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2017-18

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# CHEMISTRY

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# 27. PRACTICAL ORGANIC CHEMISTRY

## 1. PURIFICATION

### 1.1 Introduction

Organic chemistry is based on carbon compounds either natural or synthetic. Such organic compounds are in a crude form. In order to observe the properties of them, a pure compound is necessary. Purity of the compound is required for their reactions. There are various methods of purification of organic compounds based on their physical and chemical properties such as adsorption, boiling point, sublime nature, etc.

Few of them are as follows:

(a) Fractional Crystallization (b) Sublimation (c) Chromatography

(d) Distillation (e) Differential Extraction

**(a) Fractional crystallization:** Fractional crystallization is based on the solubility of a compound in a specific solvent. It is used when an organic compound is sparingly soluble in some solvent at room temperature but considerably soluble at higher temperature and impurity is highly soluble. Its solution can be heated dissolving the compound along with impurities and cooling it to form crystals of highly pure organic compound leaving impurities behind in the solution called mother liquor.

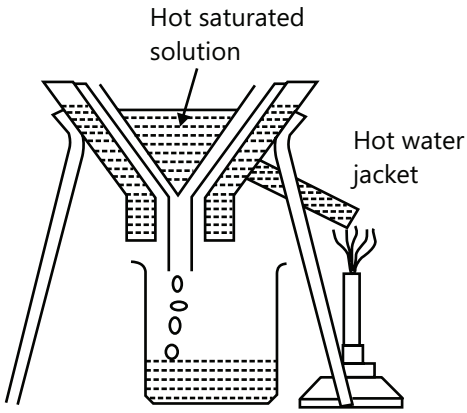



**Figure 27.1:** Hot Water funnel

**Examples:**

1. p-Xylene
2. Benzoic acid- It is sparingly soluble in cold water but highly soluble in hot water.
3. Fructose

**(b) Sublimation:** It is the property of a substance to change its state from a solid state to a vapour state without passing through a liquid state. Such compounds can be heated and separated from the impurity by separating its vapour by using the inverted funnel method.

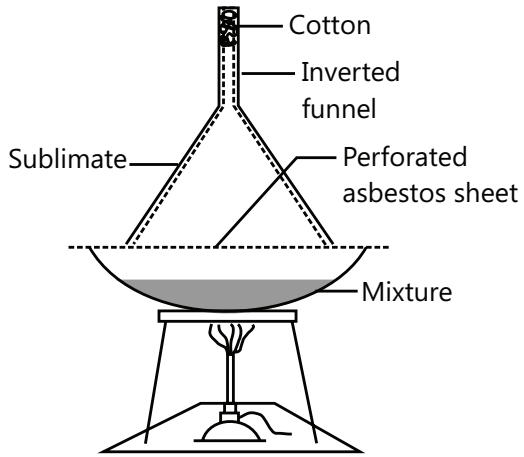



**Figure 27.2:** Sublimation

**Example:** Camphor, benzoic acid, anthracene.

**Table 27.1:** Melting Points

| Substance | M.P. | Substance | M.P. |
|---|---|---|---|
| 1,4-Dichlorobenzene | 55 | Benzoic acid | 122 |
| Naphthalene | 82 | Salicylic acid | 159 |
| 1-Naphthol | 96 | Camphor | 177 |
| Acetanilide | 114 | Caffeine | 235 |

**(c) Chromatography:** Chromatography is used for the separation of most of the compounds. There are two phases used in this technique namely stationary phase and mobile phase. Stationary phase is immobile throughout the process while mobile phase or eluent is a moving phase. Chromatography is based on its solubility in mobile phase as well as adsorption of the compound in stationary phase.

**Terms involved in chromatography:**

**(i)** **$R_f$ factor:** Retardation factor is used in identifying the product separated using paper or thin layer chromatography. $R_f$ factor

is given as: $R_f = \dfrac{\text{Migration distance of substance}}{\text{Migration distance of solvent front}}$

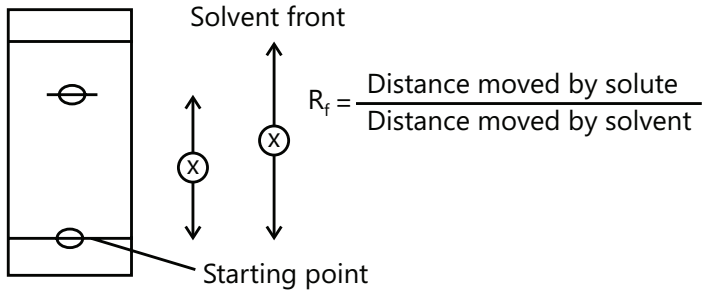



**Figure 27.3:** Chromatogram

In paper chromatography, if compounds are colourless, then ninhydrin spray is used to visualize the compounds in the form of various colours.

**(ii) Stationary Phase:** The phase in chromatography which is stationary with respect to the components of a mixture is called stationary phase. In case of column chromatography, stationary phase adsorbs components at different heights.

**(iii) Mobile Phase or Eluent:** The phase which moves along with components of a mixture is called a mobile phase or an eluent. Mobile phase determines $R_f$ factor which is dependent on the solubility of the components in a given solvent or eluent.

**The following are the different types of chromatography:**

- **Column chromatography:** Column chromatography is a separation technique in which the stationary bed is within a tube. The particles of the solid stationary phase or the support coated with a liquid stationary phase may fill the whole inside volume of the tube (packed column) or be concentrated on or along the inside tube wall leaving an open, unrestricted path for the mobile phase in the middle part of the tube (open tubular column). Differences in rates of movement through the medium are calculated to different retention times of the sample. Silica gel is a commonly used stationary phase.
- **Paper chromatography:** Paper chromatography is a technique that involves placing a small dot or line of sample solution onto a strip of chromatography paper. The paper is placed in a jar containing a shallow layer of solvent and sealed. As the solvent rises through the paper, it meets the sample mixture, which starts to travel up the paper with the solvent.
- **Thin layer chromatography (TLC):** Thin layer chromatography (TLC) is a widely employed laboratory technique and is similar to paper chromatography. However, instead of using a stationary phase of paper, it involves a stationary phase of a thin layer of adsorbent like silica gel, alumina, or cellulose on a flat, inert substrate.

  **Example:** Separation of vitamins.
- **Gas chromatography:** In this type if the stationary phase is a solid it is called solid gas chromatography. If the stationary phase is a high-boiling liquid deposit on a suitable support, it is called gas liquid chromatography. The mobile phase used is generally $N_2$, He or Ar, which do not react with the sample to be separated out. Gas chromatography is based on solubility of different gases in their stationary phase. The least soluble constituent comes out first while the most soluble comes out at the end. Thus various components of a gaseous mixture are separated. Gas chromatogram is a graph of the detector response when a gas comes out vs time.

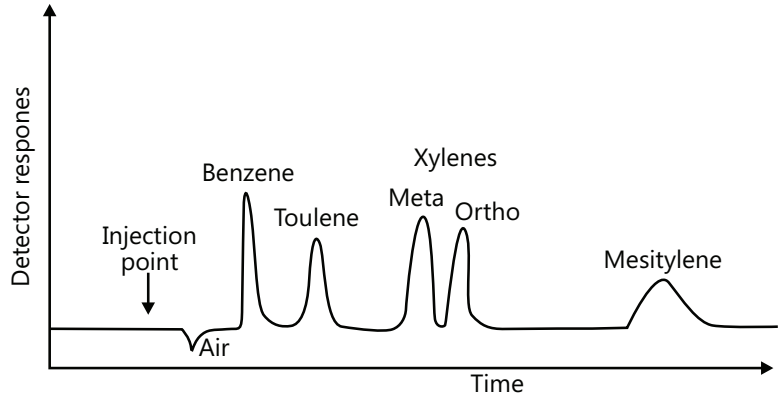



**Figure 27.4:** Plot of Detector response vs time

**Example:** Separation of amino acids.

**(d) Distillation:** There are two types of distillations based on the difference between the boiling points of the organic compound and its impurity.

**(i) Simple distillation:** This method is used if there is sufficient difference in the boiling points of volatile liquids.

**Example:** a) Chloroform ($CHCl_3$) and aniline ($PhNH_2$) can be separated by simple distillation due to large difference in their boiling points.

b) ether (b.p. 308K) and toluene (b.p. 384K)

**(ii) Fractional distillation:** This method is used to separate two volatile liquids when the difference in their boiling points is small. In such a case when one liquid starts boiling the other is also converted to vapour considerably. So, we get the vapours of both compounds. Hence, to avoid this fractionating column is used. Fractionating column opposes the vapour of one with higher boiling point and its vapour again condenses and goes to solution.

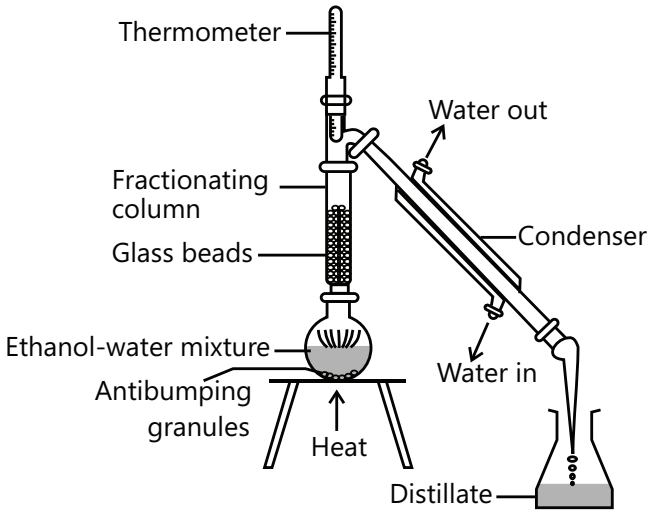



**Figure 27.5:** Distillation

**Example:** (a) Ethanol-water mixture, (b) Petroleum products are separated by fractional distillation, (c) Cyclohexane-toluene mixture, (d) Acetone (b.p. 330K) and methyl alcohol (b.p. 338K)

**(iii) Steam distillation:** This method is used to separate the compounds which are steam volatile and are insoluble in water. In this method, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and vapour is condensed and collected in a receiver. Then the compound being insoluble in water can be separated easily.

**Example:** (a) Aniline-water mixture, (b) Isolation of citral, (c) Nitro benzene

**(iv) Vacuum distillation:** The lowering of pressure on the surface of a liquid lowers its boiling point. As a result of this, a liquid can be boiled and distilled, without any decomposition, at temperature much below its normal boiling point.

**Example:** Distillation of crude oil in oil refineries, Glycerol.

**(v) Azeotropic distillation:** Azeotropic mixture is a mixture having a constant boiling point. The constituents of this mixture cannot be separated by fractional distillation. So, in this method a third component is used in distillation. The process is based on the fact that dehydrating agents like $C_6H_6$,$CCl_4$ , diethyl ether, etc. depress the partial pressure of one of the original components. As a result, the boiling point of that component is raised sufficiently and thus the other component distills over.

**Example:** Separation of ethanol and water.

**(e) Differential extraction:** This method is based on the different solubilities of an organic compound in different solvents. If a compound is soluble in water but more soluble in an organic solvent, it is separated by shaking it with an organic solvent. As a result, the organic compound gets dissolved into a organic solvent which can be extracted from water.

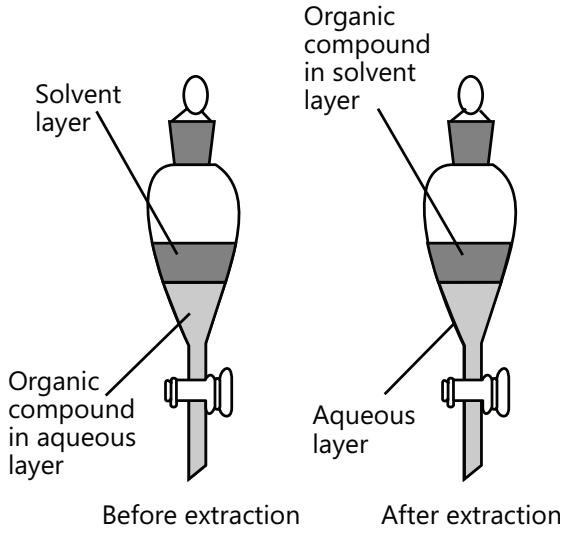



**Figure 27.6:** Separating Funnel

**Example:** (a) Iodine ($I_2$) can be purified as it is sparingly soluble in water but highly soluble in $CCl_4$ (b) Extraction of caffeine from tea

**Illustration 1:** Two volatile compounds differ in their boiling points by 20K, how will they be separated?

(a) What types of compound are purified by sublimation?

(b) How will $I_2$ be separated from KCl?

(c) How are o- and p-nitro phenols separated?

(d) How is aniline purified?

(e) How is a mixture of naphthalene and kerosene oil separated?

**Sol:** Fractional distillation.

(a) Substances whose vapour pressures become equal to the atmospheric pressure much below their b.p.

(b) Either by sublimation or by extraction with $CCl_4$ followed by evaporation.

(c) o-nitrophenol is steam volatile while p-nitro phenol is not due to intramolecular H-bonding. Hence, they are separated by steam distillation.

(d) Vacuum distillation or steam distillation.

(f) By simple distillation.

**Illustration 2:** p-nitrophenol and o-nitrophenol are separated by

(A) Crystallization

(B) Fractional crystallization

(C) Distillation

(D) Steam distillation

**Sol:** Steam distillation is used to separate the compounds which are steam volatile and are insoluble in water. This process effectively allows for distillation at lower temperatures.

# 2. QUALITATIVE ESTIMATION

## 2.1 Introduction

Qualitative estimation is used in identifying elements in a compound. While judging the properties of a compound, it is necessary to find elements constituting it. Organic compounds contain mainly C and H; in addition to these they may contain O, N, S, halogens and P.

## 2.2 Detection of Elements

### 2.2.1 Detection of C and H

Many organic compounds burn with a sooty flame or char when strongly heated. C and H are detected by heating the compound with cupric oxide (CuO) in a dry test tube. They are oxidized to $CO_2$ and $H_2O$ respectively. $CO_2$ turns lime water milky and $H_2O$ turns anhydrous $CuSO_4$ blue.

**(a)** $C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$

**(b)** $2H + CuO \xrightarrow{\Delta} Cu + H_2O$

**(c)** $CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$

**(d)** $\underset{\text{White}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{Blue}}{CuSO_4 . 5H_2O}$

### 2.2.2 Preparing Sodium Fusion Extract

Most of the organic compounds are covalent. So, it is not possible to detect elements in it due to a strong covalent bond. Therefore, it is necessary to convert them into ionic forms which can split easily in a polar medium. Sodium (Na) being strongly electropositive is used in this process by preparing sodium fusion extract. While preparing sodium fusion extract, the organic compound is strongly heated with clean sodium metal in a test tube fusing it with the sample. The fused sample is plunged into water, and a few tests are performed on the solution to identify elements in it. Following reactions occur:

$Na + C + N \xrightarrow{\Delta} NaCN$; $2Na + S \xrightarrow{\Delta} Na_2S$; $Na + X \xrightarrow{\Delta} NaX$ (X = Cl, Br, Or I)

C, N, S and X come from organic compound.

### 2.2.3 Lassaigne's Test

N, S, halogens and phosphorous present in organic compound is detected by Lassaigne's test, after preparing sodium fusion extract.

**(a)** **Test for nitrogen:** The sodium fusion extract is boiled with $FeSO_4$ and then acidified with Concentrated $H_2SO_4$. The appearance of Prussian blue colour confirms the presence of N. The following reaction occurs:

**(i)** $Fe^{2+} + 6CN^- \longrightarrow \underset{\text{Hexa cyanoferrate (II)}}{\left[Fe(CN)_6\right]^{4-}}$

**(ii)** $Fe^{2+} \xrightarrow[H_2SO_4]{\text{Conc.}} Fe^{3+} + \bar{e}$

**(iii)** $3\left[Fe(CN)_6\right]^{4-} + 4Fe^{3+} \longrightarrow \underset{\substack{\text{Ferriferro cyanide}\\ \text{(Prussian blue)}}}{Fe_4\left[Fe(CN)_6\right]_3} . H_2O$

**Exception:**

1. This test is not given by compounds which do not contain C atoms but contain N atoms.

   Example: $NH_2NH_2$ (hydrazine), $NH_2OH$ (hydroxyl amine).

   Reason: Since, these compounds do not contain carbon, in a sodium fusion extract, $CN^-$ ion will not form and Prussian blue colour is not observed.

2. This test is also not given by diazonium salts although they contain both C and N elements, because the nitrogen in them is released due to strong heating while forming a sodium fusion extract.

3. If S is also present in organic compound along with C and N, this test gives a blood red colour.

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

$$\underset{\text{Thiocyanate ion}}{3CNS^- + Fe^{+3}} \longrightarrow \underset{\substack{\text{Ferric thiocyanate}\\ \text{(Blood–red colour)}}}{Fe(CNS)_3}$$

4. If fusion is carried out with excess of sodium, the fusion gives cyanide and sulphide giving usual tests.

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

**(b) Test for sulphur:**

**(i)** The sodium fusion extract is treated with sodium nitroprusside. Appearance of violet colour confirms the presence of S.

$$\underset{\text{Sulphide ion}}{S^{2-}} + \left[Fe(CN)_5NO\right]^{2-} \longrightarrow \underset{\text{Violet colour}}{\left[Fe(CN)_5NOS\right]^{-4}}$$

**(ii)** The extract is treated with acetic acid and lead acetate is added to it. The appearance of black ppt. of lead sulphide confirms presence of S.

$$Pb^{2+} + S^{2-} \longrightarrow \underset{\text{Black ppt.}}{PbS}$$

**(c) Test for halogens:**

**(i)** Extract is acidified with $HNO_3$ and then treated with $AgNO_3$. A white ppt. soluble in $NH_4OH$ indicates the presence of Cl, a yellowish ppt. sparingly soluble in $NH_4OH$ indicates presence of Br, and a yellow ppt. insoluble in $NH_4OH$ shows presence of I.

$$AgNO_3 + NaCl \longrightarrow \underset{\substack{\text{White ppt.}\\ \text{soluble in } (NH_4OH)}}{AgCl\downarrow} + NaNO_3 \;;\; AgNO_3 + NaBr \longrightarrow \underset{\substack{\text{Pale–yellow ppt.}\\ \text{partly soluble in } (NH_4OH)}}{AgBr\downarrow} + NaNO_3$$

$$AgNO_3 + NaI \longrightarrow \underset{\substack{\text{Dark–yellow ppt.}\\ \text{insoluble in } (NH_4OH)}}{AgI\downarrow} + NaNO_3$$

If N and S are also present in the compound, this reaction forms NaCN or $Na_2S$. These ions interfere with $AgNO_3$ test. If these ions are not removed they give white ppt. which will confuse it for AgCl.

**(ii) Organic layer test:** Extract is treated with $CS_2$ and $CCl_4$ and then $Cl_2$ water is added to it. Then it is kept for some time. Appearance of orange colour in organic layer indicates the presence of Br, while a violet colour confirms iodine.

$$2Br^- + 2Cl_2 \longrightarrow \underset{\text{Orange colour}}{Br_2} + 2Cl^- \;;\; 2I^- + 2Cl_2 \longrightarrow \underset{\text{Violet colour}}{I_2} + 2Cl^-$$

**(iii)** Beilstein test: The organic compound is heated on a clean copper wire in Bunsen flame. A green coloured flash indicates chlorine, blue-green of bromine and blue of iodine. Fluorine is not detected in this test.

**Exception:** Urea ($NH_2CONH_2$) and thiourea ($NH_2CSNH_2$) do not contain halogens but still give this test.

**(d)** **Test for phosphorous:** The organic compound is heated with an oxidizing agent (sodium peroxide). Phosphorous is oxidized to phosphate. The solution is then boiled with conc. $HNO_3$ and then treated with ammonium molybdate. A canary yellow ppt. confirms the presence of phosphorous.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + \underset{\text{Ammonium molybdate}}{12(NH_4)_2MoO_4} + 21HNO_3 \longrightarrow \underset{\text{Ammonium phospho molybdate}}{(NH_4)_3PO_4.12MoO_3} + 21NH_4NO_3 + 12H_2O$$

**Exception:** If the organic compound contains arsenic (As), then it also gives the same test forming ammonium arsenomolybdate forming a canary yellow ppt.

## 2.3 Detection of Organic Groups

**(a) Hydroxyl group (alcohol and phenol)**

**1. Lucas's reagent ($ZnCl_2$; conc. HCl):** This reagent converts alcohols into the corresponding alkyl chlorides. Zinc chloride (a Lewis acid) increases the reactivity of alcohols towards acid. The test depends on the rate of reaction of primary, secondary, and tertiary alcohols with the reagent at room temperature.

**(i)** $RCH_2OH \rightarrow$ No reaction at room temperature.

**(ii)** $R_2CHOH \rightarrow R_2CHCl + H_2O$ (1 hour or maybe longer)

**(iii)** $R_3COH \rightarrow R_3CCl + H_2O$ (immediately)

To 1 mL of the alcohol in a small test tube add 6 mL of Lucas' reagent at room temperature. Close the tube with a cork, shake and allow to stand.

- **Primary alcohols -** The aqueous phase remains clear (except allyl alcohol - droplets after 7 minutes). No turbidity or cloudiness is observed.
- **Secondary alcohols -** Very slow reaction (~ 1 hour or maybe longer) when droplets of alkyl chloride may be seen. Turbidity or cloudiness is observed.
- **Tertiary alcohols -** Very fast reaction and droplets of the alkyl chloride formed almost immediately. Turbidity or cloudiness is observed.

**2. Victor meyer's test:** This test consists of the following steps:

**(i)** The given alcohol is first converted into its alkyl iodide by treating it with P & Iodine.

**(ii)** The alkyl iodide is then treated with silver nitrite (AgNO2) to convert it into a corresponding nitro alkane.

**(iii)** The nitroalkane is then treated with nitrous acid (HNO2), i.e., NaNO2 + HCl.

**(iv)** The resulting solution is finally made alkaline with aqueous NaOH or KOH. If blood red colouration appears it is a primary alcohol. If blue colouration appears it is a secondary alcohol. If the solution remains colourless, indicates a tertiary alcohol.

$$RCH_2OH + P/I_2 \longrightarrow RCH_2-I + AgNO_2 \longrightarrow RCH_2NO_2 + HONO \longrightarrow$$

$$RC(=NOH)-NO_2 + NaOH \longrightarrow \text{Blood Red colour}$$

$$R_2CH-OH + P/I_2 \longrightarrow R_2CH-I + AgNO_2 \longrightarrow R_2CHNO_2 + HONO \longrightarrow$$

$$R_2C(N=O)-NO_2 + NaOH \longrightarrow \text{Blue colour}$$

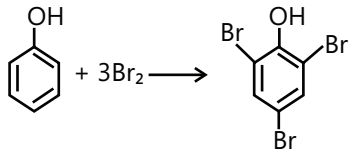
$$R_3C-OH + P/I_2 \longrightarrow R_3C-I + AgNO_2 \longrightarrow R_3C-NO_2 + HONO \longrightarrow$$

$$\text{No Reaction} + NaOH \longrightarrow \text{Colourless}$$

3. **Iodoform test:** Iodoform test is given by alcohols having $\left(CH_3-\underset{\underset{H}{|}}{C}-OH\right)$ group. In Iodoform test, the compound reacts with $I_2$ / NaOH reagent to give iodoform ($CHI_3$) which is pale yellow in colour. It is insoluble in water and has an antiseptic smell.

**(b) Phenol detection**

**(i) Bromine water:** Phenols are generally highly reactive towards electrophilic reagents and are readily brominated by bromine water. e.g.




Dissolve or suspend about 0.05 g of the compound in 2 mL of dilute hydrochloric acid and add bromine water dropwise until the bromine colour remains. A white precipitate of the bromophenol may form. Solid bromophenol derivatives can be used for the confirmation of the structure of a phenol.

**(ii) Ferric chloride test:** Most phenols react with iron (III) chloride to form coloured complexes. The colours vary - red, purple, blue or green - depending on various factors, e.g. the phenolic compound used, the solvent, concentration. Since some phenols do not give colours, a negative test must not be taken as significant without supporting information.

**(c) Aldehyde detection**

**(i) Fehling's solution:** Aldehydes reduce Fehling's solution to yellow or red copper (I) oxide.

Preparation of the reagent: Mix equal volumes of Fehling's solution I (aqueous alkaline potassium tartrate) and Fehling's solution II (copper sulphate solution).

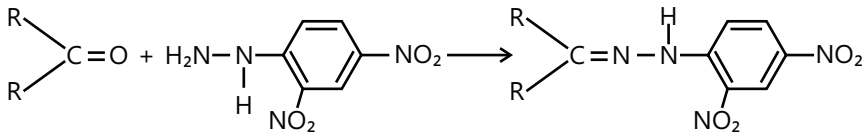
**Exception:** Only aliphatic aldehydes give this test. Aromatic aldehydes don't give this test.

**(ii) Tollen's reagent (Ammoniacal silver nitrate solution):** Aldehydes are readily oxidized to carboxylic acids and will reduce Tollen's reagent to produce a silver mirror on the inside of a clean test tube.

**Exception:** $\alpha$ -hydroxy ketones also give this test but other ketones do not. Hemiacetals and formic acid also give this test. But acetals do not.

**(d) Aldehyde or Ketone detection**

**(i) Brady's reagent (2,4-Dinitrophenylhydrazine):** A test for the carbonyl group (C=O) in aldehydes and ketones. 2,4-Dinitrophenylhydrazine gives sparingly soluble yellow or red 2,4-dinitrophenylhydrazones with aldehydes and ketones.




R,R′ = hydrogen or alkyl

**(ii) Iodoform Test:** Iodoform test is given by simple methyl ketones and acetaldehyde only i.e. compounds having $(CH_3-C=O-)$ group. In Iodoform test, the compound reacts with $I_2$ / NaOH reagent to give iodoform $(CHI_3)$ which is pale yellow in colour. It is insoluble in water and has an antiseptic smell.

**(e) Carboxylic acid:** Test with 5% aq. $NaHCO_3$

$$R-CO_2H + NaHCO_3 \longrightarrow R-CO_2-Na^+ + CO_2 + H_2O$$

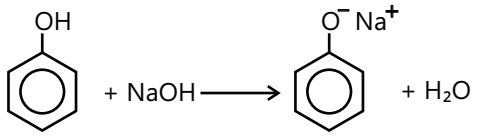
Sodium hydrogen carbonate reacts with carboxylic acids to give the sodium salt of the acid and liberates carbon dioxide. If the acid is insoluble in water and the reaction is sluggish, dissolve the acid in methanol and add carefully to a saturated sodium hydrogen carbonate solution, when a vigorous effervescence will be observed.

**(f) Distinction between alcohol, phenol and carboxylic acid**

**(i)** All alcohols react with sodium metal (Na) to evolve $H_2$ gas. But do not react with NaOH or $NaHCO_3$.

$$2CH_3CH_2OH + 2Na \longrightarrow 2CH_3CH_2ONa + H_2$$

**(ii)** All phenols react with sodium metal (Na) and NaOH. But do not react with $NaHCO_3$.




Sodium phenoxide

**(iii)** All carboxylic acids react with sodium metal (Na), NaOH and $NaHCO_3$.

**(g) Amines**

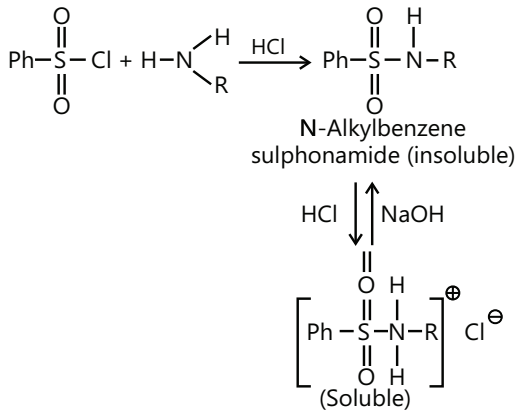
**(i) Reaction with nitrous acid:**

| AMINE | REACTION |
|---|---|
| 1° aliphatic | $\longrightarrow$ $N_2$ evolved |
| $RNH_2 + HNO_2$ | $\longrightarrow$ $ROH + N_2 + H_2O$ |
| 1° aromatic | $\longrightarrow$ Diazonium salt is formed. |
| $ArNH_2 + HNO_2$ | $\longrightarrow$ $ArN \equiv N^+$ |

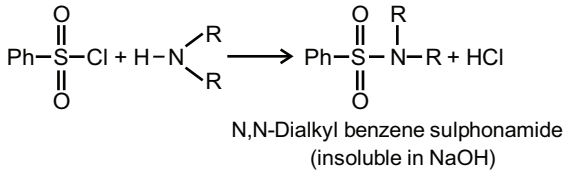
Add the cold diazonium solution and with swirling to a cold solution of 2-naphthol (0.2 g) in 5% NaOH solution (2mL). An orange-red azo dye is formed.

| | |
|---|---|
| 2° aliphatic | $\longrightarrow$ Yellow oily nitrosamines are generally formed. |
| 2° aromatic | $\longrightarrow$ $R_2NH + HNO_2 \longrightarrow R_2N-NO$ |
| 3° aliphatic | $\longrightarrow$ No visible reaction |
| 3° aromatic | $\longrightarrow$ Dialkylanilines yield green solid p-nitroso compounds (if p-position unsubstituted). |

**(ii) Hinsberg reaction:** In this test amine is shaken well with Hinsberg reagent (benzene sulphonyl chloride) in the presence of aqueous alkali (either NaOH or KOH). A primary amine will form a soluble sulfonamide salt which precipitates after addition of diluted hydrochloric acid. A secondary amine in the same reaction will directly form an insoluble sulfonamide. A tertiary amine will not react with the sulfonamide but is insoluble. After adding a dilute acid this insoluble amine is converted to a soluble ammonium salt. In this way the reaction can distinguish between the three types of amines.




A precipitate which is an insoluble compound (which is insoluble in NaOH solution also) indicates 2° amines.




3° amines do not react with the reagent.

**(iii) Reaction with Carbon disulphide ($CS_2$):** Primary amine reacts with $CS_2$ and further reacts with base due to acidic hydrogen present on nitrogen.

$R-NH_2 + CS_2 \longrightarrow R-NH-CSSH \longrightarrow$ reacts with base

Secondary amine reacts with $CS_2$ but doesn't react with a base due to the absence of acidic hydrogen.

$R_2NH + CS_2 \longrightarrow R_2.N-CSSH$ does not react with base.

Tertiary amine do not react with $CS_2$.

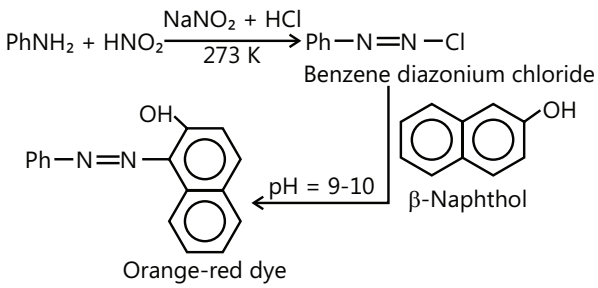
**(iv) Carbylamine test:** 1° aliphatic and aromatic amines on heating with $CHCl_3$ and KOH give an offensive smell due to the formation of carbylamine.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\substack{\text{Alkyl isocyanide}\\ \text{or}\\ \text{Alkyl carbyl amine}}}{R-NC} + 3KCl + 3H_2O$$

$$\underset{\text{Aniline}}{PhNH_2} + CHCl_3 + 3KOH \longrightarrow Ph-N\equiv C + 3KCl + 3H_2O$$

2° and 3° aliphatic and aromatic amines do not give this test.

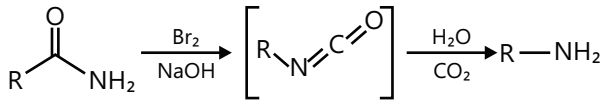
**(v) Azo-dye test:** 1° aromatic amines on heating with $NaNO_2$ and HCl give stable diazonium salts which couple with alkaline solution of β-naphthol to give orange-red azo dye.



**(h) Amides**

**(i)** Simple primary amides can be decomposed by boiling with alkali and thereby evolving ammonia which has pungent smell. E.g. $CH_3-CO-NH_2+NaOH \longrightarrow CH_3-CO_2-Na^+ + NH_3$

**(ii) Hofmann rearrangement:** Amides show Hofmann rearrangement to form a primary amine when treated with $Br_2$ / NaOH




This test confirms presence of amide.

**(i) Ester detection**

**(i) Hydroxamic acid test:** $R-CO-OR' + H_2N-OH \longrightarrow R-CO-NH-OH + R'-OH$

Esters react with hydroxylamine in the presence of sodium hydroxide to form the sodium salt of the corresponding hydroxamic acid. On acidification and addition of ferric chloride the magenta-coloured iron (III) complex of the hydroxamic acid is formed.

**(ii) Hydrolysis test:** Esters undergo saponification reaction i.e. hydrolysed with NaOH. The compound is heated with NaOH with a small amount of phenolphthalein. The initial pink colour of the solution is discharged due to the formation of acid, since phenolphthalein shows pink colour in basic medium and is colourless in acidic medium.

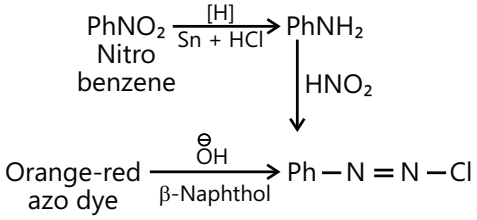
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' + NaOH \xrightarrow{\Delta} R-\overset{\overset{\displaystyle O}{\|}}{C}-ONa + R'OH$$

**(j) Nitro group detection**

**(i) Mulliken's test:** The nitro compound is dissolved in alcohol and is reduced with $Zn/NH_4Cl$ or $CaCl_2$ solution and Zn dust, and boiled. It is then filtered, cooled, and heated with ammoniacal $AgNO_3$, white to grey and the black precipitate confirms the presence of nitro group.

$$RNO_2 + 4[H] \xrightarrow[NH_4Cl]{Zn} RNHOH + H_2O$$

**(ii) Azo dye test:** Aromatic nitro compounds are first reduced to $-NH_2$ group with $SnCl_2$+conc. HCl which on reaction with nitrous acid forms diazonium salts. The stable diazonium salt forms orange red dye with alkaline solution of β -naphthol.




**(k) Sugars, Carbohydrates detection**

**(i) Molisch's test:** This is a general test for carbohydrates. Dissolve 20 - 30 mg of the compound in 2 mL water and add 0.5 mL of the reagent (a 20% solution of 2-naphthol in ethanol). Pour 2 mL of concentrated sulphuric acid from a dropper carefully down the side of the tube so that the acid forms a layer beneath the aqueous solution without mixing with it. A red colouration, changing to dark purple forms at the interface.

**(ii) Fehling's test:** This forms the reduction test of carbohydrates. Fehling's solution contains blue alkaline cupric hydroxide solution, heated with reducing sugars gets reduced to yellow or red cuprous oxide and is precipitated. Hence, formation of the yellow or brownish-red coloured precipitate helps in the detection of reducing sugars in the test solution.

**(iii) Osazone Test:** The ketoses and aldoses react with phenylhydrazine to produce a phenylhydrazone which further reacts with another two molecules of phenylhydrazine to yield osazone. Needle-shaped yellow osazone crystals are produced by glucose, fructose and mannose, whereas lactosazone produces mushroom shaped crystals. Crystals of different shapes will be shown by different osazones. Flower-shaped crystals are produced by maltose.

**(l) Proteins**

**(i) Ninhydrin test:** Amino acids also react with ninhydrin at pH = 4. The reduction product obtained from ninhydrin then reacts with $NH_3$ and excess ninhydrin to yield a blue colored substance. This test is given by only amino acids and proteins which contain free $-NH_2$ groups in their structure. Proline doesn't give this test due to absence of free $-NH_2$ group.

**(ii) Xanthoproteic test:** Some amino acids contain aromatic groups that are derivatives of benzene. These aromatic groups can undergo reactions that are characteristics of benzene and benzene derivatives. One such reaction is the nitration of a benzene ring with nitric acid. The amino acids that have activated benzene ring can readily undergo nitration. This nitration reaction, in the presence of activated benzene ring, forms yellow product.

**Example:** tyrosine, tryptophan, phenylalanine and glutamic acid.

**(iii) Millon's Test:** Millon's test is specific to phenol containing structures (tyrosine is the only common phenolic amino acid). Millon's reagent is concentrated $HNO_3$, in which mercury is dissolved. As a result of the reaction a red precipitate or a red solution is considered as positive test. A yellow precipitate of HgO is NOT a positive reaction but usually indicates that the solution is too alkaline.

**Example:** tyrosine, phenylalanine, glycine and $\beta$-naphtol.

**(iv) Biuret Test:** The Biuret Test positively identifies the presence of proteins (not less than two Peptides). The reaction in this test involves the complex formation of the proteins with $Cu^{2+}$ ions in a strongly alkaline solution.

**Example:** gelatin, casein and albumin.

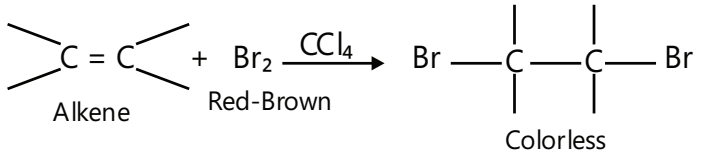
**(m) Alkene and alkyne**

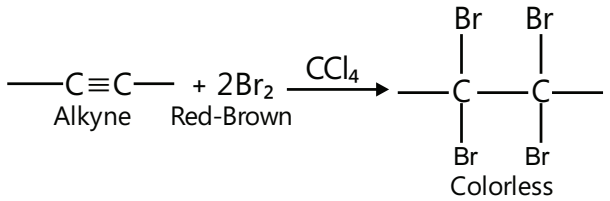
**(i) $Br_2$- water test:** The decoloration of a solution of bromine in water with dichloromethylene as catalyst is an analytical test for the presence of alkenes:

$$CH_2 = CH_2 + Br_2 \longrightarrow BrCH_2 - CH_2Br$$

It is also used as a quantitative test of unsaturation.

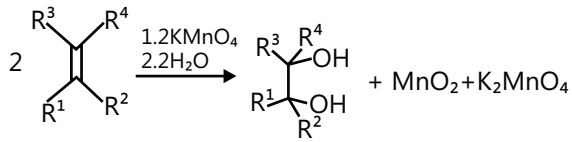
**(ii) Bromine in $CCl_4$:** Bromine will add to the carbon-carbon double bond of alkenes to produce dibromoalkanes and with alkynes to produce tetrabromoalkanes. When this reaction occurs, molecular bromine is consumed, and its characteristic dark redbrown color disappears if bromine is not added in excess. The rapid disappearance of the bromine color is a positive test for unsaturation.



**(iii) Baeyer's reagent: (Alkene only):** Baeyer's reagent is an alkaline solution of cold potassium permanganate, which is a powerful oxidant making this a redox reaction. Reaction with double or triple bonds (–C = C – or – C ≡ C –) in an organic material causes the color to fade from purplish-pink to brown. It is a syn addition reaction.

$$\underset{\text{Purple colour}}{2KMnO_4 + H_2O} \longrightarrow \underset{\text{Brownish red ppt.}}{2KOH + 2MnO_2} + 3[O]$$




$$HC{\equiv}CH + H_2O + 4[O] \longrightarrow HOOC - COOH$$

**(n) Detection of terminal alkyne**

**(i) $AgNO_3$ in ammonia:** The reactions of alkynes with certain metal cations, e.g. $Ag^+$ gives acetylides. Thus, few drops of diammine silver(I) hydroxide $Ag(NH_3)_2OH$ reacts with terminal alkynes signaled by the formation of a silver white precipitate of the silver acetylide.

$$RC \equiv C - H + Ag(NH_3)_2^+ (\text{in } NH_4OH) \longrightarrow RC \equiv C - Ag \text{ (insoluble)} + NH_3 + NH_4^+$$

**(ii) Acidic nature of terminal alkyne:** Terminal alkyne being acidic reacts with strong bases like $NaNH_2$ to form sodium acetylide.

$$H - C \equiv C - H + NaNH_2 \text{ (in ammonia or ether)} \longrightarrow H - C \equiv C - Na \text{ (sodium acetylide)} + NH_3$$

**(iii) With Grignard reagent:** Terminal alkynes react with Grignard reagent to form alkanes.

$$RC \equiv C - H + C_2H_5MgBr \text{ (in ether)} \longrightarrow RC \equiv C - MgBr + C_2H_6$$

**(o) Detection of alkoxy group**

**(i) Hot Hydroiodic Acid (HI) test:** The relatively unreactive C – O bonds in an ether can be cleaved by treatment with conc. HI to give two alkyl iodides and water. The alkyl iodides produced can react with mercuric nitrate, $Hg(NO_3)_2$ , to give the orange-red coloured mercuric iodide ($HgI_2$).

$$ROR' + 2HI \text{ (Hot)} \longrightarrow RI + R'I + H_2O$$

$$2RI + Hg(NO_3)_2 \longrightarrow \underset{\text{Vermillion coloured}}{HgI_2} + 2R - O - NO_2$$

**(ii) Cold HI Test:** When ether is treated with cold HI, the smaller alkyl group in ether forms iodide while bigger one forms alcohol in case of asymmetric ether.

$$CH_3 - CH_2 - O - CH_3 + \text{cold HI} \longrightarrow CH_3I + CH_3 - CH_2 - OH$$

## PLANCESS CONCEPTS

**Exceptions:**

- Lassaigne's test is not given by compounds which do not contain C atoms but contain N atoms.

**Example:** $NH_2NH_2$ (hydrazine), $NH_2OH$ (hydroxyl amine).

**Reason:** Since, these compounds do not contain carbon, in sodium fusion extract, $CN^-$ ion will not form and Prussian blue colour is not observed.

## PLANCESS CONCEPTS

- This test is also not given by diazonium salts although they contain both C and N elements, because the nitrogen in them is released due to strong heating while forming sodium fusion extract.
- If S is also present in organic compound along with C and N, this test gives a blood red colour.

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

$$\underset{\text{Thiocyanate ion}}{3CNS^{-}} + Fe^{+3} \longrightarrow \underset{\substack{\text{Ferric thiocyanate}\\ \text{(Blood–red colour)}}}{Fe(CNS)_3}$$

- If fusion is carried out with excess of sodium, the fusion gives cyanide and sulphide giving usual tests.

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

- In Beilstein's test, Urea $(NH_2CONH_2)$ and thiourea $(NH_2CSNH_2)$ do not contain halogens but still give the test.
- In detection of phosphorous using ammonium molybdate, if the organic compound contains arsenic (As), then it also gives this test forming ammonium arsenomolybdate forming canary yellow ppt.
- In Fehling's solution test, only aliphatic aldehydes give this test. Aromatic aldehydes don't give this test.
- In Tollen's reagent test, $\alpha$ -hydroxy ketones give this test but other ketones do not.
- All amino acids give ninhydrin test except Proline due to absence of free –NH2 group.
- 2° and 3° amines do not give carbylamine test.

**Nikhil Khandelwal (JEE 2009, AIR 94)**

## PLANCESS CONCEPTS

- Lithium is not used in Lassaigne's test even being more electropositive than sodium because it reacts slowly and its compounds are covalent with less ionic nature. Potassium is not used because it reacts vigorously and cannot be handled properly.
- In the Lassaigne's test for nitrogen, if $Fe^{3+}$ ions (with yellow colour) are in excess, it makes the blue colour of ferrocyanide to appear green.
- Tollen's test is also given by formic acid and hemiacetals. But acetals do not give this test.

**Saurabh Gupta (JEE 2010, AIR 443)**

**Illustration 3:** Lassaigne's test is not shown by diazonium salts and hydrazine $(NH_2NH_2)$ even though they contain nitrogen. Why?

**Sol:** Lassaigne's test is not given by compounds which do not contain C atoms but contain N atoms. In case of diazonim salt the nitrogen is released due to strong heating while forming sodium fusion extract.

Diazonium salts usually lose $N_2$ on heating much before they react with fused Na metal. That is why they do not give the above test. Hydrazine does not have C atoms, so it does not form NaCN and hence does not give a positive test for N. In order to test the presence of N in such compounds, during fusion with Na, some charcoal or starch is added to supply C atoms. Under these conditions, NaCN is obtained and it will give a positive test.

**Illustration 4:** The Prussian blue colour obtained in the Lassaigne's test for nitrogen is due to the formation of

(A) Iron (II) hexacyanoferrate (III) (B) Iron (III) hexacyanoferrate (II)

(C) Iron (III) hexacyanoferrate(III) (D) Iron (II) hexacyanoferrate (II)

(E) Sodium hexacyanoferrate (III)

**Sol: (B)** The Prussian blue colour obtained in the Lassaigne's test for nitrogen is due to the formation of

$$Fe^{2+} + 6CN^- \longrightarrow \underset{\text{Hexa cyanoferrate (II)}}{\left[Fe(CN)_6\right]^{4-}}$$

## 3. QUANTITATIVE ANALYSIS

Quantitative analysis of an organic compound includes the measurement of a quantity of an element in the compound. While determining molecular formula of an organic compound, it is necessary to know the percent quantity of every element present in it. There are various processes to determine this percentage based on that element.

**(a) Liebig's combustion method:** A known mass of compound is heated with CuO. The carbon present is oxidized to $CO_2$ and hydrogen to $H_2O$. The $CO_2$ is absorbed in KOH solution, while $H_2O$ vapours are absorbed in anhydrous $CaCl_2$. So, change in their weights will give percentage of C and H.

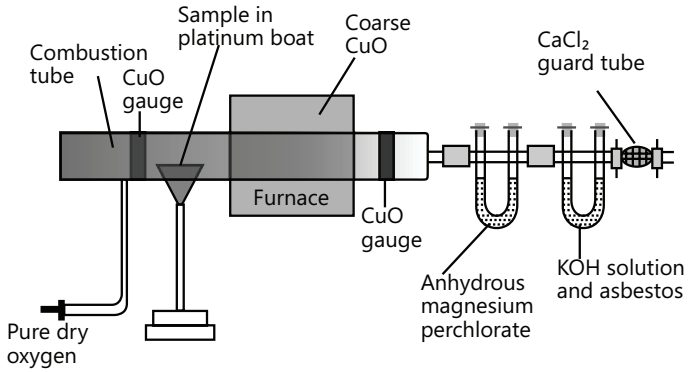



**Figure 27.7:** Combustion Tube

$$\text{Percentage of C} = \frac{12}{44} \times \frac{\text{Mass of } CO_2}{\text{Mass of compound}} \times 100;$$

$$\text{Percentage of H} = \frac{2}{18} \times \frac{\text{Mass of } H_2O}{\text{Mass of compound}} \times 100$$

**(b) Carius Method:** The Carius halogen method in analytical chemistry is a method for the quantitative determination of halogens in chemical substances. A known mass of an organic compound is heated with fuming nitric acid ($HNO_3$) in the presence of silver nitrate ($AgNO_3$) contained in a hard glass tube known as carius tube, in a furnace. Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed. This chemical test works equally well for the determination of sulfur but without the addition of silver nitrate. The sulfuric acid intermediate formed after reaction of sulfur with fuming nitric acid forms insoluble barium sulfate on the addition of barium chloride.

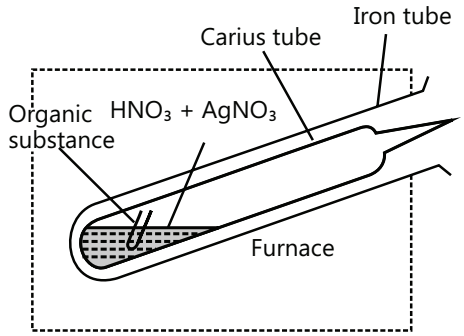



**Figure 27.8:** Carius Tube

(i) Percentage of X = $\frac{\text{Atomic mass of X}}{\text{Molecular mass of AgX}} \times \frac{\text{Mass of AgX} \times 100}{\text{Mass of compound}}$

(ii) Percentage of Cl = $\frac{35.5}{143.5} \times \frac{\text{Mass of AgCl} \times 100}{\text{Mass of compound}}$

(iii) Percentage of Br = $\frac{80}{188} \times \frac{\text{Mass of AgBr} \times 100}{\text{Mass of compound}}$

Percentage of I = $\frac{127}{235} \times \frac{\text{Mass of AgI} \times 100}{\text{Mass of compound}}$

**(c) Estimation of sulphur:** A known mass of compound is heated with fuming $HNO_3$ or sodium peroxide ($Na_2O_2$). In the presence of $BaCl_2$ solution in Carius tube. Sulphur is oxidized to $H_2SO_4$ and precipitated as $BaSO_4$. It is filtered, dried and weighed.

Percentage of S = $\frac{\text{Atomic mass of S}}{\text{Molecular mass of } BaSO_4} \times \frac{\text{Mass of } BaSO_4 \times 100}{\text{Mass of compound}} = \frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \times 100}{\text{Mass of compound}}$

**(d) Estimation of phosphorous:**

**First Method:** A known mass of compound is heated with fuming $HNO_3$ in Carius tube which converts phosphorous to $H_3PO_4$ (phosphoric acid). It is precipitated as ammonium phosphomolybdate [$(NH_4)_3PO_4.12MoO_3$] by adding $NH_3$ and ammonium molybdate. It is filtered, dried, and weighed.

Percentage of P = $\frac{\text{Atomic mass of P}}{\text{Molecular mass of ammonium phospho molybdate}} \times$

$$\frac{\text{Mass of ammonium phospho molybdate} \times 100}{\text{Mass of compound}} = \frac{31}{1877} \times \frac{\text{Mass of } (NH_4)_3.PO_4.12MoO_3 \times 100}{\text{Mass of compound}}$$

**Second Method (Carius method):** A known mass of compound is heated with fuming $HNO_3$ or sodium peroxide in Carius tube which converts phosphorous to $H_3PO_4$. Magnesia mixture $(MgCl_2 + NH_4Cl)$ is then added, which gives the precipitate of magnesium ammonium phosphate $MgNH_4.PO_4$ which on heating gives magnesium pyrophosphate $(Mg_2P_2O_7)$, which is weighed.

Percentage of P = $\frac{\text{Atomic mass of P}}{\text{Molecular mass of } Mg_2P_2O_7} \times \frac{\text{Mass of } Mg_2P_2O_7 \times 100}{\text{Mass of compound}} = \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_2 \times 100}{\text{Mass of compound}}$

**(e) Estimation of nitrogen:**

**(i) Dumas method:** A known mass of the organic compound is heated with cupric oxide in an atmosphere of carbon dioxide. The carbon and hydrogen in the compound are oxidized to carbon dioxide and water respectively, while nitrogen is set free. Any oxide of nitrogen produced during this process, is reduced back to free nitrogen by a heated copper gauze. The gaseous mixture consisting of $CO_2$, $H_2O$ and $N_2$ is collected over an aqueous solution of potassium hydroxide. All the gases except nitrogen are absorbed by the solution. The volume of gas (nitrogen) collected is measured. From the volume of nitrogen obtained the percentage of nitrogen in the compound is calculated.

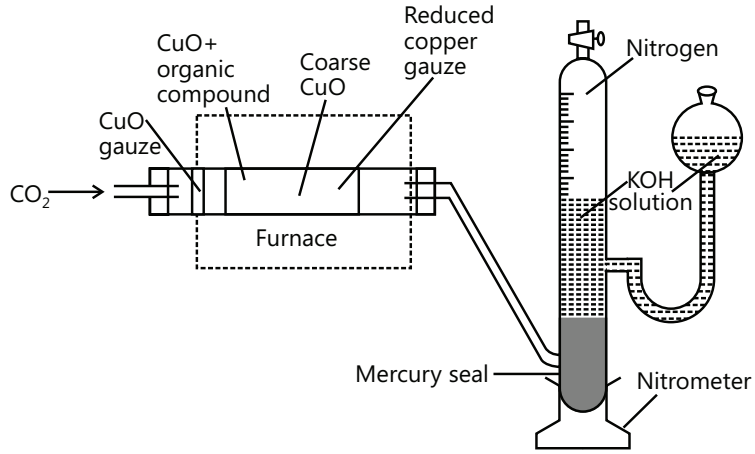



**Figure 27.9:** Dumas Apparatus

**Calculations**

Let, The mass of the organic compound taken be = Wg; Volume of nitrogen collected = $V_1$g

Atmospheric pressure = P mm Hg; Temperature at which gas is collected = $T_1$K

Therefore, Pressure of the $N_2$ gas, $P_1$ = (P - p) mm of Hg

Volume of nitrogen at STP = $\frac{P_1V_2 \times 273}{760 \times T_1}$ = V mL (Using $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$)

Mass of V mL of nitrogen at STP = $\frac{28V}{22400}$g (1 mol of $N_2$ = 28 g = 22400 mL)

Therefore, Percentage of nitrogen in the compound = $\frac{28V}{22400} \times \frac{100}{W}$

**(ii) Kjeldahl's method:** Kjeldahl's method is a faster method than Dumas' method. However, this method is used only for those organic compounds that are converted quantitatively to ammonium sulphate on heating strongly with concentrated sulphuric acid.

Kjeldahl's method cannot be used for the organic compounds,

1. Containing nitrogen in the ring, e.g., pyridine, quinoline etc.
2. Containing nitro (–$NO_2$) and diazo (–N = N–) groups.
3. Kjeldahl's method involves two steps:

- **Digestion:** A known mass (0.3 to 0.5 g) of the given organic compound is digested with concentrated $H_2SO_4$, in the presence of a small quantity of potassium sulphate and copper sulphate in a Kjeldahl's flask. Potassium sulphate raises the boiling point of sulphuric acid and copper sulphate catalyzes the digestion. In 3 to 4 hours, the organic compound is completely decomposed to form ammonium sulphate.

$$\text{Organic compound} + H_2SO_4 \xrightarrow[\text{digestion}]{Cu^{2+}} (NH_4)_2SO_4$$

- **Distillation:** The digested reaction mixture, on cooling, is transferred to a round bottomed distillation flask, and distilled with a concentrated alkali solution (NaOH). Ammonia produced is absorbed in a known volume of HCl solution of a known strength.

$$(NH_4)_2SO_4 + 2NaOH \xrightarrow{\Delta} Na_2SO_4 + 2H_2O + 2NH_3$$

$$NH_3 + HCl \longrightarrow NH_4Cl$$

The un-neutralised HCl is then back-titrated against a standard alkali. From the acid consumed, the amount of ammonia produced and hence the mass of nitrogen is calculated.

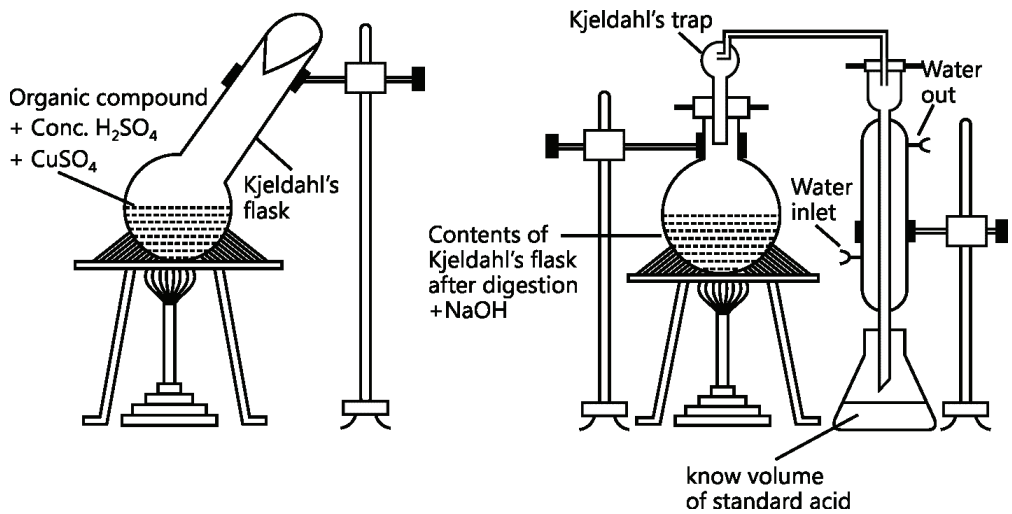



**Figure 27.10:** Kjeldahl's Method

Apparatus for the estimation of nitrogen by Kjeldahl's method

**Calculation**

Let, Mass of the organic compound = W g

Volume of the standard acid required for complete neutralization of the evolved ammonia = V mL; Normality of the standard solution of acid = N

From the law of equivalence (normality equation),

1000 mL of 1 N acid = 1000 mL of 1 N $NH_3$ = 17g $NH_3$ = 14g nitrogen

Then, V mL of N acid = V mL of $NH_3$

NV milli equivalent of acid = NV milli equivalent of ammonia

Therefore, Mass of nitrogen in the evolved ammonia = $\frac{14 \times N \times V}{1000}$ g

Then, Percentage of nitrogen in the sample = $\frac{14NV}{1000} \times \frac{100}{W} = \frac{1.4NV}{W}$

Percentage of nitrogen in the sample =

$$\frac{1.4 \times \text{Normality of HCl} \times \text{Volume of HCl used for complete neutralization of } NH_3}{\text{Mass of the compound taken}}$$

**(f) Estimation of oxygen:**

**First Method:** It is usually the difference between total percentage composition (100%) and sum of the percentage of all other elements.

Percentage of O = 100 – (Percentage of C + Percentage of H + Percentage of N +.....)

**Second Method (Aluise's method):** A known mass of compound is decomposed by heating it in the presence of $N_2$ gas. The mixture of gaseous products containing $O_2$ is passed over red hot coke when all $O_2$ is converted into CO. This mixture is heated with $I_2O_5$ in which CO is converted into $CO_2$ liberating $I_2$.

Compound $\xrightarrow{\Delta}$ Other gaseous product + $O_2$

$$2C + O_2 \xrightarrow{1373K} 2CO$$

$$I_2O_5 + 5CO \longrightarrow 5CO_2 + I_2$$

$$\text{Percentage of O} = \frac{\text{Molecular mass of } O_2}{\text{Molecular mass of } CO_2} \times \frac{\text{Mass of } CO_2 \times 100}{\text{Mass of compound}} = \frac{32}{44} \times \frac{\text{Mass of } CO_2 \times 100}{\text{Mass of compound}}$$

## 4. DETERMINATION OF EMPIRICAL FORMULAE AND MOLECULAR FORMULAE

The empirical formula of a chemical compound is a representation of the simplest whole number ratio between the elements comprising the compound. The molecular formula is the representation of the actual whole number ratio between the elements of the compound. This step by step tutorial shows how to calculate the empirical and molecular formulas for a compound.

**Problem:** A molecule with molecular weight of 180.18 g/mol is analysed and found to contain 40.00% carbon, 6.72% hydrogen and 53.28% oxygen. What are the empirical and molecular formulas of the molecule?

**Solution:** Finding the empirical and molecular formula is basically the reverse process used to calculate mass percent.

**Step 1: Find the number of moles of each element in a sample of the molecule.**

Our molecule contains 40.00% carbon, 6.72% hydrogen and 53.28% oxygen. This means a 100 gram sample contains:

40.00 grams of carbon (40.00% of 100 grams)

6.72 grams of hydrogen (6.72% of 100 grams)

53.28 grams of oxygen (53.28% of 100 grams)

**Note:** 100 grams is used for a sample size just to make the maths easier. Any sample size could be used, the ratios between the elements will remain the same.

Using these numbers we can find the number of moles of each element in the 100 gram sample. Divide the number of grams of each element in the sample by the atomic weight of the element (from the periodic table) to find the number of moles.

moles C = 40.00 g x 1 mol C/12.01 g/mol C = 3.33 moles C

moles H = 6.72 g x 1 mol H/1.01 g/mol H = 6.65 moles H

moles O = 53.28 g x 1 mol O/16.00 g/mol O = 3.33 moles O

**Step 2: Find the ratios between the number of moles of each element.**

Select the element with the largest number of moles in the sample. In this case, the 6.65 moles of hydrogen is the largest. Divide the number of moles of each element by the largest number.

Simplest mole ratio between C and H: 3.33 mol C/6.65 mol H = 1 mol C/2 mol H

The ratio is 1 mole C for every 2 moles H

Simplest ratio between O and H: 3.33 moles O/6.65 moles H = 1 mol C/2 mol H

The ratio between O and H is 1 mole O for every 2 moles of H

**Step 3: Find the empirical formula.**

We have all the information we need to write the empirical formula. For every 2 moles of hydrogen, there is one mole of carbon and one mole of oxygen. The empirical formula is $CH_2O$.

**Step 4: Find the molecular weight of the empirical formula.**

We can use the empirical formula to find the molecular formula using the molecular weight of the compound and the molecular weight of the empirical formula.

The empirical formula is $CH_2O$. The molecular weight is

molecular weight of $CH_2O$ = (1 x 12.01 g/mol) + (2 x 1.01 g/mol) + (1 x 16.00 g/mol)

molecular weight of $CH_2O$ = (12.01 + 2.02 + 16.00) g/mol

molecular weight of $CH_2O$ = 30.03 g/mol

**Step 5: Find the number of empirical formula units in the molecular formula.**

The molecular formula is a multiple of the empirical formula. We were given the molecular weight of the molecule, 180.18 g/mol. Divide this number by the molecular weight of the empirical formula to find the number of empirical formula units that make up the compound. Number of empirical formula units in compound = 180.18 g/mol/30.03 g/mol

Number of empirical formula units in compound = 6

**Step 6: Find the molecular formula.**

It takes six empirical formula units to make the compound, so multiply each number in the empirical formula by 6.

molecular formula = 6 x $CH_2O$

molecular formula = $C_{(1\times6)}H_{(2\times6)}O_{(1\times6)}$

molecular formula = $C_6H_{12}O_6$

**Sol:** The empirical formula of the molecule is $CH_2O$.

The molecular formula of the compound is $C_6H_{12}O_6$.

## PLANCESS CONCEPTS

**1. Leibig combustion method:** (Estimation of C and H)

$$\text{Percentage of C} = \frac{12}{44}\times\frac{\text{Mass of } CO_2}{\text{Mass of compound}}\times100$$

$$\text{Percentage of H} = \frac{2}{18}\times\frac{\text{Mass of } HO_2}{\text{Mass of compound}}\times100$$

**2. Carius's method ( Estimation of halogens):**

$$\text{(i) Percentage of X} = \frac{\text{Atomic mass of X}}{\text{Molecular mass of AgX}}\times\frac{\text{Mass of AgX}\times100}{\text{Mass of compound}}$$

$$\text{(ii) Percentage of Cl} = \frac{35.5}{143.5}\times\frac{\text{Mass of AgCl}\times100}{\text{Mass of compound}}$$

$$\text{(iii) Percentage of Br} = \frac{80}{188}\times\frac{\text{Mass of AgBr}\times100}{\text{Mass of compound}}$$

## PLANCESS CONCEPTS

(iv) Percentage of I = $\frac{127}{235} \times \frac{\text{Mass of AgI} \times 100}{\text{Mass of compound}}$

**3. Estimation of sulphur:**

Percentage of S = $\frac{\text{Atomic mass of S}}{\text{Molecular mass of } BaSO_4} \times \frac{\text{Mass of } BaSO_4 \times 100}{\text{Mass of compound}} = \frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \times 100}{\text{Mass of compound}}$

**4. Carius method (Estimation of phosphorous):**

Percentage of P = $\frac{\text{Atomic mass of P}}{\text{Molecular mass of } Mg_2P_2O_7} \times \frac{\text{Mass of } Mg_2P_2O_7 \times 100}{\text{Mass of compound}} = \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7 \times 100}{\text{Mass of compound}}$

**5. Dumas's method (Estimation of nitrogen):**

Percentage of nitrogen in the compound = $\frac{28V}{22400} \times \frac{100}{W}$

**6. Kjeldahl's method (Estimation of nitrogen):**

Percentage of nitrogen in the sample

$= \frac{1.4 \times \text{Normality of HCl} \times \text{Volume of HCl used for complete neutralization of } NH_3}{\text{Mass of the compound taken}}$

**7. Estimation of oxygen in general:**

Percentage of O = 100 – (Percentage of C + Percentage of H + Percentage of N +.....)

Molecular Formula= n × (Empirical formula)

**T P Varun (JEE 2012, AIR 64)**

**Illustration 6:** 0.50 gm of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5 M $H_2SO_4$ . The residual acid requires 60 ml of M/2 NaOH solution. Find the percentage of nitrogen in the compound.

**Sol:** Percentage of nitrogen present in the given compound can be determined using Kjeldahl's method. We can use the following expression, this method makes use of titration of given compound with acid, and thus it involves neutralization reaction. From the volume of acid require for complete neutralization reaction percentage of nitrogen can be determined.

Percentage of nitrogen in the sample

$= \frac{1.4 \times \text{Normality of HCl} \times \text{Volume of HCl used for complete neutralization of } NH_3}{\text{Mass of the compound taken}}$

mEq. of acid= 50 × 0.5 × 2 = 50: mEq. of base = 60 × 0.5 × 1=30

Excess of acid used to neutralise ; $NH_3$ = 50 – 30 = 20 mEq

Percentage of $N_2$ = $\frac{1.4 \times \text{mEq. of acid used}}{\text{Weight of compound}} = \frac{1.4 \times 20}{0.5} = 56.0\%$

mEq. of acid= 50 × 0.5 × 2 = 50: mEq. of base = 60 × 0.5 × 1=30

Excess of acid used to neutralise ; $NH_3$ = 50 – 30 = 20 mEq

$$\text{Percentage of } N_2 = \frac{1.4 \times \text{mEq. of acid used}}{\text{Weight of compound}} = \frac{1.4 \times 20}{0.5} = 56.0\%$$

**Illustration 7:**

(a) How is a mixture of two organic compounds separated, which have different solubilities in the same solvent?

(b) How is an organic liquid purified which decomposes below its boiling point?

(c) Why is sodium extract boiled with $HNO_3$ before testing for halogens?

(d) What type of organic compounds cannot be estimated by Kjeldahl's method?

(e) What does blood-red colouration during lassaigne's test indicate?

(f) What happens when $AgNO_3$ solution is added to bromo methane?

**Sol:** (a) By fractional crystallization.

(b) Distillation under reduced pressure i.e. vacuum distillation.

(c) To decompose NaCN or $Na_2S$ present in the Lassaigne's extract, otherwise, these will produce white precipitate with $AgNO_3$ and thus interfere with the test of halogens.

(d) Compounds containing N in the ring and those compounds in which N atom is directly linked either to an oxygen atom or another N atom such as in azo (–N = N–) and nitro ($-NO_2$) compounds.

(e) It indicates the presence of both N and S.

(f) It would not give pale-yellow precipitate of AgBr because $CH_3Br$ is a covalent compound and hence does not contain $Br^-$ ion. To get the precipitate of AgBr, $CH_3Br$ is treated with aqueous KOH to get $CH_3OH$ and $Br^-$ and then addition of $AgNO_3$. It would now give the precipitate of AgBr partly soluble in $NH_3$ or $NH_4OH$.

**Illustration 8:** 'O' 1693 gm of a volatile substance when vapourised displaced 58.9 ml of air measured at $27^0$ C and 746 mm pressure. Calculate the molar mass of the substance. (Aqueous tension at $27^0$ C =26.7 mm Hg)

**Sol:** First calculate the volume of air displaced at STP condition by using the ideal gas equation. Now using the volume term calculate the molecular mass of the given compound.

**Step I:** To convert the volume at experimental condition to volume at STP.

| | |
|---|---|
| $P_1$ = 746 – 26.7 = 719.3 mm | $P_2$ = 760 mm |
| $V_1$ = 58.9 ml | $V_2$ = ? |
| $T_1$ = 273 + 27 = 300 K | $T_2$ = 273 K |

Substituting these values in the gas equation.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}, \text{ we get } \frac{719.3\text{mm} \times 58.9\text{ml}}{300\text{K}} = \frac{760\text{mm} \times V_2\text{ml}}{273\text{K}}$$

$$\therefore\ V_2 = \frac{719.3\text{mm} \times 58.9\text{ml} \times 273\text{K}}{300\text{K} \times 760\text{mm}} = 50.73 \text{ ml}$$

$$\text{Molecular mass} = \frac{\text{Mass of substance} \times 22400}{\text{Volume of displaced air at STP}} = \frac{0.1693 \times 22400}{50.73} = 74.75 \text{ gm}$$

**Illustration 9:** 0.15 gm of an organic compound gave 0.12 gm of silver bromide by the Carius method. Find the percentage of bromide in the compound.

**Sol:** We are asked to find out the percentage of bromide in the compound. As we are provided with mass of given compound and mass of silver bromide produced by that compound by the carius method. So we can use the following expression Percentage of

$$\text{Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr}}{\text{Mass of compound}}$$

$$\text{Percentage of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr}}{\text{Mass of compound}} = \frac{80}{188} \times \frac{0.12}{0.15} \times 100 = 34.0\%$$

**Illustration 10:** 0.12 gm of an organic compound containing phosphorous gave 0.22 gm of $Mg_2P_2O_7$ by the usual analysis. Calculate the percentage of phosphorous in the compound.

**Sol:** From the given data i.e mass of $Mg_2P_2O_7$ produced and mass of given compound percentage of phosphorous can be determined using following formula:

$$\text{Percentage of phosphorus} = \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7}{\text{Mass of compound}} \times 100$$

$$\text{Percentage of phosphorus} = \frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7}{\text{Mass of compound}} \times 100 = \frac{62}{222} \times \frac{0.22}{0.12} \times 100 = 51.20\%$$

## 5. DETERMINATION OF MOLECULAR MASS

**(a) Silver Salt Method For Carboxylic Acids:** Most of the organic acids form sparingly soluble silver salts, which on ignition leave a residue of metallic silver. This forms the basis of the silver salt method for the determination of molecular mass of acids. The organic acid solution is neutralized with $NH_2OH$ and heated to boil off excess $NH_3$. It is then treated with excess of $AgNO_3$ solution and the precipitated silver salt is filtered, dried. A known mass of the dry silver salt is ignited in a crucible to a constant mass.

$$RCOOAg \xrightarrow{\Delta} Ag$$

Let the equivalent weight of acid (RCOOH) be E.

The equivalent weight of RCOOAg = E – 1 + 108 = (E +107)

Equivalent weight of Ag =108; Weight of RCOOAg = W gm

Weight of Ag = w gm; 1 equivalent of RCOOAg = 1 equivalent of Ag

$$\frac{W}{E+107} = \frac{w}{108} \;=\; \therefore\; E = \left(\frac{W \times 108}{w} - 107\right)$$

Molecular mass of an acid = E × n (basicity of an acid)

**(b) Chloroplatinate or platinichloride method for organic bases:** Organic bases form salts with HCl and the chloride give double salts with platinum chloride. Organic bases react with dibasic chloroplatinic acid $(H_2PtCl_6)$ and form double salts and are called chloroplatinates or platinichlorides. These salts leave a residue of metallic platinum on ignition.

Equivalent weight of organic base = B

Mass or weight of chloroplatinic salt = W gm

Mass or weight of platinum = w gm

Equivalent weight of platinum = 195

$$2B + H_2PtCl_6 \longrightarrow B_2H_2PtCl_6 \xrightarrow{\Delta} Pt$$

Equivalent weight of $B_2H_2PtCl_6$ = (2B + 2 + 195 + 35.5 × 6) = 2B + 410

1 equivalent of $B_2H_2PtCl_6 = 1$ equivalent of Pt $\frac{W}{2B+410} = \frac{w}{195}$ =

$$\therefore\ B = \left(\frac{W}{w} \times \frac{195}{2}\right) - 205$$

Molecular mass of the organic base = Equivalent mass × Acidity = B × n.

**(c) Victor Meyer's method:** This method is used for volatile organic compounds. A known mass of compound (W gm) is vapourised in an instrument called Victor Meyer tube. The vapours so obtained displace an equal amount of air into a graduated tube. The volume of vapours is measured and reduced to STP.

Let the volume of vapours at STP be V ml.

22400 ml of vapours are obtained from 1 mol of the compound.

V ml of vapours are obtained from $\frac{V\ ml}{22400\ ml}$ mol of compound.

$$\text{Mole} = \frac{\text{Mass of the compound (W gm)}}{\text{Molecular mass of the compound (Mw)}} = \frac{W}{Mw}$$

$$\therefore\quad \frac{W}{Mw} = \frac{V}{22400} \quad \therefore \quad Mw = \frac{W \times 22400}{V} = \frac{\text{Mass of compound} \times 22400}{\text{Volume of vapours at STP}}$$

**Illustration 10:** 0.984 gm of the chloroplatinate of a diacid base gave 0.39 gm of platinum. Calculate the molecular mass of the base.

**Sol:** Mass of platinichloride taken = 0.984 gm; Mass of platinum left = 0.39 gm

To calculate the equivalent mass of base.

Let the equivalent mass of the base be B.

∴ Molecular mass of the platininchloride $(B_2H_2PtCl_6)$ = 2B + 410.

$$\text{Now, } \frac{\text{Molecular mass of chloroplatinichloride}}{\text{Atomic mass of platinum}} = \frac{\text{Mass of platinichloride taken}}{\text{Mass of platinum left}}$$

$$\text{or} \quad \frac{2B+410}{195} = \frac{0.984}{0.39} \text{ or } B = \frac{1}{2}\left(\frac{0.984}{0.39} \times 195 - 410\right) = 41$$

Thus, the equivalent mass of the base be 41.

To calculate the molecular mass of the base,

Acidity of base = 2.

Molecular mass of base = Equivalent mass of base × acidity of base = 41 × 2 = 82

Thus, the molecular mass of base is 82.

**Illustration 11:** On analysis, 0.2 gm of a monobasic acid gave 0.505 gm of $CO_2$ and 0.0864 gm of $H_2O$ . 0.305 gm of this acid required 25 ml of N/10 NaOH for complete neutralization. Find the molecular formula of this acid.

**Sol: (a) Calculation of percentage composition**

$$\text{(i) Percentage of carbon} = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ produced}}{\text{Mass of substance taken}} \times 100 = \frac{12}{44} \times \frac{0.505}{0.2} \times 100 = 68.86\%$$

$$\text{(ii) Percentage of Hydrogen} = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ produced}}{\text{Mass of substance taken}} \times 100 = \frac{2}{18} \times \frac{0.0864}{0.2} \times 100 = 4.8\%$$

(iii) Percentage of oxygen = 100 – (Percentage of C + Percentage of H) = 100 – (68.86 + 4.8) = 26.34%

**(b) Calculation of empirical formula:**

| Element | Percentage | Atomic mass | Relative number of atoms | Simplest atomic ratio | Simplest whole number atomic ratio |
|---|---|---|---|---|---|
| Carbon | 68.86 | 12 | $\frac{68.86}{12} = 5.74$ | $\frac{5.74}{1.65} = 3.48$ | 7 |
| Hydrogen | 4.80 | 1 | $\frac{4.80}{1} = 4.80$ | $\frac{4.80}{1.65} = 2.91$ | 6 |
| Oxygen | 26.34 | 16 | $\frac{26.34}{16} = 1.65$ | $\frac{1.65}{1.65} = 1.00$ | 2 |

Hence, the empirical formula of the compound is $C_7H_6O_2$.

**(c) Calculation of molecular mass:**

mEq. Of NaOH = 25 × $\frac{1}{10}$ = 2.5 mEq. Of acid = 2.5

Equivalent of acid = 2.5 × $10^{-3}$

Equivalent of acid = Ew = $\frac{\text{Weight}}{\text{Equivalent of acid}} = \frac{0.305}{2.5 \times 10^{-3}} = 122$ gm of acid

Molecular weight of acid = Ew × n = 122 × 1 = 122

**(d) Calculation of molecular formula:**

Empirical formula $(C_7H_6O_2)$ mass of the compound = (7 × 12 + 6 × 1 + 16 × 2) = 122

$\therefore \quad n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{122}{122} = 1$

Thus, molecular formula of the compound = n × (Empirical formula) = 1 × $(C_7H_6O_2)$ = $C_7H_6O_2$

# POINTS TO REMEMBER

- Distillation process is used for the purification of liquids which boil without decomposition and contain non-volatile impurities.
- Fractional distillation process is used to separate a mixture of two or more miscible liquids which have boiling points close to each other.
- Vacuum distillation is used for liquids which decompose at a temperature below their normal boiling points.
- Steam distillation is used for separation and purification of liquid which is appreciably volatile in steam, from non-volatile components of a mixture.
- Differential extraction method is used to separate a given organic compound present in aqueous solution by shaking with a suitable organic solvent in which the compound is more soluble than water.
- Chromatography is based on the difference in rates at which the components of a mixture are absorbed as a suitable adsorbent.
- Lassaigne's test is used for detection of nitrogen, halogen and sulphur.

# Solved Examples

## JEE Main/Boards

**Example 1:** Ethylamine and diethylamine cannot be distinguished by

(A) Hinsberg test (B) Carbylamine test

(C) Iodoform test (D) Both (a) and (b)

**Sol:** Only primary amine gives carbylamine test and hinsberg reagent gives different product with primary and secondary amine. A primary amine will form a soluble sulfonamide salt which precipitates after addition of diluted hydrochloric acid. A secondary amine in the same reaction will directly form an insoluble sulfonamide. Thus these tests can be used. (C) 1° and 2° amines can be distinguished by Hinsberg test and carbylamine test.

**Example 2:** Which of the following give positive Tollen's reagent test.

(A) $(CH_2)_2$ $CO_2H$ $CO_2H$ (B) $CH_2$ $CO_2H$ $CO_2H$

(C) $CO_2H$ | $CO_2H$ (D) $HCO_2H$

**Sol:** Formic acid will get oxidized to carbon dioxide and water, this is due to the carbonyl-containing carbon in aldehydes having an attached hydrogen. (D) Formic acid is the only acid giving tollen's reagent test.

**Example 3:** Sodium nitroprusside when added to an alkaline solution of sulphide ions produces a colouration which is:

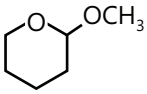
(A) Prussian blue (B) Purple

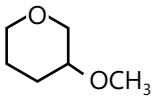
(C) Blood red (D) Turnbull Blue

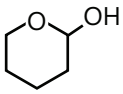
**Sol:** (C) Na + N + C + S $\longrightarrow$ NaCNS
(Sodium thiocyanate)

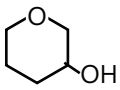
$$\underset{\text{Thiocyanate ion}}{3CNS^- + Fe^{+3}} \longrightarrow \underset{\substack{\text{Ferric thiocyanate}\\ \text{(Blood–red colour)}}}{Fe(CNS)_3}$$

**Example 4:** Which of the following give positive Tollen's test:

(A) 


(B) 


(C) 


(D) 


**Sol:** Hemiacetal due to presence of hydrogen atom at chiral carbon gives positive test with Tollen's reagent.

(C) Hemiacetals give positive Tollen's test.

**Example 5:** Give test to differentiate between 1,1-dichloroethane and 1,2-dichloroethane:

(A) 2,4-DNP then aq. KOH

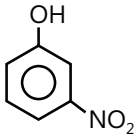
(B) Aq. KOH then 2,4- DNP

(C) $NaHSO_3$

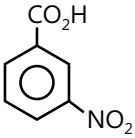
(D) Lucas reagent

**Sol:** (B) Gem dihalide forms aldehyde or ketone which gives test of 2,4-DNP

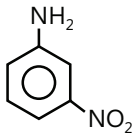
**Example 6:**



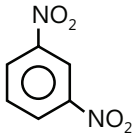

(m-nitrophenol)




(m-nitro benzoic acid)




(m-nitro aniline)




(m-dinitro benzene)

Above compounds can be differentiated by which of the following chemical test used in same order?

(A) NaOH, $NaHCO_3$, HCl (B) HCl, NaOH, $NaHCO_3$

(C) $NaHCO_3$, NaOH, HCl (D) NaOH, HCl, $NaHCO_3$

**Sol:** $NaHCO_3$ separates carboxylic acid, NaOH separates phenol. HCl further separates amine.

**Example 7:** Which of the following reagent is used for the separation of acetaldehyde from acetophenone?

(A) $NH_2OH$ (B) NaOI

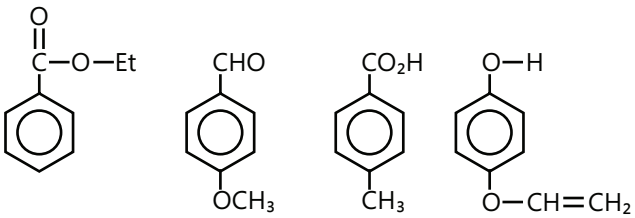
(C) Tollen's reagent (D) $C_6H_5NHNH_2$

**Sol:** ketone and aldehydes can be distinguished by Tollen's reagent as Ketones do not give Tollen's reagent test, while aldehydes do not give.

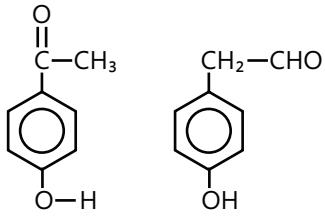
(C) Ketones do not give Tollen's reagent test, while aldehydes do not give.

## JEE Advanced/Boards

**Example 1:** Given are the isomers of $C_8H_8O_2$.



(A) (B) (C) (D)



(E) (F)

(i) Which isomer gives positive iodoform test?

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

(ii) Which isomer gives +ve Tollen's test, also reacts with $FeCl_3$?

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

(iii) Which isomer reacts with $NaHCO_3$?

(A) c (B) b (C) e (D) f

(iv) Which isomer on hydrolysis gives 1, 4-di hydroxybenzene?

(A) a (B) d (C) e (D) f

**Sol:** (i) (D) Iodoform test is given by compounds having free methyl group.

(ii) (B) Tollens test is given by aldehyde as Aldehydes are readily oxidized to carboxylic acids

(iii) (A) Acid with NaHCO3 gives brisk effervescence due to formation of Carbon dioxide

(iv) (B) Ether on hydrolysis give alcohol.

**Example 2:**

$$Ph-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{NaHCO_3^{14}} (A)\ gas\ ;\ Ph-OH \xrightarrow{Na} (B)\ gas$$

Sum of molecular mass of gas (A + B = ?)

**Sol:** Molecular mass of gas is 48; The gas formed in first reaction is $C^{14}O_2$ and from other reaction is $H_2$.

**Example 3: Statement-I:** Aniline on reaction with $NaNO_2$/HCl at 0°C followed by coupling with β-naphthol gives a dark blue coloured precipitate. and

**Statement-II:** The colour of the compound formed in the reaction of aniline with $NaNO_2$/HCl at 0°C followed by coupling with β-naphthol is due to the extended conjugation.

(A) Statement-I is true, statement-II is true; statement-II is correct explanation for statement-I

(B) Statement-I is true, statement-II is true; statement-II is not a correct explanation for statement-I

(C) Statement-I is true, statement-II is false

(D) Statement-I is false, statement-II is true

**Sol:** (D) $C_6H_5N_2Cl$ gives scarlet red coloured dye with β-naphthol.

**Example 4:** Propyne and propene can be distinguished by

(A) Conc. $H_2SO_4$ (B) $Br_2$ in $CCl_4$

(C) Dil. $KMnO_4$ (D) $AgNO_3$ in ammonia

**Sol:** Propyne being terminal alkyne forms silver ppt. with $AgNO_3$ in ammonia.

$$RC\equiv C-H + Ag(NH_3)_2^+ (\text{in } NH_4OH) \longrightarrow$$

$$RC\equiv C-Ag\ (\text{insoluble}) + NH_3 + NH_4^+$$

(D) Propyne being terminal alkyne forms silver ppt. with $AgNO_3$ in ammonia.

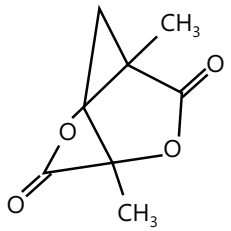
**Example 5:** 2,4-pentadione is treated with excess of KCN in acetic acid solution and finally hydrolysed with dilute

$H_2SO_4$ giving products only with molecular formula $C_7H_{12}O_6$ (dicarboylic acids). The correct statement regarding product(s) of this reaction is/are

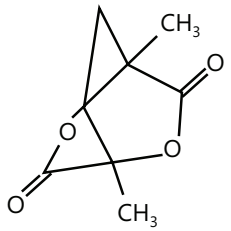
(A) Product mixture contains four stereoisomers which on fractional crystallization gives two fractions.

(B) Product mixture contains three stereoisomers which on fractional crystallization gives two fractions.

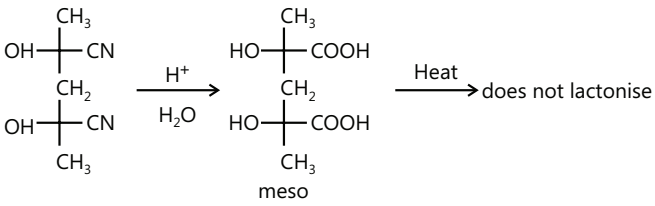
(C) Product of either fraction obtained after crystallization, on strong heating lactonizes to give the following compound:

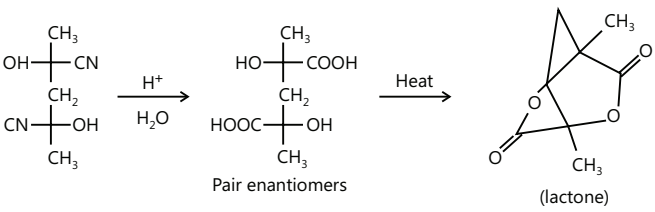


(D) Product of only one fraction obtained after crystallization, on strong heating lactonizes to give following compound:



**Sol:** (B,D) The reaction with KCN in acetic acid solution and hydrolysis with dilute $H_2SO_4$, gives a product with two chiral centers giving three stereoisomers. Nucleophilic addition occur at $sp^2$ carbons, both front and back side are equally probable. Since, product is symmetric, one meso product and a pair of enantiomers. Enantiomers having same solubility form same fraction after fractional crystallization.




**Example 6:** A hydrocarbon (A) of molecular weight 54 reacts with an excess of $Br_2$ in $CCl_4$ to give a compound (B) whose molecular weight is 593% more than that of (A). However, on catalytic hydrogenation with excess of hydrogen, (A) forms (C) whose molecular weight is only 7.4% more than that of (A). (A) reacts with $CH_3CH_2Br$ in the presence of $NaNH_2$ to give another hydrocarbon (D) which on ozonolysis yields diketone (E). (E) on oxidation gives propionic acid. Give the structures of (A) to (E) with reason.

**Sol:** To determine the molecular weights of compounds (B) and (C).

(i)The molecular weight of a compound (A) is 54 while that of compound (B), which gives on treatment with an excess of $Br_2$ in $CCl_4$, is 593% more than that of (A).

$\therefore$ Molecular weight of (B) = $\frac{(100+593)}{100} \times 54 = 374.22$

Thus, the increase in weight due to addition of Br atoms is 374.22 – 54.0 = 320.22

Since, the atomic weight of Br is 80, the number of Br atoms added = 320.22/80 = 4

As such the hydrocarbon (A) must be an alkyne.

(ii) Further, since the molecular weight of compound (C), which hydrocarbon (A) gives on catalytic hydrogenation, is only 7.4% more than that of (A), the molecular weight of (C) is

$$\frac{(100+7.4)\times 54}{100} = 57.994 = 58 \text{ (approx.)}$$

Thus, the increase in weight due to addition of H atoms = 58 – 54 = 4

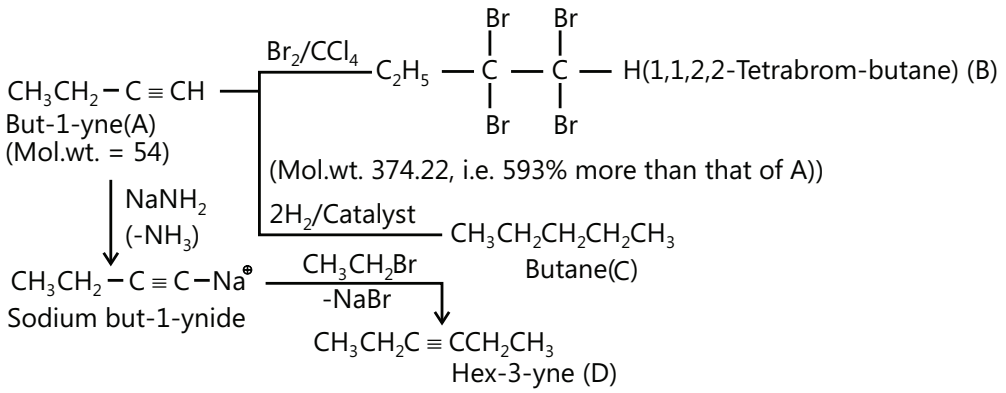
Since, the atomic weight H is 1, the number of H atoms added during catalytic hydrogenation is 4/1 = 4. Therefore, hydrocarbon (A) must be an alkyne.

To determine the structures of the hydrocarbons (A), (B), (C) and (D).

(i) The two possible structures of hydrocarbon (A) i.e. an alkyne with molecular weight 54 ($C_4H_6$) are: $CH_3CH_2 - C \equiv CH$ (But-1-yne) (I) ; $CH_3 - C \equiv CH_3$ (But-2-yne) (II)

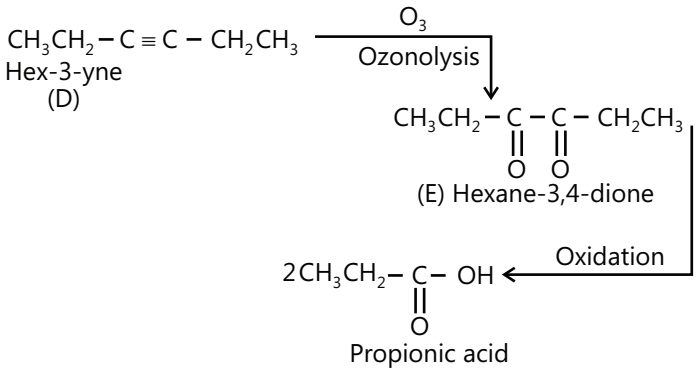
(ii) Since, (A) reacts with $CH_3CH_2Br$ in the presence of $NaNH_2$ to give another hydrocarbon (D), (A) must be a terminal alkyne i.e. but-1-yne and not but-2-yne.

(iii) If hydrocarbon (A) is but-1-yne, then the structure of the compounds (B), (C) and (D) may be worked out as follows:




To determine the structure of the diketone of (E).

Since the hydrocarbon (D) i.e. hex-3-yne on ozonolysis gives a diketone (E) which on further oxidation gives propionic acid, the diketone (E) must be hexane-3,4-dione as explained below:




Thus,

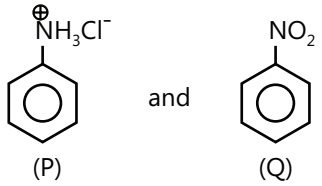
(A) = But-1-yne, (B) = 1,1,2,2 -Tetrabromobutane, (C) = Butane (D) = Hex-3-yne, and

(E) = Hexane-3, 4-dione

# JEE Main/Boards

## Exercise 1

**Q.1** Compounds (P) and (Q) can be differentiated by:




**Q.2** 0.002 gm of an organic compound was treated according to Kjeldahl's method.

$0.2 \times 10^{-4}$ mol of $H_2SO_4$ was required to neutralize $NH_3$. Calculate the percentage of $N_2$.

**Q.3** 0.12 gm of an organic compound containing phosphorous gave 0.22 gm of $Mg_2P_2O_7$ by the usual analysis. Calculate the percentage of phosphorous in the compound.

**Q.4** An organic compound containing sulphur is estimated by Carius method in which fuming $HNO_3$ is used to convert S into?

**Q.5** In organic layer test, $CS_2$ or $CCl_4$ is added to Lassaigne's extract and then $Cl_2$ water or $KMnO_4$ is added. This test is used to distinguish between?

**Q.6** A Dumas bulb full of air weighs 22.567 gm at 20°C and 755 mm pressure. Full of vapours of a substance

at 120°C and the same pressure, it weighs 22.8617 gm. The capacity of the bulb is 200 ml. Find out the molecular mass of the substance.

[Density of air = 0.00129 gm/ml

**Q.7** Percentage composition of an organic compound is as follows: $C = 10.06, H = 0.84, Cl = 89.10$

What is its molecular formula if the vapour density is 60.0?

**Q.8** The empirical formula of a compound is $CH_2$. One mole of the compound has mass of 42 g, its molecular formula is?

**Q.9** How will you separate a mixture of o-nitro-phenol and p-nitrophenol ?

**Q.10** How will you separate benzoic acid from a mixture of naphthalene and benzoic acid?

**Q.11** Suggest methods for the separation of the following mixtures:

(A) A mixture of liquid A (b.p. 365 K) and liquid B (b.p.355 K)

(B) A mixture of liquid C (b.p. 348 K) and liquid D (b.p. 478 K).

**Q.12**Will a precipitate of AgCl be formed on treating $CHCl_3$ with $AgNO_3$? Explain :

**Q.13** Name two compounds which are purified by sublimation.

**Q.14** What is the basic principle of chromatography?

**Q.15** What conclusions would you draw if the Lasagne's extract gives a blood red colouration with $FeCl_3$?

**Q.16** 0.257 g of an organic substance was heated with conc. $H_2SO_4$ and then distilled with excess of strong alkali. The ammonia gas evolved was absorbed in 50 mL of M/10 which required 23.2 mL of M/10 NaHO for neutralisation at the nitrogen in the compound.

**Q.17** 0.85 g of an organic substance was Kjeldahlised and the ammonia obtained was passed into 100 mL of M/10 $H_2SO_4$ **.** The excess acid required 154 mL of M/10 NaOH for neutralisation. Calculate .the percentage of nitrogen in the compound.

**Q.18** A ample of a 0.50 g on organic compound was heated according to Kjerldahl's method. The ammonia evolved by absorbed in 50 mL of 0.5 M $H_2SO_4$.The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

**Q.19** 0.15 g of an organic compound gave 0.12 g AgBr by carious method. Find the percentage of bromine in the compound.

**Q.20** 0.395 g of an organic compound by Carius method for the estimation of sulphur gave 0.582 g of $BaSO_4$. Calculate the percentage of sulphur in the compound.

## Exercise 2

### Single Correct Choice Type

**Q.1** In Kjeldahl's method, nitrogen present is estimated as:

(A) $N_2$ (B) $NH_3$

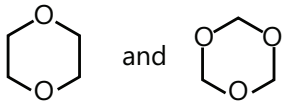
(C) $NO_2$ (D) None of these

**Q.2** A compound which doesn't give a positive test in Lassaigne's test for nitrogen is:

(A) Urea (B) Hydrazine

(C) Azobenzene (D) Phenyl hydrazine

**Q.3** Compounds (X) and (Y) can be differentiated by:



(X) (Y)

(A) $H_3O^+$ , Na (B) $H_3O^+$ , then Fehling test

(C) $H_3O^+$ , then Na (D) Both (B) and (C)

**Q.4** In Kjeldahl's method of estimation of nitrogen $K_2SO_4$ acts as:

(A) An oxidant (B) Catalytic reagent

(C) Hydrolyzing agent (D) Boiling point elevator

**Q.5** The Prussian blue colour obtained during the test of nitrogen by Lassaigne's test is due to formation of :

(A) $Fe_4[Fe(CN)_6]_3$ (B) $Na_3[Fe(CN)_6]$

(C) $Fe[Fe(CN)_6]$ (D) $Na_4[Fe(CN)_5NOS]$

**Q.6** A compound of carbon, hydrogen, and nitrogen contains the elements in the ratio 18 : 2 : 7. Calculate its empirical formula and molecular formula if its molecular mass is 108.

(A) $C_3H_4N$, $C_6H_8N_2$ (B) CHN, $C_5H_6N_3$

(C) $C_5H_6N_3$, $C_5H_6N_3$ (D) $C_2H_4N$, $C_4H_8N_2$

**Q.7** In Dumas's method for the estimation of nitrogen in an organic compound, nitrogen is estimated in the form of:

(A) Gaseous nitrogen (B) Sodium cyanide

(C) Ammonium sulphate (D) Gaseous ammonia

**Q.8** In Leibig's combustion method for estimation of C and H, if the compound contains N, which of the following is kept near the exit of the combustion tube?

(A) Silver wire (B) $PbCrO_4$

(C) Both A and B (D) Cu gauge

**Q.9** Which of the following statements are wrong? (multiple choice)

(A) The gas displaced in Victor Meyer's method is air.

(B) The simplest formula that shows the ratio of the constituent atoms present in the molecule is called molecular formula.

(C) Estimation of oxygen in an organic compound is also done by Aluise's method.

(D) An organic monobasic base B on reaction with $H_2PtCl_6$ forms an insoluble compound $B_2H_2PtCl_6$.

**Q. 10** Which of the following statement(s) is/are correct?

(A) Nitroprusside ion is $[Fe(CN)_5NO]^{2-}$.

(B) Nitroprusside ion is $[Fe(CN)_5NOS]^{2-}$

(C) Prussian blue and turn bull blue are respectively $Fe_4[Fe(CN)_5]_3$ and $Fe_3[Fe(CN)_6]_2$.

(D) Prussian blue and turn bull blue are respectively $Fe_3[Fe(CN)_6]_2$ and $Fe_4[Fe(CN)_6]_3$.

**Q.11**. Sulphur cannot be detected by

(A) Beilstein test (B) Lassaigne test

(C) Lead acetate test (D) Sodium nitroprusside test

**Q.12** If an organic compound contains both N and S; the appearance of blood red colour takes place in Lassaigne-test due to formation of

(A) NaCNS (B) $Fe(CNS)_3$ (C) NaSCN (D) $Fe(CN)_2$

**Q. 13** Layer test is used to detect the presence of

(A) Chlorine (B) Phosphorus

(C) Bromine (D) Fluorine

**Q.14** Carius method is used for the estimation of

(A) Halogens (B) Sulphur

(C) Phosphorus (D) All of these

**Q.15** During estimation of Duma's method 2.36 g of an organic compound gave 448 mL of $N_2$ (g) at NTP. The % of N in the compound is

(A) 23.7% (B) 40% (C) 47.4% (D) 12%

**Q.16** Estimation of C and H in an organic compound is done by

(A) Duma's method (B) Leibig's method

(C) Lassaigne method (D) Carius method

**Q.17** The principle involved in paper chromatography is

(A) Partition (B) Sublimation

(C) Adsorption (D) Solubility

**Q.18** Naphthalene and benzoic acid can be separated from each other best by the method of

(A) Crystallisation (B) Sublimation

(C) Distillation (D) Chromatography

**Q.19** Which of the following compound will not give Lassaigne's test for nitrogen?

(A) Azobenzene (B) Hydrazine

(C) Phenylhydrazine (D) Urea

**Q.20** What happens when $AgNO_3$ solution is added to bromo methane?

(A) Gives yellow ppt

(B) Will gives white ppt

(C) Gives yellow ppt only in presence of KOH

(D) Gives white ppt only in presence of KOH

## Previous Years Questions

**Q.1** Which of the following compounds can be detected by Molisch'stest? ***(2012)***

(A) Nitro compounds (B) Sugars

(C) Amines (D) Primary alcohols

**Q.2** Silver Mirror test is given by which one of the following compounds ? ***(2011)***

(A) Acetone (B) Formaldehyde

(C) Benzophenone (D) Acetaldehyde

**Q.3** Which of the following reagents may be used to distinguish between phenol and benzoic acid? ***(2011)***

(A) Tollen's reagent (B) Molisch reagent

(C) Neutral $FeCl_3$ (D) Aqueous NaOH

**Q.4** Biuret test is not given by ***(2010)***

(A) Carbohydrates (B) Polypeptides

(C) Urea (D) Proteins

**Q.5** The ammonia evolved from the treatment of 0.30 g of an organic compound for the estimation of nitrogen was passed in 100 mL of 0.1 M sulphuric acid. The excess of acid required 20 mL of 0.5 M sodium hydroxide solution for complete neutralization. The organic compound is ***(2004)***

(A) Acetamide (B) Thiourea

(C) Urea (D) Benzamide

**Q.6** Among the following the one that gives positive iodoform test upon reaction with $I_2$ and NaOH is: ***(2006)***

(A) $CH_3CH_2CH(OH)CH_2CH_3$ (B) $C_6H_5CH_2CH_2OH$

(C) $CH_3CH(CH_3)-CH_2OH$ (D) $Ph-CH(OH)CH_3$

**Q.7** Iodoform can be prepared from all except: ***(2012)***

(A) Ethyl methyl ketone

(B) Isopropyl alcohol

(C) 3–Methyl – 2– butanone

(D) Isobutyl alcohol

**Q.8** 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralization. The percentage of nitrogen in the compound is ***(2010)***

(A) 59.0 (B) 47.4

(C) 23.7 (D) 29.5

**Q.9** For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of $\frac{M}{10}$ sulphuric acid. The unreacted acid required 20 mL of $\frac{M}{10}$ sodium hydroxide for complete neutralization. The percentage of nitrogen in the compound is ***(2014)***

(A) 6% (B) 10% (C) 3% (D) 5%

**Q.10** In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is:

(at. mass Ag = 108 ; Br = 80) ***(2015)***

(A) 24 (B) 36 (C) 48 (D) 60

**Q.11** The hottest region of Bunsen flame shown in the figure below is: ***(2016)***

(A) Region 2 (B) Region 3

(C) Region 4 (D) Region 1

**Q.12** The distillation technique most suited for separating glycerol from spent-lye in the soap industry is: ***(2016)***

(A) Fractional distillation

(B) Steam distillation

(C) Distillation under reduced pressure

(D) Simple distillation

# JEE Advanced/Boards

## Exercise 1

**Q.1** 0.92 gm of an organic compound containing carbon, hydrogen, and oxygen was analysed by Leibig's combustion method. The increase in the mass of U-tube and the potash bulbs at the end of the operation was found to be 1.08 gm and 1.76 gm, respectively. Determine the percentage composition of the compound.

**Q.2** In an estimation of sulphur by the Carius method 0.2175 g of the substance gave 0.5825 g of $Ba_2SO_4$. What is the percentage of sulphur in the substance?

**Q.3** An organic compound having molecular mass 60 is found to contain $C = 20\%$, $H = 6.67\%$ and $N = 46.67\%$ while rest is oxygen .On heating it given $NH_3$ along with a solid residue. The solid residue give violet colour with alkaline copper sulphate solution. The compound is:

**Q.4** An hydrocarbon contains 10.5 g carbon and 1 g hydrogen. Its 2.4 g has 1 L volume at 1 atm and $127^\circ$ C. Determine the molecular formula of the Hydrocarbon.

**Q.5** 0.1877 g of an organic compound when analysed by the Duma's method yields 32 mL of most nitrogen measured at 287 k and 758 mm mercury pressure. What is percentage of nitrogen in the organic compound? (aqueous tension at $287K = 12mm$)

**Q.6** If 0.228 g of silver salt of dibasic acid gave a residue of 0.162 g of silver on ignition then what is the molecular weight of the acid?

**Q.7** 0.5 g of hydrocarbon gave 0.9 water on combustion. Calculate the percentage of carbon in hydrocarbon.

**Q.8** In a compound, C,H and N are present in $9:1:3.5$ by weight. If molecular weight of the compound is 108, then determine the molecular formula of the compound.

**Q.9** Name a method suitable for separating the mixture of iodine and sodium chloride.

**Q.10** Why is nitric acid added to sodium extract before adding silver nitrate solution for testing halogens?

**Q.11** Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

**Q.12** The $R_f$ value of A and B in a mixture determined by TLC in a solvent mixture are 0.65 and 0.42 respectively. If the mixture is separated by column chromatography using the same solvent mixture on a mobile phase, which of the two components A or B elute first?

**Q.13** A mixture contains 71 per cent of calcium sulphate and 29 per cent of camphor. Name a suitable technique of separation of the components of the mixture?

**Q.14** Suggest a suitable technique of separating naphthalene from kerosene present in a mixture.

**Q.15** Write the molecular formula of iron (III) hexacyanoferrate (II).

**Q.16** 0.2475 g of an organic compound gave on combustion 0.4950 g of carbon dioxide and 0.2025 g of water. Calculate the percentage of carbon and hydrogen in it.

**Q.17** An organic compound contains $69\%$ carbon and $4.8\%$ hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

**Q.18** On complete combustion, 0.246 g of an organic compound gave 0.198 g of carbon dioxide and 0.1014 g of water calculate the percentage composition of carbon and hydrogen in the compound.

**Q.19** In a Duma's nitrogen estimation 0.3 g of an organic compound gave 50 mL of nitrogen collected at 300 K and 715 mm pressure. Calculate the percentage of nitrogen in the compound.

(vapour pressure of water at 300 K is 15 mm).

**Q.20** During nitrogen estimation of an organic compound by Kjeldahl's method, the ammonia evolved by 0.5 g of the compound neutralised 10 mL of 1 $MH_2SO_4$. Calculate the percentage of nitrogen in the compound.

## Exercise 2

### Single Correct Choice Type

**Q.1** Prussian is formed when

(A) Ferrous sulphate reacts with $FeCl_3$

(B) Ferric sulphate reacts with $Na_4[Fe(CN)_6]$

(C) Ferrous ammonium sulphate reacts with $FeCl_3$

(D) Ammonium sulphate reacts with $FeCl_3$

**Q.2** Lassaigne's test is used to detect

(A) Nitrogen (B) Sulphur (C) Chlorine (D) All of these

**Q.3** Kjeldahl's method is used in the estimation of

(A) Nitrogen (B) Halogens (C) Sulphur (D) Oxygen

**Q.4** In sodium fusion test of organic compounds, the nitrogen of the organic compound is converted into

(A) Sodamide (B) Sodium cyanide

(C) Sodium nitrite (D) Sodium nitrate

**Q.5** A is a lighter phenol and B is an aromatic carboxylic acid. Separation of a mixture of A and B can be carried out easily by using a solution of

(A) Sodium hydroxide (B) Sodium sulphate

(C) Calcium chloride (D) Sodium bicarbonate

**Q.6** The most suitable method for separation of 1:1 mixture of ortho and para nitrophenols is

(A) Sublimation (B) Chromatography

(C) Crystallisation (D) Steam distillation

**Q.7** Lassaigne's test for the detection of nitrogen fails in:

(A) $NH_2CONHNH_2.HCl$ (B) $NH_2NH_2.HCl$

(C) $NH_2CONH_2$ (D) $C_6H_5NHNH_2.HCl$

**Q.8** An organic compound contains C = 40% O = 53.34% and H = 6.60%. The empirical formula of the compound is:

(A) $CH_2O$ (B) CHO (C) $CH_4O_2$ (D) $C_2H_2O$

**Q.9** Which of the following techniques is most suitable for purification of cyclohexanone from a mixture containing benzoic acid, isoamyl alcohol, cyclohexane and cyclohexanone?

(A) Crystallisation (B) IR spectroscopy

(C) Sublimation (D) Evaporation

**Q.10** An organic compound containing C, H and N gave the following results on analysis C = 40%, H = 13.33%, N = 46.67%. Its empirical formula would be

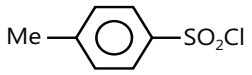
(A) $C_2H_7N_2$ (B) $CH_5N$ (C) $CH_4N$ (D) $C_2H_7N$

**Q.11** A dibasic organic acid gave the following results: C = 34.62%, H = 3.84%. Also, 0.1075 gm of this acid consumers 20 ml of 0.1 N NaOH for complete neutralisation the molecular formula of the acid.

(A) $C_4H_8O_2$ (B) $C_2H_6O$ (C) $C_3H_4O_4$ (D) $C_8H_9O_3$

### Match the Columns

**Q. 12** Match the columns with compounds in column I and the reagent to separate them in column II

| Column I | Column II |
|---|---|
| **Compounds** | **Reagent for separation** |
| (A) 1° and 2° amines | (p) $NaHSO_3$ |
| (B) Ethanal and ethanol | (q) Hinsberg reagent ($PhSO_2Cl$) or  |
| (C) $(C_2H_5)_2NH$ and butanol | (r) Dil. NaOH and distillation |
| (D) $(C_2H_5)_2C = 0$ and $CH_3COOH$ | (s) Dil. $H_2SO_4$ and steam distillation |

**Q.13** Match the columns with method of sepretion in column I with the compounds in column II

| Column I | Column II |
|---|---|
| **Methods of separation(I)** | **Compound(II)** |
| (A) Separated by treatment with dil. NaOH | (p) Toluene and aniline |
| (B) Extraction with dil. HCl, a compound passes into the aqueous layer in the form of hydrochloride salt and recovered by neutralization. | (q) Toluene and phenol |
| (C) Separated by $NaHCO_3$ solution, a compound forms salt and is recovered after acidification. | (r) Diethyl ether and chlorobenzene |
| (D) Separated by conc. $H_2SO_4$, which dissolves a compound and recovered from solution by dilution with $H_2O$ | (s) o-Cresol and benzoic acid |

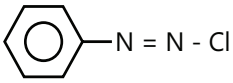
**Comprehension Type**

**Paragraph (14-23)**

Qualitative analysis of organic compounds is performed by Lassaigne's test by fusion with sodium metal, by which the covalent compounds are converted to ionic compounds. Extra elements like N, S, P and halogens are detected by their usual tests.

**Q.14** Which of the following compounds will give positive Lassaigne's test for nitrogen?

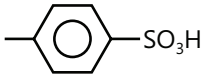
(A) $NH_2OH$ (B) $NH_2NH_2$

(C) KCN (D) 

**Q.15** Which of the following will give blood red colour in Lassaigne's test for nitrogen ?

(A) $PhNH_2$

(B) $PhNO_2$

(C) 

(D) $PhSO_3H$

**Q.16** Prussian blue colour in the detection of nitrogen in Lassaigne's test is due to formation of:

(A) $Fe_3[Fe(CN)_6]$ (B) $Fe_4[Fe(CN)_6]_3$

(C) $Fe_3[Fe(CN)_6]_2$ (D) $Fe[Fe(CN)_6]$

**Q.17** Violet colour in the detection of sulphur with sodium nitroprusside is due to formation of

(A) $Na_3[Fe(CN)_5NOS]$ (B) $Na_4[Fe(CN)_5NOS]$

(C) $Na_4[Fe(CN)_4S]$ (D) $Na_2[Fe(CN)_5S]$

**Q.18** An organic compound containing N,S, and O as extra elements is fused with metallic sodium and then extracted with distilled water. Which species is not present in the Lassaigne's extract?

(A) $NO_3^-$ (B) $CN^-$ (C) $CNS^-$ (D) $S^{2-}$

**Q.19** The Lassaigne's extract is boiled with dil.$HNO_3$ before testing for halogens because

(A) AgCN is soluble in $HNO_3$

(B) Silver halides are soluble in $HNO_3$

(C) NaCN and $Na_2S$ are decomposed by $HNO_3$.

(D) $Ag_2S$ is soluble in $HNO_3$.

**Q.20** Black precipitate in the detection of sulphur with lead acetate and acetic acid is due to formation of:

(A) $Pb_2S$ (B) PbS (C) $PbS_2$ (D) $PbSO_4$

**Q.21** Blood-red colour in the detection of both N and S in the Lassaigne's extract is due to formation of :

(A) $Fe(CNS)_2$ (B) $Fe(CNS)_3$

(C) $K_4[Fe(CN)_6]$ (D) $K_3[Fe(CN)_6]$

**Q.22** Yellow precipitate in the detection of phosphorous when an organic compound is heated with $Na_2O_2$ and then boiled with conc. $HNO_3$ followed by the addition of ammonium molybdate is due to formation of:

(A) $(NH_4)_3 . PO_4 . 12MoO_3$ (B) $(NH_4)_3 . PO_4 . 6MoO_3$

(C) $(NH_4)_3 . PO_4 . 12MoO_2$ (D) $(NH_4)_3 . PO_4 . 6MoO_2$

**Q.23** Beilstein test is given by:

(A) RX (X = Cl, Br, I) (B) Urea

(C) Thiourea (D) All of these

**Assertion Reasoning Type**

(A) If both assertion and reason are correct and reason is correct explanation of assertion.

(B) If both assertion and reason are correct and reason is not a correct explanation of assertion.

(C) If assertion is correct and reason is incorrect.

(D) If assertion is incorrect and reason is correct.

(E) If both assertion and reason are incorrect.

**Q.24 Assertion:** In organic layer test, $Cl_2$ water is added to sodium extract, which oxidises $Br^-$ and $I^-$ ions to $Br_2$ and $I_2$ respectively.

**Reason:** Reduction potential of $Cl_2$ is greater than that of $Br_2$ and $I_2$.

**Q.25 Assertion:** Hydroxylamine ($NH_2OH$) contains N, and hence gives Lassaigne's test.

**Reason:** Hydroxylamine does not contain C, so with Na metal, $CN^-$ ion is not formed.

**Q.26 Assertion:** Benzene (b.p. 353K) and methanol (b.p. 338K) are separated by simple distillation.

**Reason:** Fractional distillation is used to separate two liquids from their mixture when their boiling points differ by 20° or so.

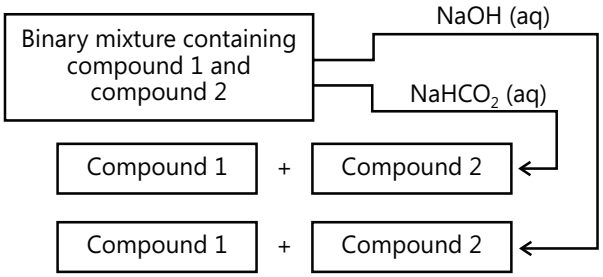
## Previous Years Questions

**Q.1** The compound that does NOT liberate $CO_2$, on treatment with aqueous sodium bicarbonate solution, is ***(2013)***

(A) Benzoic acid (B) Benzenesulphonic acid

(C) Salicylic acid (D) Carbolic acid (Phenol)

**Q.2** Identify the binary mixture(s) that can be separated into individual compounds, by differential extraction, as shown in the given scheme. ***(2012)***



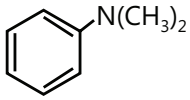

(A) $C_6H_5OH$ and $C_6H_5COOH$

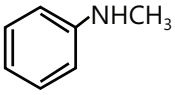
(B) $C_6H_5COOH$ and $C_6H_5CH_2OH$

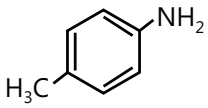
(C) $C_6H_5CH_2OH$ and $C_6H_5OH$

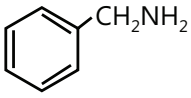
(D) $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$

**Q.3** Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with $NaNO_2$ in dil. HCl followed by addition to an alkaline solution of $\beta$ -naphthol is ***(2011)***

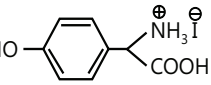
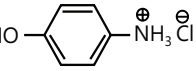
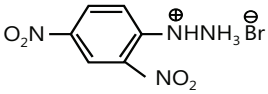
(A) 


(B) 


(C) 


(D) 


**Q.4** Match the compounds in column I with their characteristic test(s) / reaction(s) given in column II. ***(2008)***

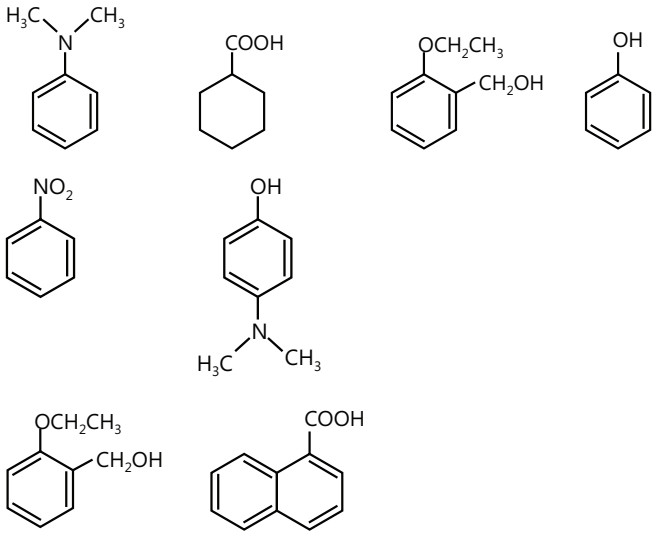
| Column I | Column II |
|---|---|
| (A) $H_2N-\overset{\oplus}{N}H_3\,\overset{-}{Cl}$ | (p) Sodium fusion extract of the compound gives Prussian blue colour with $FeSO_4$. |
| (B)   | (q) Gives positive $FeCl_3$ test. |
| (C)   | (r) Gives white precipitate with $AgNO_3$ |
| (D)   | (s) Reacts with aldehydes to form the corresponding hydrazone derivative. |

**Q.5** A hydrocarbon contains 10.5 gm of carbon for each 1 gm of hydrogen. The mass of 1 litre of hydrocarbon vapours at 127°C and 1 atm is 2.8 gm. Find out the molecular formula of the hydrocarbon. ***(1980)***

**Q.6** Match the compounds/ions in Column I with their properties / reactions in Column II. Indicate your answer by darkening the appropriate bubbles of the $4 \times 4$ matrix given in the ORS**.** ***(2007)***

| Column I | Column II |
|---|---|
| (A) $C_6H_5CHO$ | (p) Gives precipitate with 2,3 dinitrophenylhydrazine |
| (B) $CH_3C \equiv CH$ | (q) Gives precipitate with $AgNO_3$ |
| (C) $CN^-$ | (r) Is a nucleophile |
| (D) $I^-$ | (s) Is involved in cyanohydrin formation |

**Q.7** Amongst the following, the total number of compounds soluble in aqueous NaOH is: ***(2010)***



# PlancEssential Questions

## JEE Main/Boards

### Exercise 1

Q.3 Q.5 Q.9

### Exercise 2

Q.1 Q.6

### Previous Years' Questions

Q.4 Q.6 Q.7

## JEE Advanced/Boards

### Exercise 2

Q.2 Q.3 Q.5

### Previous Years' Questions

Q.2 Q.4

## Answer Key

## JEE Main/Boards

### Exercise 1

**Q.1** Ammonical $AgNO_3$ and NaOH **Q.2** 28% **Q.3** 51.20% **Q.4** $SO_4^-$

**Q.5** $Br^-$ and $I^-$ **Q.6** 86.69 **Q.7** $CHCl_3$ **Q.8** $C_3H_6$

**Q.9** Steam distillation **Q.10** Hot water

**Q.11** (a) Fractional distillation (b) Simple distillation **Q.12** $CHCl_3$ is a covalent

**Q.13** Camphor, naphthalene **Q.14** Adsorption **Q.15** Presence of N and S

**Q.16** 14.6% **Q.17** 18.4% **Q.18** 56% **Q.19** 34.04% **Q.20** 20.24%

### Exercise 2

**Single Correct Choice Type**

**Q.1** B **Q.2** B **Q.3** D **Q.4** D **Q.5** A **Q.6** A

**Q.7** A **Q.8** D **Q.9** B **Q.10** A **Q.11** B **Q.12** D

**Q.13** C **Q.14** A **Q.15** A **Q.16** D **Q.17** A **Q.18** A

**Q.19** B **Q.20** C

### Previous Years' Questions

**Q.1** B **Q.2** B,D **Q.3** C **Q.4** A **Q.5** C **Q.6** D

**Q.7** D **Q.8** C **Q.9** B **Q.10** A **Q.11** A **Q.12** C

## JEE Advanced/Boards

### Exercise 1

**Q.1** % of C = 60.03%, % of H = 13.30%, % of O = 26.67% **Q.2** 36.78%

**Q.3** $NH_2CONH_2$ **Q.4** m = 79 **Q.5** 19.90%

**Q.6** 90 **Q.7** 80% **Q.8** $C_6H_8N_2$

**Q.9** Sublimation **Q.12** A will be eluted first **Q.14** By differential extraction.

**Q.15** $Fe_4[Fe(CH)_6]_3$ **Q.16** 9.09 **Q.17** 0.506g; 0.0864g

**Q.18** 4.58% **Q.19** 17.49% **Q.20** 56%

### Exercise 2

#### Single Correct Choice Type

**Q.1** B **Q.2** D **Q.3** A **Q.4** B **Q.5** D **Q.6** D

**Q.7** B **Q.8** A **Q.9** B **Q.10** C **Q.11** C

#### Match the Columns

**Q.12** A $\rightarrow$ q; B $\rightarrow$ p; C $\rightarrow$ s; D $\rightarrow$ r **Q.13** A $\rightarrow$ q; B $\rightarrow$ p; C $\rightarrow$ s; D $\rightarrow$ r

#### Comprehension Type

**Q.14** C **Q.15** C **Q.16** B **Q.17** B **Q.18** A **Q.19** C

**Q.20** B **Q.21** B **Q.21** A **Q.22** D

#### Assertion Reasoning Type

**Q.23** A **Q.24** D **Q.25** C

### Previous Years' Questions

**Q.1** D **Q.2** B,D **Q.3** C **Q.4** A $\rightarrow$ r, s; B $\rightarrow$ p, q; C $\rightarrow$ p, q, r; D $\rightarrow$ p

**Q.5** $C_7H_8$ **Q.6** A $\rightarrow$ p, q, s; B $\rightarrow$ q; C $\rightarrow$ q, r, s; D $\rightarrow$ q, r

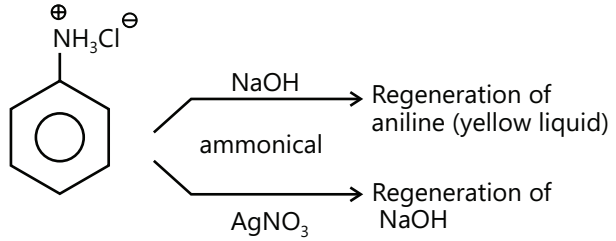
**Q.7** 5

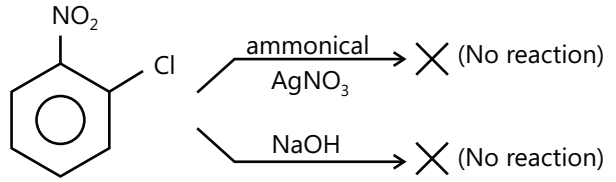
# Solutions

## JEE Main/Boards

### Exercise 1

**Sol 1:** Only phenols show colour change.




**Sol 2:** $\%N = \dfrac{(\text{Normality})_{H_2SO_4} \times (a-b) \times 0.014}{\text{Mass of sample}} \times 100 = 28\%$

**Sol 3:**

$$\%P = \frac{\text{At.mass of P}}{\text{Molar mass of } Mg_2P_2O_7} \times \frac{\text{Mass of } Mg_2P_2O_7}{\text{mass of compound}} \times 100$$

= 51.20%

**Sol 4:** An organic compound containing sulphur is estimated by Carius method in which fuming $HNO_3$ is used to convert S into $SO_4^-$

**Sol 5:** $Br^-$ and $I^-$ forms a separate layer.

**Sol 6:** Wt. of bulb = 22.567 gm; P = 755 mm

Wt. of bulb with substance = 22.8617 gm

Capacity of bulb = 200 ml.

Density of air = 0.0012.9 gm/ml

Wt. of substance = 22.8617 – 22.567 = 0.2947 gm.

m = 86.69

**Sol 7:**

| Atom | Atomic mass (a) | Percentage (b) | $\frac{b}{a} = x$ | Ration |
|---|---|---|---|---|
| C | 12 | 10.06 | $\frac{10.06}{12} = 0.83$ | 1 |
| H | 1 | 0.84 | $\frac{0.84}{1} = 0.84$ | 1 |
| CI | 35.5 | 89.10 | $\frac{89.10}{35.5} = 2.50$ | 3 |

Empirical formula = $CHCl_3$

Empirical formula mass = 12 + 1 + 106.5 = 119.5 ≈ 120

Molecular mass = 2 × VD = 2 × 60 = 120

$$n = \frac{\text{molar mass}}{\text{empirical formula mass}} = \frac{60}{60} = 1$$

Molecular formula $= (CHCl_3)_1 = CHCl_3$

**Sol 8:** Mass of 1 mol. of compound = Mol. Wt. of compound =42 mol

$\therefore$ Molecular formula = empirical formula $\times \frac{\text{Mol. wt}}{\text{EF wt.}}$

$$= CH_2 \times \frac{42}{14} = C_3H_6$$

**Sol 9:** A mixture of o-nitro phenol and p-nitro phenol can be separated by steam distillation. O-nitrophenol being less volatile distils over along with water while p-nitrophenol being non-volatile in the flask.

**Sol 10:** Benzoic acid can be separated from naphthalene by treating the mixture with hot water. Benzoic acid dissolves but naphthalene remains insoluble. On cooling pure benzoic acid crystallises out.

**Sol 11**: (a) Fractional distillation because the boiling of the two liquids differ by only $10^\circ$.

(b) Simple distillation because the boiling points of the two liquids differ much

**Sol 12:** The precipitate of AgCl will not be formed because $CHCl_3$ is a covalent compounds and does not ionize to give $Cl^-$ ions. Therefore, $Ag^+$ ions (from $AgNO_3$) to from ppt. of AgCl

**Sol 13:** Camphor, naphthalene.

**Sol 14:** The method of chromatography is based on the difference in the which the compounds of mixture are adsorbed on a suitable absorbent.

**Sol 15:** It indicates that the compound contains both N and S. During fusion, sodium thiocyanate is formed which given blood red colouration.

$$3NaSCN + FeCl_3 \rightarrow \underset{\text{Blood red}}{Fe(SCN)_3} + 3NaCl$$

**Sol 16:** Volume of $\frac{M}{10}NaOH = 23.2\,mL.of\ \frac{M}{10}HCl$

Volume of $\frac{M}{10}$ HCl unused =23.2 mL

$\therefore$ Volume of $\frac{M}{10}HCl$ required for neutralisation of

$NH_3$ = 50 – 23.2 = 26.8mL

26.8 mL of $\frac{M}{10}HCl = 26.8mL$ of $M/10\,NH_3$

1000 mL of 1 $NH_3$ solution contains nitrogen = 14 g

26.8 ml of $\frac{M}{10}NH_3$ solution contains nitrogen

$$= \frac{14 \times 26.8}{10 \times 1000}$$

Percentage of nitrogen $= \frac{14 \times 26.8 \times 100}{10 \times 1000 \times 0.257} = 14.6\%$

**Q.17:** Vol. of M/10 $H_2SO_4$ taken =100 mL Let us first calculate the volume of excess M/10 $H_2SO_4$ which was neutralised by 154 mL of M/10 NaOH

$$154 \text{ mL of } \frac{M}{10}NaOH = \frac{154}{2}\text{mL of } \frac{M}{10}H_2SO_4$$

$\therefore$ Volume of $\frac{M}{10}H_2SO_4$ left unused = 77mL

Volume of $\frac{M}{10}H_2SO_4$ used for neutralisation of $NH_3$

$$100 - 77 = 23 \text{ mL}$$

Now,

$$23 \text{ mL of } \frac{M}{10}H_2SO_4 = 2 \times 23\text{mL of } \frac{M}{10}NH_3$$

$$= 46 \text{ mL of } \frac{M}{10}NH_3$$

Now 1000 mL of 1 M $NH_3$ contain nitrogen =14 g

46 mL of $\frac{M}{10}NH_3$ contain nitrogen $= \frac{14}{1000} \times \frac{46 \times 1}{10}$

$\therefore$ Percentage of nitrogen $= \frac{14 \times 46 \times 100}{1000 \times 10 \times 0.35} = 18.4\%$

**Sol 18:** Mass of organic compound taken = 0.50 g

Vol. of 0.5 M $H_2SO_4$ taken = 50 mL

The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation

60 mL of 0.5 M NaOH solution

$= \frac{60}{2}$mL of 0.5 M $H_2SO_4$ solution

= 30mL of 0.5 M $H_2SO_4$ solution

Volume of 0.5 M $H_2SO_4$ used = 50 – 30 = 20mL

Now, 20 mL of 0.5 M $H_2SO_4 = 2 \times 20$mL of 0.5 M $NH_3$ solution

Or 1000 mL 0.5 M $NH_3$ contain nitrogen = 14

40 mL of 0.5 M $NH_3$ contain $= \frac{14 \times 40 \times 0.5}{1000}$

$$\% \text{ of N} = \frac{14 \times 40 \times 0.5}{1000 \times 0.50} \times 100 = 56\%$$

**Sol 19:** Mass of AgBr formed $= 0.12\text{g}$

$$\text{AgBr} = \text{Br}$$

$$188 \quad 80$$

188 g of AgBr contain bromine = 80 g

$$0.12 \text{ g of AgBr contain bromine} = \frac{80 \times 0.12}{188} = 0.051$$

$$\text{Percentage of bromine} = \frac{0.051}{0.15} \times 100 = 34.04\%$$

**Sol 20**: Mass of $BaSO_4 = 0.582$ g

We know $BaSO_2 = S$

$233 = 32$

233 g $BaSO_2$ contain sulphur 32 g

$$0.582 \text{ of } BaSO_2 \text{ contain sulphur} = \frac{32}{233} \times 0.582$$

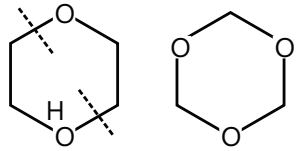
$$\text{Percentage of sulphur} = \frac{\text{Wt. of sulphur}}{\text{Wt. of xompound}} \times 100$$

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

## Exercise 2

**Sol 1: (B)** Refer kjeldahl's method.

**Sol 2: (B)** $H_2N-NH_2$ : Does not form complex.




(x) (y)

Fehling test identifies carbonly compounds.

**Sol 3: (D)** Fehling test identifies carbonyl compounds.

**Sol 4: (D)** Self-explanatory.

**Sol 5: (A)** Self-explanatory.

**Sol 6: (A)**

| C: | H: | N: |
|---|---|---|
| 18 g : | 2g : | 7 g : |
| $\frac{18}{12} = \frac{3}{2}$ : | $\frac{2}{1} = 2$ : | $\frac{7}{7} = 1$ |

$\therefore$ $C_3H_4N_3$

$$n = \frac{\text{molecular weight}}{\text{e.f.w.}} = \frac{108}{54} = 2$$

$\therefore$ Molecular formula $= C_6H_8N_4$

**Sol 7: (A)** In Dumas's method for the estimation of nitrogen in an organic compound, nitrogen is estimated in the form of gaseous nitrogen

**Sol 8: (D)** Refer text-Liebig's Combustion Method

**Sol 9: (B)** Formula showing simplest ratio is the empirical formula.

**Sol 10: (A)** Self-explanatory

**Sol 11: (B)** Belistein test is a method of determining halogens in a given compound.

**Sol 12: (D)** If both nitrogen and sulphur are present in an organic compound, sodium thiocyanate is formed which then react with $Fe^{3+}$ to form blood colour complex $[Fe(SCN)]^{2+}$

$$Na + C + N + S \rightarrow NaSC$$

$$Fe^{3+} + 2Na \rightarrow \left[Fe(SCN)\right]^{2+}$$

**Sol 13: (C)** In Lassaigne's extract when sodium iodide is treated with chlorine water the bromide oxidise to the corresponding halogens. This halogen dissolves in carbon di sulphide. Bromine impart orange colour in carbon disulphide layer.

**Sol 14: (A)** To determination of halogens.

**Sol 15 :(A)** Mass of the organic compound taken = w g

Volume of nitrogen collected = v g

1 mol of nitrogen = 28 gm = 22400ml

28v/22400 x 100/w

Percentage of nitrogen in the compound

= 28 × 448/22400 × 100/ 2.36

= 23.72 %

**Sol 16: (D)** Carbon and hydrogen present in an organic compound are estimated by 'Liebig's method'.

**Sol 17: (A)** This is useful for separating complex mixtures of compounds having similar polarity. The mobile phase is developing solutions that can travel up to the stationary phase carrying the sample along with it. In paper chromatography, the stationary phase is a uniform absorbent paper. The mobile phase is a suitable liquid solvent.

**Sol 18: (A)** Crystallisation.

**Sol 19: (B)** Hydrazine does not have C atoms, so it does not form NaCN and hence does not give a positive Lassaigne's test for nitrogen. In order to test the presence of N in such compounds, during fusion with Na, some charcoal or starch is added to supply C atoms. Under these conditions, NaCN is obtained and it will give a positive test.

**Sol 20: (C)** It would not give pale-yellow precipitate of AgBr because $CH_3Br$ is a covalent compound and hence does not contain $Br^{\Theta}$ ion. To get the precipitate of AgBr, $CH_3Br$ is treated first with aqueous KOH to get $CH_3OH$ and $Br^{\Theta}$ and then the addition of $AgNO_3$. It would now give the precipitate of AgBr partly soluble in $NH_3$ or $NH_4OH$.

## Previous Years Questions

**Sol 1: (B)** Molisch's Test : when a drop or two of alcoholic solution of $\alpha$–naphthalene added to sugar solution and then conc. $H_2SO_4$ is added along the sides of test tube, formation of violet ring takes place at the junction of two liquids.

**Sol 2: (B, D)** Silver mirror test is tollen's reagent test given by all aldehydes.

**Sol 3: (C)** Phenol gives violet coloured complex compound with neutral $FeCl_3$, benzoic acid gives pale dull yellow ppt. with neutral $FeCl_3$.

**Sol 4: (A)** It is a test characteristic of amide linkage. Urea also has amide linkage like proteins.

**Sol 5: (C)** On solving we get that $5\times10^{-3}$ mol of $H_2SO_4$ was used in reaction with organic compound.

Therefore

Moles of base × acidity of base = 2 × mol of $H_2SO_4$

Solving we get molecular mass = 60 and acidity = 2 solution. Therefore urea is the answer.

**Sol 6: (D)** Compound consists of $(CH_3-CH(OH)–)$ group which is easily oxidisable to give methyl ketone which gives iodoform reaction.

**Sol 7: (D)** Iodoform is given by (1) methyl ketones $R-CO-CH_3$

(2) Alcohols of the type $R-CH(OH)CH_3$ where R can be hydrogen also

**Sol 8: (C)** Moles of HCl reacting with

Ammonia = (moles of HCl absorbed) – (moles of NaOH solution required)

$$=\left(20\times0.1\times10^{-3}\right)-\left(15\times0.1\times10^{-3}\right)$$

= moles of $NH_3$ evolved.

= moles of nitrogen in organic compound

$\therefore$ wt. of nitrogen in org. comp = $0.5\times10^{-3}\times14$

$$= 7\times10^{-3}\text{ g}$$

$$\%\text{ wt} = \frac{7\times10^{-3}}{29.5\times10^{-3}} = 23.7\%$$

**Sol 9: (B)** As per question

| | Normality | Volume |
|---|---|---|
| $H_2SO_4$ | $\frac{N}{5}$ | 60 mL |
| NaOH | $\frac{N}{10}$ | 20 mL |

$$\left(n_{geq}\right)_{H_2SO_4} = \left(n_{geq}\right)_{NaOH} + \left(n_{geq}\right)_{NH_3}$$

$$\frac{1}{5}\times\frac{60}{1000} = \frac{1}{10}\times\frac{20}{1000} + \left(n_{geq}\right)_{NH_3}$$

$$\frac{6}{500} = \frac{1}{500} + \left(n_{geq}\right)_{NH_3}$$

$$\left(n_{geq}\right)_{NH_3} = \frac{5}{500} = \frac{1}{100}$$

$$(n_{mol})_N = (n_{mol})_{NH_3} = (n_{geq})_{NH_3} = \frac{1}{100}$$

$$(\text{Mass})_N = \frac{14}{100} = 0.14 \text{ g}$$

Percentage of "N" $= \frac{0.14}{1.4} \times 100 = 10\%$

**Sol 10: (A)**

$$\% \text{ X} = \frac{\text{Atomic mass of Br}}{\text{Molecular mass of AgBr}} \times \frac{\text{Wt. of AgBr}}{\text{Wt. of organic Bromide}} \times 100$$

Thus % Br $= \frac{80}{188} \times \frac{141}{250} \times 100 = 24$

**Sol 11: (A)** It is fact.

**Sol 12: (C)** Glycerol is high boiling liquid with B.P. 290°C. It can be separated from spent-lye by distillation under reduced pressure. Liquid is made to boil at lower temperature than normal temperature by lowering pressure on its surface, so external pressure is reduced and B.P. of liquid is lowered hence glycerol is obtained without decomposition at high temperature.

# JEE Advanced/Boards

## Exercise 1

**Sol 1:** Leibig's Combustion Method

**Potash tube:** Wt. = 1.76 gm (increase)

44 gm of $CO_2 \rightarrow 12$g C

$\therefore$ 1.76 gm of $CO_2 \rightarrow$ 'a'g C $\quad \therefore \%C = \frac{a}{0.92} \times 100$

**U-tube:** Increase = 1.08 gm

If 18 gm $H_2O \rightarrow 2$gm of $H_2$

$\therefore$ 1.08 gm $H_2O \rightarrow$ 'b'g $H_2$

$\therefore \%H = \frac{b}{0.92} \times 100$

$\therefore \%O = 100 - (\%H + \%C)$

**Sol 2:** $\underset{32g}{S}$ in organic substance $\frac{(I)HNO_3\Delta}{(II)BaCI_2} \underset{233\ g}{BaSO_4}$

$$\% \text{ of S} = \frac{32}{233} \times \frac{\text{Weight of } BaSO_4}{\text{weight of substance}} \times 100$$

$$= \frac{32}{233} \times \frac{0.5825}{0.2175} \times 100 = 36.78\%$$

**Sol 3:**

| Atom | Atomic Mass (a) | Percentage (b) | $\frac{b}{a} = x$ | Simple ratio |
|---|---|---|---|---|
| C | 12 | 20.0 | $\frac{20}{12} = 1.66$ | $\frac{1.66}{1.66} = 1$ |
| H | 1 | 6.67 | $\frac{6.67}{1} = 6.67$ | $\frac{6.67}{1.66} = 4$ |
| N | 14 | 46.67 | $\frac{46.67}{14} = 3.33$ | $\frac{3.33}{1.66} = 2$ |
| O | 16 | 26.66 | $\frac{26.66}{16} = 1.66$ | $\frac{1.66}{1.66} = 1$ |

Empirical formula $= CH_4N_2O$

Empirical formula mass $= 12 + 4 + 28 + 16 = 60$

$$n = \frac{\text{molecular mass}}{\text{empirical formula mass}} = \frac{60}{60} = 1$$

$\therefore$ Molecular formula $= (CH_4N_2O)_1 = CH_4N_2O$

$\because$ The compound gives biuret test hence, given compound is urea, i.e., $NH_2CONH_2$

**Sol 4:** $C = 10.5g = \frac{10.5}{12} mol = 0.87$ mol

$$H = 1g = \frac{1}{2} mol = 1 mol$$

$$\therefore \ (C_{0.87}H_1)_7 = C_{6.09}H_7$$

$$PV = nRT = \frac{w}{m}RT$$

$$\approx C_6H_7$$

$$1 \times 1 = \frac{2.4}{m} \times 0.082 \times 400$$

$$m = 79$$

**Sol 5:** Pressure = 785 mm,

Aqueous tension = 12 mm

$\therefore$ Actual pressure of dry $N_2$ at K = 758 – 12 = 746 mm

Volume of $N_2$ gas collected $= 32$ mL

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{760 \times V_1}{273} = \frac{746 \times 32}{287}$$

$$V_1 = 29.88 \text{ mL (at STP)}$$

$$\% \text{ of } N = \frac{28 \times V \times 100}{22400 \times w}$$

$$= \frac{28 \times 29.88 \times 100}{22400 \times 0.1877} = 19.90\%$$

**Sol 6**: Mass of silver salt = 0.228 g

Mass of silver left = 0.162 g

Basicity of acid = 2

$$\frac{\text{equivalent mass of silver salt}}{\text{equivalent mass of silver}} = \frac{\text{mass of acid taken}}{\text{mass of silver left}}$$

$$\frac{E}{108} = \frac{0.228}{0.162}$$

$$E = 152$$

Equivalent mass of acid = equivalent mass od silver salt – Equivalent mass of Ag + basicity

= 152 – 108 + 1

= 45

$\therefore$ Mol mass of acid = equivalent mass of acid $\times$ basicity

= 45 × 2 = 90

**Sol 7:**

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

$$\frac{\text{weight of } H_2O}{\text{weight of organic compound}} \times 100$$

$$= \frac{2}{18} \times \frac{0.9}{0.5} \times 100$$

$$= 20\%$$

$\therefore$ The percentage of carbon = 100 – 20 =80%

**Sol 8:**

| | C | H | N |
|---|---|---|---|
| Ratio of weights | 9 | 1 | 3.5 |
| Ration of atoms | $9/12 = 0.75$ | $1/1 = 1$ | $3.5/14 = 0.25$ |
| | $\frac{0.75}{0.25} = 3$ | $\frac{1}{0.25} = 4$ | $\frac{0.25}{0.25} = 1$ |

$\therefore$ Empirical formula $C_3H_4N$

$$n = \frac{108}{54} = 2$$

Hence, molecular formula $= (C_3H_4N) \times 2 = C_6H_8N_2$

**Sol 9:** Sublimation is used to separate the mixture of iodine and sodium chloride iodine sublimes readily.

**Sol 10:** Sodium extract is boiled with nitric acid to decompose NaCN and NaS if present.

$$NaCN + HNO_3 \rightarrow NaNO_3 + HCN \uparrow$$

$$Na_2S + HNO_3 \rightarrow 2NaNO_3 + H_2S \uparrow$$

If cyanide and sulphide ions are not decomposed, they will interfere with the test by forming precipitate of AgCN and $Ag_2S$

$$NaCN + AgNO_3 \rightarrow \underset{\text{White ppt}}{AgCN} + NaNO_3$$

$$Na_2S + 2AgNO_3 \rightarrow \underset{\substack{\text{Silver sulphide}\\ \text{(Black ppt)}}}{Ag_2S} + 2NaNO_3$$

**Sol 11:** For testing sulphur, the sodium extract is acidified with acetic acid because lead acetate is soluble and does not interfere with the test. If $H_2SO_4$ were, lead acetate will react with it forming white precipitate of lead sulphate.

$$(CH_3COO)_2 + H_2SO_4 \rightarrow \underset{\text{White ppt}}{PbSO_4} + 2CH_3COOH$$

**Sol 12:** $R_f$ value of A is 0.65, therefore, it is less strongly adsorbed as compared to compound B which has $R_f$ value of 0.42. Therefore, A will be eluted first.

**Sol 13:** The mixture can be separated by the process of sublimation. Camphor will sublime whereas calcium sulphate will be left behind.

**Sol 14:** By differential extraction.

**Sol 15:** $Fe_4\left[Fe(CH)_6\right]_3$

**Sol 16:** Wt. of organic compound $= 0.2475$ g

Wt. of $CO_2$ produced $= 0.4950$ g

Wt. of $H_2O$ produced $= 0.2025$ g

Percentage of carbon $= \frac{22}{44} \times \frac{\text{Wt. of } CO_2}{\text{Wt. of compound}} \times 100$

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

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

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

**Sol 17:** Percentage of carbon $= 69\%$

Amount of carbon in 0.20 g of compound $= 0.2 \times \frac{69}{100}$

$= 0.138$ g

Percentage of hydrogen $= 4.8\%$

Amount of hydrogen in 0.20 g of compound $= \frac{0.2 \times 4.8}{100}$

Now, $= 0.0096$ g

12g of carbon on combustion give $CO_2 = 44$ g

0.138g of carbon on combustion give $CO_2 = \frac{44}{12} \times 0.138$

$= 0.506$ g

$2H = H_2O$

2 g of hydrogen on combustion give water = 18

0.0096 g of hydrogen on combustion give water

$= \frac{18}{2} \times 0.0096 = 0.0864$ g

**Sol 18:** Wt. of organic compounds $= 0.246$ g

Wt. of $CO_2$ produced $= 0.198$ g

Wt. of $H_2O$ produced $= 0.1014$ g

Percentage of carbon $= \frac{12}{44} \times \frac{0.198 \times 100}{0.246}$

$= 20.95\%$

Percentage of hydrogen $= \frac{2}{18} \times \frac{0.1014 \times 100}{0.246} = 4.58\%$

**Sol 19:** To calculate the volume of $N_2$ at S.T.P

$V_1 = 50$ mL $\quad V_2 = ?$

$P_1 = 700$ mm $\quad P_2 = 760$ mm

$T_1 = 300$K $\quad T_2 = 273$ K

Applying $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

Or $\quad V_2 = \frac{p_1V_1T_2}{p_2T_1}$

$\therefore \quad V_2 = \frac{700 \times 50 \times 273}{760 \times 300} = 41.9$ mL

22400 mL of nitrogen at S.T.P. weigh = 28 g

41.9 mL of nitrogen at S.T.P weigh $= \frac{28 \times 41.9}{22400} = 0.0524$g

Percentage of nitrogen $= \frac{0.0524}{0.3} \times 100 = 17.49\%$

**Sol 20:** 1 M of 10 mL $H_2SO_4$ = 1 M of 20 mL of $NH_3$

1000 mL of 1 M ammonia contain $= 14$ g nitrogen

20 mL of 1 M ammonia contain $= \frac{14 \times 20}{1000}$ g nitrogen

$\therefore$ Percentage of nitrogen $= \frac{14 \times 20}{1000 \times 0.5} \times 100 = 56.0\%$

# Exercise 2

### Single Correct Choice Type

**Sol 1: (B)** Prussian is formed when Ferric sulphate reacts with $Na_4[Fe(CN)_6]$. Carbon and nitrogen of organic compound on fusion with Na gives NaCN, water soluble. This converted in sodium ferrocyanide by addition of $FeSO_4$. Ferric ions generated react with Ferro cyanide to form prussion blue ppt of ferric Ferro cyanide.

$Na + C + N \rightarrow NaCN$

$6NaCN + FeSO_4 \rightarrow Na_4[Fe(CN)_6] + Na_2SO_4$

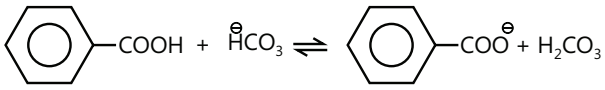
$Na_4[Fe(CN)_6 + Fe^{3+} \rightarrow Fe_4[Fe(CN)_6]_3$

**Sol 2: (D)** Lassaigne's test is used for detection of nitrogen, halogen and sulphur.

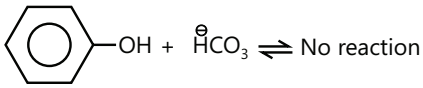
**Sol 3: (A)** Kjeldahl's method is used in the estimation of Nitrogen

**Sol 4: (B)** Sodium cyanide

**Sol 5: (D**) Sodium bicarbonate ($NaHCO_3$). Since carboxylic acids dissolve in $NaHCO_3$ but phenol do not.




A carboxylic acid soluble in organic solvent




**Sol 6: (D)** Due to intra molecular hydrogen bonding Ortho nitro phenol is more volatile than para nitro phenol which have intermolecular hydrogen bonding. In steam distillation orthonitro phenol is distil over with water and para nitro phenol remains in the flask.

**Sol 7: (B)** Hydrazine does not have C atoms, so it does not form NaCN and hence does not give a positive Lassaigne's test for nitrogen.

**Sol 8: (A)**

| Element | Percentage | At. Mass | Relative number of atoms | Simplest ratio |
|---|---|---|---|---|
| Carbon | 40/12 = 3.33 | 12 | 3.33 | 1 |
| Hydrogen | 6.60/1 = 6.60 | 1 | 6.60 | 2 |
| Oxygen | 53.34/16 = 3.33 | 16 | 3.33 | 1 |

Empirical formula = $CH_2O$

**Sol 9: (B)** As in IR spectroscopy each functional group appears at a certain peak. So it is used for the purification of cyclohexane from a mixture of benzoic acid, iso amyl alcohol, cyclohexane and cyclohexanone.

**Sol 10: (C)**

| Element | Percentage | At. Mass | Relative number of atoms | Simplest ratio |
|---|---|---|---|---|
| Carbon | 40/12 = 3.33 | 12 | 3.33 | 1 |
| Hydrogen | 13.33/1 = 13.33 | 1 | 13.33 | 4 |
| Nitrogen | 46.67/14 = 3.33 | 14 | 3.33 | 1 |

Empirical formula = $CH_4N$

**Sol 11: (C)**

**Sol:** Calculation of empirical formula:

| Element | Percentage | At. mass | Relative number or atoms | Simplest ratio of atoms |
|---|---|---|---|---|
| Carbon | 34.62 | 12 | $\frac{34.62}{12} = 2.88$ | $\frac{2.88}{2.88} = 1 \times 3 = 3$ |
| Hydrogen | 3.84 | 1 | $\frac{3.84}{1} = 3.84$ | $\frac{3.84}{2.88} = 1.33 \times 3 = 4$ |
| Oxygen | 61.54 (by difference) | 16 | $\frac{16.54}{16} = 3.84$ | $\frac{3.84}{2.88} = 1.33 \times 3 = 4$ |

Empirical formula of the acid = $C_3H_4O_4$

Empirical formula =

$$(3 \times 12) + (4 \times 1) + (4 \times 16) = 104$$

Calculation of molecular mass:

20 ml 0.1 N NaOH $\equiv$ 0.1075 gm acid

$20 \times 0.1$ ml 1 N NaOH $\equiv$ 0.1075 gm acid

$$\Rightarrow 1000 \text{ ml } 1 \text{ N NaOH} \equiv \frac{0.1075}{20 \times 0.1} \times 1000 \text{ gm acid}$$

$$\equiv 53.75 \text{ gm acid}$$

Equivalent mass of the acid = 53.75

Molecular mass of the acid = Equivalent mass $\times$ basicity

= 53.75 $\times$ 2 = 107.50

$$n = \frac{\text{Molecular mass}}{\text{Empirical mass}} = \frac{107.50}{104.0} \approx 1$$

Molecular formula = $C_3H_4O_4$

**Match the Columns**

**Sol 12:** A $\rightarrow$ q; B $\rightarrow$ p; C $\rightarrow$ s; D $\rightarrow$ r

$1^\circ$ amine + Hinsberg reagent $\rightarrow$ soluble sulfonamide $\xrightarrow[\text{dil.}]{\text{HCl}}$ ppt

$2^\circ$ amine + Hinsberg reagent $\rightarrow$ ppt.

(b) – p

$NaHSO_3 \longrightarrow$ Addition bisulphite product (white crystals)

$\downarrow C_2H_5OH$

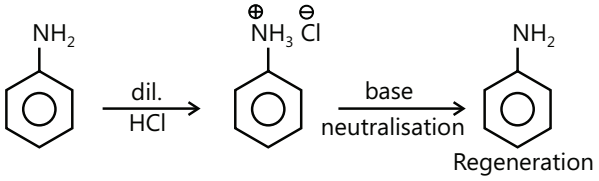
No addition product

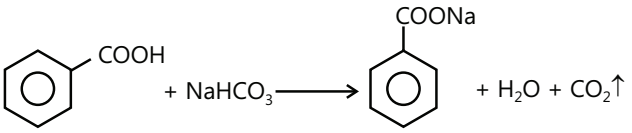
(c) – s Dil. $H_2SO_4$ converts butanol to ether, which can be separated by distillation.

(d) – r $CH_3COOH + NaOH \rightarrow \underset{\text{soluble sodium salt}}{CH_3COONa}$

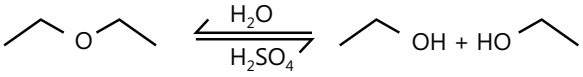
**Sol 13:** A → q; B → p; C → s; D → r

(b) – p. Aniline with dil. HCl gives anilium chloride.



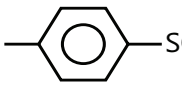

(c) – s.




(d) – r self explanatory

**Comprehension Type**

**Sol 14: (C)** KCN will give positive Lassaigne's test for nitrogen.

**Sol 15: (C)**  will give blood red colour in Lassaigne's test for nitrogen.

**Sol 16: (B)** Prussian blue colour in the detection of nitrogen in Lassaigne's test is due to formation of $Fe_4[Fe(CN)_6]_3$

**Sol 17: (B)** Violet colour in the detection of sulphur with sodium nitroprusside is due to formation of $Na_4[Fe(CN)_5NOS]$

**Sol 18: (A)** $NO_3^-$

**Sol 19: (C)** NaCN and $Na_2S$ are decomposed by $HNO_3$

**Sol 20: (B)** Black precipitate in the detection of sulphur with lead acetate and acetic acid is due to formation of PbS.

**Sol 21: (B)** Blood-red colour in the detection of both N and S in the Lassaigne's extract is due to formation of $Fe(CNS)_3$.

**Sol 22: (A)** Yellow precipitate in the detection of phosphorous when an organic compound is heated with $Na_2O_2$ and then boiled with conc. $HNO_3$ followed by the addition of ammonium molybdate is due to formation of $(NH_4)_3 . PO_4 . 12MoO_3$

**Sol 23: (D)** Beilstein test is given by all of these.

**Assertion Reasoning Type**

**Sol 24: (A)** In organic layer test, $Cl_2$ water is added to sodium extract , which oxidises $Br^-$ and $I^-$ ions to $Br_2$ and $I_2$ respectively as reduction potential of $Cl_2$ is greater than that of $Br_2$ and $I_2$.

**Sol 25: (D)** Hydroxylamine ($NH_2OH$) does not gives Lassaigne's test.

**Sol 26: (C)** Benzene (b.p. 353K) and methanol (b.p. 338K) cannot be separated by fractional distillation as fractional distillation is used to separate two liquids from their mixture when their boiling points differ by 20° or so.

## Previous Years' Questions

**Sol 1: (D)** pKa of PhOH (carbolic acid) is 9.98 and that of carbonic acid $(H_2CO_3)$ is 6.63 thus phenol does not give effervescence with $HCO_3^-$ ion.

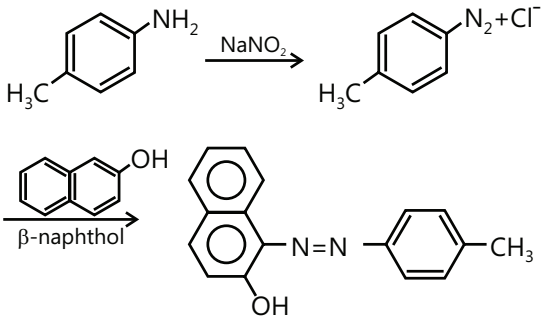
**Sol 2: (B, D)** (A) Both are soluble in NaOH, hence inseparable.

(B) Only benzoic acid $(C_6H_5COOH)$ is soluble in NaOH and $NaHCO_3$, while benzyl alcohol $(C_6H_5CH_2OH)$ is not. Hence, separable.

(C) Although NaOH can enable separation between benzyl alcohol $(C_6H_5CH_2OH)$ and phenol $(C_6H_5OH)$ as only the later is soluble in NaOH. However, in $NaHCO_3$, both are insoluble. Hence, inseparable.

(D) $\alpha$-phenyl acetic acid $(C_6H_5CH_2COOH)$ is soluble in NaOH and $NaHCO_3$. While benzyl alcohol $(C_6H_5CH_2OH)$ is not. Hence, separable.

**Sol 3: (C)** Only aromatic primary amines give this azo-dye test. Amine in option (d) is not aromatic.



**Sol 4:** A → r, s; B → p, q; C → p, q, r; D → p

Sodium fusion extract gives Prussian blue colouration, nitrogen and carbon both are present in the compound.

Phenolic group and salt of carboxylic acid gives $FeCl_3$ test. Chloride salt gives white precipitate of AgCl on treatment with $AgNO_3$.

Hydrazone formation occur effectively at pH = 4.5. The reaction proceeds in that condition only

when $H^+$ concentration is sufficient to activate the following enolization.

**Sol 5:** Carbon: Hydrogen: : 10.5 : 1

Calculation of empirical formula

| Element | Percentage | At. Mass | Relative number of atoms | Simplest ratio |
|---|---|---|---|---|
| Carbon | $\frac{10.5}{11.5}\times 100 = 91.3$ | 12 | $\frac{91.3}{12} = 7.6$ | $\frac{7.6}{7.6} = 1\times 7 = 7$ |
| Hydrogen | $\frac{1}{11.5}\times 100 = 8.7$ | 1 | $\frac{8.7}{1} = 8.7$ | $\frac{8.7}{7.6} = 1.14\times 7 = 8$ |

Empirical formula = $C_7H_8$; Empirical formula mass = (12 × 7) + (1 × 8) = 92

Calculation of molecular mass: Experimental conditions STP Conditions

$V_1 = 1$ litre $V_2 = ?$; $P_1 = 1$ atm $P_2 = 1$ atm; $T_1$ = 127 + 273 = 400 K; $T_2$ = 273 K

Applying the gas equation, we get

$$V_2 = \frac{P_1V_1}{T_1}\times\frac{T_2}{P_2} = \frac{1\times 1\times 273}{400\times 1} = 0.6825 \text{ Litre}$$

0.6825 litre of the gas weighs 2.8 gm.

∴ 22.4 litre of the gas weighs $\frac{2.8}{0.6825}\times 22.4$ = 91.89 = 92

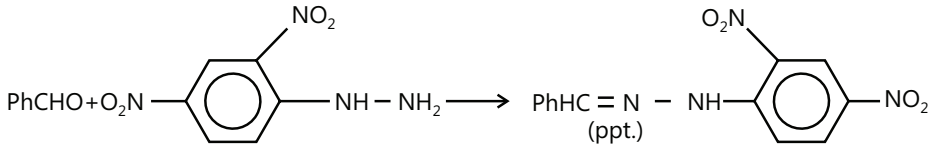
$$N = \frac{\text{Molecular mass`}}{\text{Empirical mass}} = \frac{92}{92} = 1$$

∴ Molecular formula = Empirical formula = $C_7H_8$

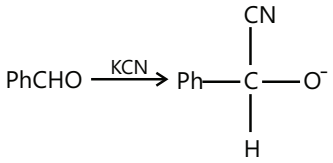
**Sol 6 :** A → p, q, s; B → q; C → q, r, s; D → q, r

(Note: Assuming $AgNO_3$ in ammoniac)

(A)

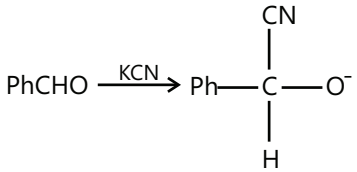



$$PhCHO + Ag_2O \xrightarrow{NH_3} PhCOO^- + Ag\downarrow$$
(White ppt.)




$$CH_3C \equiv CH \xrightarrow{\text{ammonical } AgNO_3} CH_3C{\equiv}C^- \quad Ag^+\downarrow$$
(White ppt.)

(B)

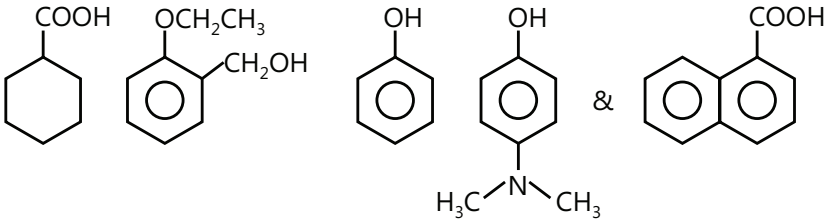



(C) $AgNO_3 + CN^- \longrightarrow AgCN\downarrow$

(D) $AgNO_3 + I^- \longrightarrow AgI\downarrow$

**Sol 7 : (5)**

Are soluble in aqueous NaOH.



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