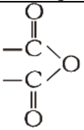
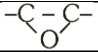
CHAPTER-01
IUPAC NOMENCLATURE

Functional Group	Prefix	Suffix	Structure
Carboxylic acid	Carboxy	– oic acid °Carboxylic acid	$-\overset{\overset{O}{\|}}{C}-OH$
Sulphonic acid	Sulpho	Sulphonic acid	$-SO_3H$
Anhydride	X	oic-anhydride	
Ester	Alkoxy carbonyl or Carbalkoxy	alkyl….oate °Carbonyl halide	$-\overset{\overset{O}{\|}}{C}-OR$
Acid halide	Haloformyl or Halocarbonyl	– oyl halide °Carbonyl halide	$-\overset{\overset{O}{\|}}{C}-X$
Acid amide	Carbamoyl / Amido	– amide °Carboxamide	$-\overset{\overset{O}{\|}}{C}-NH_2$
Carbonitrile / Cyanide	Cyano	nitrile °Carbonitrile	$-C\equiv N$
Aldehyde	Formyl or Oxo	– al °Carbaldehyde	$-\overset{\overset{O}{\|}}{C}-H$
Ketone	Keto or Oxo	– one	$-\overset{\overset{O}{\|}}{C}-$
Alcohol	Hydroxy	– ol	$-OH$
Thio alcohol	Mercapto	thiol	$-SH$
Amine	Amino	amine	$-NH_2$
Ether	Alkoxy	____	$-O-R$
Oxirane	Epoxy	____	
Nitro derivation	Nitro	____	$-NO_2$
Nitroso derivation	Nitroso	____	$-NO$
Halide	Halo	____	$-X$
Double bond	____	ene	$C=C$
Triple bond	____	yne	$C\equiv C$

Priority order:
COOH > So_3H > –COOR > –COCl > $CONH_2$ > C≡N > N ≡ C > –CHO > –COR > – OH > SH > NH_2

Important rules for Nomenclature of Alkanes

Rule 1: First of all, the longest carbon chain in the molecule is identified.

Rule 2: The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers.

Rule 3: If different alkyl groups are present, they are listed in alphabetical order.

If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing.

Rule 4: The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used.

Rule 5: The carbon atom of the branch that attaches to the root alkane is numbered 1.

Some additional rules

1. For nomenclature of complex compounds follow priority order: Main functional group > multiple bond > substituent
2. If an open chain contain two or more than two cyclic compounds then always select open chain as main chain.
3. For nomenclature of aromatic compounds, if the chain contains two or less than two carbons then use benzene as main chain. If the chain contains more than two carbons then use aliphatic chain as main chain.

ISOMERISM

Definition

Compounds having same molecular formula but differ in at least one physical or chemical or biological properties are called isomers and this phenomena is known as isomerism.

Types of Isomerism:

(1) Structural Isomerism **(2) Stereo Isomerism**

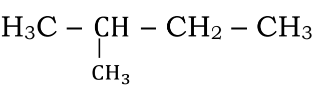
(1) Structural Isomerism: Structural isomerism is a form of isomerism in which molecules with the same molecular formula have atoms bonded together in different orders.

Types of Structural Isomerism:

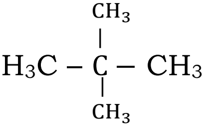
(A) Chain Isomerism: This type of isomerism is due to difference in the arrangement of carbon atoms constituting the chain.

Key points: Parent carbon chain or side chain should be different.

e.g., C_5H_{12} : $CH_3 - CH_2 - CH_2 - CH_2 - CH_3$ (n-pentane),



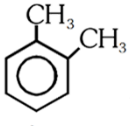
$H_3C - \underset{\substack{| \\ CH_3}}{CH} - CH_2 - CH_3$ (iso-pentene),

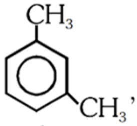


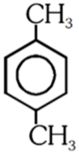
$H_3C - \overset{\substack{CH_3 \\ |}}{\underset{\substack{| \\ CH_3}}{C}} - CH_3$ (neo-pentane)

(B) Positional Isomerism: It occurs when functional groups or multiple bonds or substituents are in different positions on the same carbon chain.

Key point: Parent carbon chain remain same and substituent, multiple bond and functional group changes its position.

e.g., $C_6H_4(CH_3)_2$: 
o-xylene

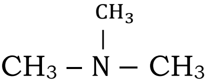
, 
m-xylene

, 
p-xylene

(C) Functional Isomerism: It occurs when compounds have the same molecular formula but different functional groups.

e.g., C_3H_9N : $CH_3 - CH_2 - CH_2 - NH_2$ (1-propanamine),

$CH_3 - CH_2 - NH_2 - CH_3$ (N-methylethanamine),

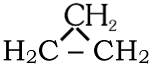

$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{N} - CH_3$ (N,N-dimethylmethanamine)

(D) Metamerism: This type of isomerism occurs when the isomers differ with respect to the nature of alkyl groups around the same polyvalent functional group.

e.g., $C_4H_{10}O$: $CH_3 - O - CH_2 - CH_2 - CH_3$ (n-propyl methylether),

$CH_3 - CH_2 - O - CH_2 - CH_3$ (diethyl ether)

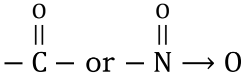
(E) Ring-Chain Isomerism: In this type of isomerism, one isomer is open chain but another is cyclic.

e.g., C_3H_6 : $CH_3 - CH = CH_2$ (propene), 
$H_2C \overset{CH_2}{\wedge} CH_2$ (cyclopropane)

- For chain, positional and metamerism, functional group must be same.
- Metamerism may also show chain and position isomerism but priority is given to metamerism.

(E) Tautomerism: This type of isomerism is due to spontaneous interconversion of two isomeric forms into each other with different functional groups in dynamic equilibrium.

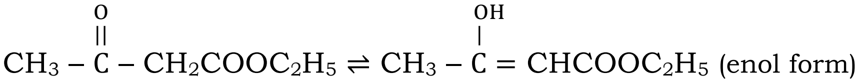
Conditions:

(I) Presence of 

$-\overset{\overset{O}{\|}}{C}-$ or $-\overset{\overset{O}{\|}}{N}\longrightarrow O$

(II) Presence of at least one α-H atom which is attached to a saturated C-atom.

e.g., Acetoacetic ester.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2COOC_2H_5 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CHCOOC_2H_5 \text{ (enol form)}$$

Enol content enhance by:

⇒ Acidity of a-H of keto form

⇒ Intra molecular H-Bonding in enol form

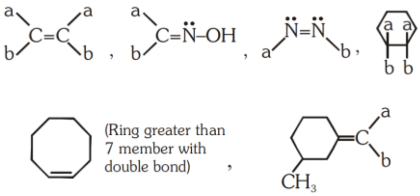
⇒ Resonance in enol form

⇒ Aromatisation in enol form

(2) Stereoisomerism: Compounds with the same molecular formula and structural formula but having difference in the spatial arrangement of atoms or groups in 3D space are called stereoisomers and the phenomenon is called stereoisomerism.

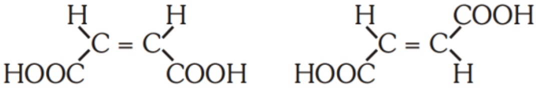
Types of Stereoisomerism:

(A) Geometrical Isomerism: It is due to restricted rotation and is observed in following systems



- Cis-trans isomerism: The cis compound is the one with the same groups on the same side of the bond, and the trans has the same groups on the opposite sides. Both isomers have different physical and chemical properties.

e.g.



cis
maleic acid

trans
fumaric acid

- General physical properties of geometrical isomer of but-2-ene

(I)	Stability	trans > cis
(II)	Dipole moment	cis > trans
(III)	Boiling point	cis > trans
(iv)	Melting point	trans > cis

Calculation of number of geometrical isomers:

Unsymmetrical	2^n
Symmetrical	$2^{n-1} + 2^{m-1}$ $m = \frac{n}{2}$ (If n is even) $m = \frac{n+1}{2}$ (If n is odd)

(B) Optical Isomerism: Compounds having same molecular and structural formula but different behaviour towards plane polarised light are called optical isomers and this phenomenon is called optical isomersim.

Types of Optical Isomers:

(I) Optically Active

- dextrorotatory (d)
- laevorotatory (ℓ)

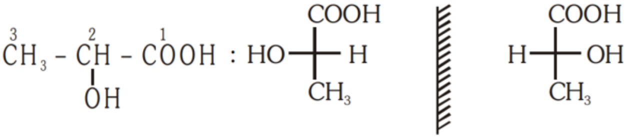
(II) Optically Inactive

- meso

Condition: Molecule should be asymmetric or chiral i.e. symmetry element (POS & COS) should be absent.

The carbon atom linked to four different groups is called chiral carbon.

Fischer projection: An optical isomer can be represented by Fischer projection which is planar representation of three-dimensional structure. Fischer projection representation of lactic acid (2-hydroxypropanoic acid)



Configuration of optical isomer:

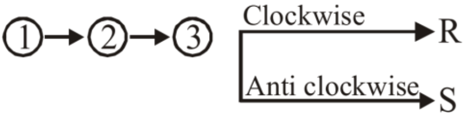
(I) Absolute configuration (R/S system)

(II) Relative configuration (D/L system)

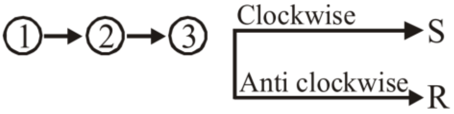
Determination of R/S configuration:

Rule-1 Assign the priority to the four groups attached to the chiral carbon according to priority rule.

Rule-2 If lowest priority (4) is bonded to vertical line then moving



Rule-3 If lowest priority (4) is bonded to horizontal line then moving



Determination of D/L System:

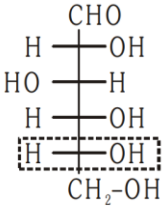
- Reference molecule glyceraldehyde
- It is used to assign configuration in carbohydrate, amino acid and similar compounds

Rule: Arrange parent carbon chain on the vertical line

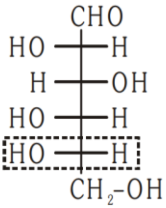
- Placed most oxidised carbon on the top or nearest to top.
- On highest IUPAC numbered chiral carbon

  If OH group on RHS → D

  If OH group on LHS → L



D-Glucose



L-Glucose

CIP Sequence Rule: The following rules are followed for deciding the precedence order of the atoms or groups: -

(I) Highest priority is assigned to the atoms of higher atomic number attached to asymmetric carbon atom.

(II) In case of isotopes, isotopes having higher atomic mass is given priority.

(III) If the first atom of a group attached to asymmetric carbon atom is same then we consider the atomic number of 2nd atom or subsequent atoms in group.

(IV) If there is a double bond or triple bond, both atoms are considered to be duplicated or triplicated.

Non-superimposable mirror images are called enantiomers which rotate the plane polarised light up to same extent but in opposite direction.

Diastereomers are stereoisomers which are not complete mirror images of each other. They have different physical and chemical properties.

Meso compounds are those compounds whose molecules are superimposable on their mirror images inspite of the presence of asymmetric carbon atom.

An equimolar mixture of the enantiomers (d & ℓ) is called racemic mixture. The process of converting d− or ℓ − form of an optically active compound into racemic form is called racemisation.

The process by which dl mixture is separated into d and ℓ forms with the help of chiral reagents or chiral catalyst is known as resolution.

Compound containing chiral carbon may or may not be optically active but show optical isomerism.

For optical isomer chiral carbon is not the necessary condition.

Calculation of number of optical isomers:

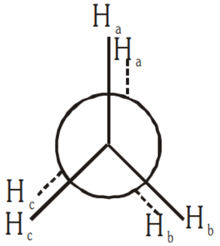
The compound	Optically active forms	Optically inactive forms (meso)
Unsymmetrical	2^{n}	Zero
Symmetrical If n = even	$2^{(n-1)}$	$2^{\left(\frac{n}{2}-1\right)}$

Symmetrical If n = odd	$2^{(n-1)} - 2^{\frac{(n-1)}{2}}$	$2^{\frac{(n-1)}{2}}$

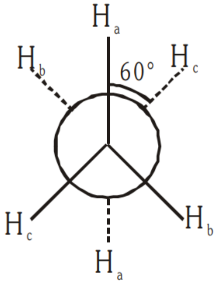
⟹ Where n = number of chiral carbons

(C) Conformational Isomerism: The different arrangement of atoms in space that results from the carbon-carbon single bond free rotation by 0-360° are called conformations or conformational isomers or rotational isomers and this phenomenon is called conformational isomerism.

Newmann Projection: Here two carbon atoms forming the s bond are represented one by circle and other by centre of the circle. Circle represents rear side C and its centre represents front side carbon. The C–H bonds of front carbon are depicted from the centre of the circle while C–H bond of the back carbon are drawn from the circumference of the circle.

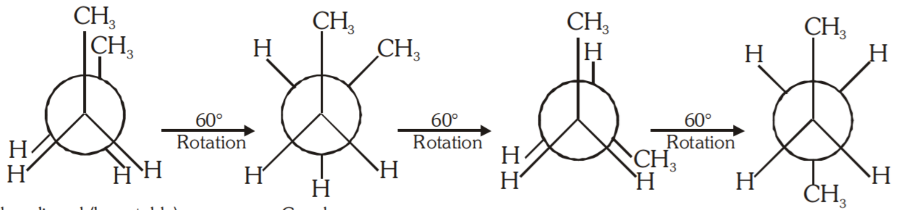


Eclipsed form (least stable)



Staggered form (most stable)

Conformations of butane: $\overset{4}{C}H_3 - \overset{3}{C}H_2 \curvearrowright CH_2 - \overset{1}{C}H_3$



Fully eclipsed (less stable)

Gauche

Partially Eclipsed form

Anti Staggered-form (most stable)

The order of stability of conformations of n-butane.

Anti-staggered > Gauche > Partially eclipsed > Fully eclipsed

Relative stability of various conformation of cyclohexane is

Chair > twist boat > boat > half chair
(Chiral)

General Organic Chemistry

Electrophiles are electron deficient species.

e.g., $H^{\oplus}$, $R^{\oplus}$, $NO_2^{\oplus}$, $X^{\oplus}$, PCl_3, PCl_5

($\overset{\oplus}{N}H_4$ and $H_3O^{\oplus}$ are not electrophile)

Nucleophiles are electron rich species.

e.g., $Cl^{\ominus}$, $\overset{\ominus}{C}H_3$, $\overset{\ominus}{O}H$, $RO^{\ominus}$, $\overset{\ominus}{C}N$, $\ddot{N}H_3$, $R\overset{..}{\underset{..}{O}}H$, $CH_2{=}CH_2$, $CH\equiv CH$

Relative electron withdrawing order (–I order):

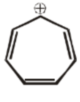
$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -COOH > -X > -OR > -OH > -C\equiv CH > -NH_2 > -C_6H_5 > -CH{=}CH_2$

Relative electron releasing order (+I order):

$-\overset{\ominus}{N}H > -O^{\ominus} > -COO^{\ominus} >$ 3° alkyl > 2° alkyl > 1° alkyl > $-CH_3$

Relative stability order

(a) Stability of carbocation


$> (Ph)_3\overset{\oplus}{C} > (Ph)_2\overset{\oplus}{C}H > Ph{-}\overset{\oplus}{C}H_2 > CH_2{=}CH{-}\overset{\oplus}{C}H_2 > (CH_3)_3\overset{\oplus}{C} > (CH_3)_2\overset{\oplus}{C}H > CH_3\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2{=}\overset{\oplus}{C}H > CH\equiv\overset{\oplus}{C}$

(b) Stability of free radical

$(Ph)_3\dot{C} > (Ph)_2\dot{C}H > Ph\dot{C}H_2 > CH_2{=}CH{-}\dot{C}H_2 > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

(c) Stability of carbanion

$(Ph)_3\overset{\ominus}{C} > (Ph)_2\overset{\ominus}{C}H > Ph-\overset{\ominus}{C}H_2 > CH_2{=}CH-\overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_3 > CH_3\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

Resonance

- Resonance involves delocalization of loan pair or π electrons.
- Resonance is a hypothetical concept
- Resonance hybrid is the real structure whereas resonating structures are imaginary.
- In resonance, we cannot change position of atoms.

Types of resonance:

1. Positive charge in conjugation with π electrons.

2. Negative charge in conjugation with π electrons.

3. π electrons in conjugation with π electrons.

4. π electrons in conjugation with lone pair.

5. π electrons in conjugation with free radical.

6. Positive charge in conjugation with lone pair.

7. Lone pair or negative charge in conjugation with vacant orbital.

Hyperconjugation

- It involves complete transfer of electrons of C–H σ bond towards positive charge or free radicals.
- It is also known as no bond resonance/Baker Nathan effect
- Stability of carbocation $\propto$ total number of α-H.
- Stability of free radical $\propto$ total number of α-H.
- Stability of alkene $\propto$ total number of α-H.

- Isotopic effect in Hyperconjugation : $CH_3 > CD_3 > CT_3$

Heat of hydrogenation (HOH)

- HOH ∝ number of π bond.
- HOH $\propto \frac{1}{stability\ of\ alkene}$

Heat of combustion (HOC)

- HOC ∝ number of carbon atoms
- HOC $\propto \frac{1}{stability}$

Bond Dissociation Energy (BDE)

- BDE $\propto \frac{1}{stability\ of\ free\ radical}$

Mesomeric Effect

- It is defined as the polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of electrons present on an adjacent atom.
- **+M Effect Order**
  $-O^- > -NH_2 > -NHR > -OR > -NHCOR > -OCOR > -Ph > -F > -Cl > -Br > -I.$
- **–M Effect Order**
  $-NO_2 > -CN > -S(=O)2-OH > -CHO > -C=O > -COOCOR > -COOR > -COOH > -CONH_2 > -COO^-$

Some Additional Points related to GOC

1. For deciding priority between different effects, always follow: Resonance > hyperconjugation > Inductive effect
2. Halogens exhibit –I as well as + M effect. In this –I > +M. Therefore, it destabilizes the ring but is ortho-para directing.

Basic Strength $\propto K_b \propto \frac{1}{pK_b}$

- **Basic strength of amine:**

  In aqueous medium

  R ⇒ $-CH_3$ $2° > 3° > NH_3$

  R ⇒ $-CH_2CH_3$ $2° > 3° > 1° > NH_3$

  In gaseous medium

  R ⇒ $-CH_3$ $3° > 2° > 1° > NH_3$

  R ⇒ $-CH_2CH_3$ $3° > 2° > 1° > NH_3$

- **Reactivity towards necleophile (NAR)**
  (A) $HCHO > CH_3CHO > (CH_3)_2CO$
  (B) $CCl_3CHO > CHCl_2CHO > CH_2ClCHO$

- **Reactivity order towards acyl nucleophilic substitution reaction**
  Acid chloride > anhydride > ester > amide

- **Order of electronic effect**
  Mesomeric > Hperconjugation > Inductive effect

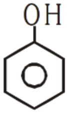
- **Stability of alkene ∝ number of α-hydrogen**
  $R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2 > \underset{\text{trans form}}{RCH{=}CHR} > \underset{\text{cis form}}{RCH{=}CHR}$
  $RCH{=}CH_2 > CH_2{=}CH_2$

- Heat of hydrogenation $\propto \frac{1}{\text{Stability of alkene}}$

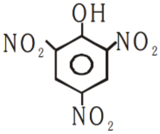
Acidic Strength $\propto$ Stability of Conjugate base $\propto K_a \propto \frac{1}{pK_a}$

(A) $H_2O > CH{\equiv}CH > NH_3$

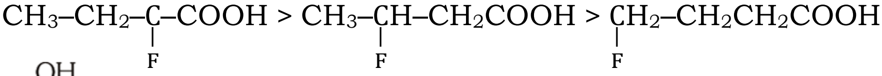
(B) $CH{\equiv}CH > CH_2{=}CH_2 > CH_3{-}CH_3$

(C) $R-SO_3H > R-COOH >$  $> R-OH$

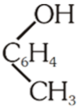
(D) $HCOOH > CH_3COOH > CH_3CH_2COOH$

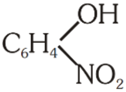
(E)  $> HCOOH > C_6H_5COOH > CH_3COOH$

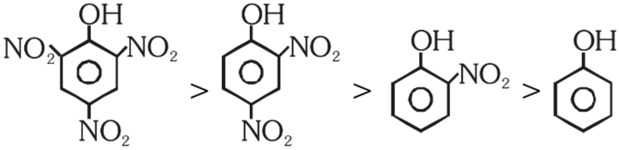
(F) $CCl_3COOH > CHCl_2COOH > CH_2ClCOOH$

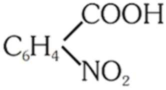
(G) 

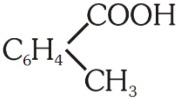
$$CH_3-CH_2-\underset{\substack{|\\F}}{C}-COOH > CH_3-\underset{\substack{|\\F}}{C}H-CH_2COOH > \underset{\substack{|\\F}}{C}H_2-CH_2CH_2COOH$$

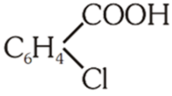
(H)  Phenol > m > p > o

(I)  p > o > m > Phenol

(J) 

(K)  o > p > m > benzoic acid

(L)  o > benzoic acid > m > p

(M)  o > m > p > benzoic acid

Purification Methods (Distillation Techniques)

Type:

(A) Simple Distillation

Conditions:

(i) When liquid sample has nonvolatile impurities.

(ii) When boiling point difference is 30 K or more.

Examples:

(i) Mixture of chloroform

(BP = 334K) and Aniline

(BP = 475K)

(ii) Mixture of Ether

(b.p. = 308K) &

Toluene (b.p. = 384K)

(iii) Hexane (342K) and

Toluene (384K)

(B) Fractional Distillation

When b.p. difference is 10K

Examples:

(i) Crude oil in petroleum industry

(ii) Acetone (329 K) and Methyl alcohol (338 K)

(C) Distillation under Reduced Pressure (Vacuum Distillation)

When liquid boils at higher temperature and it may decompose before b.p. is attained.

Examples:

(i) Concentration of sugar juice

(ii) Recovery of glycerol from spent lye.

(iii) Glycerol

(D) Steam Distillation

When the substance is immiscible with water and steam volatile.

P	=	P_1	+	P_2
Vapour Pressure		Vapour pressure Of Organic Liquid		Vapour pressure of water

Examples:

(i) Aniline is separated from water

(ii) Turpentine oil

(iii) Nitro Benzene

(iv) Bromo Benzene

(v) Naphthalene

(vi) O-Nitrophenol

LASSAIGNE'S METHOD

(detection of elements)

Element	Sodium extract	Confirmed test
Nitrogen	$Na+C+N \xrightarrow{\Delta} NaCN$	(NaCN+FeSO4 + NaOH) Boil and cool +FeCl3+conc. HCl→$Fe_4[Fe(CN)_6]_3$ Prussian blue colour

Sulphur	$2Na+S$ $\Delta \downarrow$ Na_2S	(i) Na2S+Na2(Fe(CN)5NO] Sodium nitrosorpuside $\rightarrow Na_4[Fe(CN)_5NOS]$ A deep violet colour (ii) $Na_2S+CH_3COOH+(CH_3COO)_2Pb\rightarrow$ A black ppt. (PbS↓)
Halogen	$Na+X$ $\Delta \downarrow$ NaX	$NaX+HNO_3 + AgNO_3$ (i) White ppt. soluble in aq. NH_3 confirms Cl. (ii) Yellow ppt. partially soluble in aq. NH_3 confirms Br. (iii) Yellow ppt. insoluble in aq. NH_3 confirms I.
Nitrogen and sulphur together	$Na+C+N+S$ $\Delta \downarrow$ NaCNS Sodium thiocyanate (Blood red colour)	As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both

QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Estimation of carbon and hydrogen-Leebig's method

$$C_xH_y + O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

excess

% of C = $\frac{12}{44} \times \frac{wt.of\ CO_2}{wt.\ of\ org.\ compd} \times 100$

% of H = $\frac{2}{18} \times \frac{wt.of\ H_2O}{wt.\ of\ org.\ compd} \times 100$

Notes

This method is suitable for estimation if organic compound contains C and H only. In case if other elements e.g., N, S, halogens are also present the organic compound will also give their oxides which is being absorbed in KOH and will increase the percentage of carbon and therefore following modification should be made.

Estimation of Nitrogen

Duma's method: The nitrogen containing organic compound yields nitrogen gas on heating it with copper (II) oxide in the presence of CO_2 gas. The mixture of gases is collected over potassium hydroxide solution in which CO_2 is absorbed and volume of nitrogen gas is determined.

$$\%\ of\ N = \frac{28}{22400} \times \left(\frac{\begin{matrix} Vol.of\ N_2 \\ collected \\ at\ N.T.P. \end{matrix}}{\begin{matrix} Wt.of \\ organic \\ compound \end{matrix}} \right) \times 100$$

Notes

This method can be used to estimate nitrogen in all types of organic compounds.

Kjeldahi's Method: In this method nitrogen containing compound is heated with conc. H_2SO_4 in presence of copper sulphate to convert nitrogen into ammonium sulphate which is decomposed with excess of alkali to liberate ammonia. The ammonia evolved is

$$\%\text{ of N}\,\frac{\begin{array}{c}1.4\times\text{volume of acid (ml)}\\ \times\text{normality of acid}\end{array}}{\text{wt.of organic compound}}$$

Notes

This method is simpler and more convenient and is mainly used for finding out the percentage of nitrogen in food stuff, soil, fertilizers and various agricultural products. This method cannot be used for compound having nitro groups, azo group (–N = N–) and nitrogen in the rign (pyridine, quinole etc.) Since nitrogen in these compounds is not quantitatively converted in to ammonium sulphate.