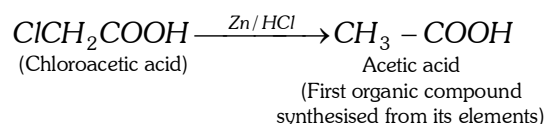
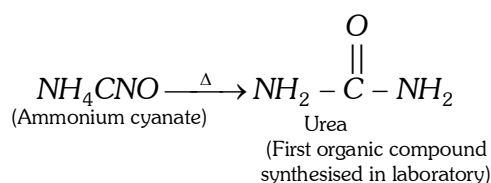


Purification, classification and nomenclature of organic compound Part 1

The word 'organic' signifies life. Therefore, all substances which were obtained directly or indirectly from living organisms, plants and animals were called organic compounds and the branch of chemistry which deals with these compounds was called organic chemistry.

Modern definition of organic chemistry : Organic chemistry is a chemistry of hydrocarbons and their derivatives in which covalently bonded carbon is an essential constituent.

Berzelius put forward a theory in 1815 known as *vital force theory*. According to this theory, "organic compounds could be prepared only by living organism under the influence of a mysterious force known as *vital force*". Accidental synthesis of urea by **Wohler** and synthesis of acetic acid by **Kolbe** led to the fall of this theory.



Berthelot prepared **methane** in laboratory and the most abundant organic compound is **cellulose** which is a polymer of glucose. **Kekule** and **Couper** proposed the tetravalency of carbon and wrote the first structural formula. In 1874, **Van't Hoff** and **Le Bel** suggested that four bonds in the most carbon compounds are directed towards the corners of a tetrahedron.

Purification and Characterisation of organic compounds

The study of organic compounds starts with the characterisation of the compound and the determination of its molecular structure. The procedure generally employed for this purpose consists of the following steps :

- (1) Purification of organic compounds
- (2) Qualitative analysis of organic compounds
- (3) Quantitative analysis of organic compounds
- (4) Determination of molecular mass of organic compounds
- (5) Calculation of Empirical formula and Molecular formula of organic compounds
- (6) Determination of structure of organic compounds by spectroscopic and diffraction methods

(1) Purification of organic compounds : A large number of methods are available for the purification of substances. The choice of method, however, depends upon the nature of substance (whether solid or liquid) and the type of impurities present in it. Following methods are commonly used for this purpose,

- (i) Simple crystallisation
- (ii) Fractional crystallisation
- (iii) Sublimation
- (iv) Simple distillation
- (v) Fractional distillation
- (vi) Distillation under reduced pressure
- (vii) Steam distillation
- (viii) Azeotropic distillation
- (ix) Chromatography
- (x) Differential extraction
- (xi) Chemical methods

(i) Simple crystallization : 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 crystallization, a suitable solvent is selected (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 crystallization, (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 crystallization are : water, alcohol, ether, chloroform, carbon-tetrachloride, acetone, benzene, petroleum ether etc.

Purification, classification and nomenclature of organic compound Part 1

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.

Note : Sometimes crystallization can be induced by adding a few crystals of the pure substance to the concentrated solution. This is called *seeding*.

(ii) **Fractional crystallization :** The process of separation of different components of a mixture by repeated crystallizations is called fractional crystallization. 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 (mother liquor). The mother liquor left after crystallization 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 crystallization 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*.

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 vaporisation 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)

(c) benzene (b. p. 353 K) and aniline (b. p. 457 K)

Note : Although the b.p. of H_2O ($100^\circ C$) and ethanol ($78.1^\circ C$) differ by $21.9^\circ C$, they can not be separated by simple distillation since they form an azeotrope.

(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.

Purification, classification and nomenclature of organic compound Part 1

Note : Fractional distillation can not be used to separate a mixture of liquids which form *azeotropes*, i.e., *constant boiling mixtures*.

(vi) **Distillation under reduced pressure** (*vacuum distillation*) : In this process, a liquid is distilled much below its boiling point. It is of special advantage for the purification of liquids which decompose near 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 Hg pressure. Similarly, sugarcane juice is concentrated in sugar industry by evaporation under reduced pressure.

(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 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 of these 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,

Purification, classification and nomenclature of organic compound Part 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
Paper or Partition chromatography	Liquid/Liquid	Qualitative and quantitative analysis of polar organic compounds (sugars, α -amino acids and inorganic compounds)

Note : * R_f value (retention factor) : The movement of the substances relative to the solvent is expressed in terms its retention factor (R_f value). This gives the relative adsorption of each component of the mixture.

$$R_f = \frac{\text{Distance moved by the substance from the base line}}{\text{Distance moved by the solvent from the base line}}$$

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.

It is also possible to estimate the components quantitatively by measuring the intensity of colours developed by them on reacting with suitable reagents.

It is determined in *Thin layer chromatography* (TLC) and *Ascending paper chromatography*.

(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 solvent selected 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 than if all the volume is used in one installment.

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 acids dissolve in NaHCO_3 solution evolving CO_2 but phenols usually do not react.

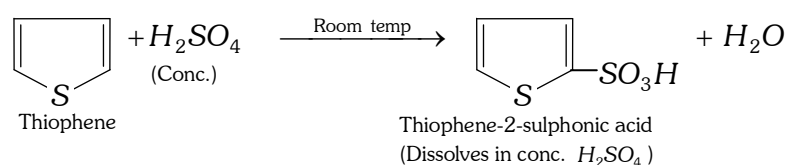
(b) Destructive distillation of wood gives *pyroligneous acid* which contains acetic acid (10%), acetone (0.5%) and methanol (3%). Acetic acid can be separated from this mixture by treating it with milk of lime when acetic acid forms the calcium salt. The reaction mixture on distillation gives a mixture of acetone and methanol (which can be

Purification, classification and nomenclature of organic compound Part 1

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.

(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.*

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

Purification, classification and nomenclature of organic compound Part 1

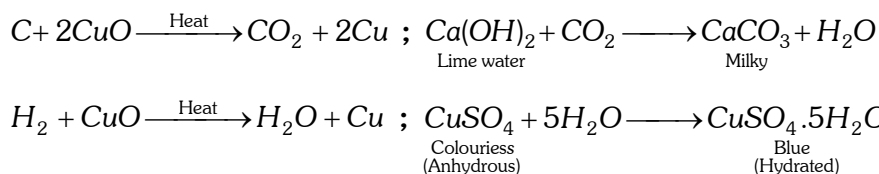
of pure compound, it is sure that the compound under test is pure. On the other hand, if the melting point of the mixture is less than the melting point of the pure compound, the compound in question is not pure.

Note : *Boiling point is not as reliable a test of purity as is the melting point for the solids. There are many liquids which are miscible with other liquids and mixtures have fixed boiling points (azeotrope). Thus other physical properties are being used for deciding the purity.

(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 seldom absent. On heating the organic compound with dry cupric oxide when 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**.



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 is 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 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.

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	$2NaCN + FeSO_4 \longrightarrow Fe(CN)_2 + Na_2SO_4$ $Fe(CN)_2 + 4NaCN \longrightarrow Na_4[Fe(CN)_6]$ $3Na_4[Fe(CN)_6] + 4FeCl_3 \xrightarrow{HCl} Fe_4[Fe(CN)_6]_3 + 12NaCl$ 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) $Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5NO.S]$ deep violet (ii) $Na_2S + (CH_3COO)_2Pb \xrightarrow{CH_3COOH} PbS \downarrow + 2CH_3COONa$ black ppt.

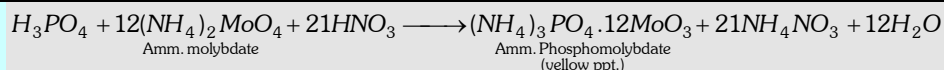
Purification, classification and nomenclature of organic compound Part 1

Halogen	$\text{Na} + \text{Cl} \xrightarrow{\Delta} \underset{\text{(S.E.)}}{\text{NaCl}}$	S.E. $+ \text{HNO}_3 + \text{AgNO}_3$ (i) White ppt soluble in aq NH_3 confirms Cl (ii) Yellow ppt partially soluble in aq. NH_3 confirms Br . (iii) Yellow ppt insoluble in aq NH_3 confirms I	$\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \underset{\text{ppt}}{\text{AgX}} \downarrow$ $\underset{\text{White ppt}}{\text{AgCl}} + 2\text{NH}_3(\text{aq}) \longrightarrow \underset{\text{soluble}}{[\text{Ag}(\text{NH}_3)_2]\text{Cl}}$
Nitrogen and sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \underset{\text{(S.E.)}}{\text{NaCNS}}$	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both.	$\text{NaCNS} + \text{FeCl}_3 \longrightarrow \underset{\text{blood red colour}}{[\text{Fe}(\text{CNS})\text{Cl}_2]} + \text{NaCl}$

Other methods for detection of elements

Element	Test
Nitrogen	<p>Soda lime test : A pinch of an organic compound is heated strongly with soda lime ($\text{NaOH} + \text{CaO}$) in a test tube. If ammonia gas evolves, it indicates nitrogen. $\text{CH}_3\text{CONH}_2 + \text{NaOH} \xrightarrow{\text{CaO}} \text{CH}_3\text{COONa} + \text{NH}_3$. This test is, however, not reliable since certain compounds like nitro, azo etc do not evolve NH_3 when heated with soda lime.</p>
Sulphur	<p>Oxidation test : Sulphur can also be tested by oxidation test. The organic compound is fused with fusion mixture (a mixture of sodium carbonate and potassium nitrate). The sulphur, if present in the organic compound, is oxidised to sodium sulphate. $\text{Na}_2\text{CO}_3 + \text{S} + 3\text{O} \longrightarrow \text{Na}_2\text{SO}_4 + \text{CO}_2$. The fused mass is dissolved in water and the solution is acidified with hydrochloric acid. Barium chloride solution is then added. The formation of a white precipitate indicates the presence of sulphur.</p> $\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \longrightarrow \underset{\text{(White ppt.)}}{\text{BaSO}_4} + 2\text{NaCl}$
Halogens	<p>Beilstein's test (copper wire test) : A clean copper wire is heated in the Bunsen flame till it does not impart any green colour to the flame. The heated end is dipped in the organic compound and heated again. The appearance of a green or bluish green flame due to the formation of volatile cupric halides indicates the presence of some halogen in the organic compound. Though this test is very sensitive yet it does not confirm the presence of halogens in an organic compound since certain organic compounds like urea, thiourea, pyridine, organic acids etc. Which do not contain halogens give this test due to the formation of volatile cupric cyanide. It does not tell as to which halogen is present.</p> <p>Special test for bromine and iodine (layer test) : Boil a portion of the Lassaigne's extract with nitric acid. Add a few drops of CS_2 and then add chlorine water slowly with constant shaking.</p> <p>An orange colouration in CS_2 layer confirms the presence of bromine where as a violet colouration in the layer confirms the presence of iodine.</p> $2\text{NaBr} + \text{Cl}_2 \longrightarrow \underset{\text{turns CS}_2 \text{ layer orange}}{2\text{NaCl} + \text{Br}_2}; \quad 2\text{NaI} + \text{Cl}_2 \longrightarrow \underset{\text{turns CS}_2 \text{ layer violet}}{2\text{NaCl} + \text{I}_2}$
Phosphorus	<p>Phosphorus is detected by fusing the organic compound with sodium peroxide when phosphorus is converted into sodium phosphate. $2\text{P} + 5\text{Na}_2\text{O}_2 \longrightarrow 2\text{Na}_3\text{PO}_4 + 2\text{Na}_2\text{O}$. The fused mass is extracted with H_2O, boiled with conc. HNO_3 and then ammonium molybdate is added. Appearance of yellow ppt. or colouration due to the formation of ammonium phosphomolybdate indicates the presence of phosphorus.</p> $\text{Na}_3\text{PO}_4 + 3\text{HNO}_3 \xrightarrow{\Delta} \text{H}_3\text{PO}_4 + 3\text{NaNO}_3$

Purification, classification and nomenclature of organic compound Part 1



Oxygen There is no satisfactory qualitative method for the detection of oxygen. However, its presence can be inferred indirectly.

(i) If the organic compound is heated alone in a dry test tube in presence of nitrogen, the formation of water drops on cooler parts of the tube may indicate the presence of oxygen.

(ii) The presence of oxygen can be inferred by testing the presence of functional groups known to contain oxygen, e.g., hydroxyl (–OH), aldehydic (–CHO), carboxyl (–COOH), etc.

(3) Quantitative analysis (Estimation of Elements) : After qualitative analysis of elements, the next step in the determination of molecular formula of an organic compound is the estimation of various elements by mass, i.e. finding the percentage composition of the substance by mass. The various methods commonly employed for the estimation of principal elements are discussed in table.

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 stream 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) $\% \text{ of C} = \frac{\text{Weight of } CO_2}{\text{Weight of org. compound}} \times \frac{12}{44} \times 100$</p> <p>(ii) $\% \text{ of H} = \frac{\text{Weight of } H_2O}{\text{Weight of org. compound}} \times \frac{2}{18} \times 100$</p>
Nitrogen	<p>(i) Duma's method : Elemental nitrogen is converted into molecular nitrogen by suitable chemical method and its volume is changed to STP data.</p> $C_xH_yN_z + CuO \longrightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + (Cu)$ <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>Oxides of nitrogen + Cu \longrightarrow N_2 + CuO</p> $\% \text{ of N} = \frac{28}{22400} \times \frac{V}{W} \times 100$ <p>Where, V = volume of N_2 in nitrometer (in ml) at NTP, W = Weight of substance taken.</p> $\% \text{ of N} = \frac{1.4 \times N_1 \times V_1}{W}$ <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>	$\% \text{ of Cl} = \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of substance taken}} \times 100$ $\% \text{ of Br} = \frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of substance taken}} \times 100$ $\% \text{ of I} = \frac{127}{235} \times \frac{\text{Mass of AgI formed}}{\text{Mass of substance taken}} \times 100$

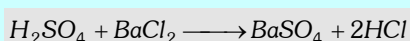
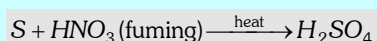
Purification, classification and nomenclature of organic compound Part 1

(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.

Sulphur

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.

$$\% \text{ of S} = \frac{32}{233} \times \frac{\text{Mass of BaSO}_4 \text{ formed (W}_1\text{)}}{\text{Mass of substance taken (W)}} \times 100$$



phosphorous

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 phosphate, $MgNH_4PO_4$, by the addition of magnesia mixture

$$\% \text{ of P} = \frac{62}{222} \times \frac{\text{Mass of Mg}_2\text{P}_2\text{O}_7 \text{ formed (W}_1\text{)}}{\text{Mass of substance taken (W)}} \times 100$$

$(MgSO_4 + NH_4OH + NH_4Cl)$. The magnesium ammonium phosphate is washed, dried and ignited when it is converted to magnesium pyrophosphate $(Mg_2P_2O_7)$.



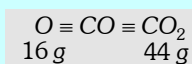
From the mass of magnesium pyro-phosphate, the percentage of phosphorus in the compound can be calculated.

Oxygen

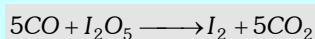
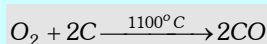
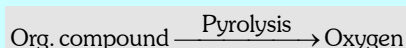
(i) The usual method of determining the percentage of oxygen in an organic compound is by the method of difference. All the elements except oxygen present in the organic compound are estimated and the total of their percentages subtracted from 100 to get the percentage of oxygen.

Percentage of oxygen = 100 – (Sum of the percentages of all other elements)

(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 .



$$\% \text{ of O} = \frac{16}{44} \times \frac{\text{mass of CO}_2}{\text{mass of org. compd.}} \times 100$$



Example : 1 The percentage of N_2 in urea is about

[KCET (Med.) 2001]

(a) 18.05

(b) 28.29

(c) 46.66

(d) 85.56

Solution: (c) Urea (NH_2CONH_2) has molecular weight 60 and weight of nitrogen is 28

Purification, classification and nomenclature of organic compound Part 1

In 60gm. of urea nitrogen present = 28gm.

In 100gm. of urea nitrogen present = $\frac{28}{60} \times 100 = 46.66\%$

Example : 2 58 ml. of $\frac{N}{5}H_2SO_4$ are used to neutralize ammonia given by 1g of organic compound. Percentage of nitrogen in the compound is

- (a) 34.3 (b) 82.7 (c) 16.2 (d) 21.6

Solution: (c) % of N = $\frac{1.4 \times \text{Normality of acid} \times \text{Volume of acid}}{\text{Mass of substance}} = \frac{1.4 \times 1 \times 58}{1 \times 5} = 16.2$

Example : 3 0.2595g of an organic substance in a quantitative analysis yielded 0.35g of the barium sulphate. The percentage of sulphur in the substance is [CPMT 2000; AFMC 2001]

- (a) 18.52g (b) 182.2g (c) 17.5g (d) 175.2g

Solution: (a) % of S = $\frac{32}{233} \times \frac{\text{wt. of } BaSO_4}{\text{wt. of organic compound}} \times 100 = \frac{32}{233} \times \frac{0.35}{0.2595} \times 100 = 18.52\%$

Example : 4 0.2g of an organic compound on complete combustion produces 0.18g of water, then the percentage of hydrogen in it is [Pb. CET 1988]

- (a) 5 (b) 10 (c) 15 (d) 20

Solution: (b) % of H = $\frac{\text{wt. of } H_2O}{\text{wt. of organic compound}} \times \frac{2}{18} \times 100 = \frac{0.18}{0.2} \times \frac{2}{18} \times 100 = 10$

Example : 5 If 0.2g of an organic compound containing carbon, hydrogen and oxygen on combustion, yielded 0.147g carbon dioxide and 0.12g water. What will be the content of oxygen in the substance [AFMC 1998]

- (a) 73.29% (b) 78.45% (c) 83.23% (d) 89.50%

Solution: (a) % C = $\frac{12}{44} \times \frac{0.147}{0.2} \times 100 = 20.045$

$$\% H = \frac{2}{18} \times \frac{0.12}{0.2} \times 100 = 6.666$$

$$\therefore \% O = (100 - 20.045 - 6.666) = 73.289 = 73.29 \text{ (approx)}$$

Example : 6 0.25g of an organic compound gave 31.1ml. of N_2 by Duma's method. Calculate the % of N in this compound. [MP PET 1997]

- (a) 16 (b) 18.32 (c) 45.46 (d) 15.55

Solution: (d) % N (By Duma's method) = $\frac{28 \times \text{Volume of } N_2 \text{ at NTP} \times 100}{22400 \times \text{weight of compound}} = \frac{28 \times 31.1 \times 100}{22400 \times 0.25} = 15.55\%$

Example : 7 0.15g of an organic compound gave 0.12g of AgBr by Carius method. The percentage of bromine in the compound is

- (a) 20 (b) 10 (c) 30 (d) 34

Solution: (d) % of Br = $\frac{80}{188} \times \frac{\text{Mass of AgBr formed}}{\text{Mass of substance taken}} \times 100 = \frac{80}{188} \times \frac{0.12}{0.15} \times 100 = 34 \text{ (Approx.)}$

Example : 8 0.50g of an organic compound was Kjeldahlised and the NH_3 evolved was absorbed in a certain volume of 1N H_2SO_4 . The residual acid required 60 cm^3 of $N/2 NaOH$. If the percentage of N is 56 then the volume of 1N H_2SO_4 taken was

- (a) 30ml. (b) 40ml. (c) 50ml. (d) 60ml.

Solution: (c) Let the vol. of 1N H_2SO_4 taken = V of ml.

Now 60ml. of $N/2 NaOH = 30 \text{ ml. of } 1N NaOH = 30 \text{ ml. of } 1N H_2SO_4$

Thus, vol. of acid left unused = 30 ml. of 1N H_2SO_4

Purification, classification and nomenclature of organic compound Part 1

\therefore vol. of 1N H_2SO_4 used = $(V - 30)$ ml.

Now % of N is given by the relation, % of N = $\frac{1.4 \times N_1 \times V}{W}$ or $56 = \frac{1.4 \times 1 \times (V - 30)}{0.50}$ or $V = 50$ ml.

(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,

$$V_2 = \frac{p_1 \times V_1}{T_1} \times \frac{273}{760}$$

22400 ml of vapours weight at NTP = M (mol. mass); V_2 ml of vapours weight at NTP = W g

$$22400 \text{ ml of vapour weight at NTP} = \frac{W}{V_2} \times 22400 = M$$

or Vapour density of substance = $\frac{\text{Mass of 1 ml of vapours at NTP}}{\text{Mass of 1 ml of hydrogen at NTP}}$

$$\text{or } V.D. = \frac{W/V_2}{0.00009} \quad (\because \text{Mass of 1 ml of } H_2 \text{ at NTP} = 0.00009 \text{ g or } 2/22400)$$

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

(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 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

Purification, classification and nomenclature of organic compound Part 1

substance in a known mass of the solvent. The molecular mass of the compound can be calculated from the following mathematical relationships :

$$(a) \text{ Elevation in boiling point : Mol. Mass} = \frac{1000 K_b \times w}{W \times \Delta T}$$

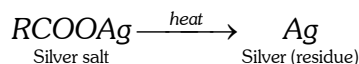
Where, K_b = Molal elevation constant of the solvent, w = Mass of the compound, W = Mass of the solvent
 ΔT = Elevation in boiling point of the solvent (determined experimentally)

$$(b) \text{ Depression in freezing point : Mol. Mass} = \frac{1000 K_f \times w}{W \times \Delta T}$$

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 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,

$$\text{Mol. mass of the acid} = \text{Equivalent mass of the acid} \times \text{basicity}$$

Calculations : (i) Mass of silver salt taken = w g (ii) Mass of metallic silver = x g

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

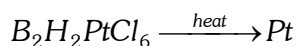
Let the equivalent mass of the acid be E . In the preparation of silver salt, a hydrogen atom of the carboxylic group is replaced by a silver atom.

$$\text{Thus, Equivalent mass of silver salt} = E - 1 + 108 = E + 107$$

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

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

(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 $B_2H_2PtCl_6$.



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

Purification, classification and nomenclature of organic compound Part 1

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 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.

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

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

$$V \text{ ml } N_1 \text{ alkali solution} \equiv w \text{ g acid}$$

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

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

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.

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

$$\text{Molecular mass of the base} = \text{Eq. mass} \times \text{acidity}$$

(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, $\text{C}_6\text{H}_{12}\text{O}_6$.

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

- Divide the percentage of each element by its atomic mass. This gives the relative number of atoms.
- Divide the figures obtained in step (i) by the lowest one. This gives the simplest ratio of the various elements present.
- 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.
- 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.

Purification, classification and nomenclature of organic compound Part 1

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

$$\text{Molecular formula} = n \times \text{Empirical formula}$$

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 as 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.

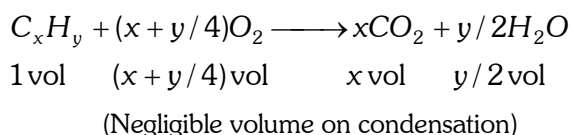
(b) The mixture is exploded by passing an electric spark between the platinum electrodes. As a result, carbon and hydrogen of the hydrocarbon are oxidised to CO_2 and H_2O vapours respectively.

(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. $2\text{NaOH} + \text{CO}_2 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$

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.



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.

Example : 9 In victor mayer's method 0.2 gm of an organic substance displaced 56 ml. of air at STP the molecular weight of the compound

[Kerala (Med.) 2003]

Purification, classification and nomenclature of organic compound Part 1

- (a) 56 (b) 112 (c) 80 (d) 28

Solution: (c) $M = \frac{W}{V_2} \times 22400$; $M = \frac{0.2}{56} \times 22400 = 80$

$M = \text{mol. wt. of compound}$
 $W = \text{Mass of organic compound}$
 $V_2 = \text{Volume of air at STP}$

Example : 10 0.24 g of a volatile liquid on vaporization gives 45ml. of vapours at NTP. What will be the vapour density of the substance. (Density of $H_2 = 0.089 \text{ gL}^{-1}$) [CBSE PMT 1996]

- (a) 95.39 (b) 39.95 (c) 99.53 (d) 59.93

Solution: (d) Vapour density = $\frac{\text{Mass of 45ml. of vapours at NTP}}{\text{Mass of 45ml. of } H_2 \text{ at NTP}} = \frac{0.24}{45 \times 0.000089} = 59.93$

(∵ Density of $H_2 = 0.089 \text{ gL}^{-1} = 0.000089 \text{ g/ml.}$)

Example : 11 If 0.228 g of silver salt of dibasic acid gave a residue of 0.162 g of silver on ignition then molecular weight of the acid is [AIIMS 2000]

- (a) 70 (b) 80 (c) 90 (d) 100

Solution: (c) Molecular weight of the acid = $\left[\frac{w}{x} \times 108 - 107 \right] \times n$

Where, $w = \text{wt. of silver salt}$, $x = \text{wt. of metallic silver}$, $n = \text{basicity of acid}$

∴ Mol. wt. of acid = $\left[\frac{0.228}{0.162} \times 108 - 107 \right] \times 2 = [152 - 107] \times 2 = 90$

Example : 12 Platinum salt of an organic base contains 32.5% platinum. Hence, equivalent weight of the base is

- (a) 95 (b) 190 (c) 600 (d) 300

Solution: (a) Equivalent weight of base (E),

$$E = \frac{1}{2} \left[\frac{w}{x} \times 195 - 410 \right] = \frac{1}{2} \left[\frac{100}{32.5} \times 195 - 410 \right] = \frac{1}{2} [600 - 410] = \frac{1}{2} \times 190 = 95$$

$\left(\begin{array}{l} w = \text{mass of platinum salt} \\ x = \text{mass of platinum} \end{array} \right)$

Example : 13 Insulin contains 3.4% sulphur. The minimum molecular weight of insulin is [MP PET 1993]

- (a) 350 (b) 470 (c) 560 (d) 940

Solution: (d) Minimum mass of sulphur = wt. of its one atom = 32

∴ 3.4 gms of sulphur present in 100 gms.; ∴ 32 gms of sulphur present in = $\frac{100 \times 32}{3.4} = 940$

Example : 14 Haemoglobin contains 0.33% of iron by weight . The molecular weight of haemoglobin is approximately 67200. The number of iron atoms (At. wt. (Fe) = 56) present in one molecule of haemoglobin are

- (a) 6 (b) 1 (c) 4 (d) 2

Solution: (c) Total wt. of Fe in haemoglobin = $\frac{0.33}{100} \times 67200 = 221.76$; At. wt. of $Fe = 56$

Total no. of Fe atoms per molecule of haemoglobin = $\frac{221.76}{56} = 3.96$; Thus no. of Fe atoms = 4

Example : 15 If a compound on analysis was found to contain $C = 18.5\%$, $H = 1.55\%$, $Cl = 55.04\%$ and $O = 24.81\%$, then its empirical formula is [AIIMS 1998]

- (a) $CHClO$ (b) CH_2ClO (c) C_2H_2OCl (d) $ClCH_2O$

Solution: (a) $C:H:Cl:O = \frac{18.5}{12} : \frac{1.55}{1} : \frac{55.04}{35.5} : \frac{24.81}{16} = 1:1:1:1$; ∴ Empirical formula = $CHClO$

Example : 16 An organic compound has been found to possess the empirical formula CH_2O and molecular weight 90. The molecular formula of it is ($C = 12$, $H = 1$ and $O = 16$) [CPMT 2000; MP PET 2002]

- (a) $C_3H_6O_3$ (b) CH_2O (c) $C_2H_6O_2$ (d) C_2H_2O

Purification, classification and nomenclature of organic compound Part 1

Solution: (a) Molecular weight = 90 ; Empirical weight of $CH_2O = 12 + 2 + 16 = 30$

$$n = \frac{\text{Molecular weight}}{\text{Empirical weight}} = \frac{90}{30} = 3$$

\therefore Molecular formula = Empirical formula $\times n = CH_2O \times 3 = C_3H_6O_3$

Example : 17 A dibasic organic acid gave the following results : C = 34.62%, H = 3.84%. 0.1075g of this acid consumes 20 ml of 0.1N NaOH for complete neutralisation. Find out the molecular formula of the acid. [Roorkee 1979]

(a) $C_3H_4O_4$ (b) $C_2H_2O_2$ (c) $C_3H_6O_2$ (d) CH_2O

Solution: (a)

Calculation of empirical formula

Element	Percentage	At. mass	Relative number of 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	$\frac{61.54}{16} = 3.84$	$\frac{3.84}{2.88} = 1.33 \times 3 = 4$

Empirical formula of the acid = $C_3H_4O_4$; Empirical formula mass = $(3 \times 12) + (4 \times 1) + (4 \times 16) = 104$

Calculation of molecular mass : 20 ml 0.1 N NaOH \equiv 0.1075g acid ; $20 \times 0.1, ml 1N NaOH \equiv 0.1075g$ acid

So 1000 ml 1N NaOH $\equiv \frac{0.1075}{20 \times 0.1} \times 1000g$ acid $\equiv 53.75g$ acid ; Eq. mass of the acid = 53.75

Mol. Mass of the acid = Eq. mass \times basicity = $53.75 \times 2 = 107.50$

$$n = \frac{\text{Mol. mass}}{\text{Emp. mass}} = \frac{107.50}{104.0} \approx 1; \quad \therefore \text{Molecular formula} = C_3H_4O_4$$

Example : 18 A hydrocarbon contains 10.5g of carbon for each one gram of hydrogen. The mass of 1 litre of hydrocarbon vapours at $127^\circ C$ and 1 atmospheric pressure is 2.8 g. Find out the molecular formula. [IIT 1980]

(a) C_6H_6 (b) C_2H_6 (c) C_3H_4 (d) C_7H_8

Solution: (d) Carbon : Hydrogen :: 10.5 : 1

Calculation of empirical formula

Element	Percentage	At. mass	Relative number of atoms	Simplest ratio
Carbon	$\frac{10.5}{115} \times 100 = 91.3$	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 = $(12 \times 7) + (1 \times 8) = 92$

Calculation of molecular mass,

Experimental conditions : $V_1 = 1$ litre, $P_1 = 1$ atm, $T_1 = 127 + 273 = 400$ K

NTP conditions : $V_2 = ?$, $P_2 = 1$ atm, $T_2 = 273$ K

Applying gas equation,

$$V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{1 \times 1 \times 273}{400 \times 1} = 0.6825 \text{ litre}$$

0.6825 litre of the gas weigh = 2.8 g

Purification, classification and nomenclature of organic compound Part 1

$$22.4 \text{ litre of the gas weigh} = \frac{2.8}{0.6825} \times 22.4 = 91.89 \approx 92$$

$$n = \frac{\text{Mol. mass}}{\text{Emp. mass}} = \frac{92}{92} = 1$$

Molecular formula = Empirical formula = C_7H_8

Example : 19 10 ml of a gaseous hydrocarbon were mixed with 100 ml of oxygen and exploded in a eudiometer tube. The volume of the residual gases was 95 ml of which 20 ml was absorbed by caustic soda and the remainder by pyrogallol. The molecular formula of the gas is

- (a) C_2H_2 (b) C_2H_4 (c) C_3H_6 (d) C_4H_8

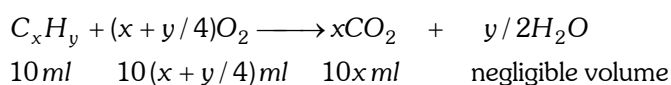
Solution: (a) Vol. after explosion and cooling i.e., vol. of CO_2 formed + unsolved O_2 = 95 ml

Vol. after introducing KOH solution, i.e., vol. of CO_2 formed = 20 ml

Vol. absorbed by alkaline pyrogallol, i.e., vol. of unsolved O_2 = 95 – 20 = 75 ml

∴ Vol. of O_2 used = 100 – 75 = 25 ml.

Applying the combustion equation,



Equating theoretical and experimental values,

$$10x = 20 \text{ and } 10(x + y/4) = 25$$

$$\therefore x = 2 \text{ and } 10(2 + y/4) = 25$$

or $y = 2$; Thus the hydrocarbon is C_2H_2

TEACHING CARE

(6) Determination of structure by spectroscopic and diffraction methods : With the advancement of scientific developments, new techniques have been designed to determine the structures of compounds.

(i) **Spectroscopic methods :** All spectroscopic methods involve either the absorption of radiation or the emission of radiation. The common types of spectroscopic methods used these days are *ultra-violet* (U. V.), *infra-red* (I. R.), *nuclear magnetic resonance* (N. M. R.), *mass spectroscopy* etc. Mass spectroscopy determines the molecular mass of the compounds. In fact, it is the best available method to determine the molecular mass. The other spectroscopic methods detect the presence of functional groups present in the molecule.

(ii) **Diffraction methods :** The diffraction methods help to determine the complete three dimensional structure of the molecules including bond length, bond angle etc. The commonly used diffraction methods are: X-ray diffraction, neutron diffraction, electron diffraction etc.

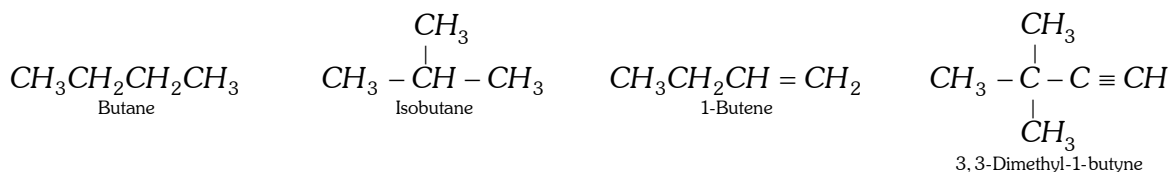
Classification of organic compounds

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,

Purification, classification and nomenclature of organic compound Part 1

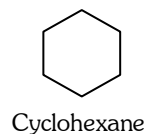
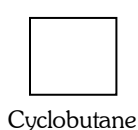


These compounds are also called as aliphatic compounds.

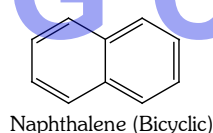
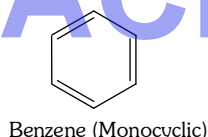
(ii) **Cyclic or closed-chain compounds** : Cyclic compounds contain at least one ring or closed chain of atoms. The compounds with only one ring of atoms in the molecule are known as *monocyclic* but those with more than one ring of atoms are termed as *polycyclic*. These are further divided into two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

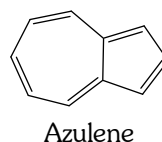
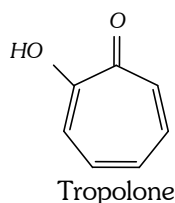


Aromatic compounds : These compounds consist of at least one benzene ring, *i.e.*, a six-membered carbocyclic ring having alternate single and double bonds. Generally, these compounds have some fragrant odour and hence, named as aromatic (*Greek word aroma meaning sweet smell*).



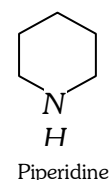
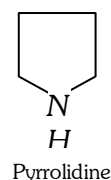
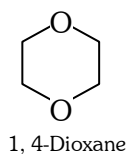
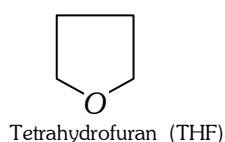
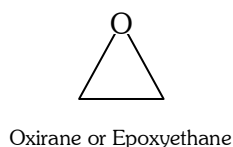
These are also called benzenoid aromatics.

Note : *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.



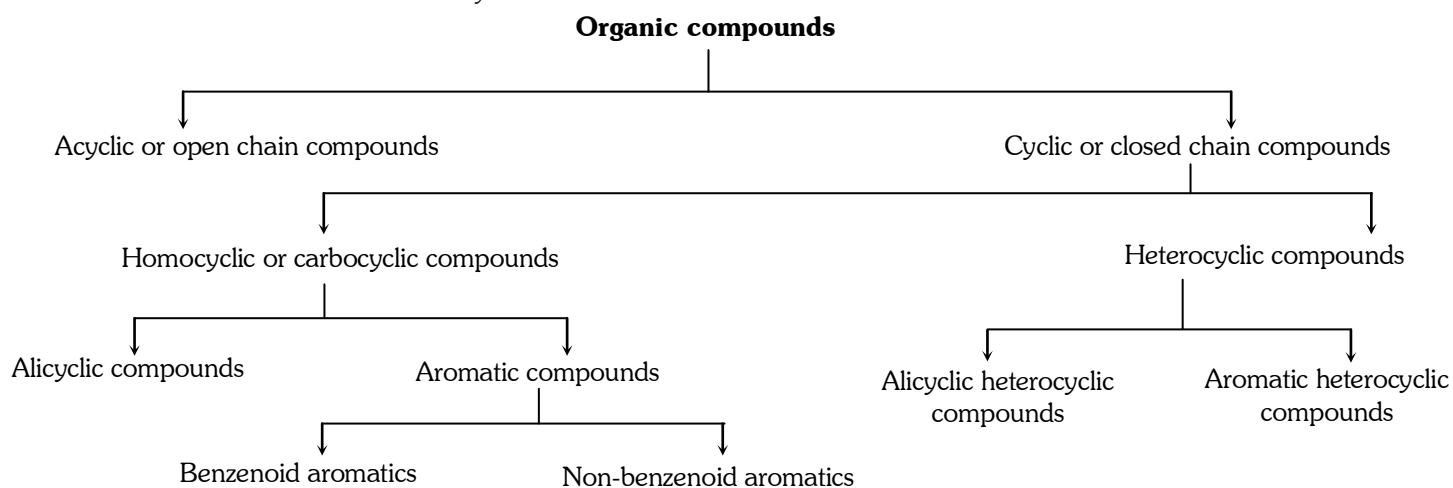
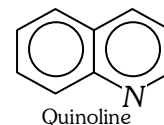
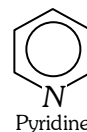
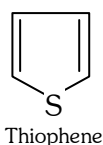
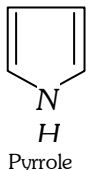
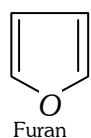
(b) **Heterocyclic compounds** : Cyclic compounds containing one or more hetero atoms (*e.g.* O, N, S etc.) in the ring are called heterocyclic compounds. These are of two types :

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



Purification, classification and nomenclature of organic compound Part 1

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



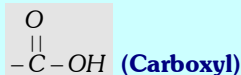
(2) Classification based on functional groups : A functional group is an atom or group of atoms in a molecule that gives the molecule its characteristic chemical properties. Double and triple bonds are also considered as functional groups.

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.

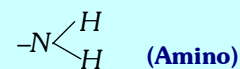
Class	Functional group	Class	Functional group
Olefins/Alkenes	$\text{>C}=\text{C}<$	Acid halides	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{X} \end{array}$ (Acylhalide)
Acetylenes/Alkynes	$-\text{C}\equiv\text{C}-$	Amides	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{NH}_2 \end{array}$ (Amide)
Alkyl Halides	$-\text{F}, -\text{Cl}, -\text{Br}, -\text{I}$ (Halo)	Acid anhydrides	$\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ -\text{C}-\text{O}-\text{C}- \end{array}$ (Anhydride)
Alcohols	$-\text{OH}$ (Hydroxy)	Esters	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}-\text{C}- \\ \end{array}$ (Ester)
Ethers	$\begin{array}{c} \quad \\ -\text{C}-\text{O}-\text{C}- \\ \quad \end{array}$ (Alkoxy)	Cyanides/Nitriles	$-\text{C}\equiv\text{N}$ (Cyano)
Aldehydes	$\begin{array}{c} -\text{C}-\text{H} \\ \\ \text{O} \end{array}$ (Aldehydic)	Isocyanides	$-\text{N}\equiv\text{C}$ (Isocyano)
Ketones	$\begin{array}{c} \text{O} \\ \\ -\text{C}- \end{array}$ (ketonic)	Nitro compounds	$\begin{array}{c} \text{O} \\ // \\ -\text{N} \end{array}$ (Nitro) ↓

Purification, classification and nomenclature of organic compound Part 1

Carboxylic acid



Amines



(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 .

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 may have values 1, 2, 3.... etc.

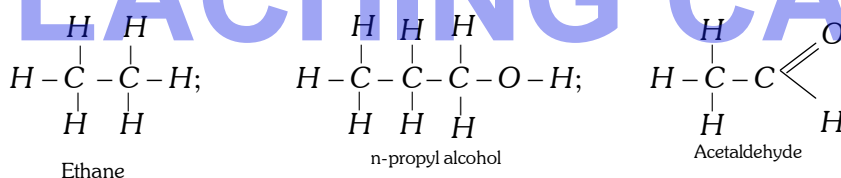
(ii) Two successive members differ in their formula by $-\text{CH}_2$ group or by 14 atomic mass units ($12 + 2 \times 1$).

(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.

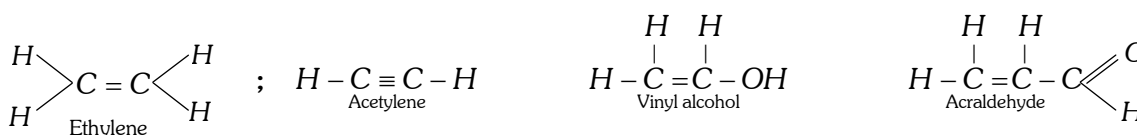
(iv) The members in any particular family have almost identical chemical properties and their physical properties such as melting point, boiling point, density, solubility etc., show a proper gradation with the increase in the molecular mass.

(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.



Note : The double bond between carbon and oxygen atoms is not a sign of unsaturation as in acetaldehyde or acetone.

Nomenclature of organic compounds

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*.

Purification, classification and nomenclature of organic compound Part 1

(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.

Common or trivial names of some organic compounds.

Compound	Common name	Compound	Common name
CH ₄	Methane	CHCl ₃	Chloroform
C ₂ H ₂	Acetylene	CHI ₃	Iodoform
H ₃ CCH ₂ CH ₂ CH ₃	n-Butane	CH ₃ CN	Acetonitrile
(H ₃ C) ₂ CHCH ₃	Isobutane	CH ₃ COOH	Acetic acid
(H ₃ C) ₄ C	Neopentane	C ₆ H ₆	Benzene
HCHO	Formaldehyde	C ₆ H ₅ CH ₃	Toluene
(H ₃ C) ₂ CO	Acetone	C ₆ H ₅ NH ₂	Aniline
CH ₃ CH ₂ OH	Ethyl alcohol	C ₆ H ₅ OH	Phenol
CH ₃ CONH ₂	Acetamide	C ₆ H ₅ OCH ₃	Anisole
CH ₃ OCH ₃	Dimethyl ether	C ₆ H ₅ COCH ₃	Acetophenone
(CH ₃ CH ₂) ₂ O	Diethyl ether	C ₆ H ₅ CONH 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.

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-

Purification, classification and nomenclature of organic compound Part 1

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.

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.

Note : *It may be noted that **extra** 'a' is added to the word root if the primary suffix to be added begins with a consonant (other than a, e, i, o, u). For example, for two double bonds, suffix is diene and if it is to be added to word root but (for 4C atoms), it becomes butadiene.

(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.

Class of org. compound	Functional group	Secondary suffix	Class of org. compound	Functional group	Secondary suffix
Alcohols	–OH	–ol	Acid chlorides	–COCl	–oyl chloride
Aldehydes	–CHO	–al	Acid amides	–CONH ₂	–amide
Ketones	>C = O	–one	Nitriles	–C≡N	–nitrile
Carboxylic acids	–COOH	–oic acid	Amines	–NH ₂	–amine
Esters	–COOR	alkyl... oate	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	Word root	Primary suffix	Secondary suffix	IUPAC name
CH ₃ CH ₂ OH	Eth	an (e)*	ol	Ethanol
CH ₃ CH ₂ CN	Prop	ane	nitrile	Propanenitrile

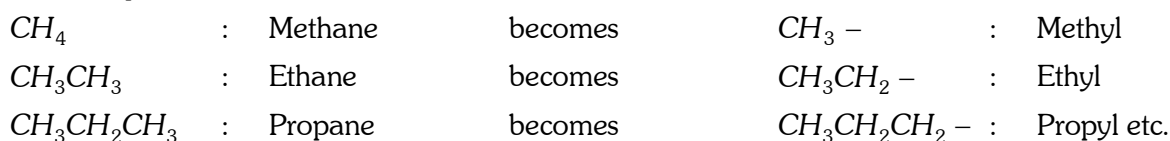
The terminal 'e' from the primary suffix has been dropped because the secondary suffix i.e. 'ol' begins with a vowel 'o'.

(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**.

Purification, classification and nomenclature of organic compound Part 1

For example,



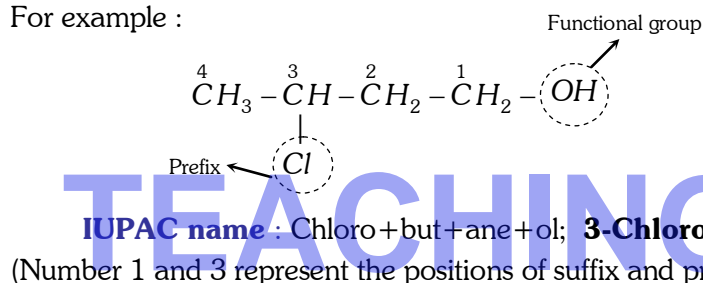
(b) *Functional groups not regarded as principal functional groups* : If a compound contains more than one functional group, then one of the functional group is regarded as principal functional group and is treated as secondary suffix. The other functional groups are regarded as substituents and are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

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

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

Prefix + word root + Primary suffix + Secondary suffix

For example :



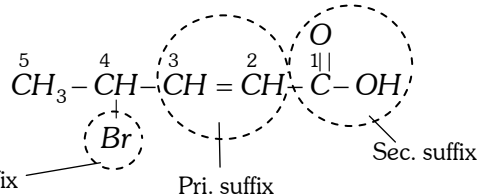
Word root : But

Primary suffix : -ane

Secondary suffix : -ol

Prefix : Chloro

TEACHING CARE



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

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

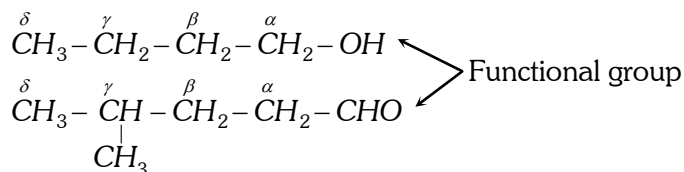
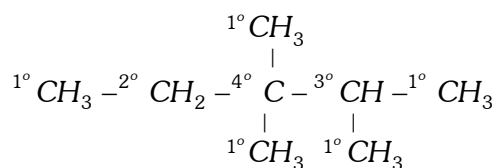
Secondary suffix : oic acid (-COOH group)

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

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

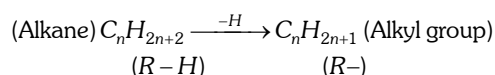
Classification of carbon atoms in organic compounds

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.

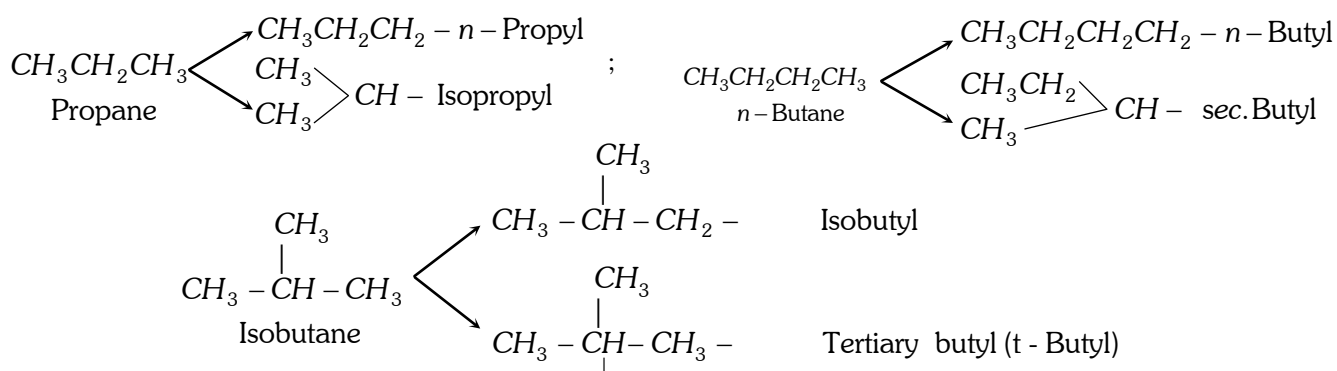


Purification, classification and nomenclature of organic compound Part 1

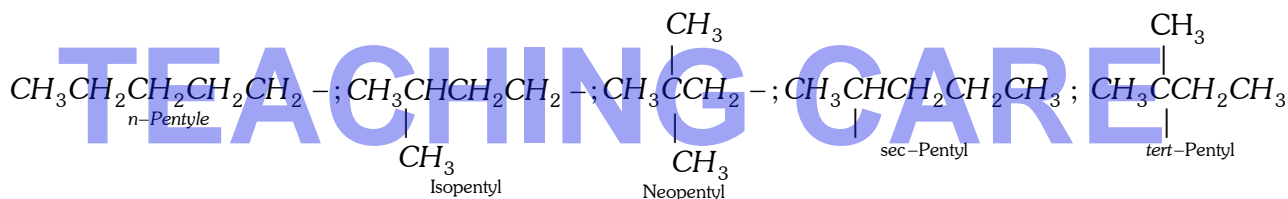
Alkyl groups are named by dropping-ane from the name of corresponding paraffin and adding the ending-yl.

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



Note : The prefix sec- or tert- before the name of the group indicate that the H-atom was removed from a secondary or tertiary carbon atom respectively.

Unsaturated groups or radicals

Group	Common name	IUPAC name	Group	Common name	IUPAC name
CH ₂ = CH -	vinyl	Ethenyl	HC ≡ C -	Acetylide	Ethynyl
CH ₂ = $\overset{2}{C}H - \overset{1}{C}H_2 -$	Allyl	2-Propenyl	HC ≡ $\overset{2}{C} - \overset{1}{C}H_2 -$	Propargyl	2-Propynyl
CH ₃ - CH = $\overset{1}{C}H -$	-	1-Propenyl			

Different classes of organic compounds

S. No.	Homologous series	Structural formula	Root word	Primary suffix	Secondary suffix	IUPAC Name
1.	Paraffins or Alkanes (C _n H _{2n+2})	$\overset{1}{C}H_4$	Meth	-ane	-	Methane
		$\overset{2}{C}H_3 - \overset{1}{C}H_3$	Eth	-ane	-	Ethane
		$\overset{3}{C}H_3 - \overset{2}{C}H_2 - \overset{1}{C}H_3$	Prop	-ane	-	Propane
		$\overset{4}{C}H_3 - \overset{3}{C}H_2 - \overset{2}{C}H_2 - \overset{1}{C}H_3$	But	-ane	-	Butane
2.	Olefins or Alkenes (C _n H _{2n})	$\overset{2}{C}H_2 = \overset{1}{C}H_2$	Eth	-ene	-	Ethene
			Prop	-ene	-	Propene

Purification, classification and nomenclature of organic compound Part 1

	$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}=\overset{1}{\text{C}}\text{H}_2$	But	-ene	-	1-Butene
	$\overset{4}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{H}_2\overset{2}{\text{C}}\text{H}=\overset{1}{\text{C}}\text{H}_2$	But	-ene	-	2-Butene
	$\overset{4}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{H}=\overset{2}{\text{C}}\text{H}\overset{1}{\text{C}}\text{H}_3$				
3. Acetylenes or Alkynes ($\text{C}_n\text{H}_{2n-2}$)	$\overset{2}{\text{C}}\text{H}\equiv\overset{1}{\text{C}}\text{H}$	Eth	-yne	-	Ethyne
	$\overset{3}{\text{C}}\text{H}_3-\overset{2}{\text{C}}\equiv\overset{1}{\text{C}}\text{H}$	Prop	-yne	-	Propyne
	$\overset{4}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{H}_2-\overset{2}{\text{C}}\equiv\overset{1}{\text{C}}\text{H}$	But	-yne	-	1-Butyne
	$\overset{4}{\text{C}}\text{H}_3-\overset{3}{\text{C}}\equiv\overset{2}{\text{C}}-\overset{1}{\text{C}}\text{H}_3$	But	-yne	-	2-Butyne
4. Monohydric Alcohols ($\text{C}_n\text{H}_{2n+1}\text{OH}$)	$\overset{1}{\text{C}}\text{H}_3\text{OH}$	Meth	-ane	-ol	Methanol
	$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{H}_2\text{OH}$	Eth	-ane	-ol	Ethanol
	$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{H}_2\text{OH}$	Prop	-ane	-ol	1-Propanol
	$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{HOH}\overset{1}{\text{C}}\text{H}_3$	Prop	-ane	-ol	2-Propanol
	$\overset{4}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{H}_2\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{H}_2\text{OH}$	But	-ane	-ol	1-Butanol
	$\overset{4}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{H}_2\overset{2}{\text{C}}\text{HOH}\overset{1}{\text{C}}\text{H}_3$	But	-ane	-ol	2-Butanol
5. Aldehydes ($\text{C}_n\text{H}_{2n}\text{O}$)	$\overset{1}{\text{H}}\overset{1}{\text{C}}\text{HO}$	Meth	-ane	-al	Methanal
	$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{HO}$	Eth	-ane	-al	Ethanal
	$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{HO}$	Prop	-ane	-al	Propanal
	$\overset{4}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{H}_2\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{HO}$	But	-ane	-al	Butanal
6. Ketones ($\text{C}_n\text{H}_{2n}\text{O}$)	$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{O}\overset{1}{\text{C}}\text{H}_3$	Prop	-ane	-one	Propanone
	$\overset{4}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{H}_2\overset{2}{\text{C}}\text{O}\overset{1}{\text{C}}\text{H}_3$	But	-ane	-one	Butanone
	$\overset{5}{\text{C}}\text{H}_3\overset{4}{\text{C}}\text{H}_2\overset{3}{\text{C}}\text{H}_2\overset{2}{\text{C}}\text{O}\overset{1}{\text{C}}\text{H}_3$	Pent	-ane	-one	2-Pentanone
	$\overset{5}{\text{C}}\text{H}_3\overset{4}{\text{C}}\text{H}_2\overset{3}{\text{C}}\text{O}\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{H}_3$	Pent	-ane	-one	3-Pentanone
7. Carboxylic acid (Mono) ($\text{C}_n\text{H}_{2n}\text{O}_2$)	$\overset{1}{\text{H}}\overset{1}{\text{C}}\text{OOH}$	Meth	-ane	-oic acid	Methanoic acid
	$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{OOH}$	Eth	-ane	-oic acid	Ethanoic acid
	$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{OOH}$	Prop	-ane	-oic acid	Propanoic acid
	$\overset{4}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{H}_2\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{OOH}$	But	-ane	-oic acid	Butanoic acid
8. Acid Chlorides (RCOCl)	$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{OCl}$	Eth	-ane	-oyl chloride	Ethanoyl chloride
	$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{OCl}$	Prop	-ane	-oyl chloride	Propanoyl chloride
	$\overset{4}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{H}_2\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{OCl}$	But	-ane	-oyl chloride	Butanoyl chloride
9. Acid amides (RCONH₂)	$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{ONH}_2$	Eth	-ane	Amide	Ethanamide
	$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{ONH}_2$	Prop	-ane	Amide	Propanamide
	$\overset{4}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{H}_2\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{ONH}_2$	But	-ane	Amide	Butanamide
10. Esters	$\overset{1}{\text{H}}\overset{1}{\text{C}}\text{OOCH}_3$	Meth	-ane	-oate	Methyl methanoate

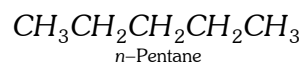
Purification, classification and nomenclature of organic compound Part 1

	(RCOOR')	$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{OOC}_2\text{H}_5$	Eth	-ane	-oate	Ethyl ethanoate
		$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{OOCH}_3$	Eth	-ane	-oate	Methyl ethanoate
		$\overset{3}{\text{C}}\text{H}_3-\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{OOC}_2\text{H}_5$	Prop	-ane	-oate	Ethyl propanoate
11.	Anhydrides	$(\text{CH}_3-\text{CO})_2\text{O}$	Eth	-ane	-oic	Ethanoic anhydride
	$(\text{RCO})_2\text{O}$	$(\text{C}_2\text{H}_5-\text{CO})_2\text{O}$	Prop	-ane	anhydride	Propanoic anhydride
					-oic anhydride	
12.	Amines	$\overset{1}{\text{C}}\text{H}_3\text{NH}_2$	Meth	-ane	amine	Methanamine
	$(\text{R}-\text{NH}_2)$		Eth	-ane	amine	Ethanamine
	Primary	$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{H}_2\text{NH}_2$	Prop	-ane	amine	1-Propanamine
		$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{H}_2\text{NH}_2$	Prop	-ane	amine	2-Propanamine
		$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}\text{NH}_2\overset{1}{\text{C}}\text{H}_3$				
13.	Cyanides or nitriles (R-CN)	$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{N}$	Eth	-ane	nitrile	Ethane nitrile
		$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{N}$	Prop	-ane	nitrile	Propane nitrile
		$\overset{4}{\text{C}}\text{H}_3\overset{3}{\text{C}}\text{H}_2\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{N}$	But	-ane	nitrile	Butane nitrile
14.	Alkyl halides	$\overset{1}{\text{C}}\text{H}_3\text{Cl}$	Meth	-ane	Chloro	Chloromethane
	$(\text{C}_n\text{H}_{2n+1}\text{X})$		Eth	-ane	Chloro	Chloroethane
		$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{H}_2\text{Cl}$	Prop	-ane	Bromo	1-Bromopropane
		$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{H}_2\text{Br}$	Prop	-ane	Bromo	2-Bromopropane
		$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}\text{Br}\overset{1}{\text{C}}\text{H}_3$				
15.	Ethers	$\overset{1}{\text{C}}\text{H}_3\text{OCH}_3$	Meth	-ane	Methoxy	Methoxymethane
	$(\text{R}-\text{O}-\text{R})$		Eth	-ane	Methoxy	Methoxyethane
		$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{H}_2\text{OCH}_3$	Eth	-ane	Ethoxy	Ethoxyethane
		$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{H}_2\text{OC}_2\text{H}_5$				
16.	Nitro compounds	$\overset{1}{\text{C}}\text{H}_3\text{NO}_2$	Meth	-ane	Nitro	Nitromethane
	$(\text{R}-\text{NO}_2)$		Eth	-ane	Nitro	Nitroethane
		$\overset{2}{\text{C}}\text{H}_3\overset{1}{\text{C}}\text{H}_2\text{NO}_2$	Prop	-ane	Nitro	1-Nitropropane
		$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}_2\overset{1}{\text{C}}\text{H}_2\text{NO}_2$	Prop	-ane	Nitro	2-Nitropropane
		$\overset{3}{\text{C}}\text{H}_3\overset{2}{\text{C}}\text{H}\text{NO}_2\overset{1}{\text{C}}\text{H}_3$				

General rules for naming organic compounds

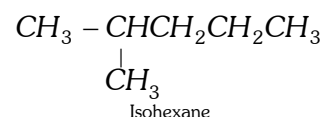
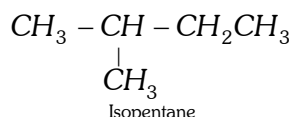
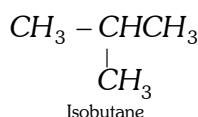
In the common system, all the isomeric alkanes (having same molecular formula) have the same parent name. The names of various isomers are distinguished by prefixes. The prefix indicates the type of branching in the molecule. For example,

(1) **Prefix n-**(normal) is used for those alkanes in which all the carbon atoms form a continuous chain with no branching.

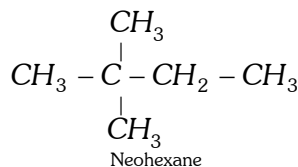
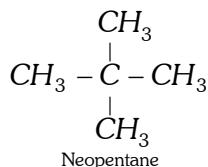


(2) **Prefix iso** is used for those alkanes in which one methyl group is attached to the next-to-end carbon atom (second last) of the continuous chain.

Purification, classification and nomenclature of organic compound Part 1



(3) **Prefix neo** is used for those alkanes which have two methyl groups attached to the second last carbon atom of the continuous chain.

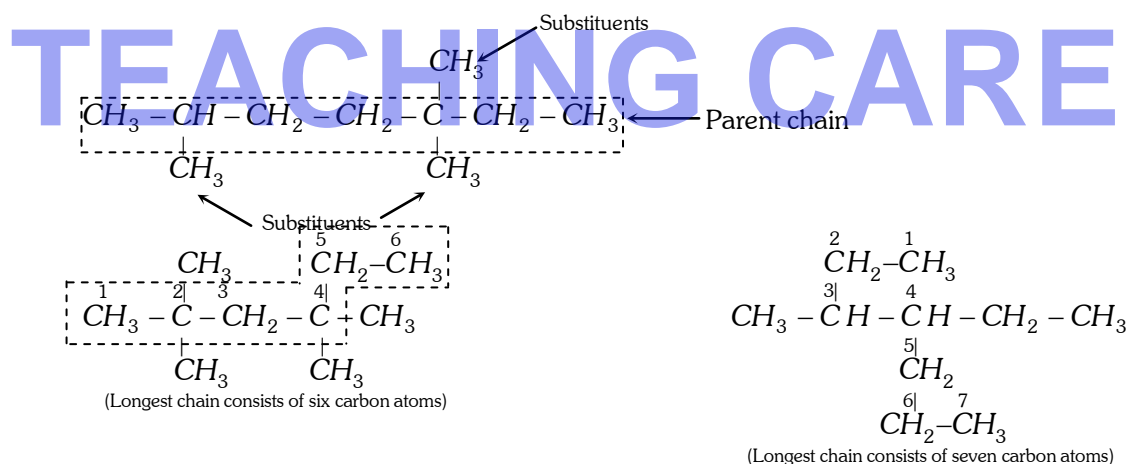


IUPAC system of nomenclature of complex compounds

The naming of any organic compound depends on the name of normal parent hydrocarbon from which it has been derived. IUPAC system has framed a set of rules for various types of organic compounds.

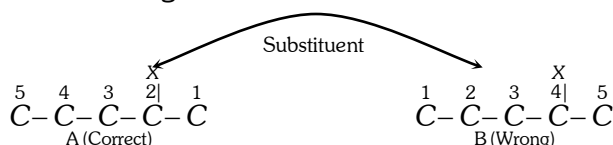
(1) **Rules for Naming complex aliphatic compounds when no functional group is present (saturated hydrocarbon or paraffins or Alkanes)**

(i) **Longest chain rule** : The first step in naming an organic compound is to select the longest continuous chain of carbon atoms which may or may not be horizontal (straight). This continuous chain is called parent chain or main chain and other carbon chains attached to it are known as side chains (substituents). Examples :

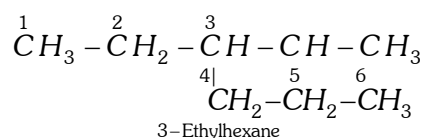
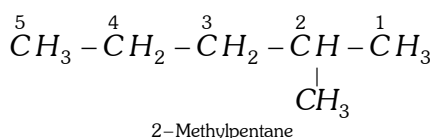


Note : *If two different chains of equal length are possible, the chain with maximum number of side chains or alkyl groups is selected.

(ii) **Position of the substituent** : Number of the carbon atoms in the parent chain as 1, 2, 3,..... etc. starting from the end which gives lower number to the carbon atoms carrying the substituents. For examples,



The number that indicates the position of the substituent or side chain is called *locant*.



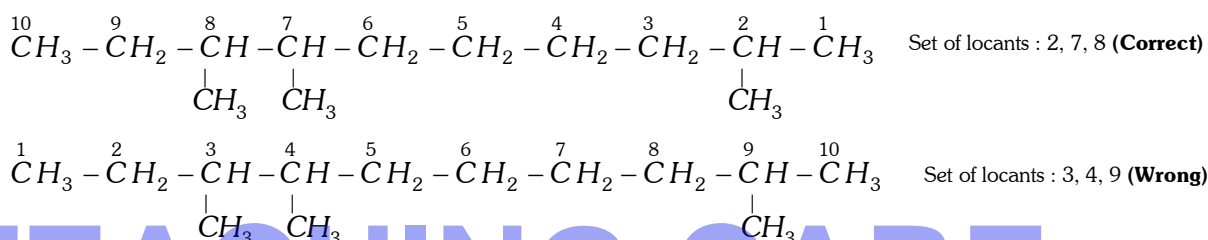
Purification, classification and nomenclature of organic compound Part 1

(iii) **Lowest set of locants** : When two or more substituents are present, then end of the parent chain which gives the lowest set of the locants is preferred for numbering.

This rule is called **lowest set of locants**. This means that when two or more different sets of locants are possible, that set of locants which when compared term by term with other sets, each in order of increasing magnitude, has the lowest term at the first point of difference. This rule is used irrespective of the nature of the substituent. For example,

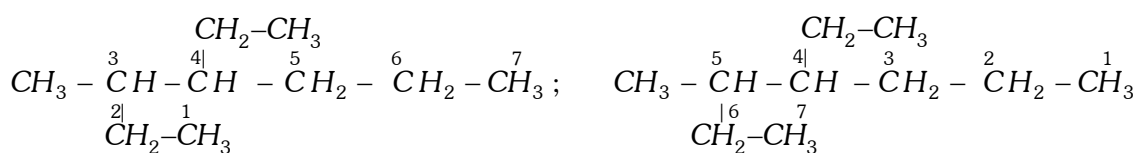


The correct set of locants is 2, 3, 5 and not 2, 4, 5. The first set is lower than the second set because at the **first difference** 3 is less than 4. (Note that first locant is same in both sets 2; 2 and the first difference is with the second locant 3, 4. We can compare term by term as 2-2, 3-4 (first difference), 5-5. **Only first point of difference is considered for preference**. Similarly for the compounds,



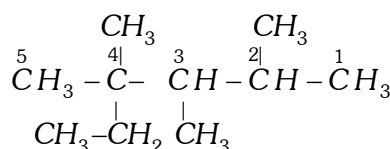
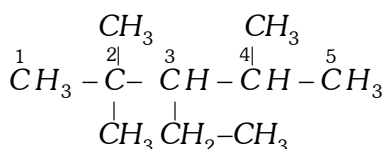
First set of locants 2, 7, 8 is lower than second set 3, 4, 9 because at the first point of difference 2 is lower than 3.

Lowest sum rule : It may be **noted** that earlier, the numbering of the parent chain containing two or more substituents was done in such a way that **sum of 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

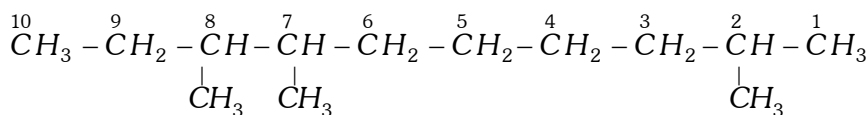
(B) wrong Sum of locants = 4+5=9



(A) Correct Sum of locants = 2+2+3+4=11

(B) Wrong Sum of locants = 2+3+4+4=13

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

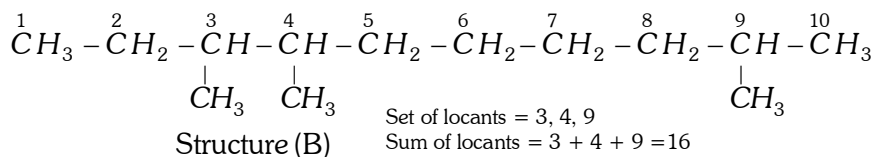


Structure (A)

Set of locants = 2, 7, 8

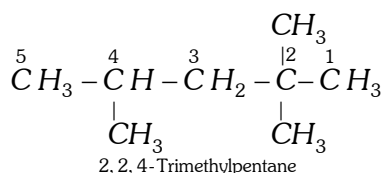
Sum of locants = 2 + 7 + 8 = 17

Purification, classification and nomenclature of organic compound Part 1



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.

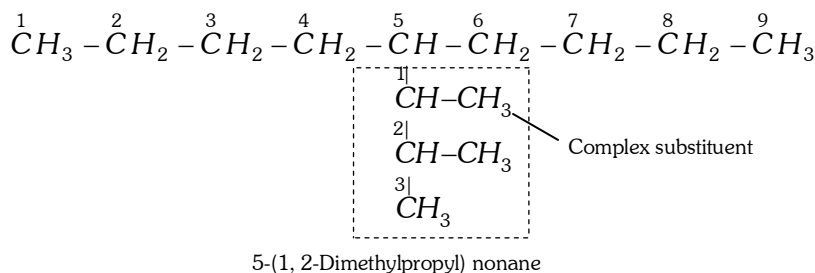


TEACHING CARE

(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,

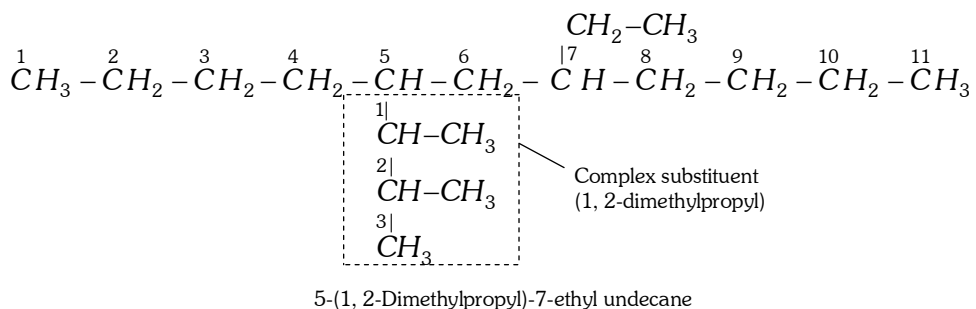


The name of the complex substituent is always written in brackets.

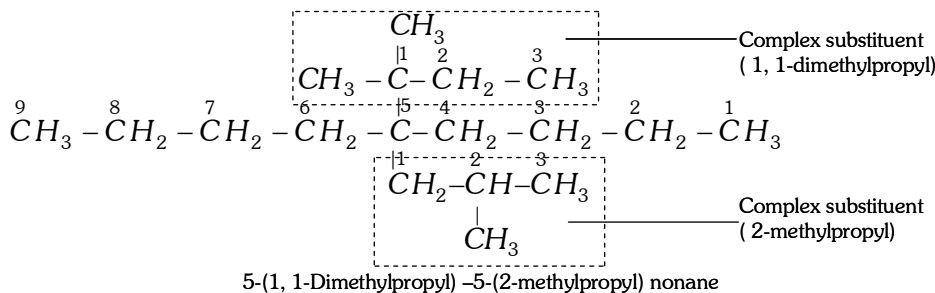
While deciding the alphabetical order of the various substituents, the name of the complex substituent is considered to begin with the first letter of the complete name. It may be **remembered** that in case of simple

Purification, classification and nomenclature of organic compound Part 1

substituents, however, the multiplying prefixes are not considered. The names of simple substituents are first alphabetized and then multiplying prefixes are inserted. For example,



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**).



TEACHING CARE