Organic Chemistry : Some Basic Principles & Techniques

Organic Compounds - Shapes and Structures

- A Swedish chemist named Berzilius proposed the vital force theory, according to which a vital force existing in living organisms is responsible for the formation of oranic compounds. However, this was proved to be incorrect when F.

  Wohler, a German chemist synthesised urea- an organic compound from ammonium cyanate, an inorganic compound.

$$\underset{\text{Ammonium cynate}}{NH_4CNO} \xrightarrow{\text{Heat}} \underset{\text{Urea}}{NH_2CONH_2}$$

- **Shape of carbon compounds**

$CH_4 \longrightarrow sp^3$ hybridised carbon
Methane
$C_2H_4 \longrightarrow sp^2$ hybridised carbon
Ethene
$C_2H_2 \longrightarrow sp$ hybridised carbon
Ethyne

- *sp* orbital has 50% '*s*' character. Thus, an *sp* hybridised carbon is more electronegative than an sp^2 (33% s character) or sp^3 (25% s-character) hybridised carbon.
- Hybridisation influences the bond length and bond enthalpy.

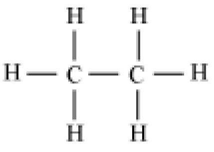
Some Characteristic Features of π-Bonds

- Parallel orientation of two *p*-orbitals on adjacent atoms is necessary for a proper sideways overlap to form π-bond.
- Rotation about C = C double bond is restricted.
- Electron charge cloud of π-bond is located above and below the plane of bonding atoms.
- Electrons are easily available to attacking reagents.

Structural Representations of Organic Compounds

- **Complete Structural Formula**

Examples:

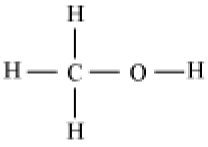


$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Ethane

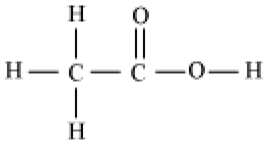
$H—C\equiv C—H$

Ethyne



$$\begin{array}{ccccccc} & & H & & & & \\ & & | & & & & \\ H & — & C & — & O & — & H \\ & & | & & & & \\ & & H & & & & \end{array}$$

Methanol



$$\begin{array}{ccccccccc} & & H & & O & & & & \\ & & | & & \| & & & & \\ H & — & C & — & C & — & O & — & H \\ & & | & & & & & & \\ & & H & & & & & & \end{array}$$

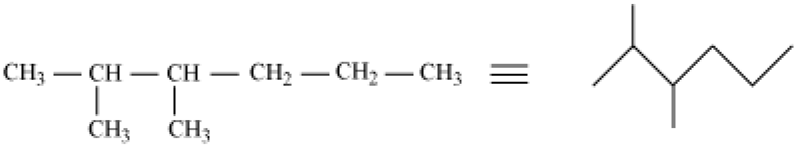
Acetic acid

- **Condensed Structural Formula**

(Structural formula obtained by omitting some or all of the dashes representing covalent bonds and then using a subscript to indicate the number of identical groups attached to an atom)

CH_3CH_3	$HC\equiv CH$	CH_3OH	CH_3COOH
Ethane	Ethyne	Methanol	Acetic acid

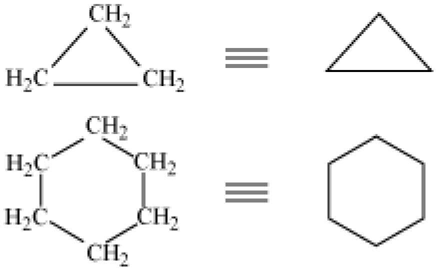
- **Bond-Line Structural Formula**
- Only lines are used to represent the structure of organic compound.
- Carbon and hydrogen atoms are not shown.
- Lines representing the C − C bonds are drawn in a *zig-zag* fashion.
- For example − bone-line formula of 2,3-dimethylhexane can be represented as



$$\begin{array}{ccccccccccc} CH_3 & — & CH & — & CH & — & CH_2 & — & CH_2 & — & CH_3 \\ & & | & & | & & & & & & \\ & & CH_3 & & CH_3 & & & & & & \end{array} \equiv$$

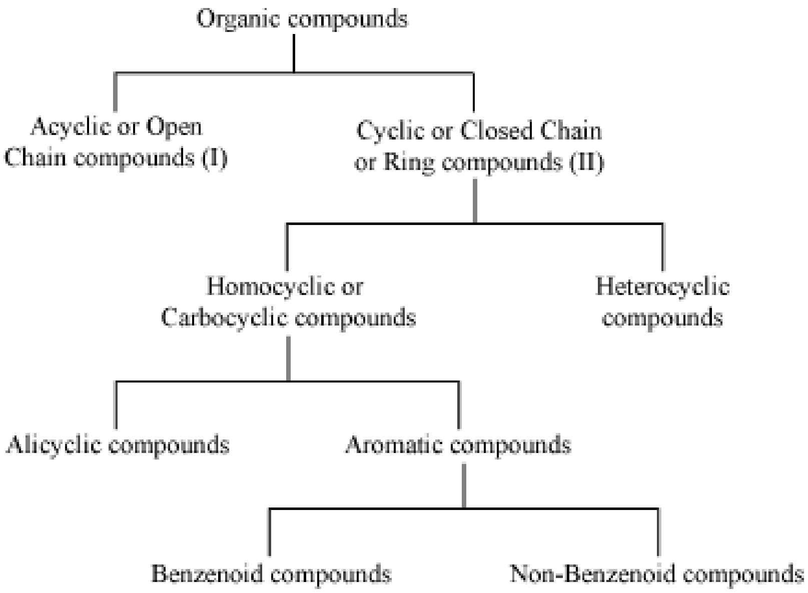
(Terminals represent methyl groups)

- In cyclic compounds,



To test your knowledge of this concept, solve the following puzzle.

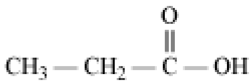
Classification of Organic Compounds



(I) Acyclic or open chain compounds consist of straight or branched chain compounds.

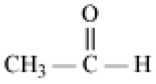
CH_3CH_3

Ethane



$CH_3-CH_2-\overset{\overset{\large O}{\|}}{C}-OH$

Propanoic acid



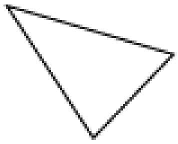
$CH_3-\overset{\overset{\large O}{\|}}{C}-H$

Acetaldehyde

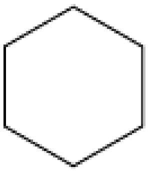
$CH_3-CH=CH_2$

Propene

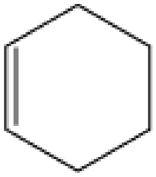
(II) Alicyclic or closed chain or ring compounds contain carbon atoms joined in the form of a ring (homocyclic). In some rings (heterocyclic), atoms other than carbon are present.



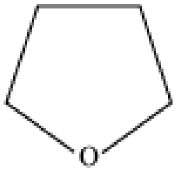
Cyclopropane



Cyclohexane



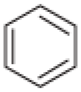
Cyclohexene



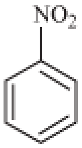
Tetrahydrofuran

Aromatic Compounds

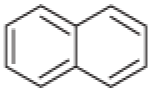
- Benzenoid aromatic compounds (include benzene and other related compounds)



Benzene

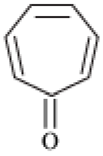


Nitrobenzene



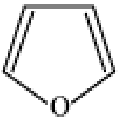
Naphthalene

- Non-benzenoid compounds (do not contain benzene ring)

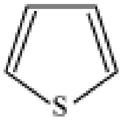


Tropolone

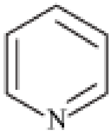
- Heterocyclic aromatic compounds



Furan



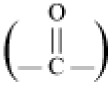
Thiophene



Pyridine

Functional Group

- An atom or group of atoms joined in a specific manner which is responsible for the characteristic chemical properties of the organic compound.

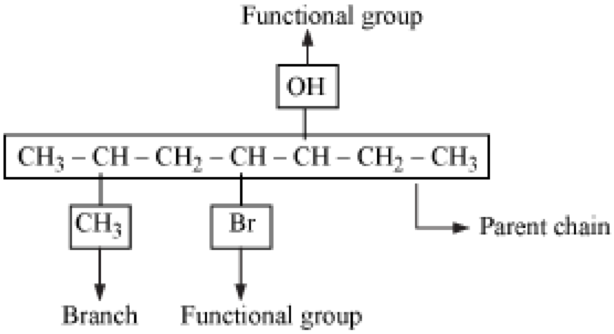
- Examples: Hydroxyl group (− OH), carboxylic acid group (− COOH), aldehyde group (−CHO), ether group (−O−), ketone group  $\left(-\overset{O}{\overset{\|}{C}}-\right)$, etc.

Homologous Series

- A group or a series of organic compounds each containing a characteristic functional group.
- The members of the series are called homologues.
- Successive members differ from each other in a molecular formula by a $-CH_2$ unit.
- Alkanes, alkenes, alkynes, alkanoic acids, amines, etc. represent homologous series.

IUPAC (International Union of Pure and Applied Chemistry) System of Nomenclature of Organic Compounds

- An organic compound can be named by identifying the parent hydrocarbon and the functional groups attached to it.



- Using prefixes and suffixes, the parent name can be modified to obtain actual name.

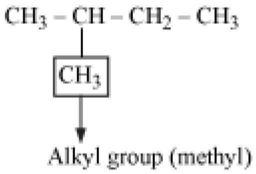
IUPAC Name of Alkanes

- **For straight chain hydrocarbons**

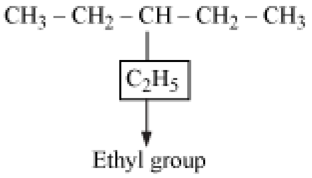
  Prefix →indicates the number of carbon atoms (except from $CH_4$to C_4H_{10})

  Suffix →‘ane’

- **Branched chain hydrocarbons**



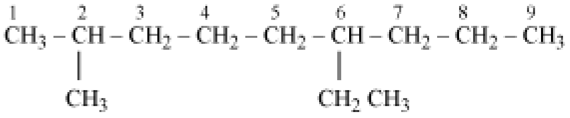
$$CH_3-\underset{\boxed{CH_3}}{\underset{|}{CH}}-CH_2-CH_3$$



$$CH_3-CH_2-\underset{\boxed{C_2H_5}}{\underset{|}{CH}}-CH_2-CH_3$$

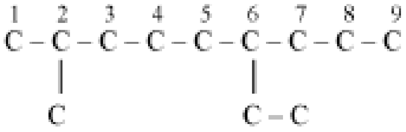
Rules for the Nomenclature of Branched Chain Alkanes

- Longest chain in the molecule is identified (called parent or root chain).



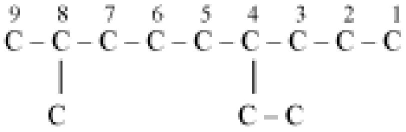
$$\overset{1}{CH_3}-\underset{CH_3}{\underset{|}{\overset{2}{CH}}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_2}-\underset{CH_2\,CH_3}{\underset{|}{\overset{6}{CH}}}-\overset{7}{CH_2}-\overset{8}{CH_2}-\overset{9}{CH_3}$$

- Numbering is done is such a way that the branched carbon atoms get the lowest possible numbers.



$$\overset{1}{C}-\underset{C}{\underset{|}{\overset{2}{C}}}-\overset{3}{C}-\overset{4}{C}-\overset{5}{C}-\underset{C-C}{\underset{|}{\overset{6}{C}}}-\overset{7}{C}-\overset{8}{C}-\overset{9}{C}$$

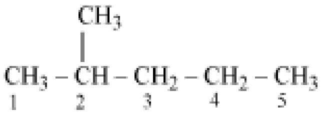
(Correct – 2, 6 positions)



$$\overset{9}{C}-\underset{C}{\underset{|}{\overset{8}{C}}}-\overset{7}{C}-\overset{6}{C}-\overset{5}{C}-\underset{C-C}{\underset{|}{\overset{4}{C}}}-\overset{3}{C}-\overset{2}{C}-\overset{1}{C}$$

(Not correct – 4, 8 position)

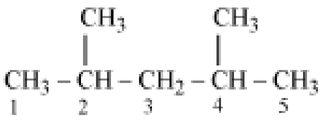
- The names of alkyl groups attached as a branch are then used as prefix in the name of parent chain. The position of the substituents is indicated by the appropriate numbers.



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

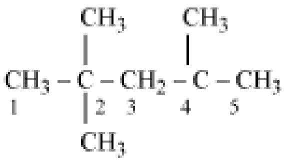
2-Methylpentane

- If two or more identical groups are present, then prefix *di* (for 2), tri (for 3), tetra (for 4) are used.



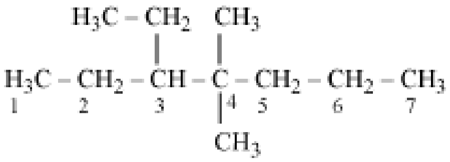
$$\underset{1}{CH_3}-\underset{2}{\overset{\overset{CH_3}{|}}{CH}}-\underset{3}{CH_2}-\underset{4}{\overset{\overset{CH_3}{|}}{CH}}-\underset{5}{CH_3}$$

2,4-Dimethylpentane



$$\underset{1}{CH_3}-\underset{\underset{CH_3}{|\,2}}{\overset{\overset{CH_3}{|}}{C}}-\underset{3}{CH_2}-\underset{4}{\overset{\overset{CH_3}{|}}{C}}-\underset{5}{CH_3}$$

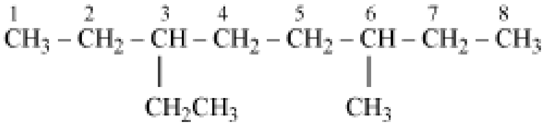
2,2,4-Trimethylpentane



$$\underset{1}{H_3C}-\underset{2}{CH_2}-\underset{3}{\overset{\overset{H_3C-CH_2}{|}}{CH}}-\underset{\underset{CH_3}{|\,4}}{\overset{\overset{CH_3}{|}}{C}}-\underset{5}{CH_2}-\underset{6}{CH_2}-\underset{7}{CH_3}$$

3-Ethyl-4,4-dimethylheptane

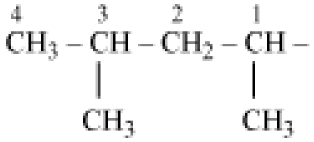
- Numbers are separated by commas.
- Lower number is given to the one coming first in the alphabetical listing.



$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{\underset{CH_2CH_3}{|}}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{6}{CH}}-\overset{7}{CH_2}-\overset{8}{CH_3}$$

3-Ethyl-6-methyloctane

- Carbon atom of the branch that attaches to the root alkane is numbered 1.

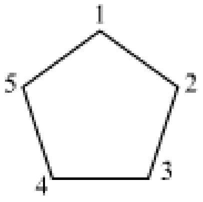


$$\overset{4}{CH_3}-\underset{\underset{CH_3}{|}}{\overset{3}{CH}}-\overset{2}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{1}{CH}}-$$

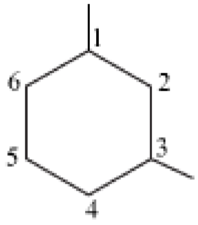
1, 3-Dimethylbutyl-

Nomenclature of Cyclic Compounds/ Cyclic Alkanes

- They are named by prefixing ‘cyclo’ to the corresponding straight chain alkane.



Cyclopentane



1,3-Dimethyl cyclohexane

Nomenclature of the Organic Compounds Having Functional Groups

- Parent chain of carbon atoms containing functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain.

- The decreasing order of priority for the functional groups is

$-COOH, -SO_3H, -COOR(R = \text{alkyl group}), COCl,$

$-CONH_2, -CN, -HC = O, > C = O, -OH, -NH_2, > C = C <, -C \equiv C -$

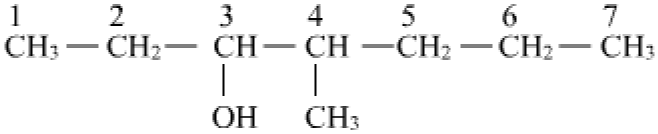
- The given table lists some functional groups and classes of organic compounds.

Class of compounds	**Functional group structure**	**IUPAC group prefix**	**IUPAC group suffix**
Alkanes	–	–	- ane
Alkenes	$>C = C<$	–	-ene
Alkynes	$-C \equiv C-$	–	-yne
Arenes	–	–	–
Halides	-X (X = F, Cl, Br, I)	halo	–
Alcohols	−OH	hydroxy	-ol

Aldehydes	−CHO	Formyl or oxo	-al
Ketones	>C = O	Oxo	-one
Nitriles	-C ≡ N	cyano	nitrile
Ethers	-R-O-R-	Alkoxy	−
Carboxylic acids	-COOH	carboxy	-oic acid
Carboxylate ions	$-COO^-$	−	−oate
Esters	-COOR	alkoxycarbonyl	-oate
Acyl halides	-COX (X = F, Cl, Br, I)	halocarbonyl	-oyl halide
Amines	$-NH_2$, >NH, >N-	amino-	−amine
Amides	$-CONH_2$, CONHR, -$CONR_2$	-carbamoyl	-amide

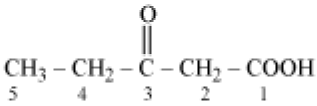
Nitro compounds	-NO_2	Nitro	−

- Examples



$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{OH}{\overset{3}{CH}}-\underset{CH_3}{\overset{4}{CH}}-\overset{5}{CH_2}-\overset{6}{CH_2}-\overset{7}{CH_3}$$

IUPAC name − 4-Methylheptan-3-ol



$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{\overset{O}{\overset{\|}{C}}}-\underset{2}{CH_2}-\underset{1}{COOH}$$

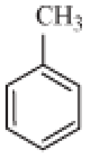
IUPAC name − 3-Oxopentanoic acid

$$\underset{6}{C}H\equiv\underset{5}{C}-\underset{4}{C}H=\underset{3}{C}H-C\underset{2}{H}=\underset{1}{C}H_2$$

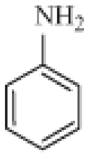
IUPAC name − Hexa −1,3-dien-5-yne

Nomenclature of Substituted Benzene Compounds

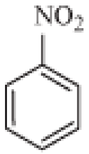
- The substituent is placed as prefix to the word benzene.



Methylbenzene

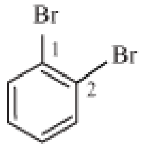


Aminobenzene

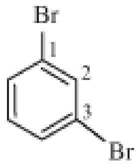


Nitrobenzene

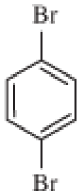
- When the benzene ring is di-substituted,



1,2-Dibromobenzene

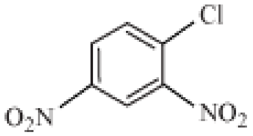


1,3-Dibromobenzene

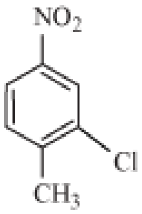


1,4-Dibromobenzene

- Substituent of the base compound is assigned number 1. The substituents appear in the name in alphabetical order. Then the other substituents are numbered in the direction in which the next substituent gets the lowest number.

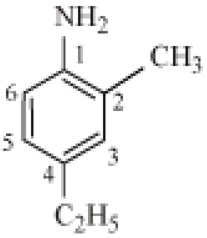


1-Chloro-2, 4- dinitrobenzene

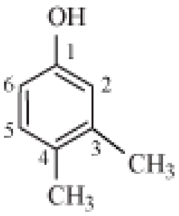


2-Chloro-1-methyl-4-nitrobenzene

- In some cases, common name of benzene derivatives is taken as the base compounds.

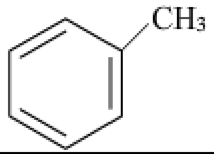
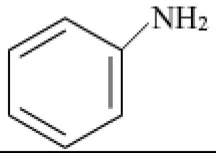
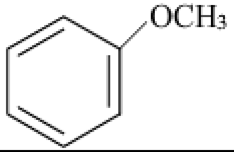
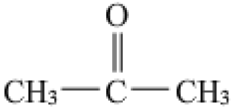
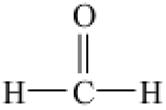


4-Ethyl-2-methylaniline



3, 4-Dimethylphenol

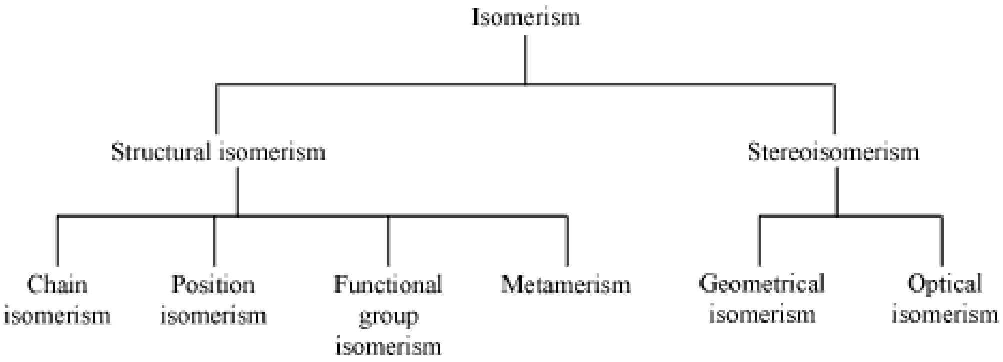
Trivial Names or Common Names of Compounds:

Compound	IUPAC Name	Trivial Name
	Metylbenzene	Toluene
	Aminobenzene	Aniline
	Methoxybenzene	Anisole
CH_3COOH	Ethanoic acid	Acetic acid
$HCOOH$	Methanoic acid	Formic acid
CH_3CHO	Ethanal	Acetaldehyde
 $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$	Propanone	Acetone
 $H-\overset{\overset{O}{\|}}{C}-H$	Methanal	Formic acid

Isomerism in Organic Compounds & Reaction Mechanism

Isomerism

Two or more compounds having the same molecular formula, but different properties are called isomers, and the phenomenon is called isomerism.

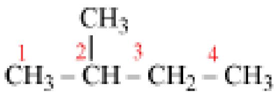


Structural Isomerism

- Compounds having the same molecular formula, but different structures are called structural isomers.
- **Chain isomerism:**
- Two or more compounds having the same molecular formula, but different carbon skeletons are referred to as **chain isomers**, and the phenomenon is called chain isomerism.
- Example −

$\overset{1}{\mathrm{CH_3}}\overset{2}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_2}}\overset{5}{\mathrm{CH_3}}$

Pentane



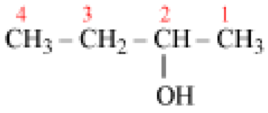
$\overset{1}{\mathrm{CH_3}} - \overset{\mathrm{CH_3}}{\overset{2|}{\mathrm{CH}}} - \overset{3}{\mathrm{CH_2}} - \overset{4}{\mathrm{CH_3}}$

2-Methylbutane

- **Position isomerism:**
- Two or more compounds differing in the position of functional group on the carbon skeleton are called **position isomers**, and the phenomenon is called position isomerism.
- Example −

$\overset{4}{\mathrm{CH_3}}\overset{3}{\mathrm{CH_2}}\overset{2}{\mathrm{CH_2}}\overset{1}{\mathrm{CH_2}}\mathrm{OH}$

Butan-1-ol



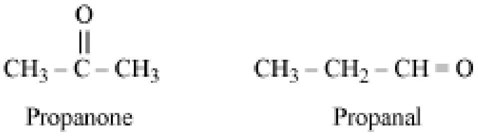
$\overset{4}{\mathrm{CH_3}} - \overset{3}{\mathrm{CH_2}} - \underset{\mathrm{OH}}{\underset{|}{\overset{2}{\mathrm{CH}}}} - \overset{1}{\mathrm{CH_3}}$

Butan-2-ol

- **Functional group isomerism:**

- Two or more compounds having the same molecular formula, but different functional groups are called **functional isomers** and the phenomenon is called functional isomerism.

- Example − propanone (ketone) and propanal (aldehyde); both have the same molecular formula C_3H_6O, but different functional groups



$CH_3-\overset{\overset{O}{||}}{C}-CH_3$ $\qquad$ $CH_3-CH_2-CH=O$

Propanone $\qquad$ Propanal

Another example −

CH_3CH_2OH	CH_3OCH_3
Ethanol	Methoxymethane
(Alcohol)	(Ether)

- **Metamerism:**

- Two or more compounds arising due to different alkyl chains on either side of the functional group in a molecule are called **metamers**, and the phenomenon is called metamerism.

- Example −

$CH_3OC_3H_7$	$C_2H_5OC_2H_5$
Methoxypropane	Ethoxyethane

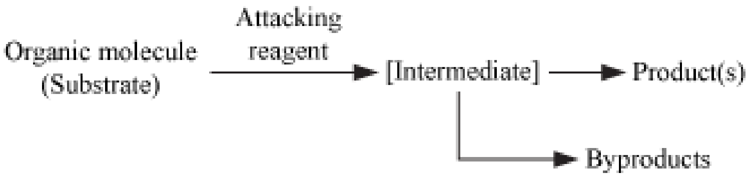
Both have the same molecular formula $C_4H_{10}O$, but have different alkyl chains on either side of the functional group (ether).

Stereoisomerism

- Compounds having the same molecular formula and having the same constitution and sequence of covalent bonds, but differing in relative positions of their atoms or groups in space are called **stereoisomers**. The phenomenon is called stereoisomerism.

- It can be classified as geometrical and optical isomerism.

Fundamental Concepts in Organic Reactions



Fission of a Covalent Bond

- **Heterolytic fission:** Bond breaks in such a way that the shared pair of electrons remains with one of the fragments

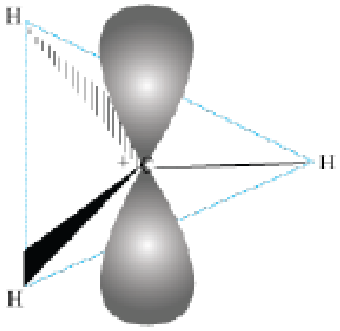
- A carbocation is the species having a carbon atom possessing sextet of electrons and a positive charge.
- Carbocations are classified as primary, secondary and tertiary.
- Example: Primary carbocation − $CH_3\overset{\oplus}{C}H_2$ (ethyl cation)

  Secondary carbocation − isopropyl cation, $(CH_3)_2\overset{+}{C}H$

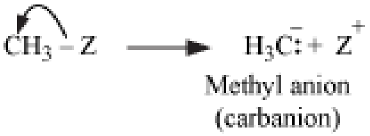
  Tertiary carbocation − *tert*-butyl cation, $(CH_3)_3\overset{+}{C}$
- The order of carbocation stability is,

$$\overset{+}{C}H_3 < CH_3\overset{+}{C}H_2 < (CH_3)_2\overset{+}{C}H < (CH_3)_3\overset{+}{C}$$

- The positively charged carbocation is *sp*^{2} hybridised. Thus, the carbocations have trigonal shape.
- Carbocations are highly unstable and reactive species.
- Due to inductive and hyperconjugation effects, the alkyl groups directly attached to the positively charged carbon stabilise the carbocations.
- The shape of methyl carbocation is as follows:



- **Heterolytic cleavage** can also give a species in which the carbon gets the shared pair (called carbanion).



- Carbanion is a carbon species carrying a negative charge on the carbon atom.
- It is an unstable and reactive species.
- The negatively charged carbanion is sp^3 hybridised.
- **Homolytic Cleavage:**
- One of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms.
- The movement of the single electron takes place, instead of a pair of electrons.
- Homolytic cleavage can be represented as,

- Free radicals are the neutral species (atoms or groups) which contain an unpaired electron. They can be classified as primary, secondary and tertiary.
- The order of stability of alkyl free radicals increases as,

$\dot{C}H_3$ <	$\dot{C}H_2CH_3$ <	$\dot{C}H(CH_3)_2$ <	$\dot{C}(CH_3)_3$
Methyl	Ethyl	Isopropyl	*Tert*-butyl
free radical	free radical	free radical	free radical

- Reactions which proceed by homolytic fission are called free radical or homopolar or non-polar reactions.

Nucleophiles and Electrophiles

- A nucleophile (Nu:) is a reagent that brings an electron pair, i.e., nucleus- seeking. Such a reaction is called a nucleophilic reaction.

  Example: Hydroxide (HO^-), cyanide (CN^-), carbanion $(R_3\bar{C}:)$, $H_2\ddot{O}:$, $R_3N:$, $R_2\ddot{N}H$

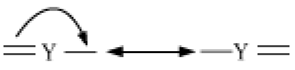
- An electrophile (E^+) is a reagent that takes away an electron pair, i.e., electron- seeking. Such a reaction is called an electrophilic reaction.

  Example: Carbocation $(\overset{+}{C}H_3)$, neutral molecules having functional groups like carbonyl group $(>C=O)$ or alkyl halides

Electron Movement, Electron Displacement Effects in Organic Compounds

Electron Movement in Organic Compounds

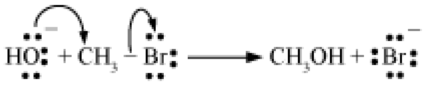
- Movement of electrons can be shown by curved arrow notation.
- Curved arrow shows how changes in bonding occur due to electronic redistribution during the reaction.
- Curved arrow starts from the point from where an electron pair is shifted and ends at a location to which the pair of electrons may move.
- From π bond to adjacent bond position



- From π bond to adjacent atom

- From atom to adjacent bond position

- For example,



Electron Displacement Effects in Covalent Bonds

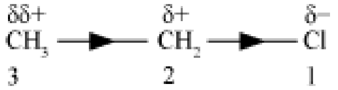
- Inductive effect and resonance effects are the examples of permanent electron displacement effects.

- Temporary electron displacement in a molecule when a reagent approaches to attack is called electromeric effect or polarisability effect.

Inductive Effect

- In a covalent bond formed by the atoms of different electronegativity, the electron density moves towards the more electronegative atom of the bond.

- A shift of electron density results in a polar covalent bond.



- C − Cl is a polar covalent bond.

- δ (delta) represents fractional electronic charge.

- (δ +) represents some positive charge and (δ −) represents some negative charge.

- The arrow pointing from δ + from δ − represents the shift of electron density.

- The polarisation of σ- bond caused by the polarisation of adjacent σ- bond is called as the **inductive effect**.

- Ability of the substituent(s) to either withdraw or donate electron density to the attached carbon atom is related to inductive effect.

- On the basis of inductive effect, the substituent can be classified as **electron-withdrawing** or **electron donating** groups relative to hydrogen.

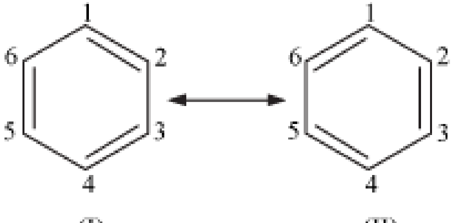
- Electron withdrawing groups −−− Halogens, nitro (-NO_2), cyano (-CN), carboxy (-COOH), ester (-COOR)

- Electron donating groups −−− Alkyl groups such as methyl (-CH_3) and ethyl (-C_2H_5)

Resonance Structure, Resonance Effect, Electromeric Effect, and Hyperconjugation

- Benzene has a uniform C − C bond length of 139 pm [an intermediate value between C − C single (154 pm) and C = C double (134 pm) bonds].

- It can be represented equally by energetically identical structures I and II.

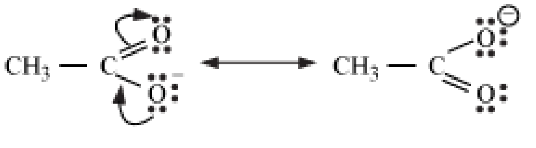


(I) (II)

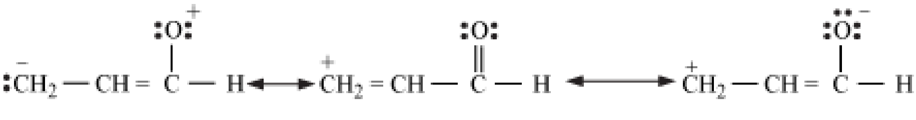
- I and II are called resonance structures (canonical structures or contributing structures).
- Resonance structures are hypothetical. They individually do not represent any real molecule.

- They contribute to the stability of the compound.

- Some more examples of resonance:



(I) (II)



- The energy of the actual structure (resonance hybrid) of the molecule is lower than that of any of the canonical structures.

- Resonance energy is the difference in energy between the actual structure and the lowest energy resonance structure.

- More the number of resonance structures, more is the resonance energy.

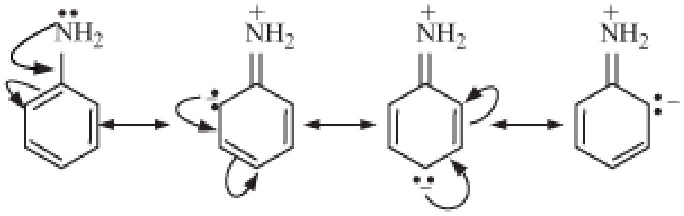
Resonance Effect (or Mesomeric Effect)

- Defined as the 'polarity produced in the molecule by the interaction of two π-bonds or between a π-bond and lone pair of electrons present on an adjacent atom'

- Designated as R or M effect

- **Positive Resonance Effect (+R Effect)**

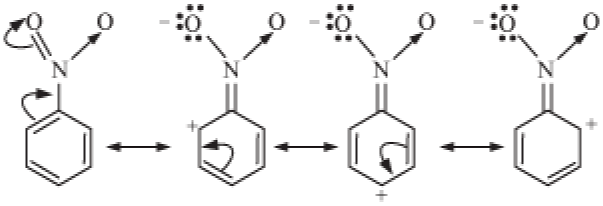
- Transfer of electrons is away from an atom or substituent group attached to the conjugated system.



- + R effect showing groups: − halogen, − OH, − OR, − OCOR, − NH_2, − NHR, − NR_2, − NHCOR

- **Negative Resonance Effect (− R Effect)**

- Transfer of electrons is towards the atom or substituent group attached to the conjugated system.



- − R effect showing groups: − COOH, − CHO, , − CN, − NO_2

Electromeric Effect

- Temporary effect

- Shown by the organic compounds having a multiple bond (a double or triple bond) in the presence of an attacking reagent only

- Designated as E effect

- Defined as the complete transfer of a shared pair of π-electrons to one of the atoms joined by multiple bonds on the demand of an attacking reagent

- **Positive Electromeric Effect (+ E Effect)**

- π- electrons of the multiple bonds are transferred to that atom to which reagent gets attached.
- For example,

- **Negative Electromeric Effect (− E Effect)**

- π-electrons of the multiple bonds are transferred to that atom to which attacking reagent does not get attached.

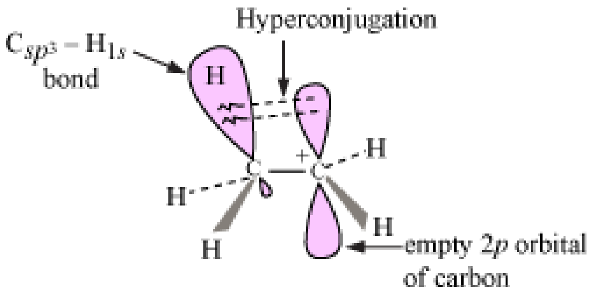
- For example,

Hyperconjugation

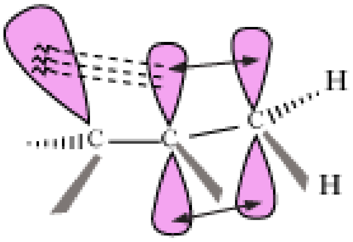
- A permanent effect

- Involves the delocalisation of σ − electrons to C − H bond of an alkyl group directly attached to an unsaturated system or to an atom with an unshared p-orbital (shown in figure)

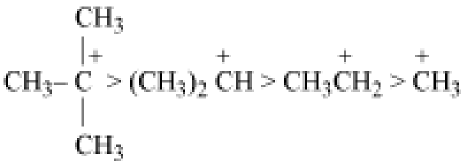
Hyperconjugation in ethyl cation:



Hyperconjugation in propene:



- On the basis of hyperconjugation effect, the relative stability of carbocations is



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{+}{C}}} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

-
- Greater the number of alkyl groups attached to a positively charged carbon atom, greater is the hyperconjugation and stabilization of the cation.
- Hyperconjugation is also called no bond resonance.

Methods of Purification of Organic Compounds

Sublimation

- Used to separate sublimable compounds from non-sublimable compounds

- **Principle:** On heating, sublimable solid substances change from solid to vapour state without passing liquid state.

Crystallisation

- Used for the purification of solid organic compounds

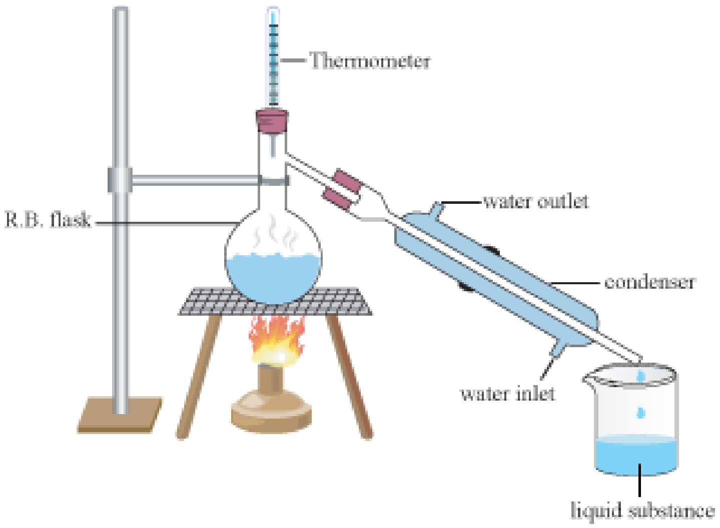
- Based on the difference in solubilities of the compound and impurities in the solvent

- The impure compound is dissolved in a 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 saturated solution, pure compound gets crystallised and is removed by filtration.

Distillation

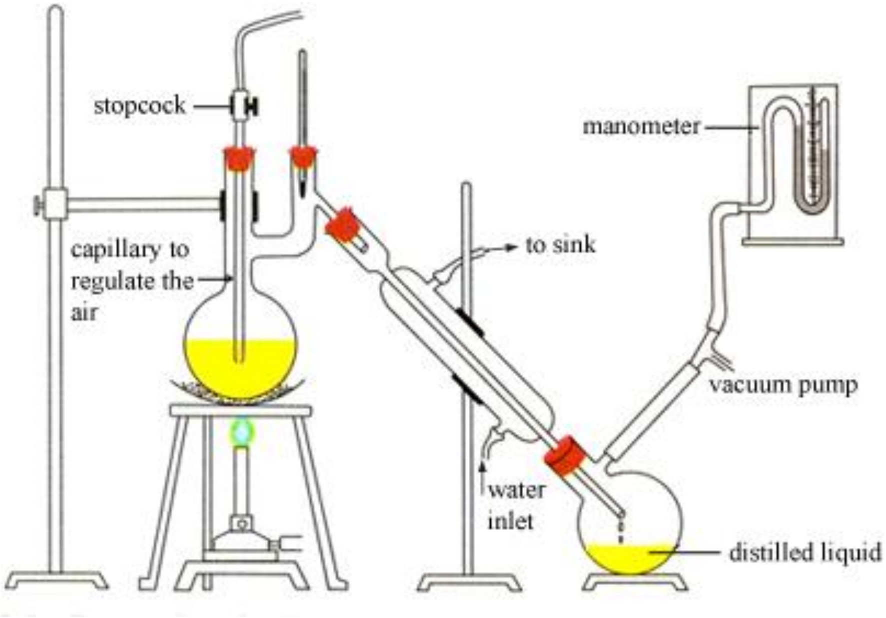
- Used to separate
- volatile liquids from non-volatile impurities
- liquids having sufficient differences in their boiling points

Example: separation of chloroform (b.p = 334 K) and aniline (b.p.= 457 K)



Distillation under Reduced Pressure

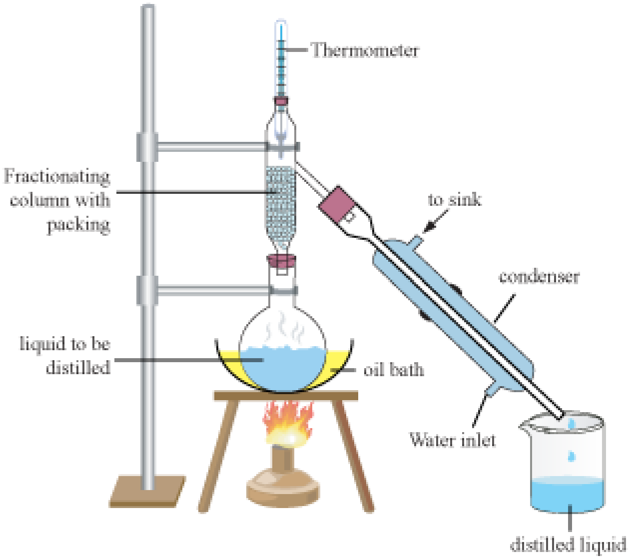
- Used to purify liquids having very high boiling points and those which decompose at or below their boiling points
- Here, the liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surfaces. Liquid boils at the temperature at which vapour pressure is equal to external pressure.



- Used to separate glycerol from spent-lye in soap industry

Fractional Distillation

- Used to separate the liquids of which the difference in boiling points is not too much
- Vapours of a liquid mixture are passed through a fractionating column (fitted over the mouth of the round bottom flask) before condensation (shown in figure).

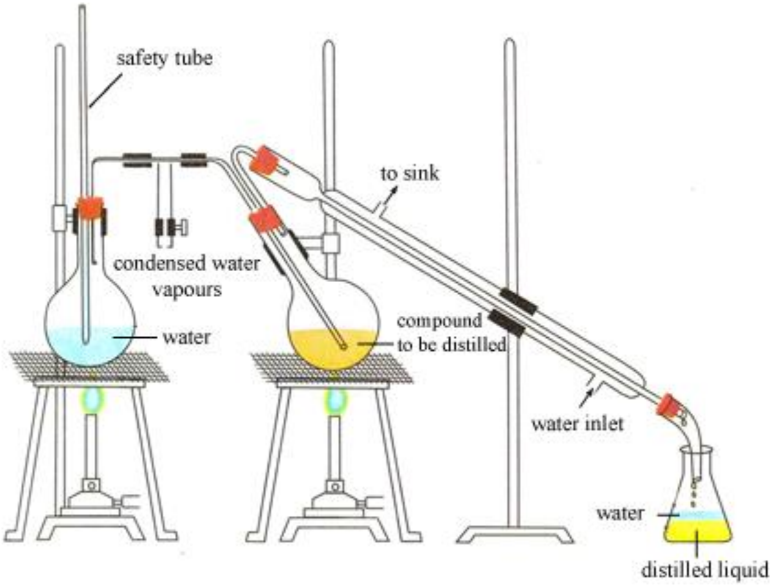


- This technique is used to separate different fractions of crude oil in petroleum industry.

Steam Distillation

- Used to separate substances which are steam volatile and are immiscible with water

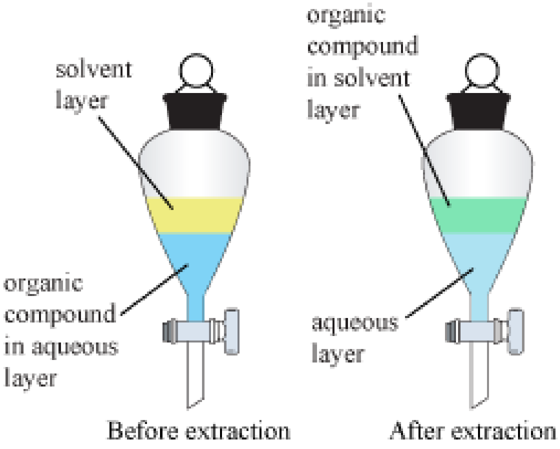
- Steam volatile component is volatilised. The vapours get condensed in the condenser and are collected as liquid in the conical flask.



- Used to separate aniline from aniline-water mixture

Differential Extraction

- An organic compound can be separated from its aqueous medium by shaking it with an organic solvent in which it is more soluble than in water.



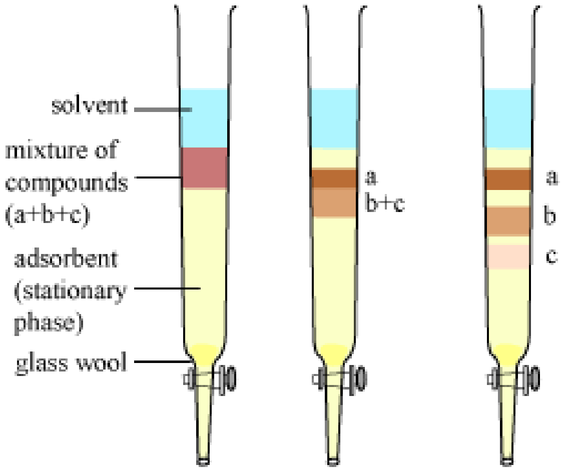
Chromatography

- Used to separate mixtures into their components, purify compounds, and also to test the purity of compounds

- Two important classes − Adsorption chromatography and partition chromatography

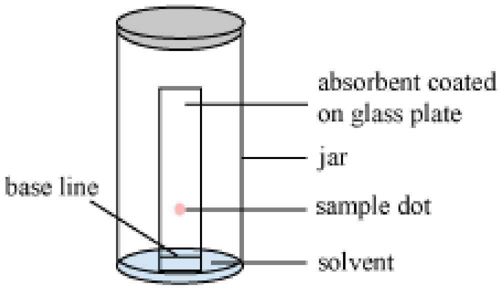
Adsorption Chromatography

- Based on the fact that different compounds are adsorbed on an adsorbent to different degrees
- Commonly used adsorbents − Silica gel and alumina
- A mobile phase is allowed to move over a stationary phase (adsorbent). Then the components of the mixture move by varying distance over the stationary phase.
- Two main types − Column chromatography and thin layer chromatography
- **Column chromatography** − This technique involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube.

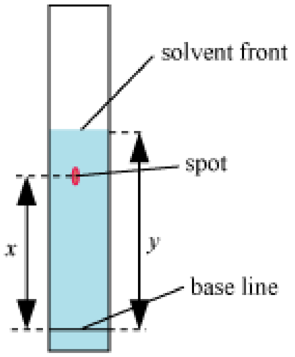


Most readily adsorbed gas (here '*a*') is retained at the top and others (*b* and *c*) come down to various distances in the column (shown in above figure).

- **Thin layer chromatography** − Involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate (shown in figure)



Developed chromatogram:

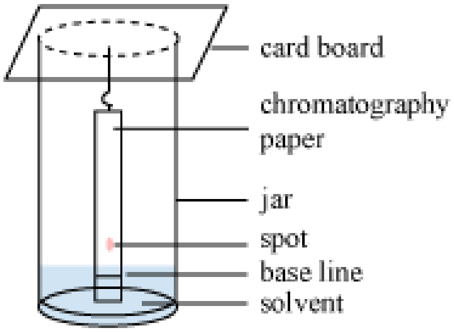


- The relative adsorption of each component of the mixture i.e., retardation factor (or R_f value) is given by,

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

Partition Chromatography

- Based on continuous differential partitioning of components of mixture between stationary and mobile phases
- Paper chromatography is a type of partition chromatography.
- For paper chromatography, chromatography paper (a special type of paper) is used which contains water trapped in it and acts as the stationary phase.



- The chromatography paper retains different components according to their differing partition in the two phases.
- The developed paper is called chromatogram.

Qualitative Analysis of Compounds

Detection of Carbon and Hydrogen

- Detected by heating a compound with copper (II) oxide
- Carbon present in the compound gets oxidised to CO_2, which is then tested with lime water (lime water turns milky)

$$C + 2CuO \xrightarrow{\Delta} 2Cu + CO_2$$
$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

- Hydrogen present in the compound is oxidised to water, which is then tested with anhydrous copper sulphate (anhydrous copper sulphate turns blue)

$$2H + CuO \xrightarrow{\Delta} Cu + H_2O$$
$$5H_2O + \underset{\text{White}}{CuSO_4} \longrightarrow \underset{\text{Blue}}{CuSO_4 \cdot 5H_2O}$$

Detection of Other Elements (N, S, P and Halogens)

Lassaigne’s Test

- Elements (N, S, P and halogens) present in the organic compound are converted from the covalent form to the ionic form by fusing the reaction with Na metal.

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

- NaCN, Na_2S and NaX, so formed, are extracted from the fused mass by boiling it with distilled water. The extract obtained is known as **sodium fusion extract**.
- **Test for Nitrogen (N)**
- Sodium fusion extract is boiled with $FeSO_4$.
- It is then acidified with sulphuric acid

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

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3 \cdot xH_2O}$$

- Formation of Prussian blue colour confirms the presence of nitrogen.
- **Test for Sulphur (S)**
- Sodium fusion extract is acidified with acetic acid and lead acetate is added to it.

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

Formation of black precipitate of lead sulphide indicates the presence of sulphur.

- When sodium fusion extract is treated with sodium nitroprusside, violet colour appears.

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

Appearance of violet colour indicates the presence of sulphur.

- **When both N and S are present** in an organic compound, sodium thiocyanate (NaSCN) is formed.

$$Na + C + N + S \longrightarrow NaSCN$$

NaSCN then gives blood red colour, and not Prussian blue, since there are no free cyanide ions.

$$Fe^{3+} + SCN^- \longrightarrow \underset{\text{Blood red}}{[Fe(SCN)]^{2+}}$$

- **Test for Halogens**
- Sodium fusion extract is acidified with HNO_3 and then treated with $AgNO_3$.

$$X^- + Ag^+ \longrightarrow AgX$$
$$X = Cl, Br \text{ or } I$$

- A white precipitate (soluble in ammonium hydroxide) indicates the presence of **chlorine**.
- A yellowish precipitate (sparingly soluble in ammonium hydroxide) indicates the presence of **bromine**.
- A yellow precipitate (insoluble in ammonium hydroxide) indicates the presence of **iodine**.
- **Test for Phosphorus**
- Compound is heated with an oxidising agent (Sodium peroxide).
- Phosphorus is then oxidised to phosphate.
- The solution of phosphate is then boiled with HNO_3 and then treated with ammonium molybdate.

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

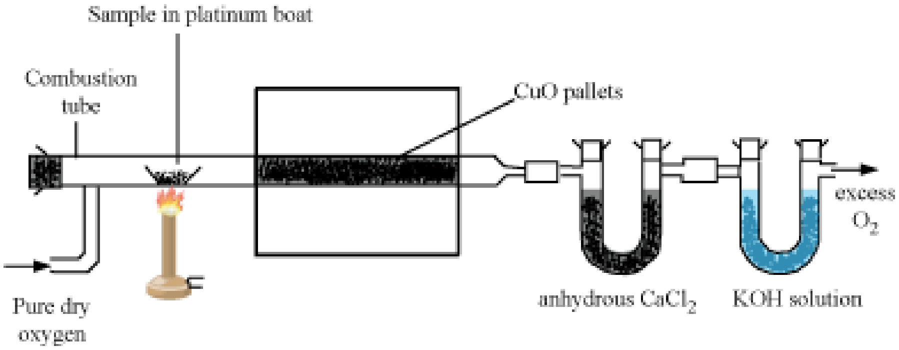
$$H_3PO_4 + \underset{\substack{\text{Ammonium} \\ \text{molybdate}}}{12(NH_4)_2MoO_4} + 21HNO_3 \longrightarrow$$

$$\underset{\substack{\text{Ammonium} \\ \text{phosphomolybdate}}}{(NH_4)_3PO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12H_2O$$

Quantitative Analysis - Carbon and Hydrogen; Nitrogen

Carbon and Hydrogen

- Organic compound of known mass is burnt in the presence of excess of oxygen and copper (**II**) oxide



- Carbon and hydrogen (present in the compound) gets oxidised to CO_2 and water respectively.

$$C_xH_y + \left(x+\frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

- The mass of water produced can be determined by passing the mixture through a weighed U-tube containing anhydrous $CaCl_2$.

- U-tube containing concentrated solution of KOH absorbs CO_2.

- The increase in the mass of $CaCl_2$ and KOH gives the amounts of water and CO_2, from which the percentages of C and H can be calculated as follows:

  Mass of the organic compound = m g

  Mass of H_2O = m_1 g

  Mass of CO_2 = m_2 g

  ∴Percentage of carbon = $\frac{12\times m_2\times 100}{44\times m}$

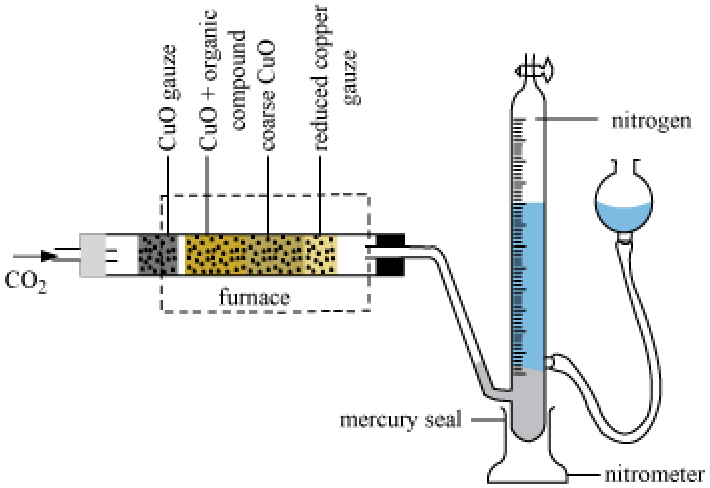
  And, percentage of hydrogen = $\frac{2\times m_1\times 100}{18\times m}$

  Nitrogen

- **Dumas Method**

- When heated with CuO in an atmosphere of CO_2, the nitrogen-containing organic compound yields free nitrogen, CO_2 and H_2O.

$$C_xH_yN_z\left(2x+\frac{y}{2}\right)CuO \longrightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x+\frac{y}{2}\right)Cu$$



- The mixture of produced N_2 and CO_2 gases is collected over an aqueous solution of KOH so that CO_2 is absorbed by it.

- Nitrogen gas is collected in the upper part of the graduated tube.

Mass of the organic compound = m g

Volume of nitrogen collected = V_1 mL

Room temperature = T_1K

Volume of nitrogen at STP = $\frac{p_1V_1 \times 273}{760 \times T_1}$

= V mL (Suppose)

Where,

p_1 = Pressure of nitrogen

V_1 = Volume of nitrogen

p_1 = Atmospheric pressure − Aqueous tension

22400 mL N_2 at STP weighs 28g.

V mL N_2 at STP weigh = $\frac{28 \times V}{22400}$ g

∴Percentage of nitrogen $= \frac{28 \times V \times 100}{22400 \times m}$

- **Kjeldahl's method**
- Compound containing nitrogen is heated with conc.H_2SO_4.
- Nitrogen gets converted into $(NH_4)_2SO_4$.
- Resulting acidic mixture is heated with an excess of NaOH.
- The liberated NH_3 gas is absorbed in an excess of a standard solution of H_2SO_4.
- Amount of NH_3 produced is determined by estimating the amount of H_2SO_4 consumed in the reaction, which is calculated by subtracting the un-reacted amount of H_2SO_4 from its total amount.

$$\text{Organic compound} + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$
$$\xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$
$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

- **Calculations:**

Mass of the organic compound = m g

Volume of H_2SO_4 of molarity M taken = V mL

Volume of NaOH of molarity M used for titration of excess of H_2SO_4 = V_1 mL

V_1 mL of NaOH of molarity M

$= \frac{V_1}{2}$ mL of H_2SO_4 of molarity M

Volume of H_2SO_4 of molarity M unused = $\left(V - \frac{V_1}{2}\right)$ mL

$\left(V - \frac{V_1}{2}\right)$ mL of H_2SO_4 of molarity M

= $2\left(V-\frac{V_1}{2}\right)$ mL of NH_3 solution of molarity *M*

1000 mL of 1 M NH_3 solution contains 17g NH_3 or 14g of N.

$2\left(V-\frac{V_1}{2}\right)$ mL of NH_3 solution of molarity *M* contains

$\frac{14\times M\times 2\left(V-\frac{V_1}{2}\right)}{1000}$ g of N.

∴Percentage of N $=\frac{14\times \mathrm{M}\times 2\left(V-\frac{V_1}{2}\right)}{1000}\times\frac{100}{m}$

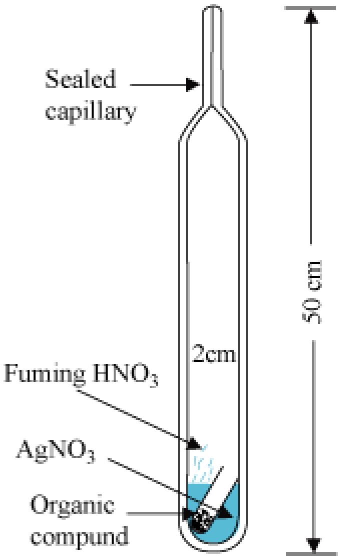
$$=\frac{1.4\times \mathrm{M}\times 2\left(V-\frac{V_1}{2}\right)}{m}$$

- This method is not applicable to the compounds containing nitrogen in nitro and azo groups; and to the nitrogen-containing ring (pyridine). This is because the nitrogen present in these compounds does not change to $(NH_4)_2SO_4$ under these conditions.

Quantitative Analysis: Halogens, Sulphur, Phosphorus and Oxygen

Halogens (Carius Method)

- An organic compound (of known mass) is heated with fuming HNO_3 in the presence of $AgNO_3$ (contained in a Carius tube) in a furnace. (shown in the figure)



- Halogens present in the compound form the corresponding silver halide (AgX).

- AgX is filtered, washed, dried and weighed.

- Calculations:

  Mass of the organic compound = m g

  Mass of AgX formed = m_1g

  1 mol of AgX contains 1 mol of ‘X’

  Mass of halogen in m_1 g of AgX $= \frac{\text{Atomic mass of 'X'} \times m_1 \text{ g}}{\text{Molecular mass of AgX}}$

  Percentage of halogen $= \frac{\text{Atomic mass of 'X'} \times m_1 \times 100}{\text{Molecular mass of AgX} \times m}\%$

  Sulphur

- An organic compound (of known mass) is heated in a Carius tube with sodium peroxide or fuming HNO_3.

- Sulphur present in the compound gets oxidised to H_2SO_4, and it gets precipitated as $BaSO_4$ by adding excess of $BaCl_2$ solution in water.

- The precipitate is filtered, washed, dried and weighed.

- Calculations:

  Mass of the organic compound taken = m g

  Mass of the barium sulphate formed = m_1g

  1 mole of $BaSO_4$ = 233 g of $BaSO_4$ = 32 g of sulphur

  m_1g of $BaSO_4$ contains $\frac{32 \times m_1}{233}$ g of sulphur.

  Percentage of sulphur $= \frac{32 \times m_1 \times 100}{233 \times m}\%$

  Phosphorus

- An organic compound (of known mass) is heated with fuming HNO_3.
- Phosphorus present in the compound is oxidised to phosphoric acid, which is precipitated as ammonium phosphomolybdate, $(NH_4)_3PO_4.12\ MoO_3$ [by adding NH_3 and ammonium molybdate].
- Calculations:

  Mass of the organic compound taken = m g

  Mass of $(NH_4)_3\ PO_4.12\ MoO_3$ = m_1g

  Molar mass of $(NH_4)_3\ PO_4.12\ MoO_3$ = 1877 g

  Percentage of phosphorus $= \frac{31 \times m_1 \times 100}{1877 \times m}\%$

  Oxygen

- Usually estimated (in terms of percentage) by the difference between the total percentage-composition (100) and the sum of the percentages of all other elements.
- Can be estimated directly as well: If an organic compound (of known mass) is heated in a stream of N_2 gas, it gets decomposed to form O_2 gas and other gaseous products.

$$\text{Compound} \xrightarrow{\text{heat}} O_2 + \text{Other gaseous products}$$

Passed over red hot coke

$$\left.2C + O_2 \xrightarrow{1373\ \text{K}} 2CO\right] \times 5 \qquad \text{(i)}$$

Passed through warm iodine pentoxide

$$\left.I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2\right] \times 2 \qquad \text{(ii)}$$

- Two moles of CO_2 are obtained from one mole of O_2, i.e., 88 g of CO_2 is obtained if 32 g of O_2 is liberated.

- Calculations:

  Mass of the organic compound = *m* g

  Mass of CO_2 produced = m_1g

  ∴ m_1 g of CO_2 is obtained from $\frac{32 \times m_1}{88}$ g of O_2

  ∴ Percentage of O_2 $= \frac{32 \times m_1 \times 100}{88 \times m}\%$