



# NOTES ON ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

The hydrides of carbon (hydrocarbons) and their derivatives are called organic compounds. The branch of chemistry which deals with these compounds is called organic chemistry. Berzelius (1808) defined organic chemistry as the chemistry of substances found in living matter and gave the vital force theory. Synthesis of urea. The first organic compound synthesised in laboratory, by Wohle gave death blow to the vital force theory.

# $(NH_4)_3SO_4 + 2KCNO \xrightarrow{-K_2SO_4} 2NH_4CNO \xrightarrow{\Delta} NH_2CONH_4$

Acetic acid is the first organic compound synthesized from its elements.

### Reasons for Large Number of Organic <mark>Compounds</mark>

(a) **Catenation** It is the tendency of self-combination and is maximum in carbon. A carbon atom can combine with other carbon atoms by single, double or triple bonds. Thus, it forms more compounds than the others.

(b) **Tetravalency and small size** Carbon being tetravalent, is capable of bonding with four other C atoms or some other monovalent atoms. Carbon can form compound with oxygen. Hydrogen, chlorine, sulphur, nitrogen and phosphorus. These compounds have specific properties depending upon the nature of the element or group attached with the carbon. Furthermore, these compounds are exceptionally stable because of the small size of carbon.

#### **General Characteristics of Organic Compounds**

- 1. These are the compounds of carbon with H, O, N, S, P, F, CI, Br and 1.
- 2. These are generall<mark>y found in living organisms. e.g., carbohydrates</mark>, proteins etc.
- 3. These may be gases, liquids or solids.
- 4. Being covalent in nature, these have low boiling point and melting point and soluble in organic solvents.
- 5. These are generally volatile and inflammable.
- 6. They do not conduct electricity because of the absence of free ions.
- 7. They possess distinct colour and odour.

# **Classification of Organic Compounds**

# 1. On the Basis of Number of C Attached

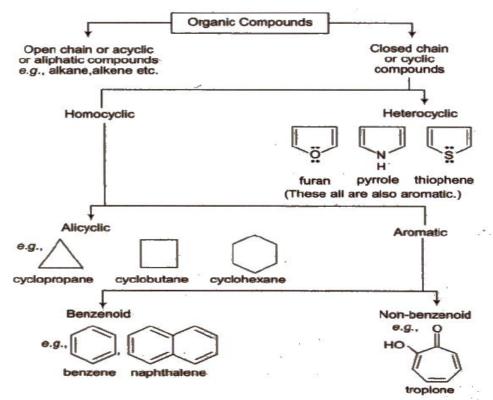
(i) **Primary carbon atom** When carbon atom is attached with one other carbon atom only, it is called primary or 1° carbon atom.

(ii) **Secondary carbon atom** When carbon atom is attached with two other carbon atoms, it is called secondary or 2° carbon atom.

(iii) **Tertiary carbon atom** When carbon atom is attached with three other carbon atoms, it is called tertiary or 3° carbon atom.

(iv) **Quaternary carbon atom** When carbon atom is attached with four other carbon atoms, it is called quaternary or 40 carbon atom.





Reactivity order of carbon atoms is as follows  $3^{\circ} > 2^{\circ} > 1^{\circ}$ .

$$\stackrel{1^{\circ}}{CH_{3}} = \stackrel{2^{\circ}}{CH_{2}} = \stackrel{CH_{3}}{CH_{3}} = \stackrel{1^{\circ}}{CH_{3}} = \stackrel{1^{\circ}}{C$$

#### On the Basis of Position of Functional Group

(i) α – carbon Carbon which is directly attached to the functional group.
(ii) β- carbon Carbon which is directly attached to the n-carbon.

#### **Classification of Hydrogen Atoms**

- 1°-hydrogen (primary) attached to 10-carbon,
- 2°-hydrogen (secondary) attached to 2°-carbon.
- **3°-hydrogen** (tertiary) attached to **3°**·carbon.
- α-hydrogen(s) Hydrogens which are attached to n-carbon atom.
- $\beta$  hydrogen(s) Hydrogens which are attached to ~-carbon atom.

$$\stackrel{\beta}{CH_3}$$
  $\stackrel{\alpha}{\longrightarrow} \stackrel{\alpha}{CH_2}$   $\stackrel{\alpha}{\longrightarrow} \stackrel{CH_2}{\longrightarrow} \stackrel{COOH}{CH_3}$   $\stackrel{\alpha}{\longrightarrow} \stackrel{\alpha}{CH_2}$   $\stackrel{COOH}{\longrightarrow}$ 

#### **Functional Group**

The atom e.g., -CI, -Br etc., or group of atoms e.g., -COOH, – CHO, which is responsible for the chemical properties of the molecule, is called functional group.

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Double and triple bonds are also functional groups.

 $R - F \leftarrow$  functional group.

R is called alkyl group, it contains only single bond; alkenyl group if contains double bond and alkynyl group if contains triple bond.

# **Homologous Series**

The series in which the molecular formula of adjacent members differ by a – CH<sub>2</sub> unit, is called homologous series and the individual members are called homologous.

# The general characteristics of this series are :

1. All the homologues contain same functional group. That's why their chemical properties are almost similar.

2. All the members of a series have same general formula

3. All the members can be prepared by almost similar methods.

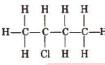
4. With increase in the molecular weight of a series, the physical properties varies gradually.

# **Representation of Different Formulae**

An organic compounds can be repres<mark>ented by the following w</mark>ays :

#### 1. Complete formula

In it, all the bonds present between any two atoms are shown clearly.



# 2. Condensed Formula

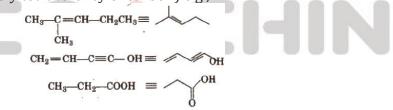
In it, all the bonds are not shown clearly.

CH<sub>3</sub>CH CH<sub>2</sub>CH<sub>3</sub> Cl Cl CH<sub>3</sub>CH(Cl)CH<sub>2</sub>CH<sub>3</sub>

# 3. Bond Line Formula

In it, every fold and free terminal represents a carbon and lines represent the bonds. e.g.,

In such formulae, it is assumed that required number of H-atoms are present, where ever, they are necessary (to satisfy tetravalency of carbon) e.g.,



#### Nomenclature of Organic Compounds Trivial System

It is the oldest system in which names are derived from source or some property. These are mainly derived from Latin or Greek names e.g., acetic acid (acetum = vinegar), oxalic acid (oxalic), malic acid (pyrusmalus), citric acid (citric), formic acid (obtained from red ant (formicidae)],



# IUPAC System

The IUPAC (International Union of Pure and Applied Chemistry) system, given in 1957, is superior and widely used. IUPAC amends these rules from time to time. Here. we are following the 1993 recommendations of IUPAC nomenclature.

Following rules are used to write the IUPAC name of an organic compound.

#### Rule I

**Longest chain rule** The chain containing the principal functional group, secondary functional group and multiple bonds as many as possible is the longest possible chain.

In the absence of functional group, secondary group and multiple bonds, the chain containing the maximum number of C-atoms will be the longest possible chain

Choose the word root from the table given below for the longest possible chain.

# Word Root for Carbon Chain

Chain length	Word root	Chain length	Word root
C1	Meth-	C <sub>7</sub> .	Hept
C <sub>2</sub>	Eth-	C <sub>8</sub>	· Oct · · ·
C <sub>3</sub>	Prop-	C <sub>9</sub>	Non
C4	But-	C <sub>10</sub>	Dec
C <sub>5</sub>	Pent	C11	Undec
C <sub>6</sub>	Hex-	C12	Dodec

### Rule 2

Lowest number rule Numbering is done in such a way so that

1. branching if present gets the lowest number.

2. the sum of numbers of side chain is lowest.

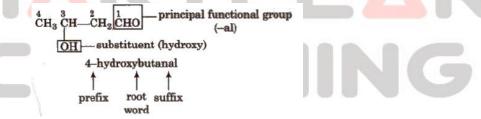
3. principal functional group gets the lowest number.

# Rule 3.

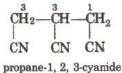
**Naming the prefixes and suffixes** Prefix represents the substituent and suffix is used for principal functional group.

Primary prefixes are cycle, bicycle, di, tri, tetra, tries. tetrakis etc.

Primary suffix are ene, ane, or yne used for double, single and triple bonds respectively. Hence. according to the rules. given above, the IUPAC name of a compound can be written as or Prefixes + Root word + Suffixes Primary prefix + secondary prefix + Root word + primary suffix + secondary suffix



If more than two similar functional groups are present, all the groups are considered as substituent, e.g.,

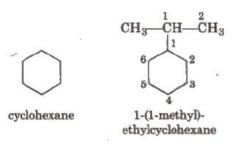


#### Naming Alicyclic Compounds

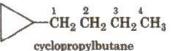
For alicyclic compounds, prefix cyclo is used e.g.,







If the alkyl chain contains a greater number of C-atoms than the ring, the ring is designated as substituent, e.g.,



If side chain contains a multiple bond or a functional group, the ring is treated as a substituent e.g.

CH<sub>3</sub>

Other examples are



# Naming Aromatic Compounds

IUPAC accepted their common trivial names e.g.,  $NH_2$ OH  $CH_3$ aniline phenol COOH CHO CN NO<sub>2</sub> benzoic acid benzaldehyde benzonitrile nitrobenzene CH2CH2CH2Br 1,4-dichlorobenzenel-bromo-3-(4-chlorophenyl) propane

#### Isomerism

The compound having same molecular formula but differ in properties are known as isomers and the phenomenon is known as isomerism.

There are two main types of isomerism i.e.,

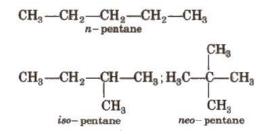
#### **1. Structural Isomerism**

In this type of isomerism, compounds have same molecular formula but different structures. It can further be of following types:

# (i) Chain Isomerism

It arises when two or more compounds have similar molecular formula but different carbon skeletons, e.g.,





#### (ii) Position Isomerism

When two or more compounds have same molecular formula but different position of functional groups or substituents, they are called positional isomers and the phenomenon is called position isomerism

$$\begin{array}{c} C_{3}H_{7}Cl\\ CH_{8}--CH_{2}--CH_{2}--Cl\\ 1-chloropropane\\ CH_{3}--CH--CH_{3}\\ i\\ Cl\\ 2-chloropropane \end{array}$$

#### (iii) Functional Isomerism

It arises when two or more compounds have the same molecular formula but different functional group. e.g., C<sub>3</sub>H<sub>6</sub>O represents an aldehyde and a ketone as

C<sub>2</sub>H<sub>6</sub>O represents an alcohol and an ether.

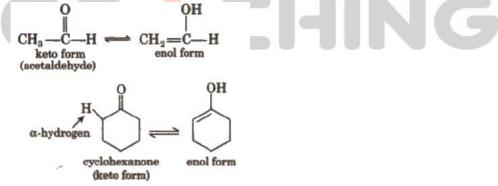
#### (iv) Metamerism

It arises due to different alkyl groups on either side of the same functional group in a molecule, e.g.,

$$CH_3 - O - C_3H_7, C_2H_5 - O - C_2H_5$$

#### (v) Tautomerism

It is a special type of functional isomerism which arises in carbonyl compounds containing  $\alpha$  – H atom e.g.,



#### 2. Stereoisomerism

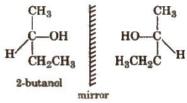
The compounds having same molecular formula but different spatial arrangement of atoms or groups are called stereoisomers and the phenomenon is called stereoisomerism.



Stereoisomerism is of three types : optical isomerism, geometrical isomerism and conformations.

#### (i) Optical Isomerism

Compounds having similar physical and chemical properties but. differ only in behaviour towards plane polarised light are called enantiomer & or optical isomers and the phenomenon is known as optical isomerism. e.g.,

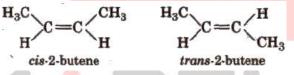


The isomer which rotate +he plane of polarised light towards right (clockwise) is known as dextrorotatory or d-form while that which rotates towards left (anticlockwise) is known as laevorotatory or l-form.

Generally asymmetric or chiral compounds show optical isomerism Chiral compounds are those which contain chiral centre i.e., chiral carbon, the carbon all the four valencies of which are satisfied by four different groups. Allenes, spiranes and biphenyl compounds, although have absence of chiral centre, but are asymmetric. That's why they are also optically active. Number of optical active isomers =  $2^n$  (where, n = chiral carbon). If two end are similar number of optical active isomers =  $2^{n-1}$  (if n = even) and meso form =  $2^{n-2/2}$ . If n = odd, number of optical active isomers =  $2^{n-1} - 2^{(n-1)/2}$ .

#### (ii) Geometrical Isomerism

The isomers having same molecular formula but different spatial arrangement of atoms about the double bond are known as geometrical isomers and this phenomenon is called geometrical isomerism, e.g.,



For exhibiting geomet<mark>rical is</mark>omerism, the essential conditions are :

1. The compound mu<mark>st contai</mark>n at least one double bond.

2. The groups present at the double bonded carbon atoms, must be different. However, one similar group should be present at the adjacent double bonded carbon atoms.

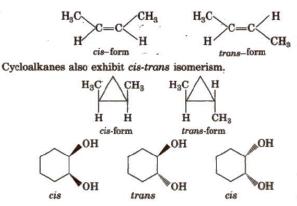
Number of geometrical isomers (if two ends are not similar =  $2^n$  where, n = number of double bonds).

#### **Types of Geometrical Isomers**

(a) **Cis-trans isomers** In cis-isomer, similar groups are present on the same side of the double bond and in trans- isomer, similar groups are present on the opposite side of the double bond. e.g.,



# mart Not



### **Attacking Reagent**

#### 1. Electrophiles or Electrophilic Reagents

These are electron deficient species i.e., behave as Lewis acids. The following species behave as electrophiles :

(i) All non-metal cations and metal cations which have vacant d- orbitals.

e.g., CI<sup>+</sup>, NO<sup>+</sup><sub>2</sub>, CH<sub>3</sub>CO<sup>+</sup> etc.

(ii) Lewis acids (incomplete octet) e.g., BF<sub>3</sub>, ZnC1<sub>2</sub> (anhydrous), FeCl<sub>3</sub> (anhydrous),

AlCl<sub>3</sub>(anhydrous), :CH<sub>2</sub> etc.

(iii) Non-metal (acidic) oxides e.g., CO<sub>2</sub>, SO<sub>2</sub> etc.

### 2. Nucleophiles or Nucleophilic Reagents

These are electron rich species i.e., behave as Lewis bases. These attack at electron deficient area.

The following species behave as nucleophiles :

- (i) All anions e.g., Cl<sup>-</sup>, NH<sub>2</sub><sup>-</sup>, OH<sup>-</sup> etc.
- (ii) Lewis bases e.g.,  $NH_3$ ,  $H_2O$ , R, R, O, R, R, O, H etc.
- (iii) Benzene, alkenes etc.

Nucleophilicity order is

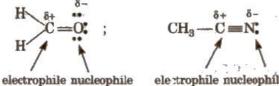
$$H^- > CH_3^- > NH_2^- > RO^- > OH^-$$

In case of same nucle<mark>ophilic s</mark>ite, nucleophilicity parallels basicity i.e., as the basicity increases, nucleophilicity also increases.

(if nucleophilic sites (or attacking atoms) are different nucleophilicity varies inversely with electronegativity)

#### 3. Amphiphiles

These species behave like both electrophiles as well as nucleophiles. Organic compounds containing a multiple bond between carbon and a more electronegative atom can act as amphiphiles, e.g.,



ele trophile nucleophile



#### **Inductive Effect**

It is just like shifting of shared pair of electrons in polar covalent molecules. If shared pair is more shifted towards the more electronegative atom, the less electronegative atom acquires slight positive charge and more electronegative atom acquires partial negative charge, e.g.,

$$\overset{+\delta}{CH_3} \rightarrow \overset{-\delta}{Cl}$$

It is a permanent effect and propagates through carbon chain.

Atoms or groups having greater electron affinity than hydrogen. are said to have electron attracting or negative inductive effect (- I) while that having, smaller electron affinity than hydrogen are said to have electron releasing or positive inductive effect (+ I) e.g.,

Here, Cl has – I effect and alkyl group has + I effect. Order of groups producing – I effect is

 $R_{3}$ N > NO<sub>2</sub> > CN > SO<sub>3</sub>H > CHO > CO > COOH > F >

$$Cl > Br > I > OH > OR > NH_2 > C_0H_5 > H$$

Order of groups producing + I effect is

$$0^- > -COO^- > 3^\circ$$
 alkyl group  $> 2^\circ$  alkyl group

>1° alkyl group > CH<sub>a</sub> > H

#### **Applications of Inductive Effect**

1. Presence of groups showing + I effect increases the stability of carbocation while presence of groups showing – I effect decreases their stability.

2. Strength of acid increases with the attachment of group showing – 1 effect and decreases with the attachment of group showing + I effect.

3. Presence of + I showing groups increases the basic strength of amines.

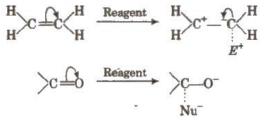
4. Reactivity of carbonyl compound is increased by – I showing groups.

5. Reactivity of alkyl halides towards S<sub>N</sub> 1 is increased by + 1 showing groups.

#### Electromeric Effect

It is defined as the polarity produced in a multiple bonded compound as a reagent approaches it. In the presence of attacking reagent, the two  $\pi$  electrons are completely transferred to any of the one atom. This effect is temporary.

This may be of + E type (when displacement of electron pair is away from the atom or group) or of – E type (when the displacement is towards the atom or group). e.g.,



#### Hyperconjugation

It involves delocalisation of  $\sigma$  electron of a C – H bond of an alkyl group attached directly to an atom of unsaturated system or to an atom with an unshared p-orbital.

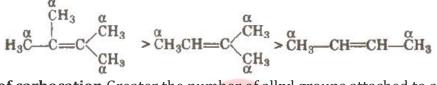


 $\begin{array}{c} \begin{array}{c} & \\ & \\ \hline \\ CH = CH_2 \end{array} \xrightarrow{H^+} CH_2 = CH = \bar{C}H_2 \end{array}$ 

This effect is also called no bond formation or Baker Nathan effect.

#### Applications of Hyperconjugation

(i) **Stability of alkenes** More the number of a-hydrogen atoms, more stable is the alkene.



(ii) **Stability of carbocation** Greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the stability.

$$(CH_{9})_{3}C^{*} > (CH_{9})_{2}CH > CH_{3}-CH_{2} > CH_{3}$$

#### **Resonance Effect**

When all the properties of a molecule cannot be shown by a single structure and two or more structures are required to show all the properties of that molecule, then the structures are called resonating structures or canonical forms and the molecule is referred as resonance hybrid. This phenomenon is called resonance.

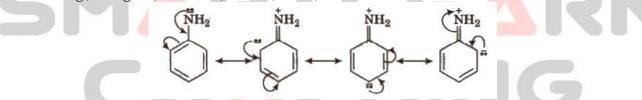
In resonance,

- 1. The arrangement of atoms must be identical in all the formulae.
- 2. The energy content of all the canonical forms must be nearly same.
- 3. Each canonical form must have the same number of unpaired electrons.

It involves delocalisation of 1t electrons. This effect may be of + R type or – R type.

#### Positive Resonance Effect (+R)

Electron donating groups with respect to conjugate system show +R effect. Central atom of functional groups should be more electronegative than the surrounding atoms or groups to show +R effect. e.g., halogens, -OH. -OR, -OCOR, -NH2,-NHCOR etc



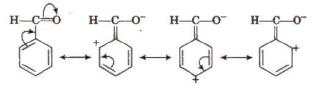
Electron donating groups producing. + R effect are ortho and para directing. 'They activate the benzene ring towards the electrophilic SUbstitution reactions except halogens. Halogens slightly deactivate the benzene ring towards the electrophilic substitution reaction. More the E.D.G. more is the basic nature.

#### Negative Resonance Effect (-R)

Electron withdrawing groups with respect to conjugate system show – R effect. Central atom of functional groups should be less electronegative than surrounding atoms or groups to show – R effect. e.g., halogens, – COOH,- COOR,- CHO,- CN,-NO<sub>2</sub> etc.







Electron withdrawing group (E.W.G.) producing – R effect are meta directing. They deactivate the benzene ring towards the electrophilic substitution reaction. More the E.W.G, more is the acidic nature.

#### **Resonance Energy**

Number of  $\pi$  bonds  $\propto$  contributing structures  $\propto$  resonance energy  $\propto$  stability. In benzene, resonance energy is 36 kcal/mol.

#### **Stability of Canonical Forms**

It can be judged by the following rules :

- 1. Non-polar structure is more stable than the polar structure.
- 2. Among polar structures, structure with maximum number of covalent bonds is most stable.
- 3. The structure with maximum charge separation is more stable.

4. Structure with positive charge on more electropositive element and negative charge on more electronegative element is more stable.

#### **Resonance and Bond order**

Bond order =  $\frac{\text{total no. of bonds betwen two atoms}}{\text{total no. of resonating structures}}$ 

e.g., 
$$\bigcirc$$
  $\longleftrightarrow$   $BO = \frac{2+1}{2} = 1.5$ 

#### **Reaction Intermediates**

These are formed as a intermediate during the course of a reaction. These are short lived and highly reactive. Free radicals, carbocations, carbanions, carbenes and nitrenes are important reactions intermediates.

#### 1. Free Radicals

These are the product of homolysis and contain an odd electron. These are highly reactive planar species with Sp<sup>2</sup> hybridisation.

Their order of stability is

$$(C_{\theta}H_{5})_{3}C > (C_{\theta}H_{5})_{2}CH > C_{\theta}H_{5}CH_{2}$$

#### 2. Carbocations

These are the product of heterolysis and contain a carbon bearing positive charge. These are electron deficient species. Carbocations contain six electrons in the valence shell. These are also planar chemical species i.e., sp<sup>2</sup> hybridised with an empty p-orbital

$$\sigma$$
 empty *p*-orbital





The stability order of carbocations is

$$(C_{\theta}H_{5})_{3}C^{+} > (C_{\theta}H_{5})_{2}CH > (CH_{3})_{3}C > C_{\theta}H_{5}CH_{2} > 2^{\circ} > CH_{2} = CH - CH_{2} > 1^{\circ} > C_{\theta}H_{5} > CH_{2} = CH$$

#### 3. Carbanions

These are also the product of heterolysis and contain a carbon bearing negative charge and 8 electrons in its valence shell

These have pyramidal shape with Sp<sup>3</sup> hybridised carbon (having one lone pair) The order of stability of carbanions is

$$(C_{\theta}H_{5})_{3}C^{-} > (C_{\theta}H_{5})_{2}CH > C_{\theta}H_{5}CH_{2} > CH_{2} = CH - CH_{2}$$

$$> CH_3 > 1^\circ > 2^\circ > 3^\circ$$
 carbanions

#### 4. Carbenes

These are divalent carbon species having two non-bonding electrons along WIth two bond pairs. These are obtained by photolysis or pyrolysis. e.g.,

$$CH_2 = C = 0 \xrightarrow{hv} cH_2 + C = 0$$

These being electron deficient behave as Lewis acids. These are of two types:

(i) **Singlet carbene** In it, the C-atom is Sp2 hybridised. Then Hybridised orbitals contain no electrons and a hybridised orbital contains two electrons :

$$\sigma$$
 empty  
 $\sigma$   $\sigma$   $sp^2$  hybridised with 2 unbonded electrons  
 $\sigma$ 

Singlet carbene has bent structure and is less stable than triplet carbene. The order of stability of singlet carbenes is

$$CH_2 > CF_2 > CCl_2 > CBr_2$$

(ii) **Triplet carbene** In it, the central C-atom is sp-hybridised. The sp – hybridised orbitals contain 1 electron each .

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unhybridised orbitals with 1 electron



Triplet carbene has linear geometry.

#### 5. Nitrene

These are neutral monovalent nitrogen species in which N atom has two unshared pair of electrons with a monovalent atom or group attached.



These are obtained by thermolysis of azides and as reactive as carbenes.





#### 6. Arynes

It contains a formal carbon-carbon triple bond in aromatic molecule.



The additional bond is formed between two neighbouring C-atoms by sideways overlapping of two Sp<sup>2</sup> orbitals. The new bond lies along with side of the ring and has little interaction with the 1t electron cloud lying above and below the ring.

The sideways overlapping is weak and thus, makes the benzene more reactive.

#### Methods of purification of organic compounds:

**Sublimation**: It is the process in which solid directly changes to gaseous form on heating and on cooling the gaseous state convert in to solid state.

The idea behind using this technique is to separate substance, that show sublimation from substance that do not sublime.

**Crystallisation**: This method is based on the difference in the solubility of compound and the impurities in the suitable solvent.

The impure compound in dissolved in a solvent in which it is sparingly soluble at room temperature, but appreciably soluble at higher temperature.

The solution is concentrated to get saturated solution.

On cooling the solution pure compound crystallizes out and is removed by filtration.

The filtrate contains impurities and small quantity of compound .

**Distillation** : This method is used to separate volatile liquids from non volatile impurities and also the liquids that have difference in their boiling points .

The liquids with different boiling point vaporise at different temperatures. Then these vapours are cooled and the liquids formed are collected separately.

Like chloroform and aniline can be easily separated by this technique as both have different boiling points.

For this technique:

(i) Take the mixture in a distillation flask. Fit the flask with a thermometer.

(ii) Arrange the apparatus as shown in the figure.

(iii) Heat the mixture slowly keeping a close watch at the thermometer and observe what happens. The vapours of one component with lower boiling point can be seen rising up in the distillation flask with the increase in temperature.

(ii) These vapours get condensed in the condenser and can be collected (as pure liquid distillate) from the condenser outlet.

**Fractional distillation**: This method is used for those liquids which have nearly same boiling points that is the difference in their boiling point is not much .So, as they have same boiling points. Therefore ,liquids from both liquids condense and formed at same time.

In this technique ,vapours of liquid mixture are passed through a fractionating column before condensation .This fractionating column is fitted over round bottom flask.

Vapours of liquid with higher boiling point condense before the vapours of liquid with lower boiling point.

On reaching the top, the vapours become pure in low boiling component and passed through the condenser. The pure liquid is collected in receiver .Each successive condensation and vaporisation unit in the fractionating column is called theoretical plate. Example: separation of





different components of crude oil

**Distillation under reduced pressure**: This method is used to purify liquids having very high boiling points and those which decompose at or below their boiling points.

Such liquids are made to boil at a temperature lower than their boiling points, by reducing the pressure on their surface. A liquid boils at a temperature, at which its vapour pressure is equal to external pressure .The pressure is reduced with the help of water pump. Example glycerol can be separated from spent-lye by this method

**Steam distillation**: This technique is applied to separate substances which are steam volatile and are immiscible in water.

In steam distillation steam from a steam generator is passed through a heated flask containing the liquid to be distilled.

The mixture of steam and the volatile organic compound is condensed and collected. Then compound is later separated from water using separating funnel.

In it the liquid boils ,when sum of vapour pressures due to organic liquid and due to water becomes equal to the atmospheric pressure.

i.e. =P<sub>1</sub> +p<sub>2</sub>

Since p<sub>1</sub> is lower than p, the organic liquid vaporises at lower temperature than its boiling point.

Example: Aniline and water can be separated by this method

**Differential extraction**: When the organic compound is present in an aqueous medium, then it is separated by shaking it with an organic solvent in which it is more soluble than in water . The organic solvent and the aqueous solution should be immiscible with each other .So, that they form two distinct layers which can be separated with separating funnel. The organic solvent is later removed by distillation or by evaporation.

**Chromatography**: It is a technique used to separate mixtures in to their components, purify. Compounds which can be solid or liquid and also test the purity of compounds. In this technique the mixture of substances are applied on to a stationary phase .Then a pure solvent or a mixture of solvents is allowed to move slowly over stationary phase .The components of mixture gets gradually separated from one another .The moving phase is mobile phase .

#### The chromatography is classified into two categories:

Adsorption chromatography Partition chromatography

Adsorption chromatography: It is based on the facts that different compounds are adsorbed on adsorbent at different degrees.

The commonly used adsorbents are silica gel and alumina.

When a mobile phase is allowed to move over a stationary phase the components of mixture move by varying distances over a stationary phase.

Depending upon differential adsorption the two types of techniques are:

Column chromatography Thin layer chromatography

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**Column chromatography**: It involves separation of mixture over a column of adsorbent packed in a glass tube.

The column is fitted with a stop cock at its lower end .The mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube.

An appropriate eluant which is liquid or a mixture of liquids is allowed to flow down the column slowly.

Depending upon the degree to which the compounds are adsorbed complete separation takes place.

The most readily adsorbed substance is retained near the top and the other comes down to various distances in the column.

**Thin layer chromatography**: This is another type of adsorption which involves separation of substances of mixture over a thin layer of adsorbent coated on glass tube.

A thin layer of adsorbent is spread over a glass plate of suitable size. The plate is known as thin layer chromatography plate.

The solution of mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate.

Then glass plate is then placed in a closed jar containing the eluant.

As the eluant rises up ,the plate the different components of mixture move along with eluant to different distances depending on their degree of adsorption .Hence, separation takes place . The relative adsorption of each component of mixture is expressed in terms of retardation factor ( $R_f$ ).

The spots of the compounds are visible on TLC plate due to their original color. The spots which are not visible to eye but fluoresce in ultraviolet light can be detected by putting the plate under ultra violet light.

# Position chromatography: It is based on the continuous differential partitioning of

components of a mixture between stationary and mobile phases.

Paper chromatography: Is a type of partition chromatography .In this a special paper called chromatography paper is used .It contains water trapped in it which acts as a stationary phase. (i)In this we take a thin strip of filter paper (25cm x 5cm approx).

(ii) Draw a line on it using a pencil, approximately 3cm above the lower edge.

(iii) Put a small drop of solution of mixture .Lets say ink from a sketch pen or fountain pen) at the centre of the line. Let the ink dry.

(iv) Attach the paper strip on the thread with the help of cello tape.

(v) Lower the filter paper strip into a large size gas jar in such a way that the drop of ink on the paper is just above the water level as shown in the figure [2.8 (b)]. Adjust the thread and fix it on the sides of gas jar with the help of cello tape.

(vi)Cover the gas jar with a lid and leave it undisturbed.

(vii) Watch carefully as the water rises up on the filter paper.

(viii) Remove the filter paper strip dry it and observe.

The paper retains different components according to their differing partition in the two phases .the paper strip is called **chromatogram.** The spots of separated coloured compounds are visible at different heights from the position of initial spot.

# Detection of carbon and hydrogen:

They are detected by heating the compound wit copper oxide. Carbon present in the compound is oxidised to Carbon-dioxide (tested with Lime water) and Hydrogen to Water(tested with anhydrous Copper sulphate).



C + CuO→Cu + Co<sub>2</sub>

Carbon copper oxide copper carbondioxide

H<sub>2</sub>+CuO→Cu+H<sub>2</sub>O Hydrogen copper oxide copper water

 $CO_2 + Ca (OH)_2 \rightarrow CaCO_3 + H_2O$ carbondioxide calcium hydroxide calcium carbonate

H<sub>2</sub>O+CuSO<sub>4</sub>→CuSO<sub>4</sub>.5H<sub>2</sub>O

#### water copper sulphate copper sulphate pentahydraye crystals

**Detection of other elements** : Nitrogen ,Sulphur, Halogen ,Phosphorous presence in organic compound are detected by Lasagne's test .The elements present in the compound are converted into covalent form in to an ionic form by fusing the compound with Sodium metal

Na+ C+ N → NaCN sodium carbon nitrogen sodium cyanide Na+S → Na<sub>2</sub>S sodium sulphur sodium sulphide Na+X→NaX sodium halogen sodium halide

**Test for Nitrogen** : The Sodium fusion extract is boiled with Ferrous Sulphate and then acidified with concentrated Sulphuric acid . The formation of Prussian Blue colour confirms the presence of Nitrogen .

 $[Fe(CN)_6]^4 + Fe^{3+} \rightarrow Fe_4[Fe(CN)_6]_3 \times H_2O$ 

**Test for Sulphur** : The Sodium fusion extract is acidified with Acetic acid with Lead acetate is added to it .A Black precipitate of Lead Sulphide indicates the presence of Sulphur.  $S^{2^{-}} + Pb^{2^{+}} -> PbS$ 

Sulphide Lead Lead Sulphide

On treating Sodium fusion extract with Sodium Nitro Prusside, the Violet colour appears that confirms Sulphur .

$$S^{2}+[Fe(CN)_{5}NO]^{2} \rightarrow [Fe(CN)_{5}NOS]$$

violet colour

**Test for halogens**: The Sodium fusion extract is acidified with Nitric acid and then treated with Silver Nitrate.

A White precipitate soluble in Ammonium hydroxide shows the presence of Chlorine.

A Yellow precipitate soluble in Ammonium hydroxide shows the presence of Bromine.

A Yellow precipitate not soluble in Ammonium hydroxide shows the presence of lodine.

X<sup>-</sup> + Ag<sup>+</sup> --> AgX

Halide Silver ion SilverHalide

**Test for phosphorous**: The compound is heated with Sodium Peroxide. The Phosphorus gets oxidised to Phosphate .Then the solution is boiled with Nitric acid and then treated with





Ammonium mol bate .A Yellow precipitate indicates phosphorous.

### Quantitative analysis

**Carbon and hydrogen:** Both of them are estimated in one experiment. A known mass of Organic compound is burnt in presence of excess of Oxygen and Copper (ii)oxide . Carbon and Hydrogen both are oxidised to form Carbon dioxide and Water.

# $C_xH_y+(x+y/4)O_2\rightarrow xCo_2+y/2H_2O$

#### Hydrocarbon oxygen carbondioxide water

The mass of Water produced is determined by passing a mixture through U-tube containing anhydrous Calcium chloride. Carbon dioxide is absorbed in another U-tube containing solution of Potassium hydroxide. The increase in mass of calcium chloride and Potassium hydroxide gives the amount of Carbon dioxide and water .From it the percentage of C and H can be calculated.

Let the mass of organic compound = mg

Mass of water =  $m_1$ Mass of carbodioxide = $m_2$ % of C = (12 x  $m_2$  x 100)/(44x)m % of H = (2 x  $m_1$  x 100)/(18x)m

Nitrogen : There are two methods for estimation of Nitrogen :

**Dumas method**: In this Nitrogen containing compound is heated with Copper oxide in an atmosphere of Carbon dioxide, yields free Nitrogen in addition to Carbon dioxide and water.

### $C_xH_yN_z+(2x+y/2)CuO \rightarrow xCo_z+y/2H_zO+z/2N_z+(2x+y/2)Cu$

The Nitrogen oxides formed are reduced to Nitrogen by passing the gaseous mixture over a heated Copper gauze. The mixture of gases so produced is collected over aqueous Potassium hydroxide which absorbs Carbon dioxide. Nitrogen is collected in the upper part of graduated tube.

Volume of N at STP =  $(P_1V_1 \times 273)/(760 \times T_1)$ 

**Kjeldahl's method**: The compound containing Nitrogen is heated with concentrated Sulphuric acid . The Nitrogen in the compound gets converted to Ammonium sulphate. The resulting acid mixture is then heated with excess Sodium hydroxide .The liberated Ammonia gas is absorbed in excess of standard solution of Sulphuric acid. The amount of Ammonia produced is determined by estimating the amount of Sulphuric acid consumed in the reaction.

 $C_xH_yN_z+(2x+y/2)CuO \rightarrow xCo_2+y/2H_2O+z/2N_2+(2x+y/2)Cu$ 

**Halogens** : For them we have Carious method. A known mass of organic compound is heated with fuming Nitric acid in the presence of Silver nitrate contained in a hard glass tube known as Carious tube in a furnace.

The Carbon and Hydrogen present in compound are oxidised to Carbon dioxide and water. The Halogens present forms the Silver halide .It is filtered, washed, dried and weighed.

Let the mass of organic compound = mg

Mass of  $AgX = m_1 g$ 1 mole of AgX contains 1 mole of X

% of Halogen = (Atomic mass of X x  $m_1$  x 100)/(molecular mass of AgX) x m

Sulphur: A known mass of organic compound is heated in Carious tube with Sodium peroxide



or fuming Nitric acid. Sulphur present is oxidised to Sulphuric acid .It is precipitated with Barium sulphate by adding excess of Barium chloride solution in water .The precipitate is filtered ,washed and dried and weighed .

Let the mass of organic compound = mg Let the mass of ammonium phosphor molybate =  $m_1$  g % of Sulphur =  $(32 \times m_1 \times 100)/(233) \times m$ 

**Phosphorous**: A known mass of organic compound is heated with fuming Nitric acid. As a result Phosphorous gets oxidised to Phosphoric acid. It is then precipitated with Ammonium molybdate .

Let the mass of organic compound = mg Let the mass of ammonium phosphor molybate =  $m_1 g$ % of Phosphorous =  $(62 \times m_1 \times 100)/(222) \times m$ 

**Oxygen**: A definite mass of organic compound is decomposed in stream of Nitrogen gas .The mixture of gaseous products containing oxygen is passed over red hot coke when all the oxygen present is converted into Carbon monoxide .Then this mixture is passed over lodine pent oxide, when CO is oxidised to Carbon dioxide producing lodine.

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