



# ORGANIC CHEMISTRY

Some Basic Principles and Techniques

Class 11 Chemistry — Unit 8

**CBSE Board 2025-26 Syllabus**

Complete Notes | Tips & Tricks | Case Studies | Expected Questions

 Prepared by: Math Love Institute | Indore & Raipur | [www.mathlove.in](http://www.mathlove.in)

★ ★ ★ COMPREHENSIVE STUDY MATERIAL FOR CLASS 11 CHEMISTRY ★ ★ ★

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## CHAPTER OVERVIEW

### Learning Objectives (NCERT CBSE 2025-26):

- **Tetravalence of carbon** and shapes of organic molecules ( $sp^3$ ,  $sp^2$ ,  $sp$  hybridisation)
- **Structural representations** — Lewis, condensed, bond-line formulas; 3D wedge-dash
- **Classification** of organic compounds: aliphatic, alicyclic, aromatic, functional groups
- **IUPAC Nomenclature** — alkanes, alkenes, alkynes, cyclic, functional groups, benzene derivatives
- **Isomerism** — structural (chain, position, functional group, metamerism) and stereoisomerism
- **Organic Reaction Mechanism** — homolytic & heterolytic fission, carbocations, carbanions, free radicals
- **Electronic effects** — inductive, resonance (mesomeric), electromeric, hyperconjugation
- **Purification techniques** — sublimation, crystallisation, distillation, chromatography
- **Qualitative analysis** — detection of C, H, N, S, halogens, phosphorus (Lassaigne's test)
- **Quantitative analysis** — estimation of C, H, N (Dumas/Kjeldahl), halogens (Carius), S, P

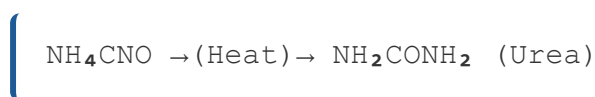
## 💡 Exam Weightage & Importance:

Unit 8 carries **significant weight in CBSE Board exams** (approximately 8–10 marks). It is the **foundation of all organic chemistry** in Class 11 and 12. Key areas for board exams:

- ✓ IUPAC nomenclature (very frequently tested)
- ✓ Structural isomerism
- ✓ Electronic displacement effects
- ✓ Lassaigne's test and qualitative analysis
- ✓ Quantitative estimation numericals (Kjeldahl, Dumas, Carius)
- ✓ Chromatography and purification methods

## 📖 Historical Background

Around 1780, chemists distinguished between **organic** (from living organisms) and **inorganic** compounds. Swedish chemist **Berzilius** proposed the "vital force" theory — that a divine force was needed to make organic compounds. This was **disproved in 1828** when **Friedrich Wöhler** synthesised **urea** (an organic compound) from ammonium cyanate (an inorganic salt):



Later, **Kolbe (1845)** synthesised acetic acid and **Berthelot (1856)** synthesised methane from inorganic sources, conclusively establishing that organic synthesis in labs is possible.



## SECTION 8.2 — TETRAVALENCE OF CARBON & SHAPES

### Carbon's Hybridisation and Bond Types

Hybridisation	Geometry	Bond Angles	Example	Bond Length
$sp^3$	Tetrahedral	$109.5^\circ$	$CH_4$ , $CCl_4$ , $C_2H_6$	Longest C–C (154 pm)
$sp^2$	Trigonal planar	$120^\circ$	$C_2H_4$ , $C_6H_6$ , $H_2C=O$	Intermediate C=C (134 pm)
$sp$	Linear	$180^\circ$	$C_2H_2$ , $HC\equiv N$	Shortest C≡C (120 pm)

### Key Rule for Hybridisation

**Greater s-character** → **greater electronegativity** → **shorter, stronger bonds**

Order of electronegativity of carbon:  $sp > sp^2 > sp^3$

Order of bond length:  $C\equiv C < C=C < C-C$

Order of bond strength:  $C\equiv C > C=C > C-C$

## Properties of $\pi$ (Pi) Bonds

- Formed by **lateral (sideways) overlap** of p-orbitals — requires parallel alignment
- Electron cloud is **above and below** the plane of bonding atoms
- **Rotation is restricted** around C=C double bond (interferes with p-orbital overlap)
- $\pi$  electrons are **easily available to attacking reagents** → most reactive sites in molecules
- $\pi$  bonds are **weaker** than  $\sigma$  bonds (less effective overlap)

## Counting $\sigma$ and $\pi$ bonds — Quick Method

- Every **single bond** = 1  $\sigma$  bond
- Every **double bond** = 1  $\sigma$  + 1  $\pi$  bond
- Every **triple bond** = 1  $\sigma$  + 2  $\pi$  bonds

**Example:**  $\text{HC}\equiv\text{C}-\text{CH}=\text{CH}-\text{CH}_3$

$\sigma$  bonds: C-C(4) + C-H(6) = **10  $\sigma$  bonds**

$\pi$  bonds: C $\equiv$ C(2 $\pi$ ) + C=C(1 $\pi$ ) = **3  $\pi$  bonds**

## SECTION 8.3 — STRUCTURAL REPRESENTATIONS

### Types of Structural Formulas

Type	Description	Example (Ethanol)
<b>Complete/Lewis</b>	Shows all atoms with bonds as dashes	H–C–C–O–H with all H shown
<b>Condensed</b>	Groups atoms, omits most dashes	CH <sub>3</sub> CH <sub>2</sub> OH
<b>Bond-line (Skeletal)</b>	Only C–C bonds as zig-zag; C and H not shown	Zig-zag line ending in –OH
<b>Wedge-Dash (3D)</b>	Solid wedge = towards observer; Dashed wedge = away	Used for chiral molecules

### Bond-Line Formula Rules

- Each **terminal point** of a line = –CH<sub>3</sub> group
- Each **line junction** = C atom with appropriate H atoms to satisfy valency
- Heteroatoms (O, N, Cl, etc.) are **always written explicitly**
- Carbon and hydrogen are **NOT written** (implied)

## SECTION 8.4 — CLASSIFICATION OF ORGANIC COMPOUNDS

### Classification Tree

ORGANIC COMPOUNDS |— I. ACYCLIC (Open-chain / Aliphatic)  
| Examples:  $\text{CH}_3\text{CH}_3$  (ethane),  $\text{CH}_3\text{COCH}_3$  (acetone) | — II.  
CYCLIC (Closed-chain / Ring) |— A. ALICYCLIC  
(carbocyclic, non-aromatic rings) | |— Homocyclic:  
Cyclopropane, Cyclohexane | — Heterocyclic (non-  
aromatic): Tetrahydrofuran | — B. AROMATIC |—  
Benzenoid: Benzene, Aniline, Naphthalene |— Non-  
benzenoid: Tropone |— Heterocyclic Aromatic: Furan,  
Thiophene, Pyridine

## ✦ Important Functional Groups (Table 8.4)

Class	Functional Group	Prefix	Suffix
Alcohols	-OH	hydroxy-	-ol
Aldehydes	-CHO	formyl-/oxo-	-al
Ketones	>C=O	oxo-	-one
Carboxylic acids	-COOH	carboxy-	-oic acid
Esters	-COOR	alkoxycarbonyl-	-oate
Amines	-NH <sub>2</sub>	amino-	-amine
Amides	-CONH <sub>2</sub>	carbamoyl-	-amide
Nitriles	-C≡N	cyano-	-nitrile
Halides	-X (F,Cl,Br,I)	halo-	—
Alkenes	>C=C<	—	-ene
Alkynes	-C≡C-	—	-yne

## 💡 Order of Priority of Functional Groups (Decreasing)

**-COOH > -SO<sub>3</sub>H > -COOR > -COCl > -CONH<sub>2</sub> > -CN > -CHO > >C=O > -OH > -NH<sub>2</sub> > >C=C< > -C≡C-**

Halogens (-F, -Cl, -Br, -I), -NO<sub>2</sub>, -OR → always prefix substituents (never suffix)



## SECTION 8.5 — IUPAC NOMENCLATURE

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### 8.5.1 — Rules for Naming Branched Alkanes

#### 6 Golden Rules of IUPAC Nomenclature







1. **Identify the longest carbon chain** (parent chain = root name)
2. **Number the chain** to give substituents the lowest possible locants
3. **Name the substituents (alkyl groups)** as prefixes, listed alphabetically
4. **Use multiplying prefixes** (di, tri, tetra...) for identical substituents; numbers separated by commas
5. **If equivalent positions**, give lower number to the substituent first in alphabetical order
6. **For cyclic compounds**, prefix 'cyclo' to the parent alkane name

## Common Alkyl Groups and Names

Group	IUPAC Name	Common Name	Abbreviation
$-\text{CH}_3$	Methyl	Me	Me
$-\text{CH}_2\text{CH}_3$	Ethyl	Et	Et
$-\text{CH}(\text{CH}_3)_2$	1-Methylethyl	Isopropyl	i-Pr
$-\text{C}(\text{CH}_3)_3$	1,1-Dimethylethyl	tert-Butyl	t-Bu
$-\text{CH}_2\text{CH}(\text{CH}_3)_2$	2-Methylpropyl	Isobutyl	—
$-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	1-Methylpropyl	sec-Butyl	s-Bu

**Note:** Prefixes iso- and neo- are part of the fundamental alkyl name (alphabetical); sec- and tert- are NOT considered in alphabetical ordering.

## Common Mistakes in Nomenclature

-  Choosing a shorter chain when a longer one exists
-  Numbering from the wrong end (must give **lowest locant set**)
-  Writing the substituents NOT in alphabetical order
-  Forgetting multiplying prefixes (di, tri) when identical groups are present
-  Considering sec- and tert- in alphabetical ordering
-  For cyclic: not assigning C1 to the most branched (most substituted) carbon

## 8.5.2 — Nomenclature of Compounds with Functional Groups

### Key Steps for Functional Group Nomenclature

1. Identify the **principal functional group** (highest priority from Table 8.4)
2. Find the **longest chain containing the principal functional group**
3. Number from the end closer to the **principal functional group**
4. Subordinate functional groups → named as **prefixes**
5. Use appropriate **suffix** from Table 8.4

### Worked Examples

1.  $\text{HOCH}_2(\text{CH}_2)_3\text{CH}_2\text{COCH}_3$  → 7-Hydroxyheptan-2-one (NOT 2-oxoheptan-7-ol; keto has priority over OH)
2.  $\text{BrCH}_2\text{CH}=\text{CH}_2$  → 3-Bromoprop-1-ene (NOT 1-bromoprop-2-ene; double bond gets lowest number)
3.  $\text{CH}_2(\text{OH})\text{CH}_2(\text{OH})$  → Ethane-1,2-diol (parent alkane fully written before diol)
4.  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$  → Buta-1,3-diene (–ne dropped before diene)
5.  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$  → 6-Hydroxyheptanal (CHO carbon is C1)

## 8.5.3 — Nomenclature of Substituted Benzene

### Rules for Benzene Derivatives

- For **monosubstituted**: substituent as prefix before "benzene" — e.g., Chlorobenzene, Nitrobenzene
- For **disubstituted**: number to give lowest locants; use o/m/p prefixes for 1,2/1,3/1,4
- For **tri or higher**: ortho/meta/para cannot be used; use numbers with lowest locant rule
- When benzene is substituent on a chain: use **phenyl** ( $C_6H_5-$ , Ph)
- Common names: toluene (methylbenzene), aniline (aminobenzene), anisole (methoxybenzene)

## SECTION 8.6 — ISOMERISM

### Classification of Isomerism

ISOMERISM |— STRUCTURAL ISOMERISM (same molecular formula, different structural arrangement) | |— 1. Chain isomerism (different carbon skeleton) | |— 2. Position isomerism (different position of substituent/FG) | |— 3. Functional group isomerism (different functional groups) | |— 4. Metamerism (different alkyl chains on each side of FG) | |— STEREOISOMERISM (same constitution, different spatial arrangement) |— Geometrical (cis-trans) isomerism |— Optical isomerism

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## Examples of Each Type of Structural Isomerism

Type	Condition	Example
<b>Chain isomerism</b>	Different carbon skeleton	$C_5H_{12}$ : n-pentane, isopentane (2-methylbutane), neopentane (2,2-dimethylpropane)
<b>Position isomerism</b>	Different position of FG/substituent	$C_3H_8O$ : propan-1-ol, propan-2-ol
<b>Functional group isomerism</b>	Different functional groups	$C_3H_6O$ : propanone (ketone) and propanal (aldehyde)
<b>Metamerism</b>	Different alkyl chains on each side of FG; same total carbon	$C_4H_{10}O$ : methoxypropane ( $CH_3OC_3H_7$ ) and ethoxyethane ( $C_2H_5OC_2H_5$ )



## SECTION 8.7 — ORGANIC REACTION MECHANISM

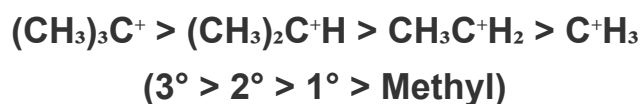
### 8.7.1 — Fission of a Covalent Bond

#### Homolytic vs. Heterolytic Cleavage

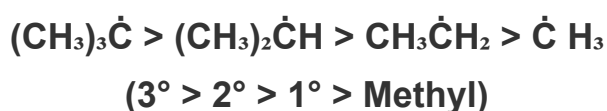
Feature	Homolytic Cleavage	Heterolytic Cleavage
<b>Electron sharing</b>	One e <sup>-</sup> to each fragment (equal split)	Both e <sup>-</sup> to one fragment
<b>Species formed</b>	Free radicals (neutral, unpaired e <sup>-</sup> )	Carbocations (+) or Carbanions (-)
<b>Arrow notation</b>	Half-headed "fish hook" arrow (→)	Full curved arrow (→)
<b>Conditions</b>	UV light, high temperature, non-polar solvents	Polar solvents, ionic conditions
<b>Reaction type</b>	Free radical (homopolar/nonpolar)	Ionic (heteropolar/polar)

## Reactive Intermediates — Stability Order

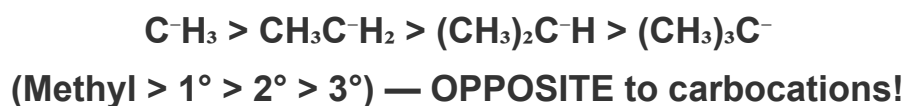
Carbocations (order: most stable → least stable):



Free radicals (order: most stable → least stable):



Carbanions (order: most stable → least stable):



### ⚠ Don't Confuse!

- Carbocation stability:  $3^\circ > 2^\circ > 1^\circ > \text{methyl}$  (more alkyl groups = more stable, due to +I and hyperconjugation)
- Carbanion stability:  $\text{methyl} > 1^\circ > 2^\circ > 3^\circ$  (more alkyl groups donate electrons = destabilise negative charge)
- Carbocation is **sp<sup>2</sup> hybridised** (trigonal planar, empty p-orbital)
- Carbanion is **sp<sup>3</sup> hybridised** (distorted tetrahedral, lone pair)

## 8.7.2 — Nucleophiles and Electrophiles

### Nucleophiles vs. Electrophiles

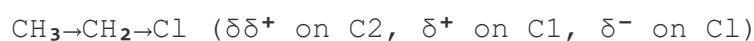
Feature	Nucleophile (Nu:)	Electrophile (E <sup>+</sup> )
<b>Meaning</b>	"Nucleus-seeking" — attacks electron-poor sites	"Electron-seeking" — attacks electron-rich sites
<b>Nature</b>	Electron-rich (donates electrons)	Electron-deficient (accepts electrons)
<b>Examples</b>	OH <sup>-</sup> , CN <sup>-</sup> , NH <sub>3</sub> , H <sub>2</sub> O, R <sub>3</sub> C: <sup>-</sup> , RO <sup>-</sup> , HS <sup>-</sup>	H <sup>+</sup> , Cl <sup>+</sup> , BF <sub>3</sub> , AlCl <sub>3</sub> , CH <sub>3</sub> <sup>+</sup> , R <sub>3</sub> C <sup>+</sup> , NO <sub>2</sub> <sup>+</sup>
<b>Attack site</b>	Electrophilic centre (δ <sup>+</sup> carbon)	Nucleophilic centre (electron-rich atom)

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## 8.7.4 to 8.7.9 — Electronic Displacement Effects

### 1. Inductive Effect (I-Effect) — Permanent

- Due to **electronegativity difference** between bonded atoms in  $\sigma$  bonds
- Transmitted through the chain; **diminishes rapidly** (negligible after 3 bonds)
- **-I effect (electron withdrawing)**:  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{COOH}$ ,  $-\text{F}$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{I}$ ,  $-\text{OH}$ ,  $-\text{OR}$
- **+I effect (electron donating)**: Alkyl groups ( $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ , tert-butyl > isopropyl > ethyl > methyl > H)
- Stronger -I effect  $\rightarrow$  **stronger acid** (stabilises carboxylate anion)



### 2. Resonance/Mesomeric Effect (R or M Effect) — Permanent

- Polarity due to interaction of  **$\pi$  bond with  $\pi$  bond** or  **$\pi$  bond with lone pair**
- Transmitted through the **conjugated system**
- **+R effect**: transfer of electrons *away* from substituent to conjugated system; *increases electron density* at certain positions
- +R groups: **-halogens**,  $-\text{OH}$ ,  $-\text{OR}$ ,  $-\text{OCOR}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{NR}_2$ , **-NHCOR**
- **-R effect**: transfer of electrons *towards* substituent from conjugated system
- -R groups:  **$-\text{COOH}$** ,  **$-\text{CHO}$** ,  **$>\text{C}=\text{O}$** ,  **$-\text{CN}$** ,  **$-\text{NO}_2$**

### 3. Electromeric Effect (E Effect) — Temporary

- Occurs **only in presence of attacking reagent** (temporary; disappears when reagent is removed)
- Complete transfer of  $\pi$ -electrons to one atom in a multiple bond
- **+E effect:**  $\pi$  electrons transferred to the atom where reagent attaches (e.g.,  $\text{H}^+$  addition to  $\text{C}=\text{C}$ )
- **-E effect:**  $\pi$  electrons transferred to the atom where reagent does NOT attach (e.g.,  $\text{CN}^-$  addition to  $\text{C}=\text{O}$ )
- When inductive and electromeric effects oppose: **electromeric effect predominates**

### 4. Hyperconjugation — Permanent

- Delocalisation of  **$\sigma$  electrons of C–H bond** of adjacent alkyl group into empty p-orbital or  $\pi$  system
- Also called "**no-bond resonance**" or "Baker-Nathan effect"
- Greater number of  $\alpha$ -hydrogen atoms  $\rightarrow$  **greater hyperconjugation**  $\rightarrow$  greater stability
- Explains stability of carbocations:  $(\text{CH}_3)_3\text{C}^+$  has 9 C–H bonds;  $\text{CH}_3^+$  has 0 (no hyperconjugation)
- Also stabilises **alkenes** and **alkylarenes**

## 🗨️ Comparing the Electronic Effects

Effect	Type	Bond Type	Transmission
Inductive	Permanent	$\sigma$ bonds	Decreases with distance
Resonance	Permanent	$\pi$ bonds/lone pairs	Through conjugated system
Electromeric	Temporary	$\pi$ bonds	At multiple bond only
Hyperconjugation	Permanent	$\sigma$ (C-H) to p/ $\pi$	Through adjacent system

### 8.7.6 — Resonance Structures

#### Rules for Writing Resonance Structures

1. Same **positions of nuclei** (atoms do not move; only electrons shift)
2. Same number of **unpaired electrons**
3. The structure with **more covalent bonds, complete octets, less charge separation** is more stable
4. Negative charge on **more electronegative** atom = more stable
5. Resonance structures are **hypothetical**; actual structure is a hybrid (resonance hybrid)
6. More contributing structures  $\rightarrow$  **lower energy resonance hybrid**  $\rightarrow$  greater stability

## Stability Order of Resonance Structures — $\text{CH}_2=\text{CH}-\text{CHO}$

Structure I:  $\text{CH}_2=\text{CH}-\text{C}(=\text{O})-\text{H}$  (most stable: all octets, no charge separation) Structure II:  $^+\text{CH}_2-\text{CH}=\text{C}(\text{O}^-)-\text{H}$  (charge separation, but negative on O) Structure III:  $^-\text{CH}_2-\text{CH}=\text{C}(\text{O}^+)-\text{H}$  (least stable: positive on O, negative on C – unfavourable)

**Stability: I > II > III**



## SECTION 8.8 — PURIFICATION METHODS

### Summary of Purification Techniques

Method	Principle	Used For	Example
<b>Sublimation</b>	Solid → vapour (without liquid state)	Sublimable compounds from non-sublimable impurities	Camphor, iodine, naphthalene
<b>Crystallisation</b>	Difference in solubility at different temperatures	Purification of solid organic compounds	Benzoic acid, sugar
<b>Simple Distillation</b>	Difference in boiling points (>25°C apart)	Volatile liquids from non-volatile impurities	Chloroform (334K) and aniline (457K)
<b>Fractional Distillation</b>	Fractionating column; successive condensation/vaporisation	Close-boiling liquids	Petroleum fractionation
<b>Distillation under reduced pressure</b>	Lowered external pressure → lower boiling point	High b.p. compounds or heat-sensitive compounds	Glycerol (from soap industry)

<b>Steam Distillation</b>	Mixture boils when $p_1 + p_2 =$ atmospheric pressure	Steam-volatile, water-immiscible compounds	Aniline from water-aniline mixture
<b>Differential Extraction</b>	Compound more soluble in organic solvent than water	Separating organic compound from aqueous solution	Separating ether-soluble from water-soluble
<b>Chromatography</b>	Differential adsorption/partition in stationary & mobile phases	Separation, purification, purity testing	TLC, column, paper chromatography

## 8.8.5 — Chromatography in Detail

### Types of Chromatography

Type	Principle	Stationary Phase	Mobile Phase
<b>Column Chromatography</b>	Differential adsorption	Silica gel or alumina in glass column	Appropriate solvent (eluant)
<b>Thin Layer Chromatography (TLC)</b>	Differential adsorption	Silica gel/alumina (0.2mm) on glass plate	Solvent (eluant)
<b>Paper Chromatography</b>	Partition (differential partitioning between stationary and mobile)	Water trapped in chromatography paper	Suitable solvent or mixture

**Retardation Factor (Rf) = Distance moved by substance from baseline (x) / Distance moved by solvent from baseline (y)**

$$0 \leq R_f \leq 1 \text{ (always)}$$

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## 💡 Detection of Colourless Spots on TLC

- **UV light** — compounds that fluoresce become visible
- **Iodine vapour** — compounds that absorb iodine appear as brown spots
- **Ninhydrin solution** — for amino acids (turns purple/pink)
- **Spray reagents** — specific for different functional groups



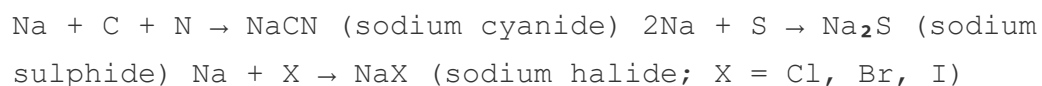
## SECTION 8.9 — QUALITATIVE ANALYSIS

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### Lassaigne's Test — Detection of N, S, Halogens, P

#### Principle of Lassaigne's Test

The organic compound is fused with metallic sodium → converts elements from **covalent to ionic form** (ionic forms are detectable)



The fused mass is dissolved in distilled water → **Sodium Fusion Extract (SFE)**

## Specific Tests from Sodium Fusion Extract

Element	Test	Reagents Added	Positive Result
<b>Nitrogen</b>	Prussian blue test	$\text{FeSO}_4$ + conc. $\text{H}_2\text{SO}_4$	Prussian blue precipitate: $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
<b>Sulphur</b>	(a) Lead acetate test	Acetic acid + $\text{Pb}(\text{CH}_3\text{COO})_2$	Black precipitate of $\text{PbS}$
<b>Sulphur</b>	(b) Sodium nitroprusside test	$\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$	Violet colour
<b>Chlorine</b>	$\text{AgNO}_3$ test	$\text{HNO}_3$ + $\text{AgNO}_3$	White ppt, soluble in $\text{NH}_4\text{OH}$
<b>Bromine</b>	$\text{AgNO}_3$ test	$\text{HNO}_3$ + $\text{AgNO}_3$	Yellowish ppt, sparingly soluble in $\text{NH}_4\text{OH}$
<b>Iodine</b>	$\text{AgNO}_3$ test	$\text{HNO}_3$ + $\text{AgNO}_3$	Yellow ppt, insoluble in $\text{NH}_4\text{OH}$
<b>Phosphorus</b>	Ammonium molybdate test	$\text{Na}_2\text{O}_2$ oxidation, then $\text{HNO}_3$ + $(\text{NH}_4)_2\text{MoO}_4$	Yellow ppt/colour (ammonium phosphomolybdate)

### ⚠ Special Cases in Lassaigne's Test

- If **both N and S** are present → sodium thiocyanate (NaSCN) forms → gives **blood red colour** with  $\text{Fe}^{3+}$ , **NO** Prussian blue (no free  $\text{CN}^-$ )
- Fix: do sodium fusion with **excess Na** → NaSCN decomposes to NaCN +  $\text{Na}_2\text{S}$
- For halogen test: if N or S is also present, **first boil with conc.  $\text{HNO}_3$**  to remove  $\text{CN}^-/\text{S}^{2-}$  that would interfere with  $\text{AgNO}_3$
- Test for C and H: heat with CuO →  $\text{CO}_2$  (tested with lime water) +  $\text{H}_2\text{O}$  (turns anhydrous  $\text{CuSO}_4$  blue)



## SECTION 8.10 — QUANTITATIVE ANALYSIS

### 8.10.1 Estimation of Carbon and Hydrogen

Burn compound in excess  $\text{O}_2/\text{CuO}$  → collect  $\text{CO}_2$  in KOH U-tube,  $\text{H}_2\text{O}$  in  $\text{CaCl}_2$  U-tube

$$\% \text{ C} = (12 \times m_2 \times 100) / (44 \times m)$$

$$\% \text{ H} = (2 \times m_1 \times 100) / (18 \times m)$$

where  $m$  = mass of compound,  $m_1$  = mass of  $\text{H}_2\text{O}$ ,  $m_2$  = mass of  $\text{CO}_2$

## 8.10.2 Estimation of Nitrogen

### (i) Dumas Method

Heat compound with CuO in CO<sub>2</sub> atmosphere → free N<sub>2</sub> collected over KOH solution

$$\% \text{ N} = (28 \times V \times 100) / (22400 \times m)$$

where V = volume of N<sub>2</sub> at STP (in mL), m = mass of compound (g)

### (ii) Kjeldahl's Method

Heat with conc. H<sub>2</sub>SO<sub>4</sub> → (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> → add NaOH → NH<sub>3</sub> → absorbed in standard H<sub>2</sub>SO<sub>4</sub> → titrate excess H<sub>2</sub>SO<sub>4</sub> with NaOH

$$\% \text{ N} = (1.4 \times M \times 2(V - V_1/2)) / m$$

where M = molarity of H<sub>2</sub>SO<sub>4</sub>, V = volume H<sub>2</sub>SO<sub>4</sub> taken, V<sub>1</sub> = volume NaOH used

⚠ **Kjeldahl's method NOT applicable to:** nitro compounds, azo compounds, nitrogen in ring (pyridine)

### 8.10.3 Estimation of Halogens — Carius Method

Heat with fuming  $\text{HNO}_3$  +  $\text{AgNO}_3$  in Carius tube  $\rightarrow$   $\text{AgX}$  precipitate

$$\% \text{ Halogen} = (\text{Atomic mass of X} \times m_1 \times 100) / (\text{Molecular mass of AgX} \times m)$$

where  $m_1$  = mass of  $\text{AgX}$ ,  $m$  = mass of compound

Halide	Mol. mass of $\text{AgX}$	Solubility in $\text{NH}_4\text{OH}$
$\text{AgCl}$	143.5	Soluble (white ppt)
$\text{AgBr}$	188	Sparingly soluble (yellowish ppt)
$\text{AgI}$	235	Insoluble (yellow ppt)

### 8.10.4 Estimation of Sulphur

Heat in Carius tube with  $\text{Na}_2\text{O}_2$  or fuming  $\text{HNO}_3$   $\rightarrow$   $\text{H}_2\text{SO}_4$   $\rightarrow$   $\text{BaSO}_4$  precipitate with  $\text{BaCl}_2$

$$\% \text{ S} = (32 \times m_1 \times 100) / (233 \times m)$$

where  $m_1$  = mass of  $\text{BaSO}_4$ ,  $m$  = mass of compound

### 8.10.6 Estimation of Oxygen

$$\% \text{ O} = 100 - (\% \text{ C} + \% \text{ H} + \% \text{ N} + \% \text{ S} + \% \text{ halogen})$$

Direct method: decompose in  $\text{N}_2 \rightarrow \text{O}_2 \rightarrow \text{CO}$  with red-hot coke  $\rightarrow \text{I}_2\text{O}_5$   
oxidises CO to  $\text{CO}_2$ , producing  $\text{I}_2$



## CASE STUDIES (CBSE Pattern)

### Case Study 1: Lassaigne's Test and Analysis

A student performed Lassaigne's test on an organic compound. On adding  $\text{FeSO}_4$  and acidifying with conc.  $\text{H}_2\text{SO}_4$ , a deep blue colour was obtained. On treating another portion with sodium nitroprusside, a violet colour appeared. On yet another portion, after acidification with  $\text{HNO}_3$  and treatment with  $\text{AgNO}_3$ , a yellowish ppt sparingly soluble in  $\text{NH}_4\text{OH}$  was obtained.

#### Q1. Which elements are present?

**Answer:** Prussian blue  $\rightarrow$  Nitrogen; Violet with nitroprusside  $\rightarrow$  Sulphur;  
Yellowish ppt with  $\text{AgNO}_3 \rightarrow$  Bromine

#### Q2. Why was $\text{HNO}_3$ added before $\text{AgNO}_3$ ?

**Answer:** Since N and S are present,  $\text{CN}^-$  and  $\text{S}^{2-}$  ions are in the SFE. These would give precipitates with  $\text{AgNO}_3$  ( $\text{AgCN}$ ,  $\text{Ag}_2\text{S}$ ) interfering with the halide test. Boiling with conc.  $\text{HNO}_3$  decomposes  $\text{CN}^-$  and  $\text{S}^{2-}$  before  $\text{AgNO}_3$  is added.

#### Q3. When both N and S are present, why is Prussian blue not obtained directly?

**Answer:**  $\text{NaSCN}$  forms (not  $\text{NaCN}$ ), so there are no free  $\text{CN}^-$  ions to form the Prussian blue complex. The thiocyanate gives blood red with  $\text{Fe}^{3+}$  instead.

## Case Study 2: Quantitative Analysis Numericals

An organic compound (0.3 g) gave 50 mL of  $N_2$  at 300K and 715 mm pressure in Dumas' method. Aqueous tension at 300K = 15 mm.

### Solution:

Actual pressure of  $N_2$  = 715 – 15 = 700 mm

Volume at STP =  $(700 \times 50 \times 273) / (760 \times 300) = 41.9$  mL

% N =  $(28 \times 41.9 \times 100) / (22400 \times 0.3) = 17.46\%$

## Case Study 3: IUPAC Naming and Isomerism

An organic compound has molecular formula  $C_4H_{10}O$ . A student claims it shows metamerism.

### Q1. Name the two metamers of $C_4H_{10}O$ (ethers).

**Answer:** Methoxypropane ( $CH_3OC_3H_7$ ) and ethoxyethane ( $C_2H_5OC_2H_5$ ). Both have different alkyl groups on each side of the  $-O-$  functional group but the same molecular formula.

### Q2. Does $C_4H_{10}O$ also show functional group isomerism?

**Answer:** Yes.  $C_4H_{10}O$  can also represent butanols (alcohols): butan-1-ol, butan-2-ol, 2-methylpropan-1-ol, 2-methylpropan-2-ol. Ethers and alcohols are functional group isomers.

### Q3. Name all types of isomerism shown.

**Answer:** Chain isomerism (among butanols), position isomerism (butan-1-ol vs butan-2-ol), metamerism (among ethers), functional group isomerism (ethers vs alcohols).

## ? EXPECTED QUESTIONS — CBSE 2025-26

### 1-Mark Questions (Very Short Answer)

1. What is the hybridisation of carbon in  $\text{CH}_2=\text{C}=\text{O}$ ? [*sp<sup>2</sup> and sp*]
2. Name the effect responsible for stability of benzene ring. [*Resonance / Delocalisation*]
3. What is the R<sub>f</sub> value in chromatography? [*Ratio of distance by substance to distance by solvent*]
4. Which method of nitrogen estimation is NOT applicable to pyridine? [*Kjeldahl's method*]
5. What colour is obtained in Lassaigne's test for sulphur with lead acetate? [*Black — PbS*]
6. Name the type of cleavage that produces free radicals. [*Homolytic cleavage*]
7. What is the shape of a methyl carbocation? [*Trigonal planar (sp<sup>2</sup> hybridised)*]
8. Give IUPAC name of  $\text{CHCl}_3$ . [*Trichloromethane*]
9. What is hyperconjugation also known as? [*No-bond resonance / Baker-Nathan effect*]
10. In steam distillation, the mixture boils when \_\_\_\_\_. [*p<sub>1</sub> + p<sub>2</sub> = atmospheric pressure*]

## 2-Mark Questions

1. Write the IUPAC names of: (a)  $(\text{CH}_3)_3\text{C}-\text{CHO}$  (b)  $\text{BrCH}_2\text{CH}=\text{CH}_2$
2. Distinguish between inductive effect and resonance effect.
3. What are nucleophiles and electrophiles? Give one example each.
4. Why is Prussian blue not formed when both N and S are present in Lassaigne's test?
5. Write all structural isomers of  $\text{C}_4\text{H}_{10}\text{O}$  (ethers).
6. Explain why a liquid vaporises below its b.p. in steam distillation.
7. In Carius method, 0.15g of compound gave 0.12g AgBr. Find % Br. [Mol. mass AgBr = 188]

## 3-Mark Questions

1. Discuss the chemistry of Lassaigne's test for nitrogen. Give reactions.
2. Explain the following with examples: (a) +I effect (b) +R effect (c) hyperconjugation
3. Explain the principle of thin layer chromatography. How are colourless compounds detected?
4. Draw resonance structures of  $\text{CH}_3\text{COO}^-$  and indicate electron shifts.
5. Compare homolytic and heterolytic bond fission with examples.
6. Give IUPAC names: (a) 3-Ethyl-4,4-dimethylheptane structure, (b) 2-Chloro-4-methylanisole, (c) 3,4-Dimethylphenol

## 5-Mark Questions (Long Answer)

1. Describe the Dumas and Kjeldahl methods for estimation of nitrogen with labelled diagrams. State their limitations.
2. Explain the various types of structural isomerism with examples for each. Draw structures.
3. Discuss the electronic displacement effects in organic chemistry: inductive, resonance, electromeric, and hyperconjugation effects with examples.
4. Describe the Carius method for estimation of (a) halogens and (b) sulphur. Give formulae used.



## EXAM STRATEGY — CHAPTER 8

### Priority Topics (High Scoring)

1. **IUPAC Nomenclature** — practice at least 30 naming problems; common in 2–3 mark questions
2. **Electronic Effects** — understand differences, not just definitions; often in 3–5 mark questions
3. **Lassaigne's Test** — write all reactions; very common as 2–3 mark question
4. **Quantitative Analysis Numericals** — master the formulas; 3 marks guaranteed
5. **Isomerism** — draw all structures for a given molecular formula
6. **Chromatography** — understand R<sub>f</sub> value; often case study material

## 🗨 Memory Tricks

**Hybridisation check:** Count "electron domains" (bonds + lone pairs) on C →  $4=sp^3$ ,  $3=sp^2$ ,  $2=sp$

**Carbocation stability:** "More carbon, more stable" (+I and hyperconjugation from alkyl groups)

**Halide precipitates in Lassaigne's test:** "White-Yellow-Yellow" (AgCl=White, AgBr=Pale Yellow, AgI=Yellow)

**Purification methods order:** "Solid → Sublimation/Crystallisation; Liquid → Distillation; Any → Chromatography"

**Kjeldahl not applicable:** "No  $NO_2$  (nitro), No  $N=N$  (azo), No ring-N (pyridine)"

**Priority order mnemonic:** "Cool Students Can Count All Categories:  $COOH > SO_3H > COOR > COCl > CONH_2 > CN > CHO > CO > OH > NH_2$ "

## LAST-MINUTE CHECKLIST

### ✓ **Must-Know for Exam**

1.  $sp$ ,  $sp^2$ ,  $sp^3$  — geometries and examples
2.  $\sigma$  and  $\pi$  bond counting rules
3. Bond-line formula reading and drawing
4. All 6 IUPAC rules for branched chain alkanes
5. Functional group priority order (at least top 7)
6. 4 types of structural isomerism with examples
7. Resonance structure rules (4 key conditions)
8. Homolytic vs heterolytic cleavage
9. Nucleophile vs electrophile — 5 examples each
10. All 4 electronic effects (nature, groups, direction)
11. Lassaigne's test — principle + reactions + results
12.  $R_f$  formula and TLC spot detection methods
13. 4 quantitative formula (C/H%, N Dumas%, N Kjeldahl%, Halogen%)
14. 8 purification methods and their principles
15. Kjeldahl limitations

## FORMULA QUICK REFERENCE

Element	Method	Formula
Carbon (%)	CuO combustion	$\% \text{ C} = (12 \times m_2 \times 100) / (44 \times m)$
Hydrogen (%)	CuO combustion	$\% \text{ H} = (2 \times m_1 \times 100) / (18 \times m)$
Nitrogen (%)	Dumas method	$\% \text{ N} = (28 \times V \times 100) / (22400 \times m)$
Nitrogen (%)	Kjeldahl's method	$\% \text{ N} = (1.4 \times M \times 2(V - V_1/2)) / m$
Halogen (%)	Carius method	$\% \text{ X} = (\text{Atomic mass of X} \times m_1 \times 100) / (\text{Mol. mass of AgX} \times m)$
Sulphur (%)	Carius method	$\% \text{ S} = (32 \times m_1 \times 100) / (233 \times m)$
Rf (TLC)	Chromatography	Rf = distance by substance / distance by solvent
Oxygen (%)	By difference	$\% \text{ O} = 100 - (\% \text{ of all other elements})$

## QUICK REVISION NOTES

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### Key Definitions

- **Catenation:** Property of carbon to form covalent bonds with other carbon atoms
- **Functional group:** Atom/group responsible for characteristic chemical properties
- **Homologous series:** Series of compounds with same FG, differing by  $-\text{CH}_2-$
- **Isomers:** Compounds with same molecular formula but different properties
- **Reaction mechanism:** Sequential account of each step describing electron movement, energetics, and rates
- **Substrate:** Reactant whose carbon is involved in new bond formation
- **Nucleophile:** Electron-rich species (donates electron pair) — nucleus-seeking
- **Electrophile:** Electron-deficient species (accepts electron pair) — electron-seeking
- **Inductive effect:** Polarisation of  $\sigma$  bond caused by electronegativity difference, transmitted through chain
- **Resonance energy:** Difference in energy between actual structure (hybrid) and lowest energy canonical structure
- **Hyperconjugation:** Delocalisation of  $\sigma$  electrons of C–H bond of alkyl group into adjacent empty p-orbital or  $\pi$  system
- **Lassaigne's test:** Sodium fusion test to detect N, S, halogens, P in organic compounds
- **Dumas method:** Estimation of N by collecting  $\text{N}_2$  gas over KOH solution
- **Kjeldahl method:** Estimation of N by converting it to  $\text{NH}_3$  and titrating with standard acid

- **Carius method:** Estimation of halogens by forming AgX precipitate

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 **Indore Branch:** Contact: +91 7869553517

 **Raipur Branch:** Raipur, Chhattisgarh

 **Website:** [www.mathlove.in](http://www.mathlove.in) |  **Email:** [info@mathlove.in](mailto:info@mathlove.in)

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