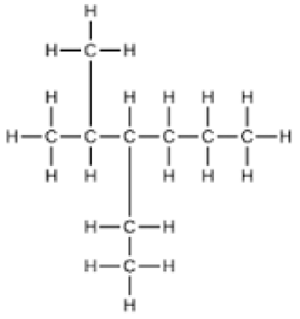
Class 11, Chapter- 12: Some Basic Principles and Techniques

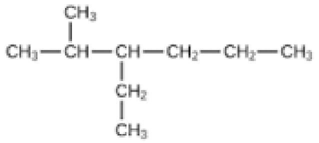
1. Hybridisation and shape of Organic Compound (Hydrocarbon):

Hydrocarbon	General Formula	Example	Hybridisation	No. of Sigma and pi bond
Alkane	C_nH_{2n+2}	CH_4 (Methane)	SP3	4 Sigma bond
		C_2H_6 (Ethane)		7 Sigma bond
Alkene	C_nH_{2n}	C_2H_4 (Ethene)	SP2	5 Sigma and 1 pi bond
		C_3H_6 (Propene)		8 Sigma and 1 pi bond
Alkyne	C_nH_{2n-2}	C_2H_2 (Ethyne)	SP	3 Sigma and 2 pi bond
		C_3H_4 (Propyne)		6 Sigma and 2 pi bond

2. Complete, condensed and bond-line structural formulas of organic compounds:

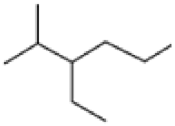


Expanded formula



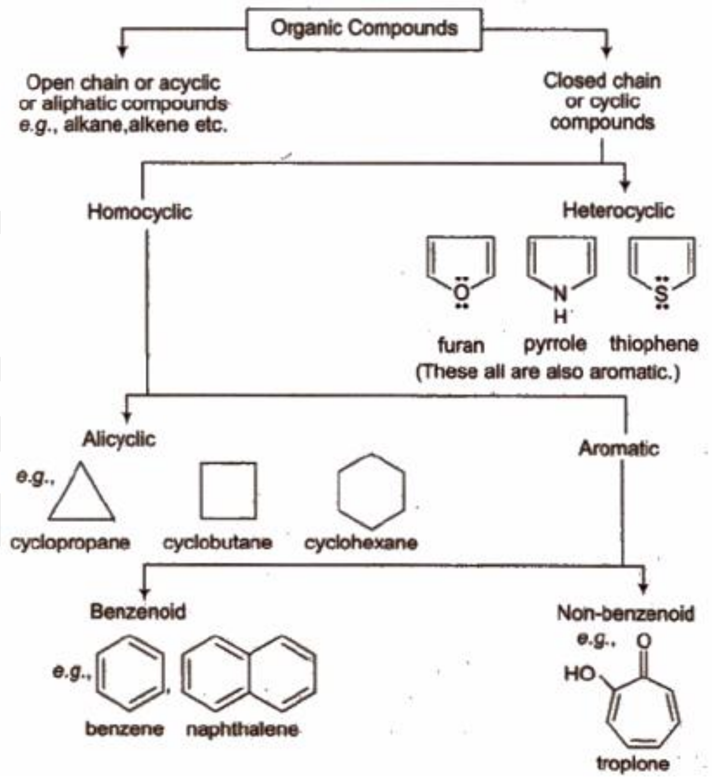
$CH_3-CH(CH_3)-CH(CH_2CH_3)-CH_2-CH_2-CH_3$

Condensed formula



Skeletal structure

3. Classification of organic compounds:



4. Characteristics of sigma and pi bonds: Refer chapter: 4

5. Rules for Nomenclature (IUPAC) of Organic Compounds:

a) The IUPAC name consists of three parts: Prefix Word root Suffix

b) Identified the longest carbon chain in the molecule.

c) The branched carbon atoms get the lowest possible numbers.

d) The names of the alkyl groups attached as a branch are then prefixed to the name of the parent alkane and its position is indicated by numbers.

e) If two substituents are found in the equivalent position, the lower number is given to the first in alphabetical order.

f) The name of the compound is written out with the substituents in alphabetical order followed by the base name (parent chain name).

g) If the same substituent occurs more than once, its indicated by a prefix (di, tri, tetra, etc.).

h) The carbon atom of the branch that attaches to the root alkane is numbered 1.

i) A cyclic (ring) hydrocarbon is designated by the prefix **cyclo-** which appears directly in front of the base name.

j) Commas are used between numbers and dashes are used between letters and numbers. There are no spaces in the name.

k) The halogen is treated as a substituent on an alkane chain. The halo- substituent is considered of equal rank with an alkyl substituent in the numbering of the parent chain.

l) Given priority to lowest numbers first double bond than triple bonds after that given priority over alkyl and halo substituents.

$CH_3-CH=CH-CH_2-CH=CH_2$

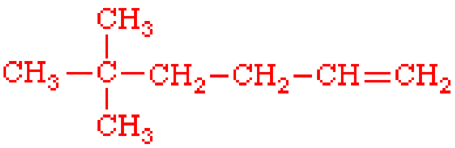
1,4-hexadiene

$CH\equiv C-CH=CH-CH=CH_2$

1,3-hexadien-5-yne

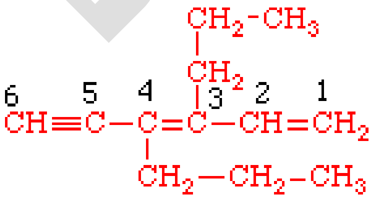
$CH_3-CH=CH-C\equiv CH$

3-penten-1-yne



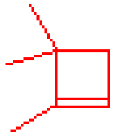
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-CH_2-CH=CH_2$

5,5-dimethyl-1-hexene



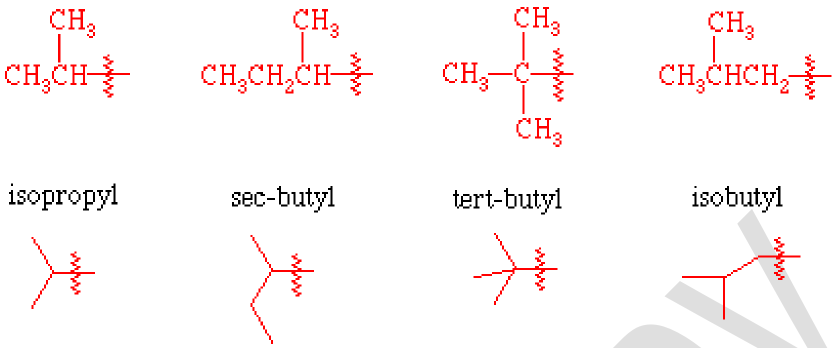
$\overset{6}{CH}\equiv\overset{5}{C}-\underset{CH_2-CH_2-CH_3}{\overset{4}{C}}=\overset{CH_2-CH_3}{\overset{|}{\overset{CH_2}{\overset{|}{\overset{3}{C}}}}}-\overset{2}{CH}=\overset{1}{CH_2}$

3,4-dipropyl-1,3-hexadien-5-yne



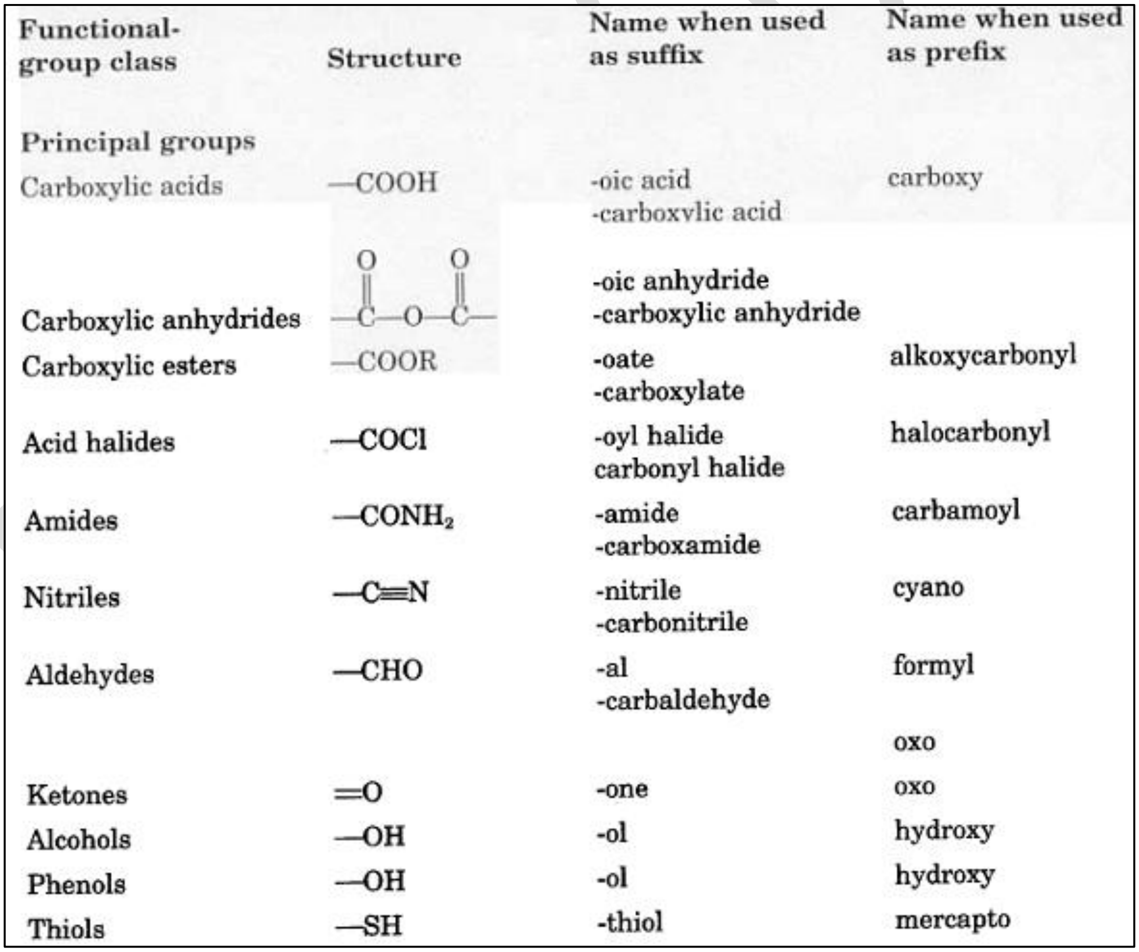
1,4,4-trimethylcyclobutene
(NOT: 2,3,3-trimethylcyclobutene)

m) There are a few common branched substituents which you should memorize. These are shown below.

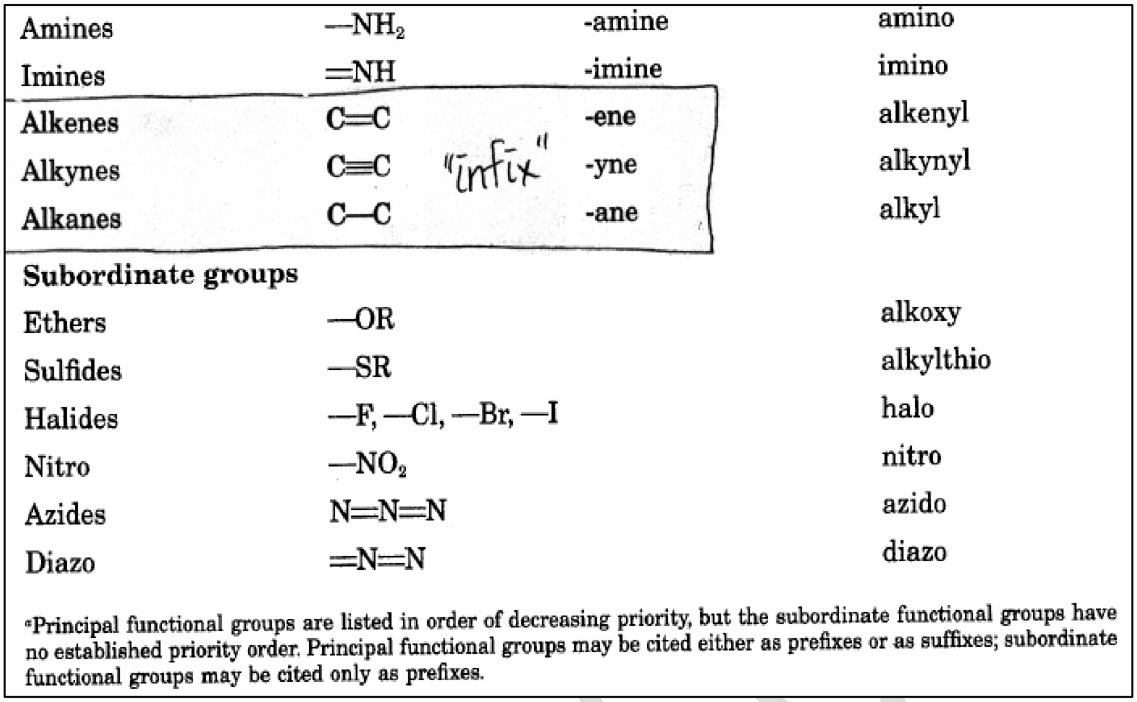


n) Nomenclature of organic compound having functional group: The functional group attached to the carbon atom gets the lowest possible number in the chain. When there are more functional groups then a priority order is followed as:

-COOH, -SO3H, -COOR, COCl, -CONH2, -CN, -HC=O, =C=O, -OH, -NH2, =C=C=,-CΞ C-.



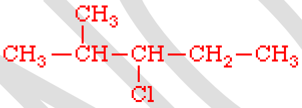
Functional-group class	Structure	Name when used as suffix	Name when used as prefix
Principal groups			
Carboxylic acids	—COOH	-oic acid -carboxylic acid	carboxy
Carboxylic anhydrides	$-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-$	-oic anhydride -carboxylic anhydride	
Carboxylic esters	—COOR	-oate -carboxylate	alkoxycarbonyl
Acid halides	—COCl	-oyl halide carbonyl halide	halocarbonyl
Amides	—CONH$_2$	-amide -carboxamide	carbamoyl
Nitriles	—C≡N	-nitrile -carbonitrile	cyano
Aldehydes	—CHO	-al -carbaldehyde	formyl
			oxo
Ketones	=O	-one	oxo
Alcohols	—OH	-ol	hydroxy
Phenols	—OH	-ol	hydroxy
Thiols	—SH	-thiol	mercapto



Amines	$-NH_2$		-amine	amino
Imines	$=NH$		-imine	imino
Alkenes	$C=C$		-ene	alkenyl
Alkynes	$C\equiv C$	“infix”	-yne	alkynyl
Alkanes	$C-C$		-ane	alkyl
Subordinate groups				
Ethers	$-OR$			alkoxy
Sulfides	$-SR$			alkylthio
Halides	$-F$, $-Cl$, $-Br$, $-I$			halo
Nitro	$-NO_2$			nitro
Azides	$N=N=N$			azido
Diazo	$=N=N$			diazo

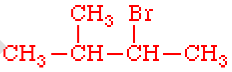
[a] Principal functional groups are listed in order of decreasing priority, but the subordinate functional groups have no established priority order. Principal functional groups may be cited either as prefixes or as suffixes; subordinate functional groups may be cited only as prefixes.

Nomenclature of Alkyl halides: The halogen is treated as a substituent (prefix) on an alkane chain. The halo- substituent is considered of equal rank with an alkyl substituent in the numbering of the parent chain.



$CH_3-CH(CH_3)-CH(Cl)-CH_2-CH_3$

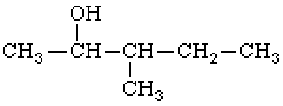
3-chloro-2-methylpentane



$CH_3-CH(CH_3)-CH(Br)-CH_3$

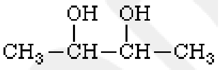
2-bromo-3-methylbutane

Nomenclature of Alcohol:



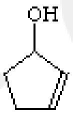
$CH_3-CH(OH)-CH(CH_3)-CH_2-CH_3$

3-methyl-2-pentanol



$CH_3-CH(OH)-CH(OH)-CH_3$

2,3-butanediol



2-cyclopenten-1-ol

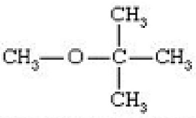
Nomenclature of Ether:

$CH_3CH_2-O-CH_2CH_3$

common name: diethyl ether
(ethyl ether or “ether”)
IUPAC name: ethoxyethane

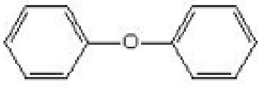
$CH_3-O-CH_2CH_3$

methyl ethyl ether
or ethyl methyl ether
methoxyethane



$CH_3-O-C(CH_3)_2-CH_3$

common name: methyl-*t*-butyl ether
(MTBE)
IUPAC name: 2-methoxy-2-methylpropane



diphenyl ether
or phenyl ether
phenoxybenzene

Nomenclature of Aldehydes

propanal

3-methylbutanal

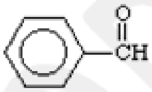
3-methyl-3-butenal

$H\overset{\overset{O}{\|}}{C}H$

methanal
(common name: formaldehyde)

$CH_3\overset{\overset{O}{\|}}{C}H$

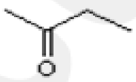
ethanal
(common name: acetaldehyde)



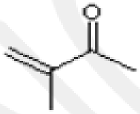
Benzaldehyde

Nomenclature of Ketones

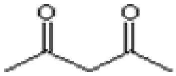
propanone
(common name: acetone)



2-butanone

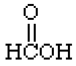


3-methyl-3-buten-2-one



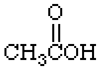
2,4-pentanedione

Nomenclature of Carboxylic Acids and Esters



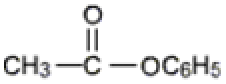
$H\overset{\overset{O}{\|}}{C}OH$

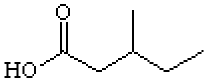
methanoic acid
(common name: formic acid)



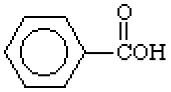
$CH_3\overset{\overset{O}{\|}}{C}OH$

ethanoic acid
(common name: acetic acid)

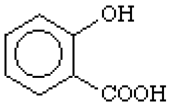
	Common name	IUPAC name
 $H-\overset{\overset{O}{\|}}{C}-OC_2H_5$	Ethyl formate	Ethyl methanoate
 $CH_3-\overset{\overset{O}{\|}}{C}-OC_6H_5$	Phenyl acetate	Phenyl ethanoate



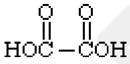
3-methylpentanoic acid



benzoic acid



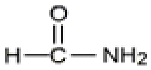
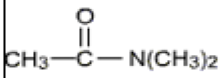
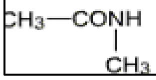
salicylic acid
(common name)



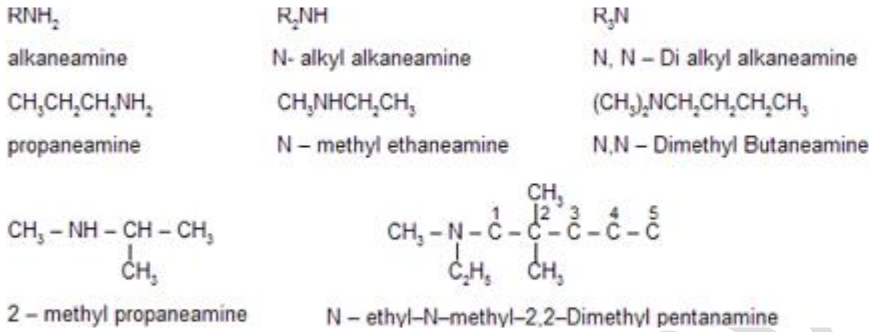
$HO\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}OH$

ethanedioic acid
(common name: oxalic acid)

Nomenclature of Amide

 $H-\overset{\overset{O}{\|}}{C}-NH_2$	Methan amide
 $CH_3-\overset{\overset{O}{\|}}{C}-N(CH_3)_2$	N,N-dimethyl acetamide
 $CH_3-\underset{\underset{CH_3}{\mid}}{CONH}$	N methyl ethanamide

Nomenclature of Amine:



RNH_2	R_2NH	R_3N
alkaneamine	N- alkyl alkaneamine	N, N – Di alkyl alkaneamine
$CH_3CH_2CH_2NH_2$	$CH_3NHCH_2CH_3$	$(CH_3)_2NCH_2CH_2CH_2CH_3$
propaneamine	N – methyl ethaneamine	N,N – Dimethyl Butaneamine

$$CH_3-NH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

2 – methyl propaneamine

$$CH_3-\underset{\displaystyle C_2H_5}{\underset{|}{N}}-\overset{1}{C}-\overset{\displaystyle CH_3}{\overset{|2}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}$$

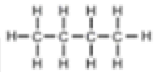
N – ethyl–N–methyl–2,2–Dimethyl pentanamine

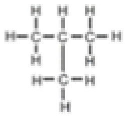
Nomenclature of substituted Benzene compound:

6. Isomerism: Two or more compounds having the same molecular formula but different physical and chemical properties are called isomers and this phenomenon is called isomerism. Its can be classified as following

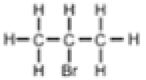
A) Structural Isomerism: There are following four types-

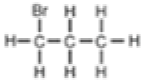
i) Branched Chain isomerism: When two or more compounds having same molecular formula but different carbon skeletons are referred to as chain isomers.





ii) Position Isomerism: Compounds which have the same structure of carbon chain but differ in position of double or triple bonds or functional group are called position isomers and this phenomenon is called Position Isomerism.



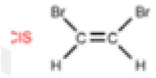


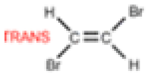
iii) Functional Isomerism: Compounds which have the same molecular formula but different functional group are called functional isomers and this phenomenon is called Functional Isomerism. e g C_2H_6O represents $CH_3 – CH_2 – OH$ and $CH_3 – O – CH_3$

iv) Metamerism: It is due to the presence of different alkyl groups on either side of functional group in the molecule. Ex. $C_4H_{10}O$ represents C_2H_5 O C_2H_5 and CH_3O C_3H_7.

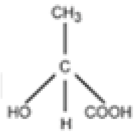
B) Sterio Isomerism: The compounds having same constitution and sequence of covalent bonds but different in relative positions of their atoms or groups in space are called Stereo isomers and that types of isomerism called Stereoisomerism. There are two types

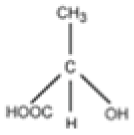
i) Geometric Isomerism: Each of two or more chemical compounds having the same molecular formula but a different geometric arrangement; are called Geometric isomers and this phenomenon is called Geometric Isomerism. An unsaturated compound or ring compound in which rotation around a carbon bond is restricted, as in cis- and trans- configurations.





ii) Optical Isomerism: The mirror images of a chiral molecule or ion are called Enantiomers or optical isomers and this phenomenon is called Optical Isomerism.



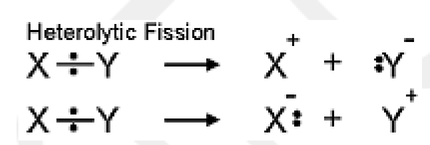


7. Fission of a Covalent Bond:

i) Heterolytic cleavage: In this cleavage the bond breaks in such a way that the shared pair of electron remains with one of the fragments. The negatively charged atom has octet configuration whereas the positively charged atom has sextet configuration.

For example, when a hydrochloric acid is cleaved then both the bonded electrons are taken by chlorine and a negative ion which can be shown as Cl^-.

$$H\text{-}Cl \rightarrow H^+ + Cl^-$$



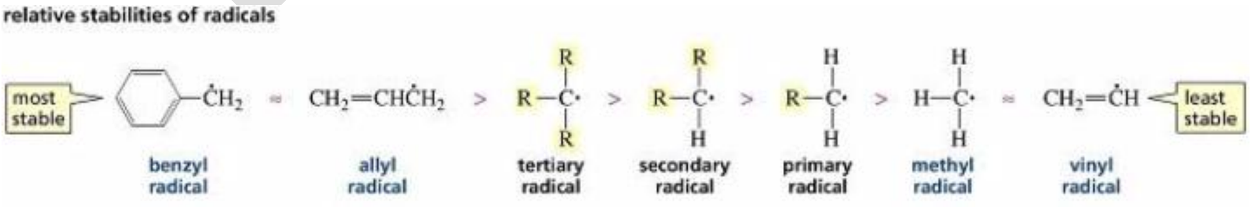
In this type of cleavage we also get carbon atoms which are negatively charged and are also called as **carbanions** and in the same way the carbon atoms which are positively charged, known as **carbocations**. The carbocations are trigonal in shape and is sp^2hybridised. Carbocations are formed due to heterolysis of C-X bond and these are very reactive towards electron rich species. Carbanions are sp^3 hybridised and are reactive towards positive charge.

ii) Homolytic Cleavage: In this cleavage the shared pair of electron goes with each of the bonded atom which results forming of species known as free radicals.

$$R - X \rightarrow R^{\cdot} + X^{\cdot}$$

Alkyl free radical

Different alkyl free radicals stability can be show in increasing order as following-

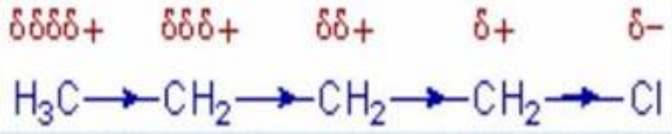


8. Nucleophiles: A reagent that brings an electron pair is called Nucleophiles (Nu:) i.e. nucleus seeking species like -OH , -CN

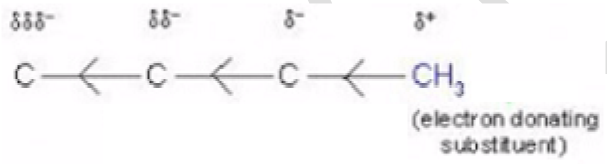
9. Electrophiles: A reagent that accept a pair of electrons to foem a new covalent bond is called Electrophiles, i.e. electron seeking e g > C= O, R3C – X, BF3, +NO2

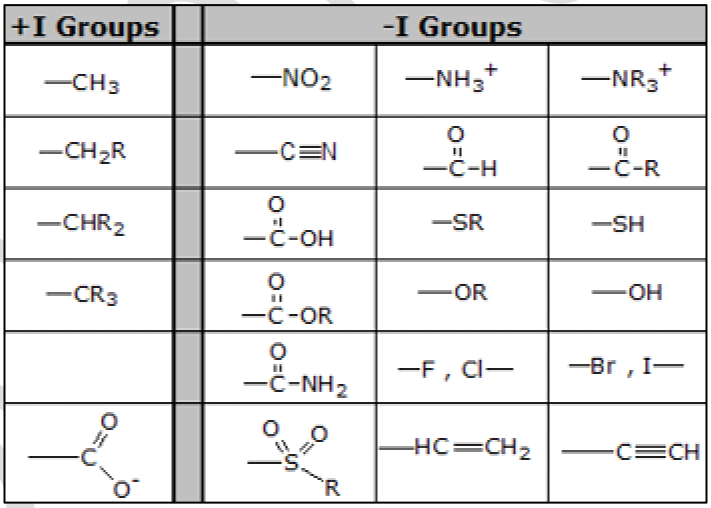
10. Inductive Effect: The polarisation of a sigma bond due to electron withdrawing effect of adjacent groups or atoms is called inductive effect.

–I effect: When the more electronegative atom or group is connected to the chain of carbon atoms then the positive charge is transferred to other carbon atom and due to this exert electron withdrawing effect and is also called –I effect.



+I effect: Some groups like alkyl groups are electron releasing in nature, this electron releasing nature is exert a +I effect. The strength of this effect is dependent on the distance between the main group and the substituent group. This effect gets weaker as the distance between these two groups increases.



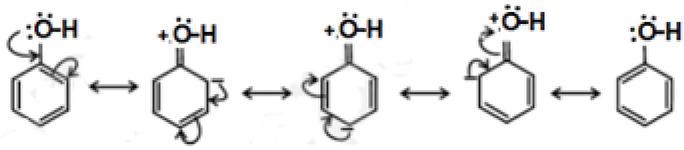


+I Groups		-I Groups		
$—CH_3$		$—NO_2$	$—NH_3^+$	$—NR_3^+$
$—CH_2R$		$—C\equiv N$	$—\overset{O}{\overset{\|\|}{C}}-H$	$—\overset{O}{\overset{\|\|}{C}}-R$
$—CHR_2$		$—\overset{O}{\overset{\|\|}{C}}-OH$	$—SR$	$—SH$
$—CR_3$		$—\overset{O}{\overset{\|\|}{C}}-OR$	$—OR$	$—OH$
		$—\overset{O}{\overset{\|\|}{C}}-NH_2$	$—F$, $Cl—$	$—Br$, $I—$
$—C(=O)O^-$		$—S(=O)_2R$	$—HC=CH_2$	$—C\equiv CH$

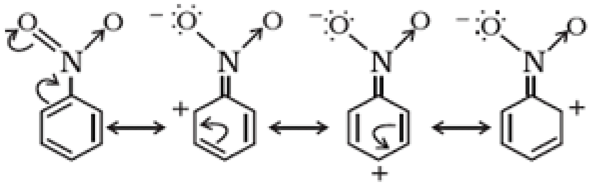
Inductive Effect of Functional Group

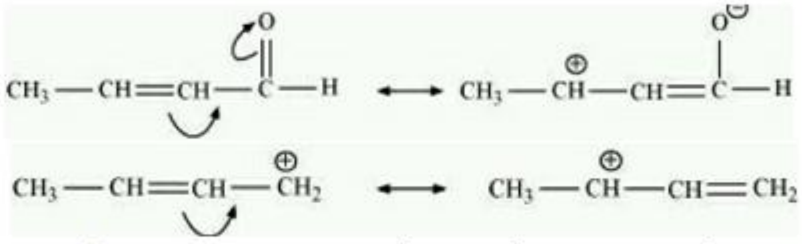
11. Resonance (Mesomeric Effect): The polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of electron present on an adjacent atom. There are two types of resonance effect:

i) Positive Resonance or Mesomeric (+R or +M) Effect: In this effect the transfer of electrons from an atom or substituent group to the conjugated system (benzene ring) through delocalization. The atoms or groups which shows +R effect are halogens,-OH, -OR,- NH2



ii) Negative Resonance or Mesomeric (- R or –M) Effect: In this effect the transfer of electrons is towards the atom or substituent group attached to the conjugated system. The atoms or groups which shows -R effect are -NO2, –COOH , -CHO , -CN



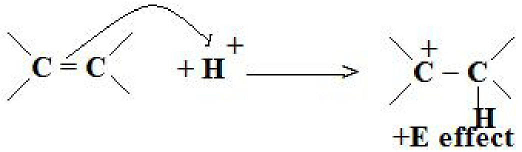


Resonance structure of some other compound

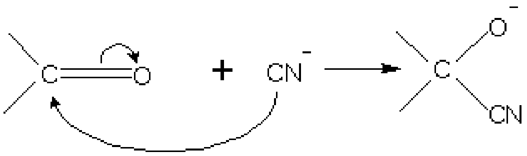
12. Electromeric Effect: The electromeric effect is the movement of electrons from one atom to another as a reagent attacks a π bond. Use curved arrow notation to show the movement of electrons during the reaction. There are two types of effect

i) Positive Electromeric Effect (+E effect): If the attacking species is an electrophile, the π electrons are transferred towards the positively charged atom. This is the +E effect.

An example is the protonation of ethene. When the H^+ comes near the double bond, the bond is polarized towards the proton.



ii) Negative Electromeric Effect (-E effect): If the attacking reagent is a nucleophile, the electrons are transferred away from the attacking reagent and into the π system. This is the –E effect.



13. Hyperconjugation: It is the interaction of the electrons in a sigma bond (usually C–H or C–C) with an adjacent empty or partially filled or filled π orbital, to give an extended molecular orbital that increases the stability of the system.

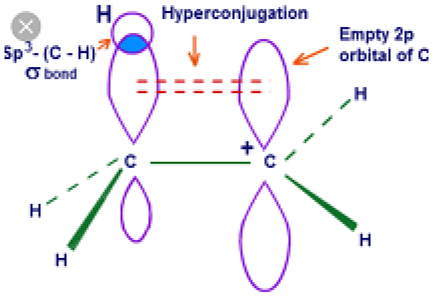
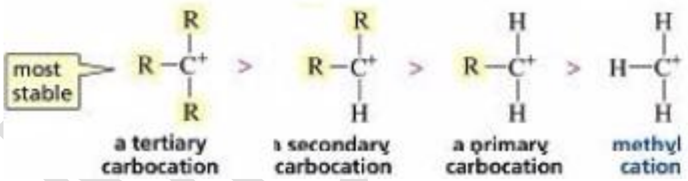


Figure: Hyperconjugation in Ethyl cation

Effect of Hyperconjugation: Bond length, dipole moments and heat of formation of molecules is affected due to hyperconjugation. Greater the number of alkyl group attached to a positively charged carbon atom, greater the hyperconjugation interaction and stabilization of the cation. So found the following relative stability of carbocation



14. Types of Organic Reaction: It can be classified in to following categories:

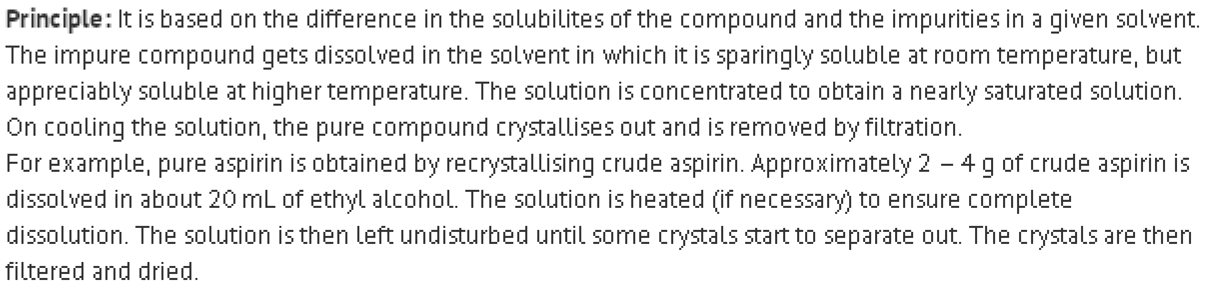
- Substitution Reaction
- Addition Reaction
- Elimination Reaction
- Rearrangement Reaction

15. Methods of Purification of Organic Compounds:

15.1. Sublimation: Sublimation is the transition of a substance directly from the solid to the gas phase without passing through the intermediate liquid phase.

This method is used to separate the sublimable compounds from non sublimable compounds. Ex Separation of Camphor

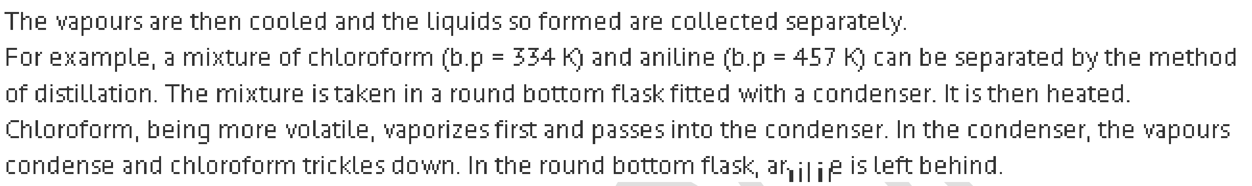
15.2. Crystallisation: Crystallisation is one of the most commonly used techniques for the purification of solid organic compound.



Principle: It is based on the difference in the solubilites of the compound and the impurities in a given solvent. The impure compound gets dissolved in the solvent in which it is sparingly soluble at room temperature, but appreciably soluble at higher temperature. The solution is concentrated to obtain a nearly saturated solution. On cooling the solution, the pure compound crystallises out and is removed by filtration.

For example, pure aspirin is obtained by recrystallising crude aspirin. Approximately 2 – 4 g of crude aspirin is dissolved in about 20 mL of ethyl alcohol. The solution is heated (if necessary) to ensure complete dissolution. The solution is then left undisturbed until some crystals start to separate out. The crystals are then filtered and dried.

15.3. Distillation: This method is used to separate volatile liquids from non volatile liquids and liquids having sufficient difference in their boiling points.



Principle: It is based on the fact that liquids having different boiling points vapourise at different temperatures. The vapours are then cooled and the liquids so formed are collected separately.

For example, a mixture of chloroform (b.p = 334 K) and aniline (b.p = 457 K) can be separated by the method of distillation. The mixture is taken in a round bottom flask fitted with a condenser. It is then heated. Chloroform, being more volatile, vaporizes first and passes into the condenser. In the condenser, the vapours condense and chloroform trickles down. In the round bottom flask, aniline is left behind.

15.4. Fractional distillation: If the boiling points of two liquids are not much, they are separated by this method. Example Separation of crude oil

15.5. Distillation under reduced pressure: This method is used to purify liquids which having high boiling points and decomposes at or below their boiling points.

Glycerol is purified by this method. It boils with decomposition at a temperature of 593K. At a reduced pressure, it boils at 453 K without decomposition.

16.6. Steam distillation: This method is used to separate substances which are steam volatile and immiscible in water. On passing steam, the compound gets heated up and the steam get condensed to water. After some time, the mixture of water and liquid starts to boil and passes through the condenser. This condensed mixture of water and liquid is then separated by using a separating funnel.

For example a mixture of water and aniline is separated by steam distillation.

15.7. Differential Extraction: When an organic compound is present in an aqueous medium it is separated by shaking it with organic solvent in which it is more soluble than in water. The aqueous solution is mixed with organic solvent in a separating funnel and shaken for sometimes and then allowed to stand for some time .when organic solvent and water form two separate layers the lower layer is run out by opening the tap of funnel and organic layer is separated. The process is repeated several times and pure organic compound is separated.

15.8. Chromatography: It is one of the most useful methods for the separation and purification of organic compounds. For example, a mixture of red and blue ink can be separated by Chromatography.

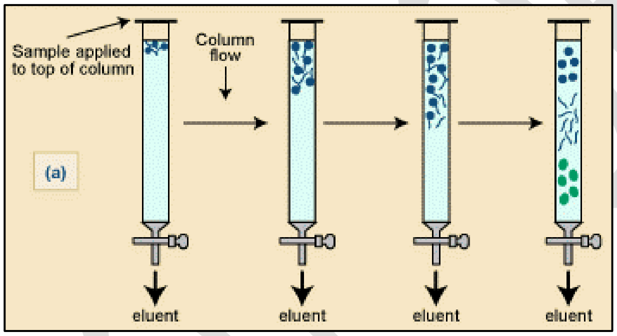
Principal: It's based on the difference in movement of individual components of a mixture through the stationary phase under the influence of mobile phase.

Based on the principal of differential adsorption, there are mainly two types of chromatographic techniques-

i) Adsorption Chromatography: It is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Silica jel or alumina is used as adsorbents. There are two types

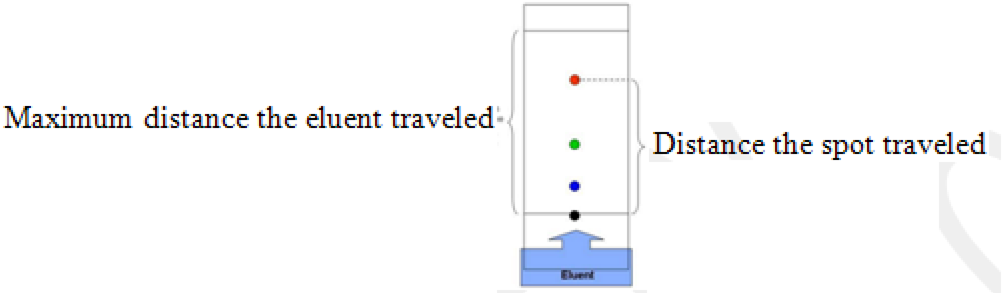
(a) Column Chromatography:

- This technique consists of a powdered adsorbent [either silica (SiO_2) or alumina (Al_2O_3)] as the stationary phase, placed in a vertical glass column.
- The mixture to be analyzed is placed on top of this vertical glass column.
- The solvent forming the mobile phase is poured from the top of the column and flow down the column.
- As the solvent flows, the solvent elutes the sample through the column and the components of the mixture begin to flow at their respective rates down the column.
- However, this technique need large volumes of solvent and any careless additions can cause disturbance to the stationary phase, leading to poor separations.



(b) Thin Layer Chromatography (TLC):

- This technique involves separation of mixture substances over a thin layer of an adsorbent (approx 0.2mm thick of silica gel or alumina) coated on a glass plate.
- A drop of solution to be analyzed is added to the TLC glass plate.
- This silica coated glass plate acts as the stationary phase. The plate is then placed in a glass chamber containing a solvent, which forms the mobile phase.
- Via capillary action, the solvent moves upwards and carries the molecules of the solution to be detected at different rates.
- The components of the solution will appear in the form of a series of spots at various locations on the plate.
- Calculations are made based on ratio of the distance that the substance travels to the distance that solvent, travels up the plate.



(ii) Partition Chromatography: It is based on the continuous differential portioning of components of a mixture between stationary and mobile phase. Paper chromatography is type of partition chromatography.

Paper chromatography:

- In this technique, the cellulose of the filter paper acts as the stationary phase.
- When a few drops of the mixture is applied to this filter paper and dipped into the container with water which act as mobile phase. The water begins to move upwards due to capillary action.
- The components are selectively retained on the paper (according to their differing partition in these two phases).
- The spots of different components travel with the mobile phase to different hights. The paper so obtained is known as a chromatogram.
- Paper chromatography is used to separate most colored compounds and is widely used in artificial and natural pigment research.
  - *Instrumentation Figure: Refer NCERT book page No. 354*

16. Qualitative analysis of organic compounds:

A) Detection of Carbon and Hydrogen: The Carbon and Hydrogen present in the Organic compound is detected by heating the compound with Copper II oxide. If carbon present in the compound, it's oxidized to CO_2 (which can be tested with lime Water) and Hydrogen is converted in to water (which can be tested with anhydrous copper sulphate which turns blue).

$C + 2CuO \rightarrow 2Cu + CO_2$

$2\ H + CuO \rightarrow Cu + H_2O$

$CO_2 + Ca\ (OH)_2 \rightarrow CaCO_3 + H2O$

$5\ H_2O + CuSO_4 \rightarrow CuSO_4.5H_2O$

B) Detection of other elements (Nitrogen, Sulphur and Halogen) by Lassaigne's Test: Lassaigne's test is used to detect the presence of elements like Nitrogen (N), Sulfur (S), Chlorine (Cl), Bromine (Br) and Iodine (I) because they elements are covalently bonded in organic compounds so for their detection, they have to be first converted to ionic form. This is done by fusing the organic compound with sodium metal. This is called Lassaigne's test. This test involves following two steps.

(i) Preparation of sodium fusion extract (SFE) (ii) Detection of elements using SFE.

i) Preparation of SFE: A small amount of organic substance is fused with small quantity of sodium metal in a fusion tube. The red hot fusion tube is then plunged into distilled water and the contents are boiled for a few minutes, then cooled it and filtered. The filtrate obtained is called sodium fusion extract (SFE) or Lassaigne's extract. It is usually alkaline. If it is not alkaline, a few drops of NaOH solution may be added to make it alkaline.

ii) Detection of elements using SFE: Thus obtained SFE is used to detect the presence of elements like N,S,Cl, Br & I. The elements in the organic compound react with sodium during fusion reaction as follows:

$Na + C + N \rightarrow NaCN$ (if N is present)

$2Na + S \rightarrow Na_2S$ (if S is present)

$Na + S + C + N \rightarrow NaSCN$ (if both N & S are present if insufficient amount of Na is used)

$Na + X \rightarrow NaX$ (If halogens are present) ; Where X = Cl/Br/I

Hence SFE may contain any of or all of ionic forms of respective elements.

a) Test for Nitrogen: The sodium fusion extract is boiled with iron II sulphate it form ferrocyanide ions. Now add 2 to 3 drops of $FeCl_3$ solution and acidified with conc. H_2SO_4, it produces ferricferrocyanide which is Prussian blue in color and indicates the presence of nitrogen.

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

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} Fe_4[Fe(CN)_6]_3.xH_2O$$

Ferric ferrocyanide (Prussian blue)

b) Test for Sulphur:

i) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur.

$S^{2-} + Pb^{2+} \rightarrow PbS$ (Black)

ii) If few drops of sodium nitro prusside treated with SFE, appearance of a deep violet color which indicates the presence of sulfur.

$S^{2-} + [Fe(CN)_5NO]^{2-} \rightarrow [Fe(CN)_5NOS]^{4-}$ (Vilot color)

Nitro prusside ion

c) When both N & S are present: If both N & S are present in the organic compound and SFE is prepared with **insufficient amount of Na metal**, then the thiocyanate ion (SCN^-) is formed instead of cyanide ion (CN^-).

The thiocyanate ions reacts with Fe^{3+} to give a blood red coloration due to formation of $[Fe(SCN)]^{2+}$.

$Fe^{3+} + SCN^-$ -------------> $[Fe(SCN)]^{2+}$ (Blood red)

Note: If sodium fusion is carried out with **excess of sodium**, the thiocyanate, SCN^- is decomposed to give CN^- & S^{2-}. Hence in this case, sulfur and nitrogen are to be identified in separate tests.

$NaSCN + 2Na \rightarrow NaCN + Na_2S$

d) Test for Halogens: The sodium fusion extract is first acidified with nitric acid and then treated with silver nitrate. If we found

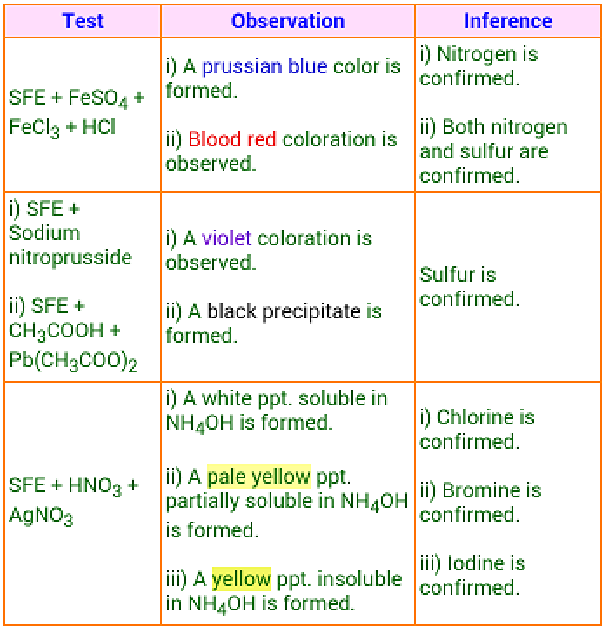
- A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine.
- A yellowish ppt. partially soluble in ammonium hydroxide shows the presence of bromine
- A yellowish ppt. insoluble in ammonium hydroxide shows the presence of iodine.

$X^- + Ag^+ \rightarrow AgX$ (Where X = Cl, Br and I)

Note: i) It is not possible to detect the presence of fluorine since the solubility of AgF is more and thus no precipitate is formed.

ii) If nitrogen or sulfur are present in the organic compound, the formation of black precipitates of AgCN or AgS may interfere during the test for halogens. So require to remove CN^- and S^{2-} from the SFE. This is done by boiling the SFE with conc. HNO_3 acid to almost dryness. The CN^- and S^{2-} ions are removed as HCN and H_2S gases. Chemical reaction involved can be represents as $NaCN + HNO_3 \rightarrow NaNO_3 + HCN$

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



Test	Observation	Inference
SFE + $FeSO_4$ + $FeCl_3$ + HCl	i) A prussian blue color is formed. ii) Blood red coloration is observed.	i) Nitrogen is confirmed. ii) Both nitrogen and sulfur are confirmed.
i) SFE + Sodium nitroprusside ii) SFE + CH_3COOH + $Pb(CH_3COO)_2$	i) A violet coloration is observed. ii) A black precipitate is formed.	Sulfur is confirmed.
SFE + HNO_3 + $AgNO_3$	i) A white ppt. soluble in NH_4OH is formed. ii) A pale yellow ppt. partially soluble in NH_4OH is formed. iii) A yellow ppt. insoluble in NH_4OH is formed.	i) Chlorine is confirmed. ii) Bromine is confirmed. iii) Iodine is confirmed.

Summary sheet of Lassaigne's Test

C) Test for Phosphorus: The compound is heated with an oxidising agent (Na_2O_2 sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow coloration or precipitate indicates the presence of phosphorus.

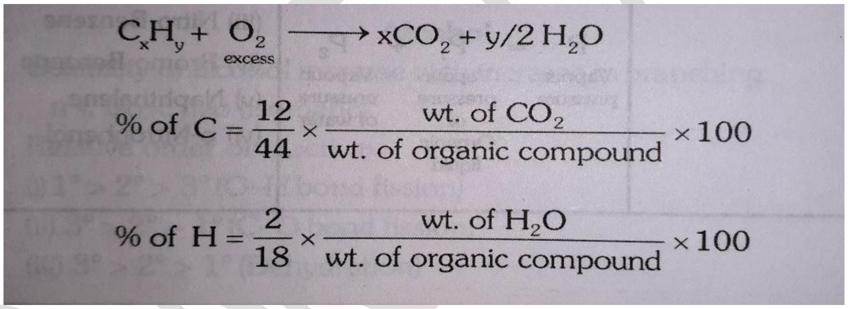
$Na_3PO_4 + 3HNO_3 \rightarrow H_3PO_4 + 3NaNO_3$
$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \rightarrow (NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O$
Ammonium molybdate Ammonium phosphomolybdate

17. Quantitative Analysis of Organic Compound:

A) Estimation of Carbon and Hydrogen: A known mass of organic compound is burnt in the presence of oxygen and CuO then carbon and hydrogen are oxidised to CO_2 and water.

$$\text{Organic compound} + O_2 \rightarrow CO_2 + H_2O$$

Passing the mixture in U tube which containing $CaCl_2$, absorbed the water and another connected U tube which containing concentrated solution of KOH, absorbed CO_2. An increase the mass of $CaCl_2$ and KOH gives the amount of water and CO_2 from which the percentage of carbon and hydrogen can be calculated.



$$C_xH_y + \underset{\text{excess}}{O_2} \longrightarrow xCO_2 + y/2\,H_2O$$

$$\%\text{ of C} = \frac{12}{44} \times \frac{\text{wt. of } CO_2}{\text{wt. of organic compound}} \times 100$$

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

B) Estimation of Nitrogen: There are two methods for estimation of nitrogen:

i) Dumas Method:

- This method can be used to estimate Nitrogen in all types of organic compounds
- A known mass of organic compound is heated with excess of CuO in the presence of CO_2 gas. This leads to the release of CO_2, H2O and N_2.
- The mixture of gases is collected over KOH solution in which CO_2 and water is absorbed and volume of nitrogen is collected in the upper part of the graduated tube.
- The volume of N_2 thus obtained is converted into percentage by applying the following equation:

$$\text{Volume of Nitrogen at STP} = \frac{P_1V_1 \times 273}{760 \times T_1}$$

$$\%N = \frac{28 \times \text{vol of } N_2 \text{ at STP} \times 100}{22400 \times \text{mass of the substance taken}}$$

ii) Kjeldahl's Method:

- This method cannot be used for compound having nitro groups, azo groups (-N = N-) and nitrogen in the ring (pyridine, quinole, etc.).
- A known mass of organic compound is heated with conc. H_2SO_4 in presence of $CuSO_4$ in a long necked flask called Kjeldahl's flask.
- Nitrogen present in the organic compound is quantitatively converted into $(NH_4)_2SO_4$ which liberate ammonia on treating with NaOH.
- Liberate ammonia gas is absorbed by a known excess of a standard acid such as H_2SO_4 or HCl.

Organic Compound + $H_2SO_4 \rightarrow (NH_4)_2SO_4$
$(NH_4)_2SO_4 + NaOH \rightarrow Na_2SO_4 + 2NH_3 + 2H_2O$
$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4$

The volume of acid unused is found by titration against a standard alkali solution. From the volume of the acid used, the percentage of nitrogen is determined by applying the following equation-

$$\%N = \frac{1.4 \times \text{Molarity of the acid} \times \text{Basicity of the acid} \times \text{Vol of the acid used}}{\text{Mass of the substance taken}}$$

C) Estimation of Chlorine (Carius method):

- A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass test tube known as carius tube in a furnace.
- Carbon and hydrogen present in the compound are oxidized to carbon dioxide and water.
- The halogen present in the forms of silver halide.

$$\text{Percentage of Chlorine} = \frac{35.5}{143.5} x \frac{\text{Mass of AgCl}}{\text{Mass of Organic compound}} x 100$$

D) Estimation of Bromine (Carius method):

$$\text{Percentage of Bromine} = \frac{80}{188} x \frac{\text{Mass of AgBr}}{\text{Mass of Organic Compound}} x \ 100$$

E) Estimation of Iodine (Carius method):

$$\text{Percentage of Iodine} = \frac{127}{235} \times \frac{\text{Mass of AgI}}{\text{Mass of Organic Compound}} \times 100$$

F) Estimation of Sulphur:

- A fixed mass of an organic compound containing sulphur is heated in a Carius tube containing sodium peroxide or fuming nitric acid.
- Sulphur present in the organic compound is oxidized to sulphuric acid.
- It is then precipitated as barium sulphate by the addition of barium chloride solution in water.
- The precipitate is then washed, filtered, dried and weighed. The mass of barium sulphate is used in calculating the percentage of sulphur in the given organic compound.

$S + HNO_3 \rightarrow H_2SO_4$
$H_2SO_4 + BaCl_2 \rightarrow BaSO_4$

$$\text{Percentage of Sulphur} = \frac{32}{233} \times \frac{\text{Mass of BaSO4} \times 100}{\text{Mass of Organic Compound}}$$

G) Estimation of Phosphorous:
Method 1:

- known mass of an organic compound is heated with fuming nitric acid where upon phosphorus present in the compound is oxidized to phosphoric acid.
- It is precipitated as ammonium phosphomolybdate, (NH4)3PO4.12 MoO3, by adding ammonia and ammonium molybdate.
- The yellow precipitate is filtered, washed, dried and weighed.

$$\text{\% of phosphorous} = \frac{31 \times m_1 \times 100}{1877 \times m}$$

Method 2:

- A known mass of compound is heated with fuming HNO3 in Carius tube which converts to H3PO4.
- Magnesia mixture (MgCl2 + NH4Cl) is then added, which gives the precipitate of magnesium ammonium phosphate (MgNH4PO4) which on heating gives magnesium pyrophosphate (Mg2P2O7), which is weighed.

P + HNO3 → H3PO4

H3PO4 + Mg2+ NH4OH → MgNH4PO4
MgNH4PO4 → Mg2P2O7 + NH3 + H2O

From the mass of magnesium pyrophosphate, the percentage of phosphorus in the compound can be calculated.

$$Percentage\,of\,Phosporus = \frac{62}{222}x\frac{Mass\ of\ Mg_2P_2O_7}{Mass\ of\ Organic\ compound}x100$$

H) Estimation of Oxygen (Aluise's method): A known amount of organic compound is subjected to pyrolysis (decomposition by heat) in a stream of nitrogen. The oxygen and other gaseous products formed during pyrolysis are passed over heated carbon at 1100°C. The oxygen combines with carbon forming carbon monoxide.

Organic Compound → Oxygen + Gaseous products
$O_2 + 2C$ (graphite) → 2CO
The gas is then passed through a tube containing iodine pentoxide at 175°C to liberate iodine:
$5CO + I_2O_5 \rightarrow I_2 + 5CO_2$
The percentage of oxygen can be derived from the amount of carbon dioxide or iodine produced.
The resulting gaseous mixture (CO_2 or I_2) is passed through potassium iodide which absorbs iodine and the CO_2 left is then absorbed in KOH. Knowing the increase of weight of KOH i.e., the weight of CO_2, the percentage of oxygen can be calculated.
Suppose the mass of the organic compound taken = m g
Mass of CO_2= m1 g

$$Percentage\,of\ Oxygen = \frac{16}{44}x\frac{Mass\ of\ CO_2}{Mass\ of\ Organic\ compound}x100$$

Summary sheet of Quantitative Analysis

Quantitative Analysis	Reagent	Final Product ppt
Carbon and Hydrogen	C + H + CuO---------Burn------------------------------------>	CO2 (absorbed by KOH) / H2O (Abs by CaCl2)
Halogen	X + Fuming HNO3 + AgNO3------------Heat------------->	AgX ppt
Sulphur	S + Fuming HNO3 ----Heat in Carius Tube------------> H2SO4	
	H2SO4 + BaCl2 ------------>	BaSO4 ppt
Phosphorus a)	P + Fuming HNO3 -----Heat----------> H3PO4	
	H3PO4 + NH3 + Ammo. Molybdate--------------------->	Ammo. Phosphomolybdate (NH4)3PO4.12 MoO3
b)	P + H3PO4 + Magnesia mixture --> Magnesium ammo. Phosphate	
	Magnesium ammo. Phosphate -----> Heat---------- >	Mag. Pyrophosphate ppt (Mg2P2O8)
Oxygen	Organic Compd----decomposed by heating----> O2 + Other gases	
	2C (Red hot coke) + O2-----1373K temp---------> 2CO	
	5CO + I2O5--->	I2 + 5CO2