
(II)	Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+} Bi^{3+}, Sb^{3+}, Sn^{2+}, As^{3+}	H_2S gas in presence of dil. HCl	Sulphides (CuS, As_2S_3 etc.)	K_{sp} values of IInd group sulphides are low, hence precipitated by low $[S^{2-}]$ ion. HCl (due to H^+ common ion) decreases the ionisation of weak acid H_2S which gives low $[S^{2-}]$ ions. Hence, group II sulphides are precipitated while others with high K_{sp} values are not precipitated.
(III)	Al^{3+}, Cr^{3+}, Fe^{3+}	NH_4OH in presence of NH_4Cl	Hydroxides [$Al(OH)_3$ etc.]	K_{sp} values of IIIrd group hydroxides are low. NH_4Cl decreases ionisation of weak NH_4OH due to common ion effect. Low $[OH^-]$ is only sufficient to precipitate group III cations as their hydroxides.
(IV)	Zn^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}	H_2S in ammoniacal medium	Sulphides (ZnS, NiS etc.)	K_{sp} values of sulphides of group IV are high. Ionisation of H_2S increases in basic medium. Hence, group IV cations are precipitated as sulphides due to increasing $[S^{2-}]$.
(V)	Ca^{2+}, Ba^{2+}, Sr^{2+}	$(NH_4)_2CO_3 + NH_4Cl$	Carbonates ($CaCO_3$, $BaCO_3$, $SrCO_3$)	K_{sp} values of carbonates are less than that of group VI (Mg^{2+}) hence, precipitated before Mg^{2+}.
(VI)	Mg^{2+} (Na^+, K^+) also included	$NH_4OH + Na_2HPO_4$ (only for Mg^{2+})	White precipitate ($MgHPO_4$)	
Zero	NH_4^+	Dilute NaOH	NH_3 gas is evolved	

Preparation of Original Solution

To prepare transparent solution of salt, following solvents are used strictly in the order given below

(i) Cold water	(ii) Hot water
(iii) Dilute HCl	(iv) Conc. HCl

Note HNO_3 or H_2SO_4 cannot be used to prepare original solution because both are oxidising agents.

1. **Analysis of Group I Cations** (Basic Radicals)

In cold original solution, dilute HCl is added drop by drop. Formation of white precipitate indicates the presence of group I. Cations of group I are precipitated as chlorides such as AgCl, $PbCl_2$ and Hg_2Cl_2. Among these chlorides, only $PbCl_2$ is soluble in hot water. Hence, hot filtrate contain Pb^{2+} ions.

Test for Lead

Experiment	Observation	Inference
Hot filtrate is taken in the test tube and add K_2CrO_4.	Yellow ppt. of $PbCrO_4$ is obtained which is soluble in NaOH but insoluble in CH_3COOH.	Indicates the presence of Pb^{2+}.
Hot filtrate is taken in the test tube and add KI	Yellow ppt. of PbI_2 is formed.	Pb^{2+} confirmed
Dilute H_2SO_4 is added to hot filtrate and mixture is cooled.	White precipitate of $PbSO_4$ is obtained which is soluble in CH_3COONH_4 solution.	Pb^{2+} confirmed

Reactions Involved in the above Tests of Pb^{2+}

- $\underset{\text{(Cold O.S.)}}{Pb^{2+}} + \underset{\text{From HCl}}{2Cl^-} \longrightarrow \underset{\text{White ppt.}}{PbCl_2\downarrow}$

$PbCl_2$ is soluble in hot water, hence filtrate contains $PbCl_2$.

- $\underset{\text{(Hot and soluble)}}{PbCl_2} + K_2CrO_4 \longrightarrow \underset{\text{Yellow ppt.}}{PbCrO_4\downarrow} + 2KCl$

$$PbCrO_4 + 4NaOH \longrightarrow \underset{\substack{\text{Sodium plumbite}\\ \text{(soluble)}}}{Na_2PbO_2} + Na_2CrO_4$$

- $PbCl_2 + 2KI \longrightarrow \underset{\text{Yellow}}{PbI_2} + 2KCl$
- $PbCl_2 + H_2SO_4 \longrightarrow \underset{\text{White ppt.}}{PbSO_4\downarrow} + 2HCl$

$$PbSO_4 + 2CH_3COONH_4 \longrightarrow \underset{\text{Soluble}}{(CH_3COO)_2Pb} + (NH_4)_2SO_4$$

2. **Analysis of Group II Cations**

Add dilute HCl in filtrate of group I and pass H_2S gas in warm solution. Formation of coloured ppt. indicates the presence of group II cations.

Sulphides of group II B cations (As_2S_3, SnS, Sb_2S_3) are soluble in yellow ammonium sulphide while sulphides of group II A (PbS, CdS, CuS, Bi_2S_3) cations are soluble in HNO_3 (HgS is soluble in *aqua-regia*).

Tests for Copper

Experiment	Observation	Inference
Take black ppt. of CuS in the test tube and add HNO_3.	Blue coloured solution is obtained	It indicates the presence of Cu^{2+}
Divide blue solution obtained into three parts.		
(i) Add CH_3COOH and $K_4[Fe(CN)_6]$ to first part.	Chocolate brown ppt. is formed	Cu^{2+} confirmed
(ii) Add aqueous NH_3 (excess) in second part of blue solution.	Deep blue solution is obtained	Cu^{2+} confirmed
(iii) Add KSCN is the third part of blue solution.	Black ppt. is obtained	Cu^{2+} confirmed

Reactions Involved in the above Test of Cation (Cu^{2+})

- $\underset{\substack{\text{Black}\\ \text{ppt.}}}{3CuS} + 8HNO_3 \longrightarrow \underset{\text{Soluble blue}}{3Cu(NO_3)_2} + 2NO + 3S + 4H_2O$
- $Cu(NO_3)_2 + 2CH_3COOH \longrightarrow (CH_3COO)_2Cu + 2HNO_3$

$$2(CH_3COO)_2Cu + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Chocolate brown ppt.}}{Cu_2[Fe(CN)_6]} + 4CH_3COOK$$

- $Cu^{2+} + 4NH_3(\text{excess}) \longrightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4]^{2+}}$
- $Cu(NO_3)_2 + 2KSCN \longrightarrow \underset{\text{Black ppt.}}{Cu(SCN)_2} + 2KNO_3$

3. **Analysis of Group III Cations**

(Fe^{3+}, Al^{3+}, Cr^{3+})

Add few drops of conc. HNO_3 in the filtrate of group II to remove H_2S. Add NH_4Cl and NH_4OH. Group III cations (if present) are precipitated as their hydroxides. [($Fe(OH)_3$-red brown ppt. $Cr(OH)_3$ dirty green ppt. $Al(OH)_3$-white gelatinous ppt).

I. **Tests for Aluminium** (Al^{3+})

Experiment	Observation	Inference
Add NaOH solution in excess to white gelatinous ppt.	White gelatinous ppt. dissolves due to the formation of sodium meta-aluminate.	It indicates the presence of Al^{3+}
In soluble meta-aluminate add NH_4Cl and boil	White gelatinous ppt. of $Al(OH)_3$ reappears	Al^{3+} confirmed

Reactions Involved in the above Test of Cation Al^{3+}

- $\underset{\text{White ppt.}}{Al(OH)_3} + NaOH \longrightarrow \underset{\substack{\text{Sodium meta-aluminate}\\ \text{(soluble)}}}{NaAlO_2} + 2H_2O$
- $NaAlO_2 + NH_4Cl + H_2O \xrightarrow{\Delta} NaCl + \underset{\substack{\text{White}\\ \text{gelatinous}}}{Al(OH)_3} + NH_3$

II. **Tests for Iron** (Fe^{3+})

Experiment	Observation	Inference
Add dilute HCl in red brown ppt. and divide it into two parts.	Precipitate dissolves	Fe^{3+} confirmed
• Add $K_4[Fe(CN)_6]$ in the first part of the above solution.	Dark blue colour is obtained	Fe^{3+} confirmed
• Add KCNS in the second part of the solution.	Dark (Blood) red colour is obtained	Fe^{3+} confirmed

Reactions Involved in the above Test of Cation Fe^{3+}

- $Fe(OH)_3 + \underset{\text{Reddish brown ppt.}}{3HCl} \longrightarrow \underset{\text{Soluble}}{FeCl_3} + 3H_2O$
- $4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\substack{\text{Ferric ferrocyanide}\\ \text{(dark blue colour)}}}{Fe_4[Fe(CN)_6]_3} + 12KCl$
- $FeCl_3 + \underset{\substack{\text{Potassium}\\ \text{sulphocyanide}}}{KCNS} \longrightarrow \underset{\substack{\text{Ferrithiocyanate}\\ \text{(blood red colour)}}}{[Fe(CNS)]Cl_2} + KCl$

4. **Analysis of Group IV Cations**

(Zn^{2+}, Ni^{2+}, $CO^{2+}$and Mn^{2+})

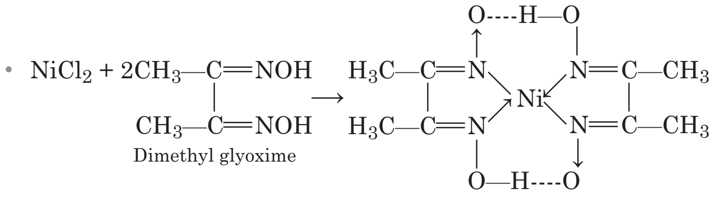
Add NH_4OH to the filtrate of group III and pass H_2S. In alkaline medium, H_2S is highly ionised so, concentration of S^{2-} is high. Due to this, group IV cations are precipitated as sulphides (ZnS, MnS, CoS and NiS).

I. **Tests for Nickel**

Experiment	Observation	Inference
Dissolve black ppt of NiS in *aqua-regia* (3 part conc. HCl + 1 part conc. HNO_3) and divide it into two parts.	Soluble chloride is formed	It indicates the presence of Ni^{2+}
• Add NH_4OH and dimethyl glyoxime to the solution	Cherry red ppt.	Ni^{2+} confirms
• Add potassium cyanide solution and heat and add $NaOH/Br_2$ water and again heat.	Black ppt. is obtained	Ni^{2+} confirms

Reactions Involved in the Test of Cation Ni^{2+}

- $3NiS + \underbrace{6HCl + 2HNO_3}_{\textit{Aqua-regia}} \longrightarrow 3NiCl_2 + 2NO + 3S + 4H_2O$



- $NiCl_2 + 2CH_3—C{=}NOH \,/\, CH_3—C{=}NOH$

Dimethyl glyoxime

Cherry red ppt.
(Dimethyl glyoximate)

- $NiCl_2 + 4KCN \longrightarrow \underset{\substack{\text{Potassium}\\ \text{nickelocyanide}}}{K_2[Ni(CN)_4]} + 2KCl$

$$2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O$$

$$2K_2[Ni(CN)_4] + NaOBr + 4NaOH \longrightarrow Ni_2O_3 + 4KCN + 4NaCN + NaBr + 2H_2O$$

II. **Tests for Zinc**

Experiment	Observation	Inference
Dissolve white ppt. of ZnS in dil. HCl and divide it into two parts.	Soluble chloride is formed.	It indicates the presence of Zn^{2+}.
• Add NaOH in the solution. White ppt. is obtained which is soluble in excess of NaOH.	White ppt. of ZnS reappears on passing H_2S into soluble sodium zincate solution	Zn^{2+} confirms
• Solution is acidified with acetic acid and add $K_4[Fe(CN)_6]$	Bluish white ppt. is obtained	Zn^{2+} confirms

Reactions Involved in the Test of Cation Zn^{2+}

- $ZnS + 2HCl \longrightarrow ZnCl_2 + H_2S$
- $ZnCl_2 + 2NaOH \longrightarrow \underset{\text{White ppt.}}{Zn(OH)_2\downarrow} + 2NaCl$

$$Zn(OH)_2 + 2NaOH \longrightarrow \underset{\substack{\text{Sodium zincate}\\ \text{(soluble)}}}{Na_2ZnO_2} + 2H_2O$$

$$Na_2ZnO_2 + H_2S \longrightarrow 2NaOH + \underset{\text{White ppt.}}{ZnS\downarrow}$$

- $2ZnCl_2 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Bluish white ppt.}}{Zn_2[Fe(CN)_6]\downarrow} + 4KCl$

5. **Analysis of Group V Cations**

(Ba^{2+}, Sr^{2+}, Ca^{2+})

Boil off H_2S from the filtrate of group IV and add NH_4OH and $(NH_4)_2CO_3$.

Formation of white ppt. indicates the presence of group V cations. Group V cations are precipitated as their carbonates ($CaCO_3$, $BaCO_3$ and $SrCO_3$).

I. **Tests for Barium**

Experiment	Observation	Inference
Dissolve the ppt. in acetic acid and heat it gently and add potassium chromate solution and again heat.	Yellow ppt. appears	Ba^{2+} confirms

Reactions Involved in the Test of Cation Ba^{2+}

- $\underset{\text{White ppt.}}{BaCO_3} + 2CH_3COOH \xrightarrow{\Delta} (CH_3COO)_2Ba + H_2O + CO_2$
- $(CH_3COO)_2Ba + K_2CrO_4 \longrightarrow \underset{\substack{\text{Barium chromate}\\ \text{(yellow ppt.)}}}{BaCrO_4\downarrow} + 2CH_3COOK$

II. **Tests for Calcium**

Experiment	Observation	Inference
Dissolve the ppt. in acetic acid ,add ammonium oxalate solution (excess) and heat.	White ppt. appears	Ca^{2+} confirmed
Acidified white ppt. obtained above by adding dilute CH_3COOH and add $KMnO_4$ solution drop wise and HCl	Pink colour of $KMnO_4$ disappears	Ca^{2+} confirmed

Reactions Involved in the Test of Cation Ca^{2+}

- $\underset{\text{White ppt.}}{CaCO_3} + 2CH_3COOH \xrightarrow{\Delta} (CH_3COO)_2Ca + H_2O + CO_2$
- $(CH_3COO)_2Ca + (NH_4)_2C_2O_4 \longrightarrow \underset{\text{White ppt.}}{CaC_2O_4 \downarrow} + 2CH_3COONH_4$
- $5CaC_2O_4 + \underset{\text{Pink}}{2KMnO_4} + 16HCl \longrightarrow 5CaCl_2 + \underset{\text{Colourless}}{2MnCl_2} + 10CO_2 + 8H_2O + 2KCl$

6. Analysis of Group VI Cation (Mg^{2+})

Tests for Ammonium

Experiment	Observation	Inference
Filtrate of group V is heated with NH_4OH and Na_2HPO_4.	A fine crystalline ppt. on scratching the side of the test tube.	Mg^{2+} confirmed

Reactions Involve in the Test of Cation Mg^{2+}

$$MgCl_2 + \underset{\substack{\text{Disodium}\\\text{hydrogen}\\\text{phosphate}}}{Na_2HPO_4} + NH_4OH \longrightarrow \underset{\substack{\text{Magnesium ammonium}\\\text{phosphate (white ppt.)}}}{Mg(NH_4)PO_4} + 2NaCl + H_2O$$

7. Analysis of Zero Group Cation, (NH_4^+)

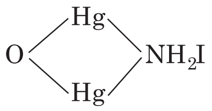
Ammonium salts are decomposed by alkali and NH_3 is liberated which can be identified by a number of methods.

Tests for Ammonium

Experiment	Observation	Inference
Take small amount of mixture in the test tube and heat it with NaOH solution.	Smell of ammonia	NH_4^+ confirmed
Bring the moistened glass rod with conc. HCl near the mouth of the test tube.	White fumes are formed	NH_4^+ confirmed
Take small amount of salt in the test tube and add NaOH and heat. Add Nessler's reagent to the solution.	Brown ppt. is obtained	NH_4^+ confirmed

Reactions Involved in the Tests of Cation NH_4^+

- $\underset{\text{From mixture}}{NH_4Cl} + NaOH \xrightarrow{\Delta} NH_3(g) + NaCl + H_2O$
- $NH_3(g) + HCl \longrightarrow \underset{\substack{\text{Ammonium}\\\text{chloride}\\\text{(white fumes)}}}{NH_4Cl}$
- $NH_3 + 3\ NaOH + \underset{\substack{\text{Nessler's}\\\text{reagent}}}{2K_2HgI_4} \longrightarrow$



$$O\langle^{Hg}_{Hg}\rangle NH_2I + 4KI + 3NaI + 2H_2O$$

Iodide of Millon's base (brown ppt.)

Practice Exercise

ROUND I Topically Divided Problems

Qualitative Organic Analysis

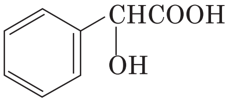
1. In organic analysis, the reagent 2, 4-dinitrophenyl hydrazine is used for the detection of which of the following functional groups ?

(a) Alcohol (b) Acid
(c) Aldehyde (d) Amines

2. An organic compound gave positive iodoform and Tollen's tests. The organic compound is

(a) CH_3CH_2OH (b) $CH_3CH_2CH_2CHO$
(c) CH_3CHO (d) CH_3COCH_3

3. A compound liberates CO_2 with $NaHCO_3$ and also gives colour with neutral $FeCl_3$ solution. The compound can be

(a)


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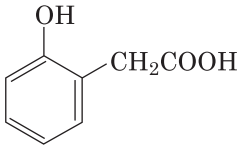
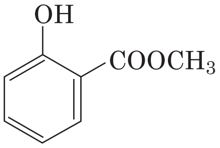
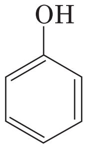


(c)


(d)


4. The reagent which does not react with both, acetone and benzaldehyde is ***(NCERT Exemplar)***

(a) sodium hydrogen sulphite
(b) phenyl hydrazine
(c) Fehling's solution
(d) Grignard reagent

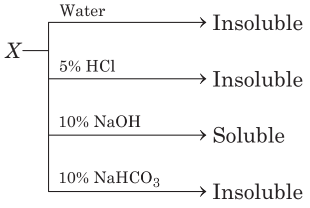
5. Phenol can be distinguished from ethanol by the reactions with ***(NCERT Exemplar)***

(a) Br_2/CCl_4 (b) Na
(c) neutral $FeCl_3$ (d) All of these

6. Compound '*A*' reacts with $CHCl_3$ and KOH gives offensive smelling compound. Compound '*A*' can be

(a) quaternary aliphatic amine
(b) primary aromatic amine
(c) secondary amine
(d) tertiary amine

7. An organic compound *X* showing the following solubility profile is



(a) *o*-toluidine (b) oleic acid
(c) *m*-cresol (d) benzamide

Chemistry Involved in the Preparation of Compounds

8. During the preparation of acetanilide from aniline a small amount of zinc is added to the reaction mixture because

(a) zinc induces the precipitation
(b) zinc prevents the reduction of aniline during the reaction
(c) zinc reduces the coloured impurities in the aniline and also prevents its oxidation during the reaction
(d) zinc forms a white crystalline complex with aniline

9. In the preparation of *p*-nitro acetanilide from aniline, nitration is not done by nitrating mixture (a mixture of conc. H_2SO_4 and conc. HNO_3) because

(a) on nitration it gives *o*-nitro acetanilide
(b) it gives a mixture of *o*-and *p*-nitroaniline
(c) $-NH_2$ group gets oxidised
(d) it forms a mixture of *o*-and *p*-nitro acetanilide

10. Which of the following compounds cannot used in preparation of iodoform ?

(a) CH_3CHO (b) CH_3COCH_3
(c) HCHO (d) 2-propanol

11. Which of the following statement is wrong about aniline yellow?

(a) It is carcinogenic
(b) It is also called *p*-aminoazobenzene
(c) It is an acid dye
(d) It is also called 4-phenylazoaniline

12. Which of the following substances is not used in the preparation of Mohr's salt ?

(a) Ferrous sulphate (b) Ammonium sulphate
(c) Dil. sulphuric acid (d) All are used

Chemistry Involved in the Titrimetric Analysis

13. Phenolphthalein is an indicator for acid-base titration, it exists as

(a) benzenoid form in acid and quinonoid form in basic solution
(b) quinonoid form in acid and benzenoid form in basic solution
(c) quinonoid form in both
(d) benzenoid form in both

14. In the titration of oxalic acid *vs* potassium permanganate, potassium permanganate acts as

(a) external indicator (b) self indicator
(c) reductant (d) Both (b) and (c)

15. In the reaction of $KMnO_4$ with an oxalate in acidic medium, MnO_4^- is reduced to Mn^{2+} and $C_2O_4^{2-}$ is oxidised to CO_2. Hence, 50 mL of 0.04 M $KMnO_4$ is equivalent to

(a) 100 mL of 0.1 M $H_2C_2O_4$ (b) 50 mL of 0.2 M $H_2C_2O_4$
(c) 50 mL of 0.1 M $H_2C_2O_4$ (d) 25 mL of 0.1 $H_2C_2O_4$

16. 0.5 g mixture of $K_2Cr_2O_7$ and $KMnO_4$ was treated with excess of KI in acidic medium. I_2 liberated required 100 cm^3 of 0.15 N $Na_2S_2O_3$ solution for titration. The percentage amount of $K_2Cr_2O_7$ in the mixture is

(a) 85.36% (b) 14.64% (c) 58.63% (d) 26.14%

17. Which of the following will oxidise 126 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) in acidic medium ?

(a) 1/3 mole of $K_2Cr_2O_7$ (b) 2 mole of $K_2Cr_2O_7$
(c) 1/3 mole of $KMnO_4$ (d) 5/2 mole of $KMnO_4$

18. The titration of Mohr's salt *vs* $KMnO_4$ is an example of redox titration. In this titration, $KMnO_4$ oxidises only ferrous salt to the ferric salt (no effect on other ions) but we can not use ferrous sulphate in place of Mohr's salt because

(a) it is less stable than Mohr's salt
(b) in air it is oxidised to ferric sulphate
(c) in air it loses water of crystallisation
(d) All of the above

19. Which of the following statements is not true ?

(a) An acidified solution of $K_2Cr_2O_7$ liberates iodine from iodides
(b) In acidic solution, dichromate ions are converted to chromate ions
(c) $(NH_4)_2Cr_2O_7$ on heating undergo exothermic decomposition to give Cr_2O_3
(d) Potassium dichromate is used as a titrant for estimation of Fe^{2+} ions

Analytical Chemistry

20. While titrating dilute HCl solution with aqueous NaOH, which of the following will not be required?

(a) Pipette and distilled water ***(JEE Main 2020)***
(b) Burette and porcelain tile
(c) Bunsen burner and measuring cylinder
(d) Clamp and phenolphthalein

21. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after sometime because ***(NCERT Exemplar)***

(a) CO_2 is formed as the products
(b) reaction is exothermic
(c) MnO_4^- catalyses the reaction
(d) Mn^{2+} acts as auto-catalyst

22. Why is HCl not used to make the medium acidic in oxidation reaction of $KMnO_4$ in acidic medium? ***(NCERT Exemplar)***

(a) Both HCl and $KMnO_4$ act as oxidising agent
(b) $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent
(c) $KMnO_4$ is a weaker oxidising agent than HCl
(d) $KMnO_4$ acts as a reducing agent in the presence of HCl

23. 100 mL of HCl + 35 mL of NaOH, colour of methyl orange in the solution will be

(a) red
(b) yellow
(c) can't be predicted
(d) methyl orange is not suitable indicator

Chemical Principles Involved in the Qualitative Salt Analysis

24. Which statement is correct?

(a) Fe^{2+} gives brown colour with ammonium thiocyanate
(b) Fe^{2+} gives blue precipitate with potassium ferricyanide
(c) Fe^{3+} gives brown colour with potassium ferricyanide
(d) Fe^{3+} gives red colour with potassium ferrocyanide

25. An aqueous solution of colourless metal sulphate *M* gives a white precipitate with NH_4OH. This was soluble in excess of NH_4OH. On passing H_2S through this solution a white ppt. is formed. The metal *M* in the salt is

(a) Ca (b) Ba (c) Al (d) Zn

26. A white sodium salt dissolves readily in water to give a solution which is neutral to litmus. When silver nitrate solution is added to the solution, a white precipitate is obtained which does not dissolve in dil. HNO_3. The anion could be
(a) CO_3^{2-} (b) Cl^- (c) SO_4^{2-} (d) S^{2-}

27. A laboratory reagent imparts green colour to the flame. On heating with solid $K_2Cr_2O_7$ and conc. H_2SO_4, it evolves a orange red gas. Identify the reagent.
(a) $CaCl_2$ (b) $BaCl_2$
(c) $CuCl_2$ (d) None of these

28. Which reagent can be used to identify nickel ion?
(a) Resorcinol
(b) Dimethyl glyoxime
(c) Diphenyl benzidine
(d) Potassium ferrocyanide

29. Which of the following reagents can be used to distinguish between sodium carbonate and sodium sulphite?
(a) Lime water (b) Baryta water
(c) Acidified $K_2Cr_2O_7$ solution (d) H_2SO_4 solution

30. The gas liberated on treating a mixture of two salts with dil. H_2SO_4 turns lime water milky and turbidity disappears with the passage of excess of gas. The aqueous solution of mixture gives white crystalline ppt. with NaCl solution. The filtrate gives a black precipitate, when H_2S is passed into it. The aqueous solution of mixture on heating gives reddish brown gas and when treated with ammonium hydroxide and excess of disodium hydrogen phosphate gives a white crystalline precipitate. The mixture contains
(a) $CO_3^{2-}, Pb^{2+}, NO_3^{2-}, Mg^{2+}$
(b) $CO_3^{2-}, Pb^{2+}, NO_3^{2-}, Ca^{2+}$
(c) $CO_3^{2-}, Pb^{2+}, Cl^-, Mg^{2+}$
(d) $CO_3^{2-}, Pb^{2+}, Cl^-, Ca^{2+}$

31. In Nessler's reagent for the detection of ammonia the active species is
(a) Hg_2Cl_2 (b) Mg^{2+} (c) Hg_2I_2 (d) HgI_4^{2-}

32. Nessler's reagent is used to detect
(a) CrO_4^{2-} (b) PO_4^{3-}
(c) MnO_4^- (d) NH_4^+

33. $K_4[Fe(CN)_6]$ cannot be used to test
(a) Fe^{3+} (b) Zn^{2+}
(c) Cd^{2+} (d) Cr^{3+}

Chemical Principles Involved in Some Experiments

34. Four samples of acids and bases are taken for an experiment
(1) 100 mL of 1 M NaOH and 100 mL of 1 M HCl
(2) 100 mL of 2 M KOH and 100 mL of 1 M H_2SO_4
(3) 100 mL of 1 M CH_3COOH and 100 mL of 1 M NaOH
(4) 100 mL of 0.5 M KOH and 100 mL of 0.5 M HNO_3
Now for each sample enthalpy of neutralisation is calculated. Now the result shows that
(a) enthalpy of neutralisation calculated in each case is found same
(b) in case (1) and (4), the value of enthalpy of neutralisation is same
(c) in case (1) and (2) and (4) the value of enthalpy calculated is same
(d) the value of enthalpy calculated is different for each sample

35. Match Column I with Column II. *(JEE Main 2021)*

	Column I Test/Reagents/Observation(s)		**Column II** (Species detected)
A.	Lassaigne's test	1.	Carbon
B.	Cu(II) oxide	2.	Sulphur
C.	Silver nitrate	3.	N, S, P, and halogen
D.	The sodium fusion extract gives black precipitate with acetic acid and lead acetate.	4.	Halogen specifically

Codes

	A	B	C	D		A	B	C	D
(a)	3	1	2	4	(b)	1	4	3	2
(c)	3	1	4	2	(d)	1	2	4	3

36. In the kinetic study of reaction of iodide ion with hydrogen peroxide, a known volume of sodium thiosulphate solution is added to
(a) oxidise iodide ion to iodine
(b) reduce iodine to iodide ion
(c) form a soluble blue complex
(d) induce the reaction rate

37. One desires to prepare a positively charged sol of silver iodide. This can be achieved by
(a) adding a little $AgNO_3$ solution to KI solution in slight excess
(b) adding a little KI solution to $AgNO_3$ solution in slight excess
(c) mixing equal volumes of equimolar solutions of $AgNO_3$ and KI
(d) None of the above

38. Leveling bulb is used during experiment to study kinetics of the dissociation of hydrogen peroxide to ensure
(a) uniform pressure difference between the room and the gases in the system
(b) pressure within the reaction vessel is same as that in the room
(c) same temperature as that of room
(d) None of the above

39. In case of weak acid and strong base, the heat of neutralisation is less than 13.7 kcal because some part of heat is utilised in
(a) dissociation of base
(b) association of base
(c) dissociation of acid
(d) association of acid

40. The methods used for the preparation of lyophilic and lyophobic sols are respectively
(a) oxidation and reduction
(b) dissolution in water and peptisation
(c) peptisation and oxidation
(d) All of the above

ROUND II Mixed Bag

1. For the given aqueous reaction which of the statement(s) is false?

$KI + K_3[Fe(CN)_6] \xrightarrow{\text{Dil. } H_2SO_4}$ brownish yellow solution.

$\downarrow ZnSO_4$

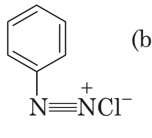
Colourless solution $\longleftarrow$ (White ppt. + brownish yellow filtrate)

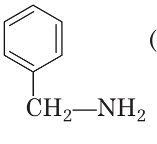
$\downarrow$

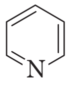
(a) The first reaction is redox reaction
(b) White ppt. is $Zn_3[Fe(CN)_6]_2$
(c) Addition of filtrate to starch solution gives blue colour
(d) White ppt. is soluble in NaOH solution

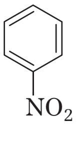
2. An organic compound '*A*' burns with a sooty flame. It is negative towards Tollen's reagent test and positive for Brady's reagent test. The compound '*A*' is
(a) acetophenone
(b) acetone
(c) salicylic acid
(d) benzaldehyde

3. Nitrogen can be estimated by Kjeldahl's method for which of the following compound ? *(JEE Main 2021)*

(a)


(b)


(c)


(d)


4. $CuSO_4$ decolourises on addition of KCN, the product is
(a) $[Cu(CN)_4]^{2-}$
(b) $[Cu(CN)_4]^{3-}$
(c) $Cu(CN)_2$
(d) CuCN

5. 50 mL of 0.5 M oxalic acid is needed to neutralise 25 mL of sodium hydroxide solution. The amount of NaOH in 50 mL of the given sodium hydroxide solution is *[JEE Main 2019]*
(a) 4 g (b) 80 g
(c) 20 g (d) 10 g

6. If Fe^{3+} and Cr^{3+} both are present in group III of qualitative analysis, then distinction can be made by *(AIEEE 2002)*
(a) addition of NH_4OH in the presence of NH_4Cl when only $Fe(OH)_3$ is precipitated
(b) addition of NH_4OH in the presence of NH_4Cl when $Cr(OH)_3$ and $Fe(OH)_3$ both are precipitated and on adding Br_2 water and NaOH, $Cr(OH)_3$ dissolves
(c) precipitate of $Cr(OH)_3$ and $Fe(OH)_3$ as obtained in (b) are treated with conc. HCl when only $Fe(OH)_3$ dissolves
(d) Both (b) and (c)

7. How H_2S is liberated in laboratory?
(a) $FeSO_4 + H_2SO_4$
(b) $FeS +$ dil. H_2SO_4
(c) $FeS +$ conc. H_2SO_4
(d) Elementary $H_2 +$ elementary S

8. On addition of conc. H_2SO_4 to a chloride salt, colourless fumes are evolved but in case of iodide salt, violet fumes come out. This is because
(a) H_2SO_4 reduces HI to I_2 *(NCERT Exemplar)*
(b) HI is of violet colour
(c) HI gets oxidised to I_2
(d) HI changes to HIO_3

9. A brown ring is formed in the ring tests for NO_3^- ion. It is due to the formation of *(NCERT Exemplar)*
(a) $[Fe(H_2O)_5(NO)]^{2+}$ (b) $FeSO_4 \cdot NO_2$
(c) $[Fe(H_2O)_4(NO_2)]^{2+}$ (d) $FeSO_4 \cdot HNO_3$

10. In qualitative analysis, when H_2S is passed through an aqueous solution of salt acidified with dilute HCl, a black ppt. is obtained. On boiling the precipitate with dil. HNO_3, it forms a solution of blue colour. Addition of excess of aqueous solution of NH_3 to this solution gives ***(NCERT Exemplar)***

(a) deep blue ppt. of $Cu(OH)_2$

(b) deep blue solution of $[Cu(NH_3)_4]^{2+}$

(c) deep blue solution of $Cu(NO_3)_2$

(d) deep blue solution of $Cu(OH)_2 \cdot Cu(NO_3)_2$

Numeric Value Questions

11. The volume strength of 8.9 M H_2O_2 solution calculated at 273 K and 1 atm is .... ($R = 0.0821$ L atm K^{-1} mol^{-1}) (rounded off to the nearest integer).

12. 3.92 g of ferrous ammonium sulphate (Mohr's salt) react completely with 50 mL $\frac{N}{10}$ $KMnO_4$ solution.

The percentage purity of the sample is ……… .

13. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralise 10 mL of this solution is ……… mL.

14. In Duma's method of estimation of nitrogen, 0.1840 g of an organic compound gave 30 mL of nitrogen collected at 287 K and 758 mm of Hg pressure.

The percentage composition of nitrogen in the compound is …… .

[Given : Aqueous tension at 287 K = 14 mm of Hg] ***(JEE Main 2021)***

15. Volume of 0.02 M MnO_4^- solution required to oxidise 90.0 mL of 0.1 M Fe^{2+} solution is …… (mL).

16. 25 mL of the given HCl solution requires 30 mL of 0.1 M sodium carbonate solution. The volume of this HCl solution required to titrate 30 mL of 0.2 M aqueous NaOH solution

Answers

Round I

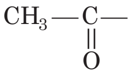
1. (c)	**2.** (c)	**3.** (b)	**4.** (c)	**5.** (a)	**6.** (b)	**7.** (c)	**8.** (c)	**9.** (c)	**10.** (a)
11. (c)	**12.** (d)	**13.** (a)	**14.** (b)	**15.** (c)	**16.** (b)	**17.** (a)	**18.** (d)	**19.** (b)	**20.** (c)
21. (d)	**22.** (b)	**23.** (a)	**24.** (b)	**25.** (d)	**26.** (b)	**27.** (b)	**28.** (b)	**29.** (c)	**30.** (a)
31. (d)	**32.** (d)	**33.** (d)	**34.** (c)	**35.** (c)	**36.** (b)	**37.** (b)	**38.** (b)	**39.** (c)	**40.** (b)

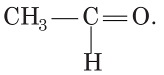
Round II

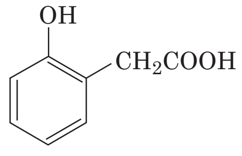
1. (b)	**2.** (a)	**3.** (b)	**4.** (b)	**5.** (a)	**6.** (d)	**7.** (b)	**8.** (c)	**9.** (a)	**10.** (b)
11. (100)	**12.** (50)	**13.** (40)	**14.** (19)	**15.** (40)	**16.** (25)				

Solutions

Round I

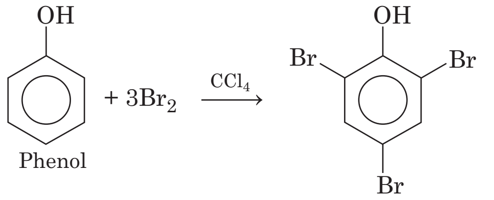
1. 2,4-DNP test in used for the detection of aldehydes.
2. The compound which contains — CHO group, gives positive Tollen's test and the compound with  $CH_3—\underset{\overset{\|}{O}}{C}—$ group gives positive iodoform test.

   Thus, the structure of the compound should be  $CH_3—\underset{\overset{|}{H}}{C}═O$.
3. The compound liberates CO_2 with $NaHCO_3$, so it contains — COOH group and it also gives colour with neutral $FeCl_3$ solution, so it also contains a —OH group directly attached to the benzene ring (i.e. phenol). Hence, the structure of the compound is



4. Benzaldehyde does not reduce Fehling's solution (a distinction from other aldehydes).

   Acetone (ketone) also does not give any test with Fehling's solution.
5. Aqueous or alcoholic solution of phenol with excess of bromine water gives a yellowish white precipitate.



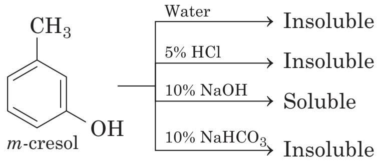
Phenol

2,4,6-tribromophenol

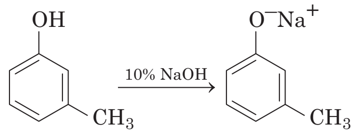
   Phenols on treatment with neutral $FeCl_3$ form violet, red, blue or green coloured complexes.

6. $RNH_2 + CHCl_3 + 3KOH \longrightarrow RNC + 3KCl + 3H_2O$

   (where, R may be alkyl or aryl group)
7. *m*-cresol is the given organic compound that shows the following solubility profile.

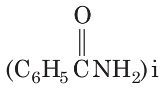


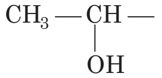
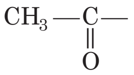
   m-cresol on reaction with 10% NaOH forms 3-methyl sodium phenoxide ion.

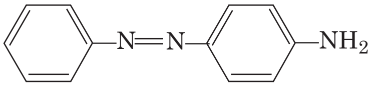


It does not react with H_2O, 5% HCl and 10% $NaHCO_3$.

Oleic acid ($C_{18}H_{34}O_2$) is soluble in 10% NaOH and 10% $NaHCO_3$ due to the presence of —COOH group.

Benzamide  $(C_6H_5\overset{\overset{O}{\|}}{C}NH_2)$ is insoluble in 5% HCl, 10% NaOH and 10% $NaHCO_3$ due to the presence of $—CONH_2$ group. ***o*-toluidine** is soluble in 5%. HCl due to presence of basic group ($—NH_2$) attached to ring.

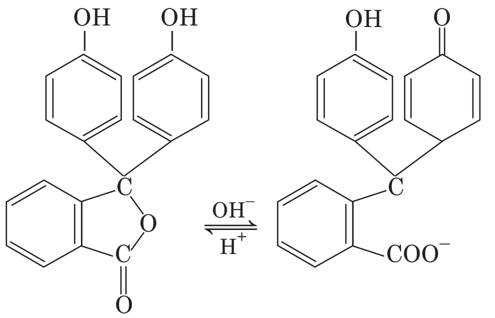
10. Formaldehyde cannot produce iodoform, as only those compound which contains either  $CH_3—\underset{\underset{OH}{|}}{CH}—$ group or  $CH_3—\underset{\overset{\|}{O}}{C}—$ group on reaction with iodine and sodium hydroxide (alkali) yield iodoform.

11. 

Aniline yellow
(*p*-amino azobenzene or 4-phenyl azoaniline)

Statement (c) is incorrect. As it is an a basic dye.

12. $(NH_4)_2SO_4 + FeSO_4 \cdot 7H_2O \longrightarrow \underset{\text{Mohr's salt}}{FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O} + H_2O$
13. Phenolphthalein is colourless in acid solution (benzenoid form) and pink in alkali (basic) solution (quinonoid form).

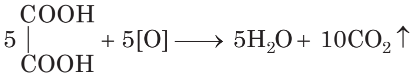


Colourless (acidic medium) benzenoid form

Red (alkaline medium) quinonoid form

14. In the titration of oxalic acid *vs* $KMnO_4$, $KMnO_4$ acts as a oxidant as well as a self indicator.

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



$$5\begin{array}{l}COOH\\|\\COOH\end{array} + 5[O] \longrightarrow 5H_2O + 10CO_2\uparrow$$

15. Equivalent mass of $MnO_4^- = \frac{\text{molar mass}}{7-2} = \frac{\text{molar mass}}{5}$

Equivalent mass of $C_2O_4^{2-} = \frac{\text{molar mass}}{2(4-3)} = \frac{\text{molar mass}}{2}$

Milliequivalent of $KMnO_4 = 50 \times 5 \times 0.04 = 10$ = M. eq. of $H_2C_2O_4 = 50 \times 2 \times 0.1 = 10$.

16. Let the amount of $K_2Cr_2O_7$ in the mixture be x g, then amount of $KMnO_4$ will be $(0.5 - x)$ g

$$\therefore \quad \left(\frac{x}{49} + \frac{0.5 - x}{31.6}\right) = \frac{100 \times 0.15}{1000}$$

where, 49 is eq. wt. of $K_2Cr_2O_7$ and 3.16 is eq. wt. of $KMnO_4$ on solving we get $x = 0.0732$ g percentage of

$$K_2Cr_2O_7 = \frac{0.0732 \times 100}{0.5} = 14.64\%$$

17. 126 g of oxalic acid = 1 mol of $H_2C_2O_4$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

1 mole of oxalate ion require = 2/5 mol $KMnO_4$

$$Cr_2O_7^{2-} + 3C_2O_4^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 6CO_2 + 7H_2O$$

1 mole of oxalate ion require = 1/3 mol $K_2Cr_2O_7$.

20. Titration (neutralisation) of dil. HCl solution with aqueous NaOH will require the following steps and apparatus.

NaOH solution made with distilled water and solid NaOH is taken in a burette and then it is fitted with a clamp.

A given volume of standard HCl solution (dilute) is then pipetted out and taken in a conical flask for titration. Then, few drops of phenolphthalein indicator is added in this HCl solution.

So, we do not require measuring cylinder and bunsen burner as the titration takes place at room temperature.

21. $$5C_2O_4^{2-} + \underset{\text{Purple}}{2MnO_4^-} + 16H^+ \longrightarrow \underset{\substack{\text{Colourless} \\ \text{(auto-catalyst)}}}{2Mn^{2+}} + 8H_2O + 10CO_2 \uparrow$$

22. Because $KMnO_4$ oxidises HCl into Cl_2 which is also an oxidising agent.

$$2Cl^- \longrightarrow Cl_2 + 2e^-] \times 5$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$

23. When 100 mL HCl is added to 35 mL NaOH then 35 mL of HCl is utilised to neutralise NaOH while 65 mL HCl remains as such.

Hence, solution becomes acidic. In acidic solution, the colour of methyl orange is red due to presence of Me^+ ions as,

$$\underset{\substack{\text{Methyl orange} \\ \text{(yellow)}}}{MeOH} \rightleftharpoons \underset{\text{Red}}{Me^+} + OH^-$$

24. The blue precipitate of Fe^{2+} ions with potassium ferricyanide is due to the formation of Turnbull's blue $K\overset{II}{Fe}[\overset{III}{Fe}(CN)_6]$ product.

$$Fe^{2+} + \underset{\text{Potassium ferricyanide}}{K_3[Fe(CN)_6]} \longrightarrow \underset{\text{Turnbull's blue}}{K\overset{II}{Fe}[\overset{III}{Fe}(CN)_6]} + 2K^+$$

26. NaCl is a salt of strong acid and strong base, hence on dissolution will give neutral solution. As white ppt. is obtained by the addition of $AgNO_3$ to the solution of Na salt, it can be of AgCl.

Further, AgCl is also insoluble in HNO_3. Hence, the anion is Cl^-.

$$NaCl + AgNO_3 \longrightarrow AgCl \downarrow HNO_3$$

27. Ba^{2+} ion imparts green colour to the flame and Cl^- ion forms chromyl chloride (which is orange red in colour) when treated with $K_2Cr_2O_7$ and conc. H_2SO_4. Thus, the reagent is

$$Ba^{2+} + 2Cl^- \longrightarrow BaCl_2$$
$$2BaCl_2 + K_2Cr_2O_7 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2BaSO_4 + \underset{\substack{\text{Chromyl chloride} \\ \text{(orange red gas)}}}{2CrO_2Cl_2} + 3H_2O$$

31. $[HgI_4]^{2-} + NH_4Cl + 4OH^- \longrightarrow NH_2HgOHgI$

32. Nessler's reagent $K_2[HgI_4]$ in alkaline medium is used to detect NH_4^+ ion.

33. (a) $4FeCl_3 + 3K_4[Fe(CN)_6] \longrightarrow \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3} + 12KCl$

For option (b) and (c), reaction is given below

$$M^{2+} + [Fe(CN)_6]^{4-} \xrightarrow[\text{of } CH_3COOH]{\text{In presence}} \underset{\text{Bluish white ppt.}}{M_2[Fe(CN)_6] \downarrow}$$

$M = Zn^{2+}, Cd^{2+}$

34. As in cases (1), (2) and (4), the acids and bases taken are strong and the enthalpy of neutralisation of all strong acids with strong bases is same, i.e. – 57.3 kJ.

35. (A) → (3), (B) → (1), (C) → (4), (D) → (2)

36. In the given experiment following reaction occurs

$$H_2O_2 + 2I^- + 2H^+ \longrightarrow 2H_2O + I_2$$

Iodine liberated in this reaction reacts with sodium thiosulphate solution and is reduced to iodide ions.

$$I_2 + \underset{\text{Thiosulphate ion}}{2S_2O_3^{2-}} \xrightarrow{\text{Fast}} \underset{\text{Tetrathionate ion}}{S_4O_6^{2-}} + 2I^-$$

37. $KI + AgNO_3$ (slight excess) $\longrightarrow AgI + KNO_3$

$$AgNO_3 \longrightarrow Ag^+ + NO_3^-$$
$$AgI(s) + Ag^+ \longrightarrow \underset{\text{Silver iodide sol}}{[AgI] \quad Ag^+}$$

38. The main purpose of using leveling bulb is to assure that pressure within the reaction vessel is same as that in the room.

Round II

1. $\overset{+3}{K_3[Fe(CN)_6]} + \overset{-1}{KI}\text{ (excess)} \xrightarrow{\text{Dil. } H_2SO_4}$

$$\overset{+2}{K_4[Fe(CN_6]} + \underset{\substack{\text{Brownish yellow}\\ \text{solution}}}{\overset{-1,0}{KI_3}}$$

$$K_4[Fe(CN)_6] + ZnSO_4 \longrightarrow \underset{\text{White ppt.}}{K_2Zn[Fe(CN)_6]}$$

$$\underset{\substack{\text{Brownish}\\ \text{yellow}\\ \text{filtrate}}}{I_3^-} + 2Na_2S_2O_3 \longrightarrow \underset{\substack{\text{Clear}\\ \text{solution}}}{Na_2S_4O_6} + 2NaI + \underset{\substack{\text{Turns starch}\\ \text{solution blue}}}{I_2}$$

$K_2Zn[Fe(CN)_6]$ reacts with NaOH as

$$K_2Zn[Fe(CN)_6] + 4NaOH \longrightarrow [Zn(OH)_4]^{2-} + [Fe(CN)_6]^{4-}$$

2. Since, given compound '*A*' burns with flame therefore, it must be aromatic compound. Again when it reacts with Brady's reagent (acidic 2, 4-dinitrophenyl hydrazine solution), it yields orange precipitate. Therefore, it must be aldehyde or ketone. But ketone does not perform Tollen's reagent test therefore, it must be a ketone. Hence, '*A*' is acetophenone .

3. Kjeldahl method is not applicable to compounds containing nitrogen in nitro group, azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulphate under these conditions.

4. $CuSO_4$ decolourises on addition of KCN. The product is CuCN along with $(CN)_2$ but in excess of KCN, colourless potassium tetracyanocuperate (I) is obtained.

$$CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + [K_2SO_4] \times 2$$

$$\underset{\text{Unstable}}{2Cu(CN)_2} \rightleftharpoons 2CuCN + \underset{\text{Cyanogen}}{(CN)_2}$$

$$CuCN + 3KCN \rightleftharpoons \underset{\text{Colourless}}{K_3[Cu(CN)_4]}$$

5. The reaction takes place as follows,

$$H_2C_2O_4 + 2NaOH \longrightarrow Na_2C_2O_4 + 2H_2O$$

Now, 50 mL of 0.5 M $H_2C_2O_4$ is needed to neutralise 25 mL of NaOH.

$\therefore$ M. eq. of $H_2C_2O_4$ = M.eq. of NaOH

$$50 \times 0.5 \times 2 = 25 \times M_{\text{NaOH}} \times 1$$

$$M_{\text{NaOH}} = 2\text{ M}$$

$$\text{Now, molarity} = \frac{\text{number of moles}}{\text{volume of solution (in L)}}$$

$$= \frac{\text{weight / molecular mass}}{\text{volume of solution (in L)}}$$

$$2 = \frac{w_{\text{NaOH}}}{40} \times \frac{1000}{50}$$

$$w_{\text{NaOH}} = \frac{2 \times 40 \times 50}{1000} = 4\text{ g}$$

6. $2NaOH + Br_2 \longrightarrow NaOBr + NaBr + H_2O$

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

$$2Cr(OH)_3 + 4NaOH + 3[O] \longrightarrow \underset{\text{Yellow solution}}{2Na_2CrO_4} + 5H_2O$$

7. $FeS + H_2SO_4\text{(dilute)} \longrightarrow FeSO_4(aq) + H_2S(g)$

8. $\underset{\text{Chloride salt}}{NaCl} + H_2SO_4 \longrightarrow NaHSO_4 + \underset{\text{Colourless}}{HCl\uparrow}$

$$\underset{\text{Iodide salt}}{NaI} + H_2SO_4 \longrightarrow NaHSO_4 + HI$$

$$2HI + H_2SO_4 \longrightarrow \underset{\text{Violet colur}}{I_2\uparrow} + SO_2 + 2H_2O$$

9. Brown ring test

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{Brown complex}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$$

In the ring test of NO_3^- ion, Fe^{2+} ion reduces nitrate ion to nitric oxide, which combines with Fe^{2+} (*aq*) ion to form brown complex.

10. On passing H_2S gas in the aqueous solution of salt in the presence of dilute. HCl, black ppt. of CuS is formed.

$$3CuS + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 3S + 4H_2O$$

$$Cu^{2+} + 4NH_4OH \longrightarrow \underset{\text{Deep blue complex}}{[Cu(NH_3)_4]^{2+}} + 4H_2O$$

11. "x vol" $H_2O_2 = \dfrac{x}{11.2}$ M H_2O_2

So, $\dfrac{x}{11.2} = 8.9$

$\Rightarrow \quad x = 11.2 \times 8.9 = 99.68 \simeq 100$

So, at NTP volume strength of 8.9 M H_2O_2 solution is 100 vol.

12. Eq. of $KMnO_4$ used $= \dfrac{50 \times 1}{1000 \times 10} = 0.005$

$\therefore$ Eq. of Mohr's salt reacted $= 0.005$

$\therefore$ Weight of Mohr's salt needed $= 0.005 \times 392 = 1.96$ g

Thus, percentage purity of Mohr's salt

$$= \frac{1.96}{3.92} \times 100 = 50\%$$

13. Normality of oxalic acid $= \dfrac{6.3 \times 1000}{63 \times 250} = 0.4$

$$N_1V_1 = N_2V_2$$

$$V_1 \times 0.1 = 10 \times 0.4$$

$$V_1 = 40\text{ mL}$$

14. In Duma's method of estimation of nitrogen. 0.1840 g of organic compound gave 30 mL of nitrogen which is collected at 287 K and 758 mm of Hg.

Given : Aqueous tension at 287 K = 14 mm of Hg.

Hence, actual pressure = (758 – 14) = 744 mm of Hg.

$$\text{Volume of nitrogen at STP} = \frac{273 \times 744 \times 30}{287 \times 760}$$

$$V = 27.935 \text{ mL}$$

$\because$ 22400 mL of N_2 at STP weights = 28 g.

$\therefore$ 27.94 mL of N_2 at STP weights

$$= \left(\frac{28}{22400} \times 27.94\right) \text{g} = 0.0349 \text{ g}$$

$$\text{Hence, \% of nitrogen} = \left(\frac{0.0349}{0.1840} \times 100\right) = 18.97\%$$

Round off. Answer = 19 %

15. $MnO_4^- + 5Fe^{2+} \longrightarrow 5Fe^{3+} + Mn^{2+}$

$$M_1V_1(MnO_4^-) = 5N_1V_1(MnO_4^-) \text{ milliequivalent}$$

$$M_2V_2(Fe^{2+}) = 5N_2V_2(Fe^{2+}) \text{ milliequivalent}$$

$$N_1V_1(MnO_4^-) = N_2V_2(Fe^{2+})$$

$$5 \times 0.02 \times V_1 = 40 \times 0.1$$

$$V_1 = \frac{40 \times 0.1}{5 \times 0.02}$$

$$V_1 = 40 \text{ mL}$$

16. The reaction of HCl with Na_2CO_3 is as follows

$$2HCl + Na_2CO_3 \longrightarrow 2NaCl + H_2O + CO_2$$

We know that, M_{eq} of HCl = M_{eq} of Na_2CO_3

$$\frac{25}{1000} \times 1 \times M_{HCl} = \frac{30}{1000} \times 0.1 \times 2$$

$$M_{HCl} = \frac{30 \times 0.2}{25} = \frac{6}{25} \text{ M}$$

The reaction of HCl with NaOH is as follows

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Also, M_{eq} of HCl = M_{eq} of NaOH

$$\frac{6}{25} \times 1 \times \frac{V}{1000} = \frac{30}{1000} \times 0.2 \times 1$$

$$V = 25\text{`} \text{ mL}$$