

(i) **Simple crystallisation** : This is the most common method used to purify organic solids. It is based upon the fact that whenever a crystal is formed, it tends to leave out the impurities. For crystallisation, a suitable solvent is one (a) which dissolves more of the substance at higher temperature than at room temperature (b) in which impurities are either insoluble or dissolve to an extent that they remain in solution (in the mother liquor) upon crystallisation, (c) which is not highly inflammable and (d) which does not react chemically with the compound to be crystallized. The most commonly used solvents for crystallisation are : water, alcohol, ether, chloroform, carbon- tetrachloride, acetone, benzene, petroleum ether etc.

Examples : (a) Sugar having an impurity of common salt can be crystallized from hot ethanol since sugar dissolves in hot ethanol but common salt does not.

(b) A mixture of benzoic acid and naphthalene can be separated from hot water in which benzoic acid dissolves but naphthalene does not.

(ii) **Fractional crystallisation** : The process of separation of different components of a mixture by repeated crystallisations is called fractional crystallisation. The mixture is dissolved in a solvent in which the two components have different solubilities. When a hot saturated solution of this mixture is allowed to cool, the less soluble component crystallises out first while the more soluble substance remains in solution. The mother liquor left after crystallisation of the less soluble component is again concentrated and then allowed to cool when the crystals of the more soluble component are obtained. The two components thus separated are recrystallized from the same or different solvent to yield both the components of the mixture in pure form.

Fractional crystallisation can be used to separate a mixture of $KClO_3$ (less soluble) and KCl (more soluble).

(iii) **Sublimation** : Certain organic solids on heating directly change from solid to vapour state without passing through a liquid state, such substances are called *sublimable* and this process is called *sublimation*.

$$\text{Solid} \xrightleftharpoons[\text{Cool}]{\text{Heat}} \text{Vapour}$$

The *sublimation process* is used for the separation of sublimable volatile compounds from non sublimable impurities. The process is generally used for the purification of camphor, naphthalene, anthracene, benzoic acid $NH_4Cl, HgCl_2$, solid SO_2 , Iodine and salicylic acid etc containing non-volatile impurities.

(iv) **Simple distillation** : Distillation is the joint process of vapourisation and condensation. This method is used for the purification of liquids which boil without decomposition and contain non-volatile impurities. This method can also be used for separating liquids having sufficient difference in their boiling points. This method can be used to separate a mixture of

(a) chloroform (b. p. 334 K) and aniline (b. p. 457 K)

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

(v) **Fractional distillation** : This process is used to separate a mixture of two or more miscible liquids which have boiling points close to each other. Since in this process, the distillate is collected in fractions under different temperatures, it is known as fractional distillation. This process is carried out by using *fractionating columns*. Fractionating column is a special type of long glass tube provided with obstructions to the passage of the vapour upwards and that of liquid downwards. This method may be used to separate a mixture of acetone (b. p. 330 K) and methyl alcohol (b. p. 338 K) or a mixture of benzene and toluene. One of the technological applications of fractional distillation is to separate different fractions of crude oil in petroleum industry into various useful fractions such as gasoline, kerosene oil, diesel oil, lubricating oil etc.

(vi) **Distillation under reduced pressure** : This method is used for the purification of high boiling liquids and liquids which decompose at or below their boiling points.

The crude liquid is heated in distillation flask fitted with a water condenser, receiver and vacuum pump. As the pressure is reduced, the liquid begins to boil at a much lower temperature than its normal boiling point. The vapour is condensed by water condenser and the pure liquid collects in the receiver.

Glycerol which decomposes at its boiling point (563 K) under atmospheric pressure can be distilled without decomposition at 453 K under 12 mm of Hg. Similarly, sugarcane juice is concentrated in sugar industry by evaporation under reduced pressure which saves a lot of fuel.

(vii) **Steam distillation** : This method is applicable for the separation and purification of those organic compounds (solids or liquids) which (a) are insoluble in water (b) are volatile in steam (c) possess a high vapour pressure (10-15 mm Hg) at 373 K and (d) contain non-volatile impurities.

Aniline (b. p. 457 K) can be purified by steam distillation since it boils at a temperature of 371.5 K in

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presence of steam. Other compounds which can be purified by steam distillation are: nitrobenzene, bromobenzene, *o*-nitrophenol, salicylaldehyde, *o*-hydroxyacetophenone, essential oils, turpentine oil etc.

(viii) **Azeotropic distillation** : Azeotropic mixture is a mixture having constant boiling point. The most familiar example is a mixture of ethanol and water in the ratio of 95.87 : 4.13 (a ratio present in rectified spirit). It boils at 78.13°C. The constituents of an azeotropic mixture can't be separated by fractional distillation. Hence a special type of distillation (azeotropic distillation) is used for separating the constituents of an azeotropic mixture.

In this method a third compound 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 will distil over.

Dehydrating agents having low boiling point (e.g. C_6H_6 , CCl_4 , ether) depress the partial pressure of alcohol more than that of water; on the other hand, dehydrating agents having high boiling point (glycerol, glycol) depress the partial pressure of water more than that of alcohol.

(ix) **Chromatography** : This is a modern method used for the separation of mixtures into its components, purification of compounds and also to test the purity of compounds. The name chromatography is based on the Greek word '*chroma*' meaning colour and '*graphy*' for writing because the method was first used for the separation of coloured substances found in plants. This method was described by **Tswett** in 1906.

(a) **Principle of chromatography** : The technique of chromatography is based on the difference in the rates at which the components of a mixture move through a porous medium (called *stationary phase*) under the influence of some solvent or gas (called *moving phase*). Thus, this technique consists of two phases- one is a stationary phase of large surface area while the second is a moving phase which is allowed to move slowly over the stationary phase. *The stationary phase is either a solid or a liquid while the moving phase may be a liquid or a gas.*

(b) **Types of chromatography** : Depending upon the nature of the stationary and the mobile phases, the different types of chromatographic techniques commonly used are in a given table,

Table : 22.1

Type of Chromatography	Mobile/Stationary Phase	Uses
Adsorption or column chromatography	Liquid/Solid	Large scale separations
Thin-layer chromatography	Liquid/Solid	Qualitative analysis (identification and characterization of organic compounds)
High performance liquid chromatography	Liquid/Solid	Qualitative and quantitative analysis
Gas-liquid chromatography (GLC)	Gas/Liquid	Qualitative and quantitative analysis
Partition chromatography or ascending paper chromatography	Liquid/Liquid	Qualitative and quantitative analysis of polar organic compounds (sugars, α -amino acids and inorganic compounds)

It is constant for a given substance (component) under a given set of conditions. Therefore, it is possible to identify the various components by determining their R_f values.

(x) **Differential extraction** : This method is used for the separation of an organic compound (solid or liquid) from its aqueous solution by shaking with a suitable solvent (e.g. ether, benzene, chloroform, carbon tetrachloride etc.) in a separating funnel. The selected solvent should be immiscible with water but should dissolve the organic compound to an appreciable extent.

It is important to note that extraction is more efficient (i.e., more complete) when a given volume of the extracting solvent is used in several installments.

This method is normally applied to *nonvolatile compounds*. For example, *benzoic acid can be extracted from its water solution using benzene.*

(xi) **Chemical methods** : Besides these physical methods, a number of chemical methods have also been used to separate a mixture of organic compounds. These methods are based upon the distinguishing chemical properties of one class of organic compounds from the others. For example,

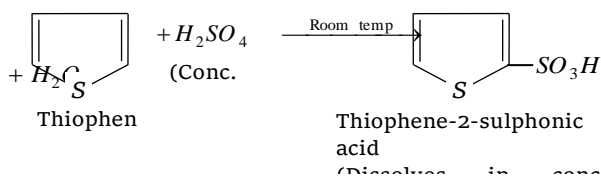
(a) Phenols can be separated from carboxylic acids on treatment with an aqueous solution of $NaHCO_3$. Since carboxylic acids dissolve in $NaHCO_3$ solution evolving CO_2 but phenols usually do not react.

(b) Destructive distillation of wood gives *pyroligneous acid* which contains acetic acid (10%),

acetone (0.5%) and methanol (3%). Acetic acid can be separated from this mixture by treating it with milk of lime when acetic acid forms the calcium salt. The reaction mixture on distillation gives a mixture of acetone and methanol (which can be further separated by fractional distillation into individual components as mentioned above) while the calcium salt remains as residue in the flask. The calcium salt is then decomposed with dil HCl and distilled to afford acetic acid.

(c) A mixture of 1°, 2° and 3° amines can be separated using either benzenesulphonyl chloride (*Hinsberg's reagent*) or diethyl oxalate (*Hoffmann's method*).

(d) *Purification of commercial benzene* : Commercial benzene obtained from coal-tar distillation contains 3-5% thiophene as an impurity which can be removed by extraction with conc. H_2SO_4 . This purification is based upon the fact that thiophene undergoes sulphonation much more easily than benzene. Thus, when commercial benzene is shaken with conc. H_2SO_4 in a separating funnel, thiophene undergoes sulphonation to form thiophene-2-sulphonic acid which dissolves in conc. H_2SO_4 while benzene does not.



After this treatment, the benzene layer is removed, washed with water to remove unreacted H_2SO_4 , dried over anhyd. $CaCl_2$ and then distilled to give pure benzene.

(e) *Absolute alcohol from rectified spirit* : The rectified spirit (ethanol : H_2O , 95.87:4.13 by weight) is kept over a calculated amount of active quick lime (CaO) for few hours and then refluxed. During this process, water present in rectified spirit combines with CaO to form $Ca(OH)_2$. When the resulting mixture is distilled, absolute alcohol distils over leaving behind, $Ca(OH)_2$.

Drying of Organic Substances. (1) *For solids* : Most solids are dried first by pressing them gently between folds of filter papers. Compounds which neither decompose on heating nor melt below $100^\circ C$ are dried by keeping them in steam or oven maintained at $110^\circ C$. Substances, which decompose on heating are

dried by keeping them in a vacuum desiccator containing a suitable dehydrating agent like fused $CaCl_2$, conc. H_2SO_4 , P_4O_{10} , solid KOH or $NaOH$, etc (desiccant).

(2) *For liquids* : Organic liquids are generally dried by keeping them over night in contact with a dehydrating (desiccating) agent which does not react chemically with the liquid to be dried. Commonly used *dehydrating agents* are quick lime, anhydrous $CaCl_2$, fused $CuSO_4$ or $CaSO_4$, KOH , metallic sodium or potassium, etc.

Criteria of purity of organic compounds : The purity of an organic compound can be ascertained by determining its some physical constants like m.p., b.p., specific gravity, refractive index and viscosity. In usual practice, sharp m.p. (in case of solids) and boiling point (in case of liquids) are used as criteria for purity because their determination is feasible in the laboratory. *A pure organic solid has a definite and sharp (sudden, rapid and complete) melting point, while an impure substance has a lower and indefinite melting point.*

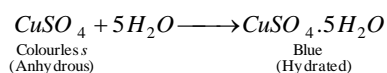
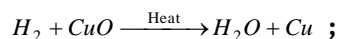
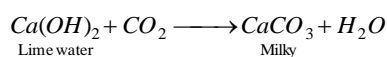
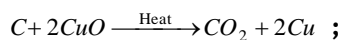
(1) **Mixed melting point** : The melting point of two thoroughly mixed substances is called mixed melting point. This can also be used for ascertaining the purity of a compound .

The substance, whose purity is to be tested, is mixed with a pure sample of the same compound. The melting point of the mixture is determined. If the melting point of the mixture is sharp and comes out to be the same as that of pure compound, it is sure that the compound under test is pure. On the other hand, if the melting point of the mixture is less than the melting point of the pure compound, the compound in question is not pure.

(2) **Qualitative analysis** : (Detection of Elements)

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

Carbon is an essential constituent of an organic compound whereas hydrogen is nearly always present. On heating the organic compound with dry cupric oxide, carbon is oxidized to CO_2 and hydrogen to H_2O . CO_2 is detected by lime water which turns milky while H_2O is detected by anhydrous $CuSO_4$ (white) which turns it blue. This method is known as **copper oxide test**.



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If the substance under investigation is a volatile liquid or gas, the vapours are passed over heated copper oxide kept in combustion tube and the gaseous products are tested as above.

Lassaigne method

This is used to detect nitrogen, halogen and sulphur. Organic compounds are fused with dry sodium in a fusion-tube and fused mass after extraction with H_2O is boiled and filtered. Filtrate called sodium extract (S.E.) is used to detect elements (other than C and H) and the tests are given in the table.

• Organic compounds being covalents normally do not have ionisable groups, hence direct test is not possible.

• Fusion with Na forms soluble salt (like $NaCl, NaCN$ etc.) which can be easily detected.

• This test fails in case of diazo compounds.

• Sometimes when the amount of nitrogen present is small, the prussian blue is present in colloidal form and the solution looks green.

Table : 22.2 Lassaigne method (Detection of elements)

Element	Sodium Extract (S.E.)	Confirmed Test	Reaction
Nitrogen	$Na + C + N \xrightarrow{\Delta} NaCN$ (S.E.)	S.E. + $FeSO_4 + NaOH$, boil and cool + $FeCl_3 + conc. HCl$ Blue or green colour	$2NaCN + FeSO_4 \longrightarrow Fe(CN)_2 + Na_2SO_4$ $Fe(CN)_2 + 4NaCN \longrightarrow Na_4[Fe(CN)_6]$ Sodium ferrocyanide $3Na_4[Fe(CN)_6] + 4FeCl_3 \xrightarrow{HCl} Fe_4[Fe(CN)_6]_3 + 12NaCl$ Ferric ferrocyanide (Prussian blue)
Sulphur	$2Na + S \xrightarrow{\Delta} Na_2S$ (S.E.)	(i) S.E. + sodium nitroprusside (ii) S.E. + $CH_3CO_2H + (CH_3CO_2)_2Pb$ A black ppt.	(i) $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NO.S]$ or Sodium nitroprusside (Purple) $Na_3[Fe(ONSNa)(CN)_5]$ Sodium thionitroprusside (Violet) (ii) $Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH} PbS \downarrow + 2CH_3COONa$ black ppt.
Halogen	$Na + X \xrightarrow{\Delta} NaX$ (S.E.) (X = Cl, Br, I)	S.E. + $HNO_3 + AgNO_3$ (i) White ppt soluble in aq NH_3 confirms Cl. (ii) Pale yellow ppt partially soluble in aq. NH_3 confirms Br. (iii) Yellow ppt insoluble in aq NH_3 confirms I.	$NaX + AgNO_3 \xrightarrow{HNO_3} AgX \downarrow$ ppt $AgCl + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]Cl$ White ppt soluble $AgBr + 2NH_3(aq) \longrightarrow [Ag(NH_3)_2]Br$ Yellow ppt. Partially soluble $AgI + NH_3(aq) \longrightarrow Insoluble$
Nitrogen and sulphur together	$Na + C + N + S \xrightarrow{\Delta} NaCNS$ (S.E.) with excess of Na the thiocyanate formed decomposes into cyanide and sulphide. $NaCNS + 2Na \rightarrow NaCN$ $+Na_2S$	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.	$3NaCNS + FeCl_3 \longrightarrow [Fe(SCN)_3]$ or $[Fe(SCN)]Cl_2 + 3NaCl$ Ferric sulphocyanide (Blood red colour)

Table : 22.3 Other methods for detection of elements

Element	Test
Nitrogen	Soda lime test : A pinch of an organic compound is heated strongly with soda lime ($NaOH + CaO$) in a test tube. If ammonia gas evolves, it indicates nitrogen. $CH_3CONH_2 + NaOH \xrightarrow{CaO} CH_3COONa + NH_3$. Acetamide This test is, however, not reliable since certain compounds like nitro, azo etc do not evolve NH_3 when heated with soda lime.

Table : 22.4 Quantitative estimation of elements in organic compounds

Element	Method and its principle	Formula
Carbon and Hydrogen	<p>Liebig's combustion method : In this method, a known weight of organic compound is heated with pure and dry cupric oxide in a steam of pure and dry oxygen, when carbon is oxidised to carbon dioxide while hydrogen is oxidised to water. From the weight of CO_2 and H_2O, the percentage of C and H can be calculated.</p> $C_xH_y + \left(x + \frac{y}{4}\right)O_2 \xrightarrow{\Delta} xCO_2 + \frac{y}{2}H_2O$	<p>(i) % of C = $\frac{\text{Weight of } CO_2}{\text{Weight of org. compound}} \times \frac{12}{44} \times 100$</p> <p>(ii) % of H = $\frac{\text{Weight of } H_2O}{\text{Weight of org. compound}} \times \frac{2}{18} \times 100$</p>
Nitrogen	<p>(i) Duma's method : Elemental nitrogen is converted into molecular nitrogen by a suitable chemical method and its volume is changed to STP data.</p> $C + 2H + 3CuO \rightarrow CO_2 + H_2O + 3Cu$ $2N + 2CuO \rightarrow N_2 + \text{oxide of nitrogen}$ <p>Oxides of nitrogen + Cu \longrightarrow $N_2 + CuO$</p> <p>(ii) Kjeldahl's method : Nitrogen in organic compound is converted into NH_3 by suitable chemical method which, in turn, is absorbed by V_1 mL of $N_1H_2SO_4$.</p> $N(\text{from organic compound}) + \text{conc. } H_2SO_4 \xrightarrow{\Delta} (NH_4)_2SO_4$ $(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O + 2NH_3$	<p>% of N = $\frac{28}{22400} \times \frac{V}{W} \times 100$</p> <p>Where, V = volume of N_2 in nitrometer (in ml) at NTP, W = Weight of substance taken;</p> $\% \text{ of N} = \frac{1.4 \times N \times V}{W}$ <p>Note : This method is, however, not applicable to compounds containing nitrogen in the ring (e.g. Pyridine, quinoline etc) and compounds containing nitro and azo ($-N=N-$) groups since nitrogen in these compounds is not completely converted into $(NH_4)_2SO_4$ during digestion.</p>
Halogens	<p>(i) Carius method : The method is based on the fact that when an organic compound containing halogen (Cl, Br, or I) is heated in a sealed tube with fuming nitric acid in presence of silver nitrate, silver halide is formed. From the mass of silver halide formed, the percentage of the halogen can be calculated.</p> <p>(ii) Schiff's and Piria method : In this method the accurately weighed organic compound (0.15 - 0.25 g) is taken in a small platinum crucible with a mixture of lime and sodium carbonate, ($CaO + Na_2CO_3$). It is now heated strongly and then cooled and dissolved in dilute nitric acid in a beaker. The solution is then filtered and the halide is precipitated with silver nitrate solution. Halogen is now calculated as in Carius method.</p>	<p>% of Cl = $\frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of substance taken}} \times 100$</p> <p>% of Br = $\frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of substance taken}} \times 100$</p> <p>% of I = $\frac{127}{235} \times \frac{\text{Mass of AgI formed}}{\text{Mass of substance taken}} \times 100$</p>
Sulphur	<p>Carius method : When an organic compound containing sulphur is heated with fuming nitric acid, sulphur is oxidised to sulphuric acid. This is precipitated as barium sulphate by adding barium chloride solution. From the amount of barium sulphate, percentage of sulphur can be calculated.</p> $S + HNO_3(\text{fuming}) \xrightarrow{\text{heat}} H_2SO_4$ $H_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2HCl$ <p style="text-align: center;">white ppt</p>	<p>% of S = $\frac{32}{233} \times \frac{\text{Mass of } BaSO_4 \text{ formed}}{\text{Mass of substance taken}} \times 100$</p>
phosphorus	<p>Carius method : The organic compound containing phosphorus is heated with fuming nitric acid. Phosphorus is oxidised to phosphoric acid. It is precipitated as magnesium ammonium</p>	<p>% of P = $\frac{62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7 \text{ formed}}{\text{Mass of substance taken}} \times 100$</p>



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	<p>phosphate, $MgNH_4PO_4$, by the addition of magnesia mixture ($MgSO_4 + NH_4OH + NH_4Cl$). The magnesium ammonium phosphate is washed, dried and ignited when it is converted to magnesium pyrophosphate ($Mg_2P_2O_7$).</p> $2MgNH_4PO_4 \xrightarrow{\text{heat}} Mg_2P_2O_7 + 2NH_3 + H_2O$ <p>From the mass of magnesium pyro-phosphate, the percentage of phosphorus in the compound can be calculated.</p>	
Oxygen	<p>(i) The usual method of determining the percentage of oxygen in an organic compound is by the method of difference. All the elements except oxygen present in the organic compound are estimated and the total of their percentages subtracted from 100 to get the percentage of oxygen.</p> <p>(ii) Aluise's method ∴ Organic compound containing oxygen is heated with graphite and CO formed is quantitatively converted into CO_2 on reaction with I_2O_5.</p> <p style="text-align: center;">Org. compound $\xrightarrow{\text{Pyrolysis}}$ Oxygen</p> $O_2 + 2C \xrightarrow{1100^\circ C} 2CO$ $5CO + I_2O_5 \longrightarrow I_2 + 5CO_2$	<p>Percentage of oxygen = 100 - (Sum of the percentages of all other elements)</p> $\begin{matrix} O \equiv CO \equiv CO_2 \\ 16 \text{ g} \quad \quad 44 \text{ g} \end{matrix}$ $\% \text{ of } O = \frac{16}{44} \times \frac{\text{mass of } CO_2}{\text{mass of org. compd.}} \times 100$

(4) **Determination of Molecular Mass** : The molecular mass of the organic compounds can be determined by various methods.

(i) **Physical methods for volatile compounds**

(a) **Victor Meyer's method** : Molecular mass of volatile liquids and solids can be easily determined from the application of **Avogadro hypothesis** according to which the mass of 22.4 litres or 22400ml of the vapour of any volatile substance at NTP is equal to the molecular mass of the substance.

In Victor Meyer's method, a known mass of the volatile substance is vaporised in a Victor Meyer's tube. The vapours formed displace an equal volume of air into a graduated tube. The volume of air collected in graduated tube is measured under experimental conditions. This volume is converted to NTP conditions.

Calculations : Mass of the organic substance = W g

Let the volume of the air displaced be = V_1 ml ;

Temperature = T_1 K

Pressure (after deducting aqueous tension)

= p_1 mm

Let the volume at NTP be = V_2 ml

Applying gas equation, $V_2 = \frac{p_1 \times V_1}{T_1} \times \frac{273}{760}$

∴ V_2 ml of vapours weight at NTP = W g

∴ 22400 ml of vapour weight at NTP =

$$\frac{W}{V_2} \times 22400 = M$$

Alternatemethod : Vapour density of substance

$$= \frac{\text{Mass of 1 ml of vapours at NTP}}{\text{Mass of 1 ml of hydrogen at NTP}}$$

or $V. D. = \frac{W / V_2}{0.00009}$ (∵ Mass of 1 ml of H_2 at

NTP

= 0.00009 g or 2 / 22400)

or $V. D. = \frac{W}{V_2 \times 0.00009}$;

Mol. Mass, $M = 2 \times V. D. = \frac{2W}{V_2 \times 0.00009}$

(b) **Hofmann's method** : The method is applied to those substances which are not stable at their boiling points, but which may be volatilised without decomposition under reduced pressure. A known mass of the substance is vaporised above a mercury column in a barometric tube and the volume of the vapour formed is recorded. It is then reduced to NTP conditions. The molecular mass of the organic

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substance can be calculated by the application of following relationship,

$$\text{Mol. Mass} = \frac{\text{Mass of the substance}}{\text{volume of the vapours at NTP}} \times 22400$$

(ii) **Physical methods for Non-volatile substances** : The molecular mass of a non-volatile organic compound can be determined by noting either the elevation in boiling point of the solvent (Ebullioscopic method) or the depression in freezing point of the solvent (Cryoscopic method) produced by dissolving a definite mass of the substance in a known mass of the solvent. The molecular mass of the compound can be calculated from the following mathematical relationships :

(a) *Elevation in boiling point* : Mol. Mass

$$= \frac{1000 K_b \times w}{W \times \Delta T}$$

Where, K_b = Molal elevation constant of the solvent, w = Mass of the compound, W = Mass of the solvent

ΔT = Elevation in boiling point of the solvent (determined experimentally)

(b) *Depression in freezing point* : Mol. Mass

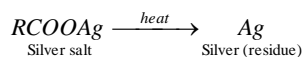
$$= \frac{1000 K_f \times w}{W \times \Delta T}$$

Where, K_f = Molal depression constant of the solvent, w = Mass of the compound, W = Mass of the solvent

ΔT = Depression in freezing point of the solvent (determined experimentally)

(iii) Chemical methods

(a) *Silver salt method for acids* : It is based on the fact that silver salt of an organic acid on heating gives residue of metallic silver.



From the mass of the silver salt taken and the mass of the silver residue obtained, the equivalent mass of the silver salt can be calculated.

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

Knowing the equivalent mass of silver salt, the equivalent mass of the acid can be obtained. The molecular mass of an acid can be determined with the help of the following relationship,

Mol. mass of the acid = Equivalent mass of the acid \times basicity

Calculations : (i) Mass of silver salt taken = wg

(ii) Mass of metallic silver = xg

$$\frac{\text{Eq. mass of silver salt}}{\text{Eq. mass of silver}} = \frac{w}{x}; \text{ Eq. mass of silver salt} = \frac{w}{x} \times 108$$

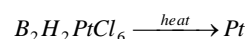
Let the equivalent mass of the acid be E . In the preparation of silver salt, a hydrogen atom of the carboxylic group is replaced by a silver atom.

Thus, Equivalent mass of silver salt = $E - 1 + 108 = E + 107$

$$\text{Thus, } E + 107 = \frac{w}{x} \times 108 \text{ or } E = \left[\frac{w}{x} \times 108 - 107 \right]$$

If n be the basicity of the acid, then Mol. Mass of the acid = $\left[\frac{w}{x} \times 108 - 107 \right] \times n$

(b) *Platinichloride method for bases* : Organic bases combine with chloroplatinic acid, H_2PtCl_6 to form insoluble platinichlorides, which, on ignition, leave a residue of metallic platinum. Knowing the mass of platinum salt and the mass of metallic platinum, the molecular mass of the platinum salt can be determined. Let B represents one molecule of the base. If the base is mono-acidic, the formula of the salt will be $B_2H_2PtCl_6$.



$$\frac{\text{Molecular mass of the salt}}{\text{Atomic mass of platinum}} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}}$$

Let E be the equivalent mass of the base.

Molecular mass of the salt

$$= 2E + 2 + 195 + 213 = 2E + 410$$

$$\text{So } \frac{2E + 410}{195} = \frac{w}{x} = \frac{\text{Mass of platinum salt}}{\text{Mass of platinum}};$$

$$2E = \left[\frac{w}{x} \times 195 - 410 \right]; E = \frac{1}{2} \left[\frac{w}{x} \times 195 - 410 \right]$$

Mol. mass of the base = Eq. mass \times acidity = $E \times n$

where n is the acidity of the base.

(c) *Volumetric method for acids and bases* : Molecular mass of an acid can be determined by dissolving a known mass of the acid in water and titrating the solution against a standard solution of an alkali using phenolphthalein as an indicator. Knowing the volume of alkali solution used, the mass of the acid,

which will require 1000 ml of a normal alkali solution for complete neutralisation can be calculated. This mass of the acid will be its equivalent mass.

$\underbrace{1000 \text{ ml } 1N \text{ alkali solution}}_{\text{One gram equivalent of alkali}} \equiv \text{One gram equivalent of the acid}$

Calculations : Suppose w g of the organic acid requires V ml N_1 alkali solution for complete neutralisation.

V ml N_1 alkali solution $\equiv w$ gm acid

So 1000 ml N_1 alkali solution $\equiv \frac{w}{V \times N_1} \times 1000$ g acid
 \equiv one gram equivalent acid

Equivalent mass of the acid $\equiv \frac{w}{V \times N_1} \times 1000$

Thus, Molecular mass of the acid = Eq. mass \times basicity

In the case of organic bases, the known mass of the base is titrated against a standard solution of an acid. Knowing the volume of the acid solution used, the mass of the organic base which will require 1000 ml of a normal acid solution for complete neutralisation can be calculated. This mass will be the equivalent mass of the base.

$\underbrace{1000 \text{ ml } N \text{ acid solution}}_{\text{One gram equivalent of the acid}} \equiv \text{One gram equivalent of the base}$

base

Molecular mass of the base = Eq. mass \times acidity

(5) Calculation of Empirical and Molecular formula

(i) **Empirical formula** : Empirical formula of a substance gives the simplest whole number ratio between the atoms of the various elements present in one molecule of the substance. For example, empirical formula of glucose is CH_2O , i.e. for each carbon atom, there are two H-atoms and one oxygen atom. Its molecular formula is however, $C_6H_{12}O_6$.

Calculation of empirical formula : The steps involved in the calculation are as follows,

(a) Divide the percentage of each element by its atomic mass. This gives the relative number of atoms.

(b) Divide the figures obtained in step (i) by the lowest one. This gives the simplest ratio of the various elements present.

(c) If the simplest ratio obtained in step (ii) is not a whole number ratio, then multiply all the figures with

a suitable integer i.e., 2, 3, etc. to make it simplest whole number ratio.

(d) Write down the symbols of the various elements side by side with the above numbers at the lower right corner of each. This gives the empirical or the simplest formula.

(ii) **Molecular formula** : Molecular formula of a substance gives the actual number of atoms present in one molecule of the substance.

Molecular formula = $n \times$ Empirical formula

Where, n is a simple integer 1, 2, 3,..... etc. given by the equation,

$$n = \frac{\text{Molecular mass of the compound}}{\text{Empirical formula mass of the compound}}$$

where the molecular mass of the compound is determined experimentally by any one of the methods discussed former, empirical formula mass is calculated by adding the atomic masses of all the atoms present in the empirical formula.

(iii) Molecular formula of gaseous hydrocarbons (Eudiometry)

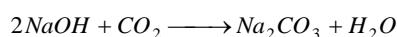
Eudiometry is a direct method for determination of molecular formula of gaseous hydrocarbons without determining the percentage composition of various elements in it and without knowing the molecular weight of the hydrocarbon. The actual method used involves the following steps,

(a) A known volume of the gaseous hydrocarbon is mixed with an excess (known or unknown volume) of oxygen in the eudiometer tube kept in a trough of mercury.

(b) The mixture is exploded by passing an electric spark between the platinum electrodes. As a result, carbon and hydrogen of the hydrocarbon are oxidised to CO_2 and H_2O vapours respectively.

(c) The tube is allowed to cool to room temperature when water vapours condense to give liquid water which has a negligible volume as compared to the volume of water vapours, Thus, the gaseous mixture left behind in the eudiometer tube after explosion and cooling consists of only CO_2 and unused O_2 .

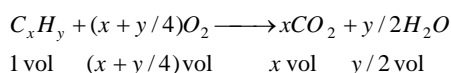
(d) Caustic potash or caustic soda solution is then introduced into the eudiometer tube which absorbs CO_2 completely and only unused O_2 is left behind.



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Thus, the decrease in volume on introducing NaOH or KOH solution gives the volume of CO_2 formed. Sometimes, the volume of O_2 left unused is found by introducing pyrogallol and noting the decrease in volume.

Calculation : From the volume of CO_2 formed and the total volume of O_2 used, it is possible to calculate the molecular formula of gaseous hydrocarbon with the help of the following equation.



(Negligible volume on condensation)

From the above equation, it is evident that for one volume of hydrocarbon,

(a) $(x + y/4)$ volume of O_2 is used

(b) x volume of CO_2 is produced

(c) $y/2$ volume of H_2O vapours is produced which condense to give liquid H_2O with negligible volume.

(d) Contraction on explosion and cooling

$$= [(1 + x + y/4) - x] = 1 + y/4$$

By equating the experimental values with the theoretical values from the above combustion equation, the values of x and y and hence the molecular formula of the gaseous hydrocarbon can be easily determined.

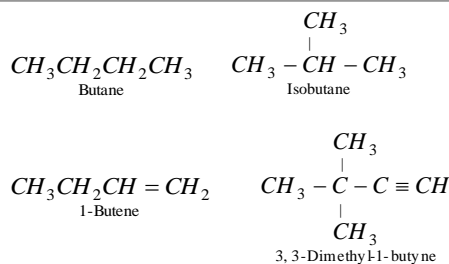
(6) **Determination of structure by spectroscopic and diffraction methods** : The structures of organic substances are determined by spectroscopic and diffraction methods.

Classification of organic compounds

Organic compounds have been classified on the basis of carbon skeleton (structure) or functional groups or the concept of homology.

(1) Classification based on structure

(i) **Acyclic or open-chain compounds** : Organic compounds in which all the carbon atoms are linked to one another to form open chains (straight or branched) are called acyclic or open chain compounds. These may be either saturated or unsaturated. For example,



These compounds are also called as aliphatic compounds.

(ii) **Cyclic or closed-chain compounds** : Cyclic compounds contain at least one ring or closed chain of atoms. The compounds with only one ring of atoms in the molecule are known as *monocyclic* but those with more than one ring of atoms are termed as *polycyclic*. These are further divided into two subgroups.

(a) **Homocyclic or carbocyclic** : These are the compounds having a ring or rings of carbon atoms only in the molecule. The carbocyclic or homocyclic compounds may again be divided into two types :

Alicyclic compounds : These are the compounds which contain rings of three or more carbon atoms. These resemble with aliphatic compounds than aromatic compounds in many respects. That is why these are named alicyclic, *i.e.*, aliphatic cyclic. These are also termed as polymethylenes. Some of the examples are,



Cyclopropane

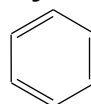


Cyclobutane

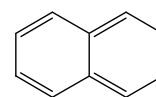


Cyclohexane

Aromatic compounds : These compounds consist of at least one benzene ring, *i.e.*, a six-membered carbocyclic ring having alternate single and double bonds. Generally, these compounds have some fragrant odour and hence, named as aromatic (*Greek word aroma meaning sweet smell*).



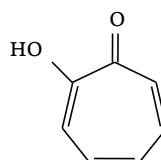
Benzene



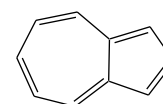
Naphthalene

These are also called benzenoid aromatics.

Non-benzenoid aromatics : There are aromatic compounds, which have structural units different from benzenoid type and are known as Non-benzenoid aromatics *e.g.* Tropolone, azulene etc.



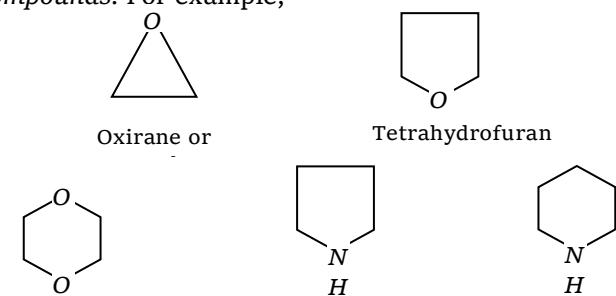
Tropolone



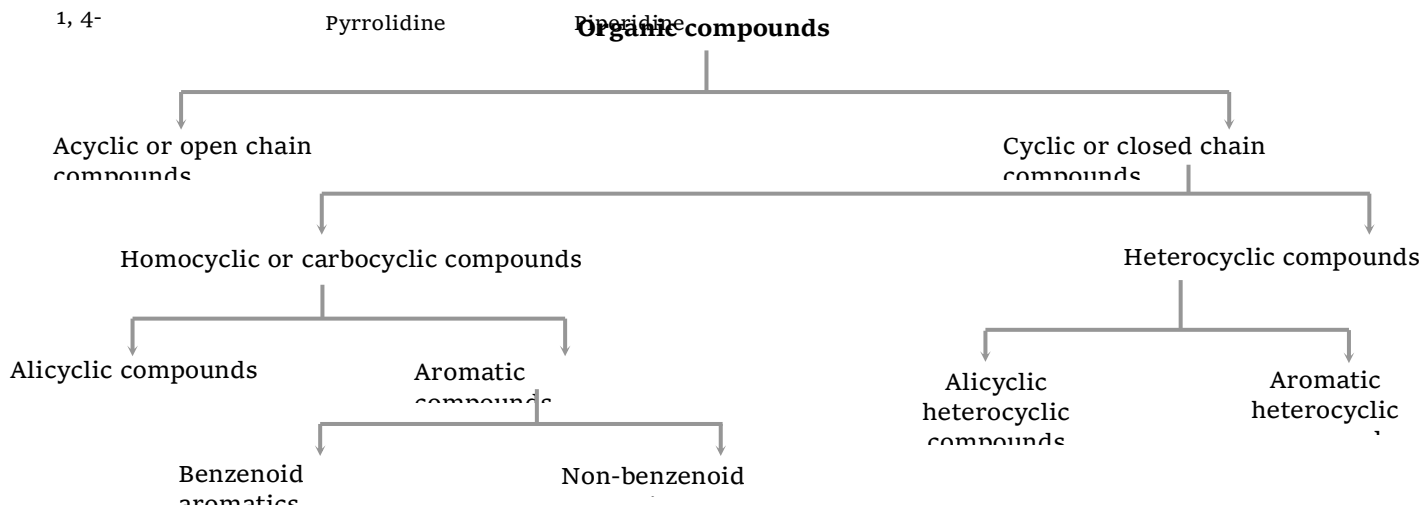
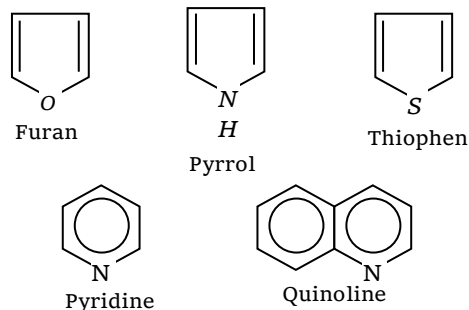
Azulene

(b) *Heterocyclic compounds* : Cyclic compounds containing one or more hetero atoms (e.g. O, N, S etc.) in the ring are called heterocyclic compounds. These are of two types :

Alicyclic heterocyclic compounds : Heterocyclic compounds which resemble aliphatic compounds in their properties are called *Alicyclic heterocyclic compounds*. For example,



Aromatic heterocyclic compounds : Heterocyclic compounds which resemble benzene and other aromatic compounds in most of their properties are called *Aromatic heterocyclic compounds*. For example,



(2) Classification based on functional groups :

A *functional group* is an atom or group of atoms in a molecule that gives the molecule its characteristic chemical properties. Double and triple bonds are also considered as functional groups.

All compounds with the same functional group belong to the same class. Various classes of compounds having some of the common functional groups are listed in the table.

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Table : 22.5

Class	Functional group	Class	Functional group
Olefins/Alkenes (ene)	$\text{>C} = \text{C} <$	Acid halides (Alkanoyl halides)	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{X} \end{array}$ (Acylhalide)
Acetylenes/Alkynes (yne)	$-\text{C} \equiv \text{C}-$	Amides (Alkanamides)	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{NH}_2 \end{array}$ (Amide)
Alkyl Halides	$-\text{F}, -\text{Cl}, -\text{Br}, -\text{I}$ (Halo)	Acid anhydrides (Alkanoic anhydrides)	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ -\text{C}-\text{O}-\text{C}- \end{array}$ (Anhydride)
Alcohols (Alkanols)	$-\text{OH}$ (Hydroxy)	Esters (Alkylalkanoates)	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}-\text{C}- \\ \end{array}$ (Ester)
Ethers (Alkoxyalkanes)	$\begin{array}{c} \quad \\ -\text{C}-\text{O}-\text{C}- \\ \quad \end{array}$ (Alkoxy)	Cyanides/Nitriles (Alkanenitrile)	$-\text{C} \equiv \text{N}$ (Cyano)
Aldehydes (Alkanals)	$\begin{array}{c} -\text{C}-\text{H} \\ \\ \text{O} \end{array}$ (Aldehydic)	Isocyanides	$-\text{N} \rightleftharpoons \text{C}$ (Isocyano)
Ketones (Alkanones)	$\begin{array}{c} \text{O} \\ \\ -\text{C}- \end{array}$ (Carbonyl)	Nitro compounds (Nitroalkanes)	$\begin{array}{c} \text{O} \\ // \\ -\text{C} \\ \backslash \\ \text{O} \end{array}$ (Nitro) ↓
Carboxylic acid (Alkanoic acid)	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{OH} \end{array}$ (Carboxyl)	Amines	$\begin{array}{c} \text{H} \\ / \\ -\text{C} \\ \backslash \\ \text{H} \end{array}$ (Amino)

(3) **Homologous series** : A homologous series can be defined as a group of compounds in which the various members have similar structural features and similar chemical properties and the successive members differ in their molecular formula by CH_2 group.

Characteristics of homologous series

(i) All the members of a series can be represented by the general formula. For example, the members of the alcohol family are represented by the formula $\text{C}_n\text{H}_{2n+1}\text{OH}$ where n have values 1, 2, 3..... etc.

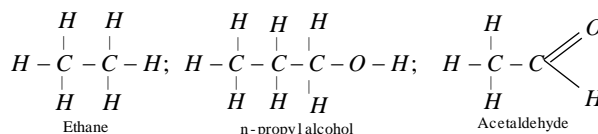
(ii) Two successive members differ in their formula by $-\text{CH}_2$ group or by 14 atomic mass units $(12 + 2 \times 1)$.

(iii) Different members in a family have common functional group e.g., the members of the alcohol family have $-\text{OH}$ group as the functional group.

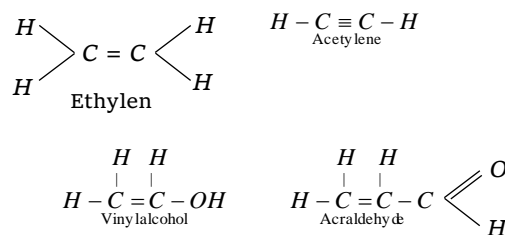
(iv) The members in any particular family have almost identical chemical properties and their physical properties such as melting point, boiling point, density, solubility etc., show a proper gradation with the increase in the molecular mass.

(v) The members present in a particular series can be prepared almost by similar methods known as the general methods of preparation.

(4) **Saturated and unsaturated compounds** : If, in an organic compound containing two or more carbon atoms, there are only single bonds between carbon atoms, then the compound is said to be saturated, e.g. ethane, n -propyl alcohol, acetaldehyde etc.



On the other hand, if the compound contains at least one pair of adjacent carbon atoms linked by a multiple bond, then that compound is said to be **unsaturated**, e.g. ethylene, acetylene, vinyl alcohol, acraldehyde etc.



Nomenclature of organic compounds

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Nomenclature means the assignment of names to organic compounds. There are two main systems of nomenclature of organic compounds.

(1) **Trivial system** : This is the oldest system of naming organic compounds. The trivial name was generally based on the source, some property or some other reason. Quite frequently, the names chosen had Latin or Greek roots. For example,

(i) Acetic acid derives its name from vinegar of which it is the chief constituent (Latin : *acetum* = vinegar).

(ii) Formic acid was named as it was obtained from red ants. The Greek word for the red ants is *formicus*.

(iii) The names oxalic acid (*oxalus*), malic acid (*pyrus malus*), citric acid (*citrus*) have been derived from botanical sources given in parentheses.

(iv) Urea and uric acid have derived their names from urine in which both are present.

(v) The liquid obtained by the destructive distillation of wood was named as wood spirit. Later on, it was named methyl alcohol (Greek : *methu* = spirit; *hule* = wood).

(vi) Names like glucose (sweet), pentane (five), hexane (six), etc. were derived from Greek words describing their properties or structures.

(vii) Methane was named as marsh gas because it was produced in marshes. It was also named as fire damp as it formed explosive mixture with air.

Table : 22.6 Common or trivial names of some organic compounds.

Compound	Common name	Compound	Common name
CH_4	Methane	$CHCl_3$	Chloroform
C_2H_2	Acetylene	CHI_3	Iodoform
$H_3CCH_2CH_2CH_3$	<i>n</i> -Butane	CH_3CN	Acetonitrile
$(H_3C)_2CHCH_3$	Isobutane	CH_3COOH	Acetic acid
$(H_3C)_4C$	Neopentane	C_6H_6	Benzene
$HCHO$	Formaldehyde	$C_6H_5CH_3$	Toluene
$(H_3C)_2CO$	Acetone	$C_6H_5NH_2$	Aniline
CH_3CH_2OH	Ethyl alcohol	C_6H_5OH	Phenol
CH_3CONH_2	Acetamide	$C_6H_5OCH_3$	Anisole
CH_3OCH_3	Dimethyl ether	$C_6H_5COCH_3$	Acetophenone
$(CH_3CH_2)_2O$	Diethyl ether	$C_6H_5CONH_2$	Benzamide

(2) **IUPAC system** : In order to rationalise the system of naming, an *International Congress of Chemists* was held in Geneva in 1892. They adopted certain uniform rules for naming the compounds.

The system of nomenclature was named as *Geneva system*. Since then the system of naming has been improved from time to time by the *International Union of Pure and Applied Chemistry* and the new system is called *IUPAC system* of naming. This system of nomenclature was first introduced in 1947 and was modified from time to time. The most exhaustive rules for nomenclature were first published in 1979 and later revised and updated in 1993. The rules discussed in the present chapter are based on guide books published by IUPAC in 1979 (**Nomenclature of Organic Chemistry**

by J. Rigandy and S.P. Klesney) and 1993 (**A Guide to IUPAC Nomenclature for Organic Chemistry** by R. Panico, W.H. Powell and J.C. Richer). With the help of this system, an organic compound having any number of carbon atoms can be easily named.

IUPAC System of Naming Organic Compounds :

In the IUPAC system, the name of an organic compound consist of three parts : (i) Word root (ii) Suffix (iii) Prefix

(i) **Word root** : The word root denotes the number of carbon atoms present in the chain.

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Table : 22.7

Chain length	Word root	Chain length	Word root
C ₁	Meth-	C ₁₁	Undec-
C ₂	Eth-	C ₁₂	Dodec-
C ₃	Prop-	C ₁₃	Tridec-
C ₄	But-	C ₁₄	Tetradec-
C ₅	Pent-	C ₁₅	Pentadec-
C ₆	Hex-	C ₁₆	Hexadec-
C ₇	Hept-	C ₁₇	Heptadec-
C ₈	Oct-	C ₁₈	Octadec-
C ₉	Non-	C ₁₉	Nonadec-
C ₁₀	Dec-	C ₂₀	Eicos

(ii) **Suffix** : The word root is linked to the suffix which may be primary or secondary or both.

(a) **Primary suffix** : A primary suffix is added to the word root to indicate whether the carbon chain is saturated or unsaturated.

Table : 22.8

Type of carbon chain	Primary suffix	General name
Saturated (C - C)	-ane	Alkane
Unsaturated (C = C)	-ene	Alkene
Unsaturated (C ≡ C)	-yne	Alkyne

If the parent chain contains two, three or more double or triple bonds, then the numerical prefixes such as **di** (for two), **tri** (for three), **tetra** (for four), etc. are added to the primary suffix.

(b) **Secondary suffix** : A secondary suffix is then added to the word root after the primary suffix to indicate the functional group present in the organic compound.

Table : 22.9

Class of org. compound	Functional group	Secondary suffix
Alcohols	-OH	-ol
Aldehydes	-CHO	-al
Ketones	> C = O	-one
Carboxylic acids	-COOH	-oic acid
Esters	-COOR	alkyl... oate
Acid chlorides	-COCl	-oyl chloride
Acid amides	-CONH ₂	-amide
Nitriles	-C≡N	-nitrile

Amines	-NH ₂	-amine
Thiol	-SH	thiol

It may be noted that while adding the secondary suffix to the primary suffix, the terminal 'e' of the primary suffix (*i.e.* ane, ene and yne) is dropped if the secondary suffix begins with a vowel but is retained if the secondary suffix begins with a consonant. For example

Organic compound	CH ₃ CH ₂ OH	CH ₃ CH ₂ CN
Word root	Eth	Prop
Primary suffix	an (e)*	ane
Secondary suffix	ol	nitrile
IUPAC name	Ethanol	Propanenitrile

The terminal 'e' from the primary suffix has been dropped because the secondary suffix *i.e.* 'ol' begins with a vowel 'o'.

(iii) **Prefix** : There are many groups which are not regarded as functional groups in the IUPAC name of the compound. These are regarded as **substituents** or **side chains**. These are represented as **prefixes** and are placed before the word root while naming a particular compound. These may be :

(a) **Alkyl groups** : These groups contain one hydrogen atom less than the alkane. These are named by substituting the suffix **ane** of the name of the corresponding alkane by **yl**. *i.e.* alkane - ane + yl = **alkyl**.

For example,

CH ₄	:	Methane becomes
CH ₃ -	:	Methyl
CH ₃ CH ₃	:	Ethane becomes
CH ₃ CH ₂ -	:	Ethyl
CH ₃ CH ₂ CH ₃	:	Propane becomes
CH ₃ CH ₂ CH ₂ -	:	Propyl etc.

(b) **Functional groups not regarded as principal functional groups** : If a compound contains more than one functional group, then one of the functional group is regarded as principal functional group and other is treated as secondary suffix. The other functional groups are regarded as substituents and are indicated by prefixes.

Table : 22.10

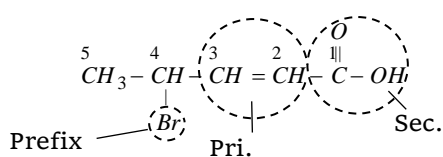
Substituent	Prefix
-F	Fluoro

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-Cl	Chloro
-Br	Bromo
-I	Iodo
-NO	Nitroso
-N=N-	Diazo
-OCH ₃	Methoxy
-OC ₂ H ₅	Ethoxy
-NO ₂	Nitro
-NH ₂	Amino
-OH	Hydroxo

Thus, a complete IUPAC name of an organic compound may be represented as:

Prefix + word root + Primary suffix + Secondary suffix



Word root : Pent (five C - C - C - C - C)

Primary suffix : ene (double bond at C - 2)

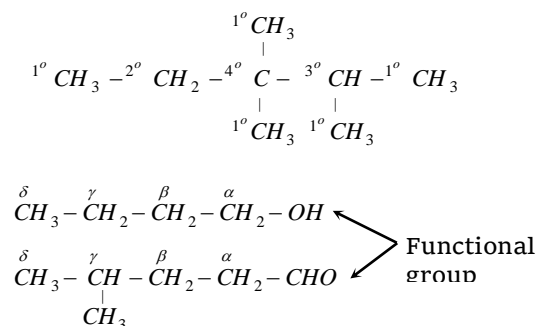
Secondary suffix : oic acid (-COOH group)

Prefix : Bromo (-Br group at C - 4)

IUPAC name : Bromo + pent + ene + oic acid or 4-Bromopent -2-en-1-oic acid

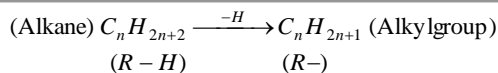
Classification of carbon atoms in organic compounds

The carbon atoms in an alkane molecule may be classified into four types as *primary* (1°), *secondary* (2°), *tertiary* (3°) and *quaternary* (4°). The carbon atoms in an organic compound containing functional group can be designated as α , β , γ , δ .



Alkyl groups

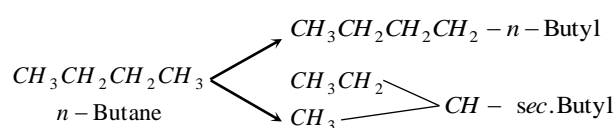
These are univalent groups or radicals obtained by the removal of one hydrogen atom from a molecule of a paraffin. The symbol 'R' is often used to represent an alkyl group.



Alkyl groups are named by dropping -ane from the name of corresponding paraffin and adding the ending -yl.

Parent saturated hydrocarbon	Name of the alkyl group	Structure
Methane	Methyl	CH ₃ -
Ethane	Ethyl	CH ₃ - CH ₂ -
Propane	n-Propyl	CH ₃ - CH ₂ - CH ₂ -
Butane	n-Butyl	CH ₃ - CH ₂ - CH ₂ - CH ₂ -

Alkyl groups derived from saturated hydrocarbons having three or more carbon atoms exist in isomeric forms.



Similarly, removal of different H atoms in pentane gives the following radicals :

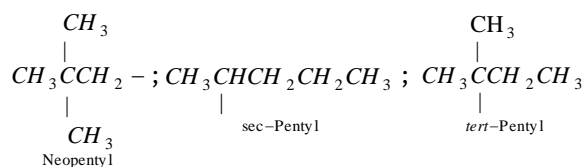
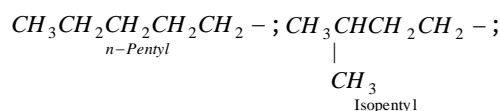


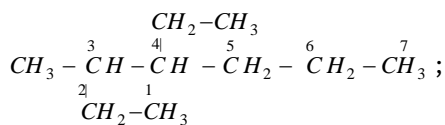
Table : 22.11 Unsaturated groups or radicals

Group	Common name	IUPAC name
CH ₂ = CH -	Vinyl	Ethenyl
CH ₂ = ² CH - ¹ CH ₂ -	Allyl	2-Propenyl
CH ₃ - CH = ¹ CH -	-	1-Propenyl
HC ≡ C -	Acetylide	Ethynyl
HC ≡ ² C - ¹ CH ₂ -	Propargyl	2-Propynyl

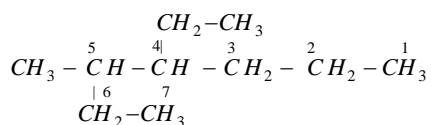
General rules for naming organic compounds

In the common system, all the isomeric alkanes (having same molecular formula) have the same parent name. The names of various isomers are distinguished by prefixes. The prefix indicates the type of branching in the molecule. For example,

the locants is the lowest. This rule is called **lowest sum rule**. For example, the carbon chain of alkanes given below should be numbered as indicated in structures A and not according to structure B.

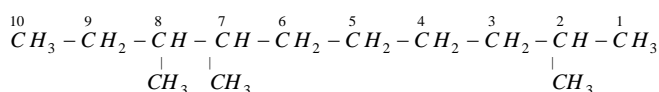


A (correct) Sum of locants = 3+4=7

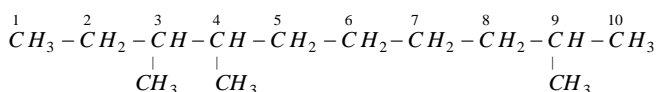


B (wrong) Sum of locants = 4+5=9

According to latest IUPAC system of nomenclature, the lowest set of locants is preferred even if it violates the lowest sum rule. For example,



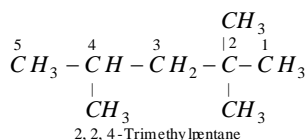
Structure (A) Set of locants = 2, 7, 8
(Correct) Sum of locants = 2 + 7 + 8



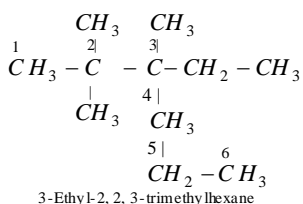
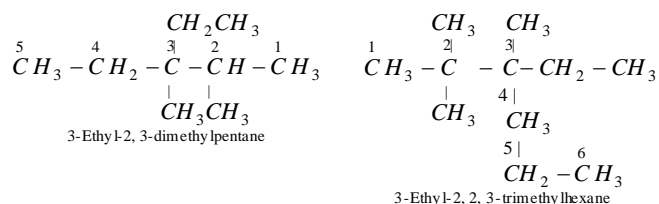
Structure (B) Set of locants = 3, 4, 9
(Wrong) Sum of locants = 3 + 4 + 9

This compound is numbered as 2, 7, 8 and not as 3, 4, 9 in accordance with latest lowest set of locants rule, even though it violates lowest sum rule.

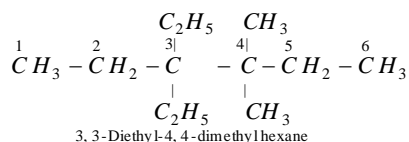
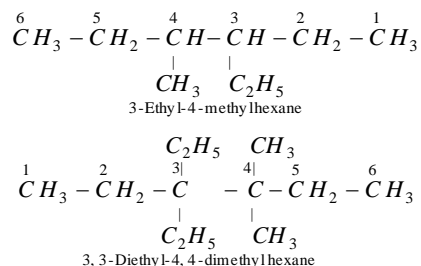
(iv) **Presence of more than one same substituent** : If the same substituent or side chain occurs more than once, the prefixes di, tri, tetraetc., are attached to the names of the substituents. For example,



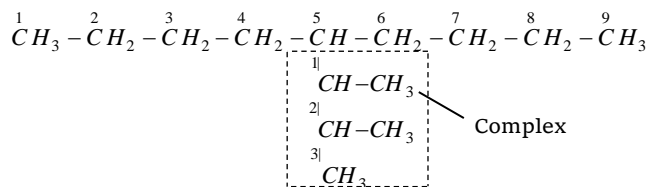
(v) **Naming different substituents** : If two or more different substituents or side chains are present in the molecule, they are named in the alphabetical order along with their appropriate positions.



(vi) **Naming different substituents at equivalent position** : In case, there are different alkyl substituents at equivalent positions, then numbering of the parent chain is done in such a way that the alkyl group which comes first in the alphabetical order gets the lower number.



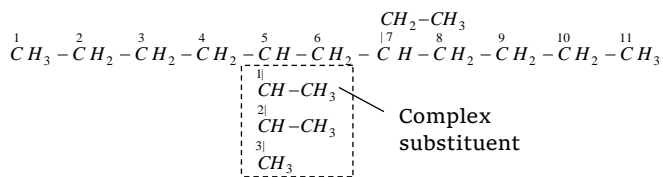
(vii) **Naming the complex substituents** (or substituted substituents) : If the substituent on the parent chain is complex (i.e. it is branched) it is named as substituted alkyl group by numbering the carbon atom of this group attached to the parent chain as 1. The name of such substituent is given in brackets in order to avoid confusion with the numbering of the parent chain. For example,



5-(1, 2-Dimethylpropyl)

The name of the complex substituent is always written in brackets.

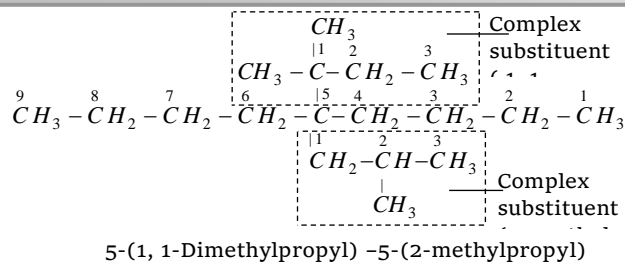
While deciding the alphabetical order of the various substituents, the name of the complex substituent is considered to begin with the first letter of the complete name. It may be **remembered** that in case of simple substituents, however, the multiplying prefixes are not considered. The names of simple substituents are first alphabetized and then multiplying prefixes are inserted. For example,



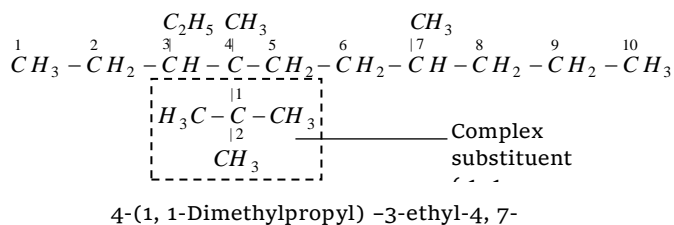
5-(1, 2-Dimethylpropyl)-7-ethyl

It may be noted that dimethyl propyl (a complex substituent) is alphabetized under **d** and not under **m**. Therefore, it is cited before ethyl (e).

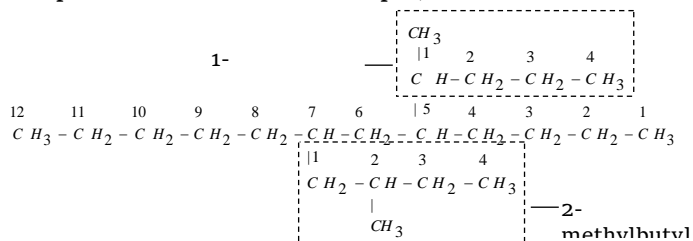
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The substituent dimethyl is cited first because it is alphabetized under *d*. Similarly,

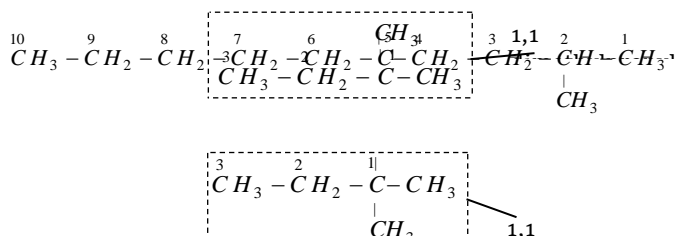


When the names of two or more complex substituents are composed of identical words, priority for citation is given to the substituent which has lowest locant at the first cited point of difference within the complex substituent. For example,



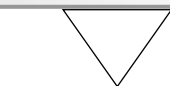
The substituent (1-methylbutyl) is written first because it has lower locant than the substituent (2-methylbutyl).

When the same complex substituent (substituted in the same way) occurs more than once, it is indicated by the multiplying prefix *bis* (for two), *tris* (for three), *tetra kis* (for four) etc.



(viii) **Cyclic hydrocarbons** :- These compounds contain carbon chain skeletons which are closed to form rings. The saturated hydrocarbons with ring of carbon atoms in the molecule are called *cycloalkanes*. These have the general formula C_nH_{2n} .

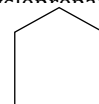
The cyclic compound is named by prefixing **cyclo** to the name of the corresponding straight chain alkane. For example,



C_3H_6 ,
Cyclopropane



C_4H_8 , Cyclobutane

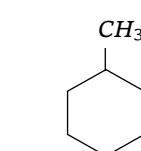


C_5H_{10} ,
Cyclopentane

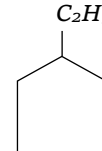


C_6H_{12} ,
Cyclohexane

If side chains are present, then the rules given in the previous section are applied. For example,

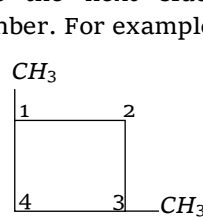


Methylcyclohexane

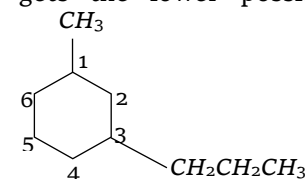


Ethylcyclopentane

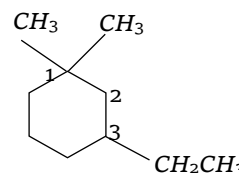
When more than one side chains are present, the numbering is done beginning with one side chain so that the next side chain gets the lower possible number. For example,



1,3-Dimethylcyclobutane

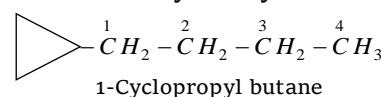


1-Methyl-3-propylcyclohexane
(Not 5-Methyl-1-propyl)

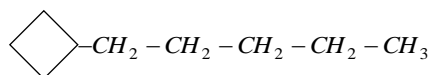


3-Ethyl-1, 1-dimethylcyclohexane
(Not 1-Ethyl-3,3-)

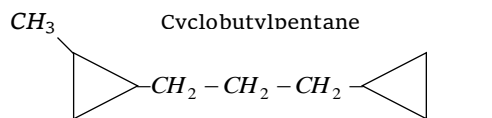
When a single ring system is attached to a single chain with a greater number of carbon atoms or when more than one ring system is attached to a single chain, then it is named as cycloalkylalkanes. For example,



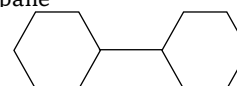
1-Cyclopropyl butane



1-Cyclobutylpentane



1, 3-Bis(2-methylcyclopropyl)propane



Cyclohexyl

In case of substituted cycloalkenes, the double bond is given the lowest possible number and numbering is done in such a way that the substituents get the lowest number.

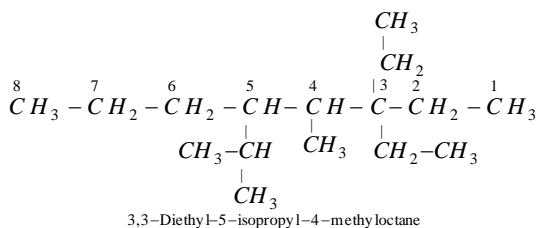


3-Methylcyclohex-1-ene 2, 3-Dimethylcyclopent-

According to the IUPAC system of Nomenclature, certain trivial or semi-systematic names may be used for unsubstituted radicals. For example, the following names may be used,

$(\text{CH}_3)_2\text{CH}-$	Isopropyl
$\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-$	Sec-Butyl
$(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}_2-$	Isopentyl
$\text{CH}_3-\text{CH}_2-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-$	tert-Pentyl
$(\text{CH}_3)_2\text{CH}-\text{CH}_2-$	Isobutyl
$(\text{CH}_3)_3\text{C}-$	tert-Butyl
$(\text{CH}_3)_3\text{C}-\text{CH}_2-$	Neopentyl
$(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}-$	Isohexyl

However, when these are substituted, these names cannot be used as such. For example,



It may be noted that while writing the substituent's name in alphabetical order, the prefixes *iso*- and *neo*- are considered to be part of the fundamental name. However, the prefixes *sec*- and *tert*- are not considered to be the part of the fundamental name.

(2) Rules for IUPAC names of polyfunctional organic compounds

Organic compounds which contain two or more functional groups are called polyfunctional compounds. Their IUPAC names are obtained as follows,

(i) **Principal functional group** : If the organic compound contains two or more functional groups, one

of the functional groups is selected as the principal functional group while all the remaining functional groups (also called the secondary functional groups) are treated as substituents. The following order of preference is used while selecting the principal functional group.

Sulphonic acids > *carboxylic acids* > *anhydrides* > *esters* > *acid chlorides* > *acid amides* > *nitriles* > *aldehydes* > *ketones* > *thiols* > *alcohols* > *alkenes* > *alkynes*.

All the remaining functional groups such as halo (fluoro, chloro, bromo, iodo), nitroso ($-\text{NO}$), -nitro ($-\text{NO}_2$), amino ($-\text{NH}_2$) and alkoxy ($-\text{OR}$) are treated as substituents.

Table : 22.12

Order of preference	Prefix	Suffix (ending)
$-\text{SO}_3\text{H}$	Sulpho	Sulphonic acid
$-\text{COOH}$	Carboxy	- oic acid
$-\text{COOR}$	Alkoxy carbonyl	Alkyl alkanoate
$-\text{COX}$	Haloformyl	Oyl halide
$-\text{CONH}_2$	Carbamoyl	- amide
$-\text{C}\equiv\text{N}$	Cyano	- nitrile
$-\text{CHO}$	Formyl	- al
$>\text{C}=\text{O}$	Keto	- one
$-\text{OH}$	Hydroxy	- ol
$-\text{NH}_2$	Amine	- amine
$\text{C}=\text{C}$	-	- ene
$-\text{C}\equiv\text{C}-$	-	- yne
$-\text{O}-$	Epoxy	-
$-\text{X}$	Halo	-
$-\text{NO}_2$	Nitro	-

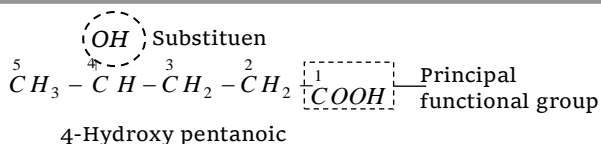
(ii) **Selecting the principal chain** : Select the longest continuous chain of carbon atoms containing the principal functional group and maximum number of secondary functional groups and multiple bonds, if any.

(iii) **Numbering the principal chain** : Number the principal chain in such a way that the principal functional group gets the lowest possible number followed by double bond and triple bond and the substituents, *i.e.*

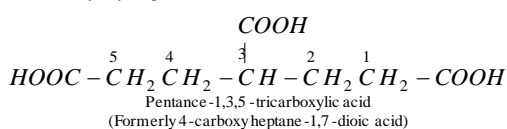
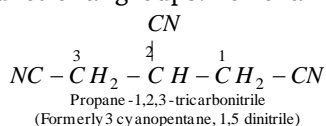
Principal functional group > double bond > triple bond > substituents

(iv) **Alphabetical order** : Identify the prefixes and the positional numbers (also called locants) for the secondary functional groups and other substituents and place them in alphabetical order before the word root.

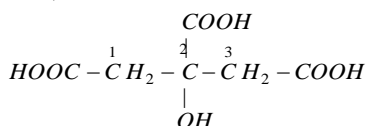
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(3) **Polyfunctional compounds containing more than two like functional groups** : According to latest convention (1993 recommendations for IUPAC nomenclature), if an unbranched carbon chain is directly linked to more than two like functional groups, the organic compound is named as a derivative of the parent alkane which does not include carbon atoms of the functional groups. For example,



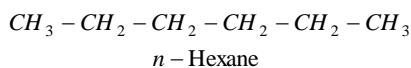
Following the above rule, citric acid may be named as,



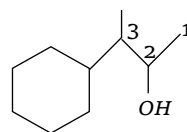
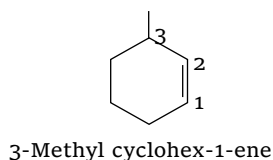
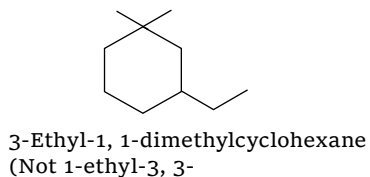
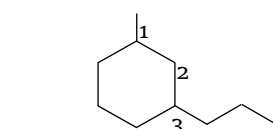
2-Hydroxypropane-1, 2, 3-tricarboxylic acid
 (formerly 3-carboxy-3-hydroxypentane-1, 5-dioic acid)

Bond-line Notation of organic compounds

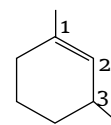
Sometimes, the bonds between carbon atoms are represented by lines. For example, *n*-hexane has a continuous chain of six carbon atoms which may be represented as,



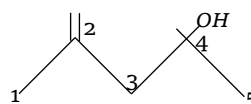
In this notation, the carbon atoms are represented by line ends and intersections. It is assumed that the required number of hydrogen atoms are present wherever they are necessary to satisfy the tetravalency of carbon. A single line represents a single bond (C - C), two parallel lines represent a double bond (C = C) and three parallel lines represent a triple bond (C ≡ C). For example,



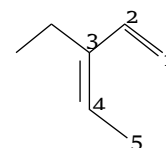
3-Cyclohexyl butan-2-ol



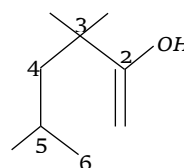
1, 3-Dimethyl cyclohex-1-



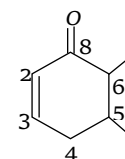
4-Hydroxy-4-methyl pentan-2-



3-Ethyl penta-1, 3-diene



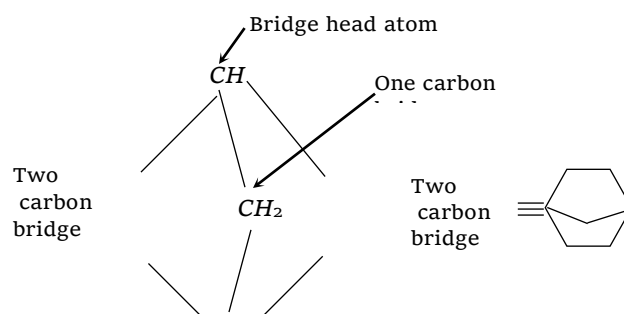
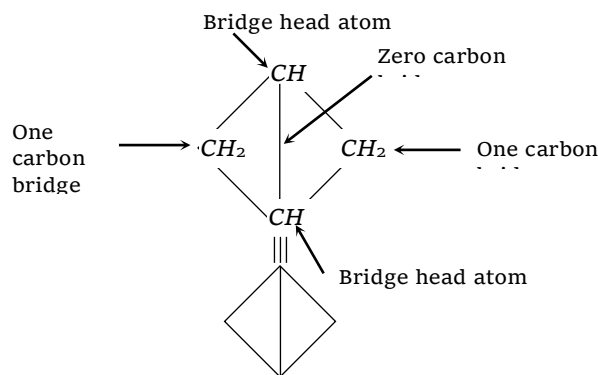
3, 3, 5-trimethylhex-1-en-2-



5, 6-Dimethylcyclohex-2-en-1-

Nomenclature of Bicyclic compounds

Many hydrocarbons and their derivatives contain two fused or bridged rings. The carbon atoms common to both rings are called bridge head atoms and each bond or chain of carbon atoms connecting both the bridge head atoms is called as bridge. The bridge may contain 0, 1, 2.... etc. carbon atoms. For example,





These bicyclic compounds are named by attaching the prefix 'bicyclo' to the name of the hydrocarbon having the same total number of carbon atoms as in the two rings. The number of carbon atoms in each of the three bridges connecting the two bridge head carbon atoms is indicated by arabic numerals, i.e., 0, 1, 2.....etc. These arabic numerals are arranged in descending order; separated from one another by full stops and then enclosed in square brackets. The complete IUPAC name of the hydrocarbon is then obtained by placing these square brackets containing the arabic numerals between the prefix bicyclo and the name of alkane. For example,



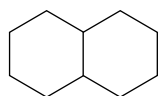
Bicyclo [2, 2, 1] heptane
(also called norbornane)



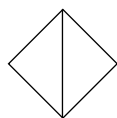
Bicyclo [3, 1, 1] heptane



Bicyclo [2, 2, 2] octane

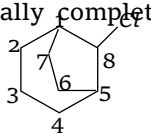


Bicyclo [4, 4, 0] decane
(also called decalin)

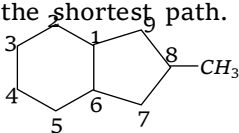


Bicyclo [1, 1, 0] butane

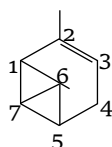
If a substituent is present, the bicyclic ring system is numbered. The numbering begins with one of the bridge head atoms, proceeds first along the longest bridge to the second bridge head atom, continues along the next longest bridge to the first bridge head atom and is finally completed along the shortest path. For example,



8-Chlorobicyclo [3, 2, 1]



8-Methylbicyclo [4, 3, 0]

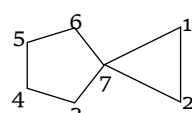


2, 6, 6-Trimethylbicyclo [3, 1, 1] hept-

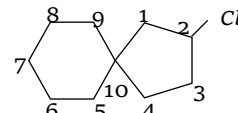
Nomenclature of spiro compounds

Compounds in which one carbon atom is common to two different rings are called **spiro compounds**. The IUPAC name for a spiro compound begins with the word spiro followed by square brackets containing the

number of carbon atoms, in ascending order, in each ring connected to the common carbon atom and then by the name of the parent hydrocarbon corresponding to the total number of the carbon atoms in the two rings. The position of substituents are indicated by numbers; the numbering beginning with the carbon atom adjacent to the spiro carbon and proceeding first around the smaller ring and then to the spiro atom and finally around the larger ring. For example,



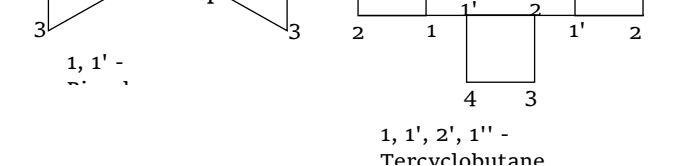
Spiro [2.4]



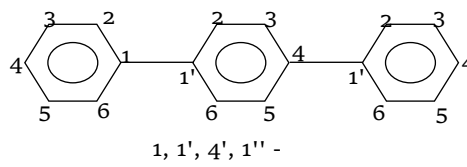
2-Chlorospiro [3.5]

Nomenclature of special compounds

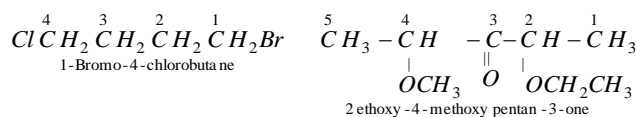
Unbranched assemblies consisting of two or more identical hydrocarbon units joined by a single bond are named by placing a suitable numerical prefix such as *bi* for two, *ter* for three, *quater* for four, *quinque* for five etc. before the name of the repetitive hydrocarbon unit. Starting from either end, the carbon atoms of each repetitive hydrocarbon unit are numbered with unprimed and primed arabic numerals such as 1, 2, 3...., 1', 2', 3' 1'', 2'', 3''.... etc. The points of attachment of the repetitive hydrocarbon units are indicated by placing the appropriate locants 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 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963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000.



As an exception, unbranched assemblies consisting of benzene rings are named by using appropriate prefix with the name phenyl instead of benzene. For example,

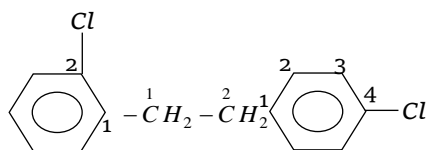


□ If two atoms/groups of same preference occupy identical positions from either end of the parent chain, the lower number must be given to the atom/group whose prefix comes first in the alphabetical order. For example,



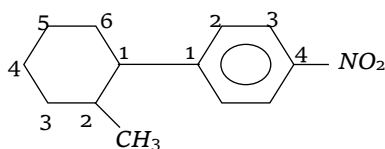
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□ When two or more prefixes consist of identical words, the priority for citation is given to that group which contains the lowest locant at the first point of difference. For example,



1-(2-chlorophenyl)-2-(4-chlorophenyl)

□ If a compound contains a benzene ring coupled to an alicyclic ring, it is named as a derivative of benzene, i.e. compound having lowest state of hydrogenation. For example,



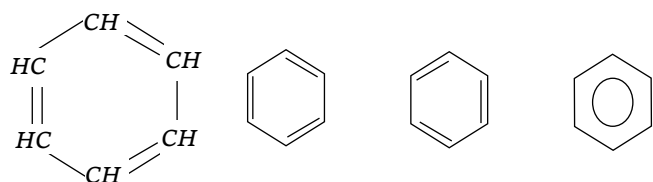
1-(2-Methylcyclohexyl)-4-nitro

In the common system of nomenclature, prefixes iso and neo are used only for compounds containing an isopropyl group, $(CH_3)_2CH$ and a tert-butyl group, $(CH_3)_3C$ respectively at the end of the carbon chain.

Nomenclature of simple aromatic compounds

Aromatic compounds are those which contain one or more benzene rings in them. An aromatic compound has two main parts : (1) Nucleus, (2) Side chain

(1) **Nucleus** : The benzene ring represented by regular hexagon of six carbon atoms with three double bonds in the alternate positions is referred to as **nucleus**. The ring may be represented by any of the following ways,



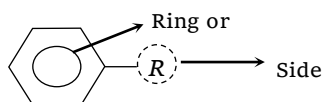
(i)

(ii)

(iii)

(iv)

(2) **Side chain** : The alkyl or any other aliphatic group containing at least one carbon atom attached to the nucleus is called **side chain**. These are formed by replacing one or more hydrogen atoms in the ring by alkyl radicals i.e., R (R may be $-CH_3$, $-C_2H_5$, $-C_3H_7$ etc.)



If one atom of hydrogen of benzene molecule is replaced by another atom or group of atoms, the derivative formed is called **monovalent substituted derivative**. It can exist only in one form because all the six hydrogens of benzene represent equivalent positions. For example, C_6H_5X , where X is a monovalent group.

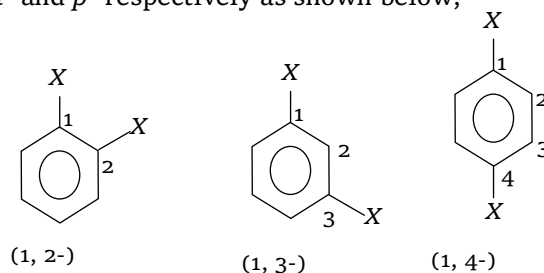
When two hydrogen atoms of benzene are replaced by two monovalent atoms or group of atoms, the resulting product disubstituted benzene derivative can have three different forms. These forms are distinguished by giving the numbers. The position occupied by the principle functional group is given as 1 and the other position is numbered in a clockwise direction which gives lower locant to the substituents.

(i) **Ortho** (or 1, 2-) : The compound is said to be ortho (or 1, 2-) if the two substituents are on the adjacent carbon atoms.

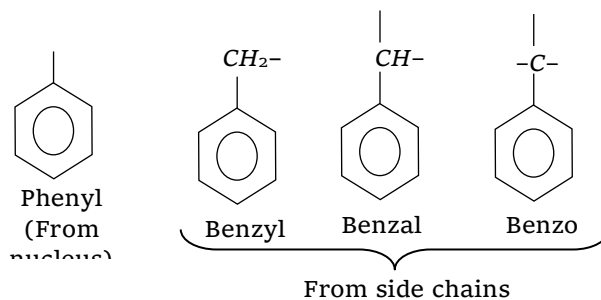
(ii) **Meta** (or 1, 3-) : The compound is said to be meta or (1, 3-) if the two substituents are on alternate carbon atoms.

(iii) **Para** (or 1, 4-) : The compound is said to be para or (1, 4-) if the two substituents are on diagonally situated carbon atoms.

Ortho, meta and para are generally represented as o-, m- and p- respectively as shown below,

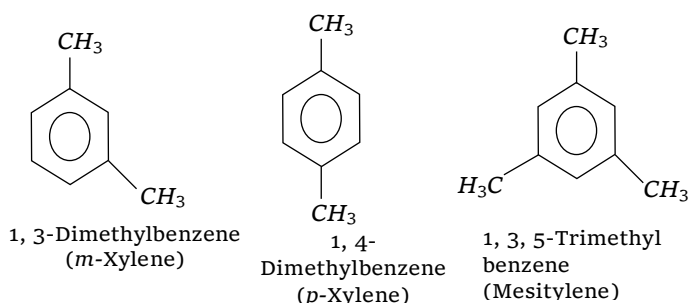
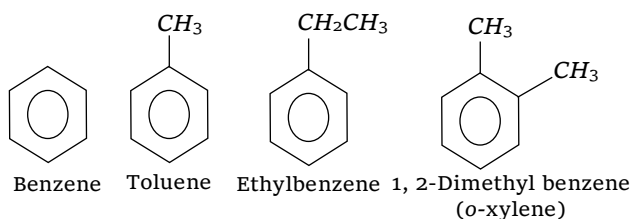


Aryl group : The radicals obtained by removal of one or more hydrogen atoms of the aromatic hydrocarbon molecules are known as aryl radicals or aryl groups. For example,

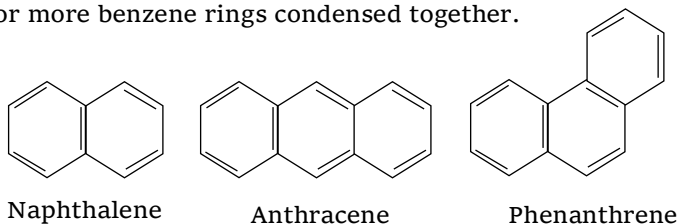


Nomenclature of different aromatic compounds : The names of few simple aromatic compounds are given below :

Hydrocarbons

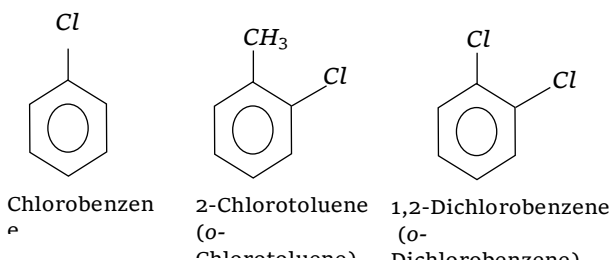


The aromatic hydrocarbons may also contain two or more benzene rings condensed together.

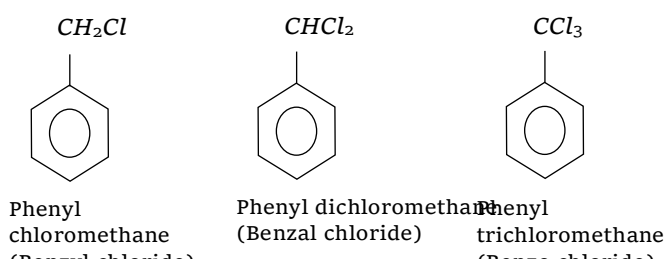


Halogen derivatives

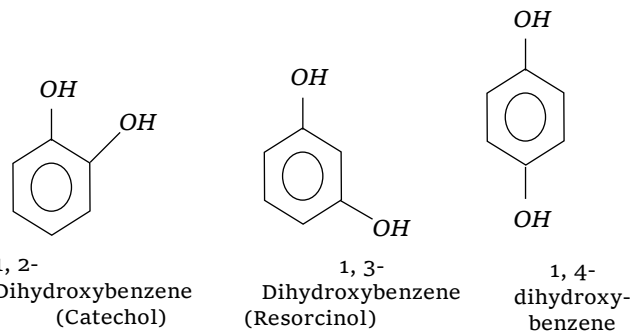
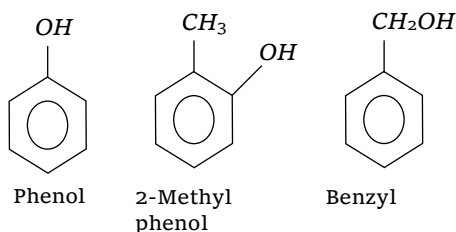
Nuclear substituted



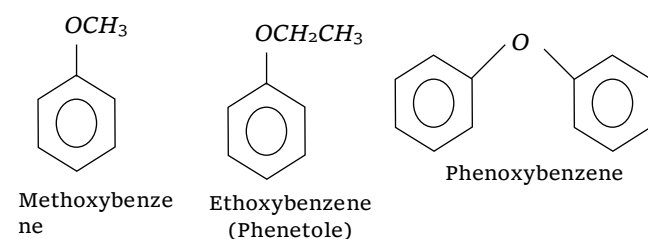
Side chain substituted



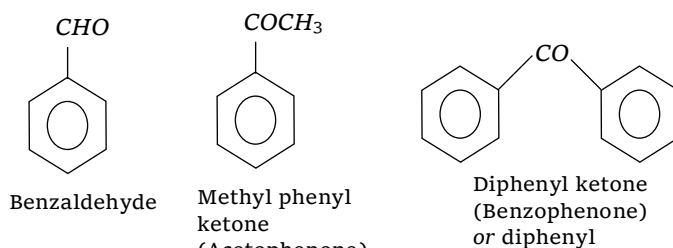
Hydroxy derivatives



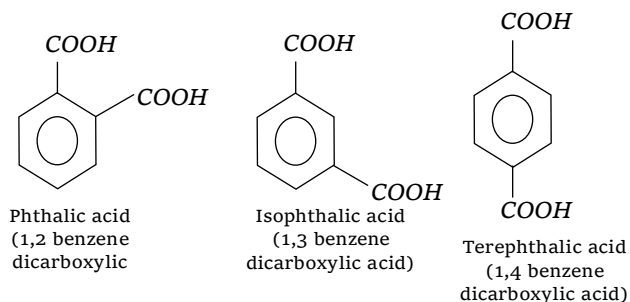
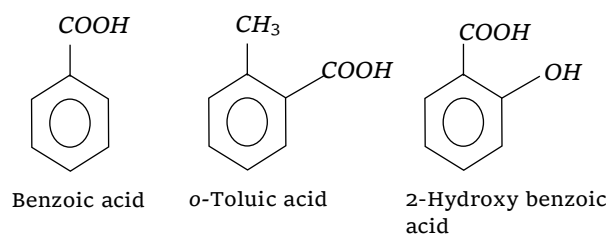
Ethers



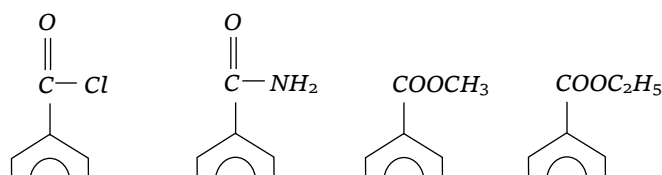
Aldehydes and ketones (Nuclear substituted)

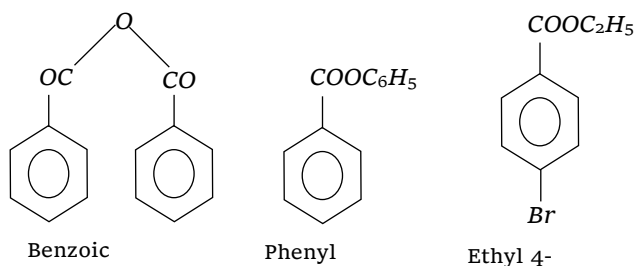


Carboxylic acids (Nuclear substituted)

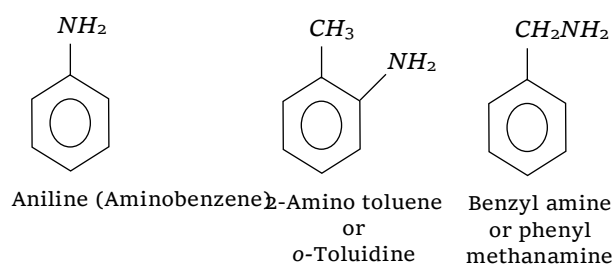


Acid derivatives

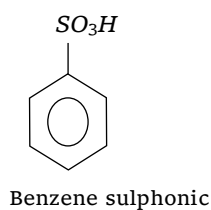




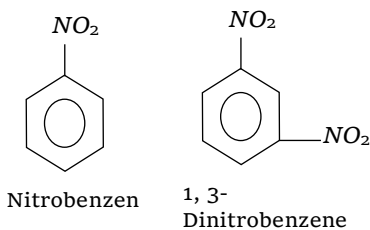
Amino derivatives (Nuclear substituted)



Sulphonic acids

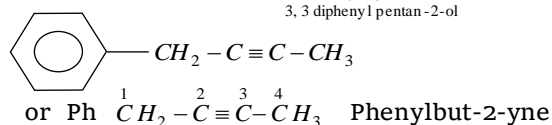
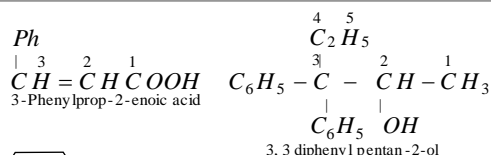
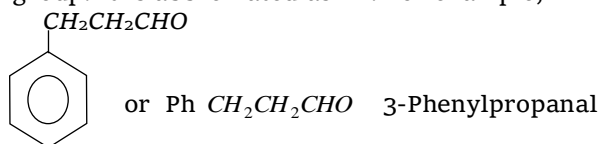


Nitro derivatives

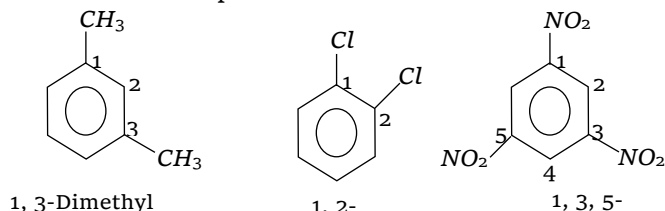


Some tips for nomenclature of aromatic compounds : For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word benzene. It may be noted that common names of many substituted benzene compounds are still universally used. Some important tips for nomenclature of organic compounds are given below,

(i) When the benzene ring is named as substituent on the other molecule, it is named as **phenyl group**. It is treated in the nomenclature just like the name of an alkyl group. It is abbreviated as Ph. For example,

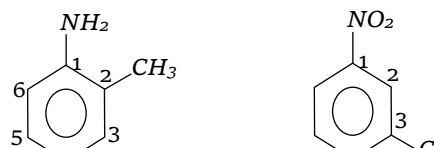
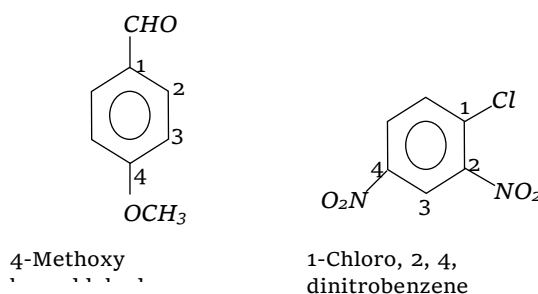
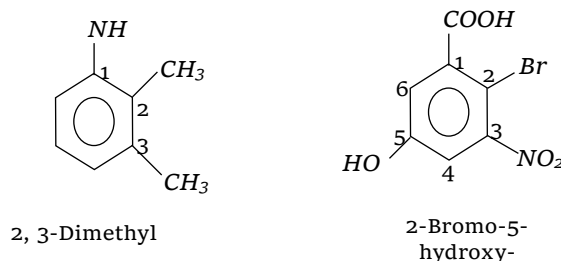
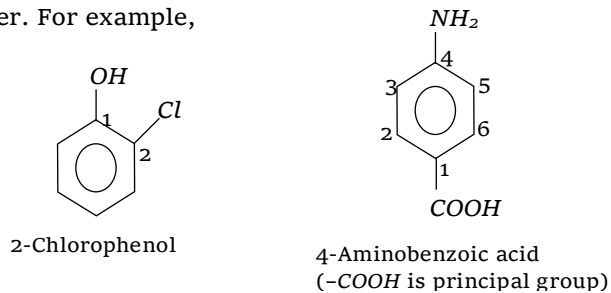


(ii) Disubstituted, trisubstituted or tetrasubstituted benzenes are named by using the numbers for the positions of the substituents.



(iii) If different groups are attached to the benzene ring, then the following rules are kept in mind,
 (a) The principal group is fixed as number 1.
 (b) The numbering of the chain is done in any direction (clockwise or anticlockwise) which gives lower number to the substituents.

(c) The substituents are written in alphabetical order. For example,



Tips & Tricks

✍ Steam distillation may be regarded analogous to distillation under reduced pressure.

✍ Seeding-sometimes crystal formation can be initiated by the addition of crystals of a substance. It is known as seeding.

✍ Vanillin can be extracted from vanilla beans by Soxhlet extractor.

✍ Concentration of raw juice in sugar factories is done by vacuum distillation.

✍ Lithium is not used in Lassaigne's test because it reacts slowly and its compounds are covalent. Potassium is also 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 ferric ferrocyanide to appear green.

✍ In Kjeldahl's method for estimation of nitrogen, potassium sulphate is added to raise the boiling point of sulphuric acid.

✍ Ter Meulen's method is used for the estimation of nitrogen, Stepanow's method, Schiff's and Piria method for halogen and messenger's method for the estimation of sulphur.

