## Message from the CEO

Education is the foundation of every successful society, and books are the most reliable medium for spreading knowledge. Scholar Publications was founded with the vision to provide students and educators with high-quality, authentic, and curriculum-aligned academic content.

Books publication is not just our identity — it is our legacy. We are not merely associated with publishing; we are committed to strengthening the intellectual and academic foundation of our nation.

The development of each book begins with careful selection of authors. We publish only those books that are written by renowned, experienced, and field-expert professors, ensuring both academic strength and relevance to examination requirements.

Our mission goes beyond publishing — we aim to distribute knowledge effectively to every school and college across Punjab. Our trained marketing team regularly engages with teachers, collects their feedback, and provides them with content that is truly beneficial for both instructors and students.

We are grateful to Allah Almighty for choosing us for this important mission, and we pray that our efforts bring positive change to Pakistan's educational landscape.

**Warm regards,**
**Muhammad Shahid Qureshi**
**CEO, Scholar Publications**
**Urdu Bazar, Lahore**
**0300 – 9441414**


**Published by:**
Muhammad Shahid Qureshi
Scholar Publications
Qazafi Market, Urdu Bazar,
Lahore - Pakistan
042 - 37231595
37241133

**Edition: 2026-27**

**Composed by:**
Atiq ur Rehman

**Designed by:**
Adeel Akram

**Printed at:**
Nasir Baqir Printers
Rattigon Road, Lahore



All Rights Reserved. This book, in whole or in part, May not br reproduced, stored in a retrieval system, Or transmitted, in any form or by any means, electronic, mechanical, photocopy, recordings, in any Language or otherwise, without prior written Permission from publisher.


# Table of Contents


**17 Group 2 Elements**

| | |
|---|---|
| Theory | 01 |
| Answer Key of Topic-wise MCQs | 14 |
| Solution Check Understandings | 14 |
| Exercise Multiple Choice Questions | 15 |
| Short Answer Questions | 16 |
| Constructed Response Questions | 17 |
| Descriptive Questions | 17 |
| Additional Short Answer Questions | 17 |
| Self-Assessment | 21 |
| Entrance Test MCQs | 21 |

**18 Transition Metals**

| | |
|---|---|
| Theory | 23 |
| Answer Key of Topic-wise MCQs | 43 |
| Solution Check Understandings | 43 |
| Exercise Multiple Choice Questions | 43 |
| Short Answer Questions | 44 |
| Constructed Response Questions | 46 |
| Descriptive Questions | 47 |
| Additional Short Answer Questions | 47 |
| Self-Assessment | 49 |
| Entrance Test MCQs | 50 |

**19 Basics of Organic Chemistry**

| | |
|---|---|
| Theory | 51 |
| Answer Key of Topic-wise MCQs | 73 |
| Solution Check Understandings | 73 |
| Exercise Multiple Choice Questions | 73 |
| Short Answer Questions | 74 |
| Constructed Response Questions | 75 |
| Descriptive Questions | 78 |
| Additional Short Answer Questions | 79 |
| Self-Assessment | 82 |
| Entrance Test MCQs | 83 |

**20 Aromatic Hydrocarbons**

| | |
|---|---|
| Theory | 85 |
| Answer Key of Topic-wise MCQs | 103 |
| Solution Check Understandings | 103 |
| Exercise Multiple Choice Questions | 104 |
| Short Answer Questions | 105 |
| Constructed Response Questions | 108 |
| Descriptive Questions | 109 |
| Additional Short Answer Questions | 110 |
| Self-Assessment | 113 |
| Entrance Test MCQs | 114 |

**21 Halogenoalkanes**

| | |
|---|---|
| Theory | 115 |
| Answer Key of Topic-wise MCQs | 129 |
| Exercise Multiple Choice Questions | 129 |
| Short Answer Questions | 130 |
| Constructed Response Questions | 131 |
| Descriptive Questions | 133 |
| Additional Short Answer Questions | 133 |
| Self-Assessment | 137 |
| Entrance Test MCQs | 138 |

**22 Hydroxy Compounds**

| | |
|---|---|
| Theory | 139 |
| Answer Key of Topic-wise MCQs | 152 |
| Exercise Multiple Choice Questions | 153 |
| Short Answer Questions | 154 |
| Constructed Response Questions | 157 |
| Descriptive Questions | 157 |
| Additional Short Answer Questions | 158 |
| Self-Assessment | 162 |
| Entrance Test MCQs | 163 |

**23 Carbonyl Compounds and Carboxylic Acids**

| | |
|---|---|
| Theory | 165 |
| Answer Key of Topic-wise MCQs | 183 |
| Exercise Multiple Choice Questions | 184 |
| Short Answer Questions | 185 |
| Constructed Response Questions | 186 |
| Descriptive Questions | 187 |
| Additional Short Answer Questions | 189 |
| Self-Assessment | 193 |
| Entrance Test MCQs | 194 |

**24 Organic Nitrogen Compounds**

| | |
|---|---|
| Theory | 197 |
| Answer Key of Topic-wise MCQs | 214 |
| Exercise Multiple Choice Questions | 214 |
| Short Answer Questions | 215 |
| Constructed Response Questions | 218 |
| Descriptive Questions | 219 |
| Additional Short Answer Questions | 220 |
| Self-Assessment | 223 |
| Entrance Test MCQs | 224 |



CamScanner

**25 Organic Synthesis**

| | |
|---|---|
| Theory | 225 |
| Answer Key of Topic-wise MCQs | 237 |
| Exercise Multiple Choice Questions | 237 |
| Short Answer Questions | 238 |
| Constructed Response Questions | 240 |
| Descriptive Questions | 240 |
| Additional Short Answer Questions | 241 |
| Self-Assessment | 242 |
| Entrance Test MCQs | 243 |

**26 Polymers**

| | |
|---|---|
| Theory | 245 |
| Answer Key of Topic-wise MCQs | 258 |
| Exercise Multiple Choice Questions | 259 |
| Short Answer Questions | 260 |
| Constructed Response Questions | 262 |
| Descriptive Questions | 262 |
| Additional Short Answer Questions | 263 |
| Self-Assessment | 266 |
| Entrance Test MCQs | 267 |

**27 Bio Chemistry**

| | |
|---|---|
| Theory | 269 |
| Answer Key of Topic-wise MCQs | 288 |
| Exercise Multiple Choice Questions | 288 |
| Short Answer Questions | 289 |
| Constructed Response Questions | 291 |
| Descriptive Questions | 292 |
| Additional Short Answer Questions | 293 |
| Self-Assessment | 295 |
| Entrance Test MCQs | 296 |

**28 Chromatography**

| | |
|---|---|
| Theory | 297 |
| Answer Key of Topic-wise MCQs | 304 |
| Exercise Multiple Choice Questions | 304 |
| Short Answer Questions | 305 |
| Constructed Response Questions | 306 |
| Descriptive Questions | 307 |
| Additional Short Answer Questions | 308 |
| Self-Assessment | 311 |
| Entrance Test MCQs | 312 |

**29 Spectroscopy-1**

| | |
|---|---|
| Theory | 313 |
| Answer Key of Topic-wise MCQs | 328 |
| Exercise Multiple Choice Questions | 329 |
| Short Answer Questions | 330 |
| Constructed Response Questions | 332 |
| Descriptive Questions | 333 |
| Additional Short Answer Questions | 333 |
| Self-Assessment | 335 |
| Entrance Test MCQs | 336 |

**30 Spectroscopy-2 NMR**

| | |
|---|---|
| Theory | 337 |
| Answer Key of Topic-wise MCQs | 356 |
| Exercise Multiple Choice Questions | 356 |
| Short Answer Questions | 357 |
| Constructed Response Questions | 358 |
| Descriptive Questions | 360 |
| Additional Short Answer Questions | 360 |
| Self-Assessment | 363 |
| Entrance Test MCQs | 364 |

**31 Materials and Energy**

| | |
|---|---|
| Theory | 365 |
| Answer Key of Topic-wise MCQs | 381 |
| Exercise Multiple Choice Questions | 381 |
| Short Answer Questions | 382 |
| Constructed Response Questions | 383 |
| Descriptive Questions | 384 |
| Additional Short Answer Questions | 384 |
| Self-Assessment | 387 |
| Entrance Test MCQs | 388 |

**32 Medicine, Agriculture and Industry**

| | |
|---|---|
| Theory | 389 |
| Answer Key of Topic-wise MCQs | 403 |
| Exercise Multiple Choice Questions | 404 |
| Short Answer Questions | 405 |
| Constructed Response Questions | 407 |
| Descriptive Questions | 408 |
| Additional Short Answer Questions | 409 |
| Self-Assessment | 411 |
| Entrance Test MCQs | 412 |

**33 Water**

| | |
|---|---|
| Theory | 413 |
| Answer Key of Topic-wise MCQs | 428 |
| Exercise Multiple Choice Questions | 429 |
| Short Answer Questions | 430 |
| Constructed Response Questions | 431 |
| Descriptive Questions | 432 |
| Additional Short Answer Questions | 433 |
| Self-Assessment | 435 |
| Entrance Test MCQs | 436 |

| | |
|---|---|
| Pairing Scheme | 437 |
| Model Paper | 438 |




17 CHAPTER

# GROUP 2 ELEMENTS

## Student Learning Outcomes (SLOs)

[C-12- B-01 to C-12-B-14]

- Describe the properties and trends of Group 2 elements, including their electron configurations, reactivity, and common compounds such as oxides, hydroxides and carbonates.
- Explain the reactivity of Group 2 elements in terms of their electron configuration and valence electrons.
- Explain the chemical reactivity of Group 2 elements, including their reactions with oxygen, water, and acids (Be, Mg, Ca).
- Explain the term reactivity series and its application in predicting the outcome of chemical reactions.
- Explain the term basic oxide and its application in the formation of Group 2 compounds.
- Compare the properties and reactivity of Group 2 elements with group 1 in the periodic table.
- Understand the term thermal decomposition and its application in the analysis of Group 2 compounds especially carbonates and nitrates.
- Use the term thermal decomposition and its application in the analysis of Group 2 compounds especially carbonates and nitrates.
- Describe qualitatively the trend in the thermal stability of the nitrates and carbonates including the effect of ionic radius on the polarization of the large anion.
- Explain the trend in solubility of group 2 sulphates and hydroxides using terms enthalpy of hydration and enthalpy of solution.
- Describe qualitatively the variation in solubility and of enthalpy change of solution, $\Delta H^{\circ}_{sol}$, of the hydroxides and sulphates in terms of relative magnitudes of the enthalpy change of hydration and the lattice energy"
- Explain the term complex ion and its application in the formation of Group 2 compounds.
- Explain the extraction and purification process of Group 2 elements and their compounds.
- Describe the industrial and everyday uses of Group 2 compounds, including their role in medicine and agriculture.

**Q.1 What are Group 2 elements? State their reactivity and uses.** S/Q

**Ans.** Group 2 elements (Be, Mg, Ca, Sr, Ba, Ra) are the **s-block elements** present in Group 2 of the periodic table.

- They are called alkaline earth metals because of their metallic nature and occurrence in the earth's crust.
- Their reactivity lies between that of highly reactive alkali metals and less reactive transition metals.
- Calcium and magnesium are among the eight most widely occurring elements in the earth's crust.

➢ **Uses:**

- Beryllium is used to make copper alloys harder for aerospace materials.
- Magnesium is an important component of chlorophyll, the green matter in plants.
- Magnesium, calcium, strontium and barium are used in fireworks because they produce vibrant flame colours.



Figure: Most firework colours are due to Group 2 element

CamScanner

# PROPERTIES AND TRENDS OF GROUP 2 ELEMENTS

**Q.2 State the electronic configuration and general properties of Group 2 elements.** S/Q

**Ans. Electronic configuration of Group 2 Elements:**

- All Group 2 elements have two electrons in their outermost s-subshell.
- Their general outer electronic configuration is $ns^2$. Therefore, they show similar chemical properties. They are called alkaline earth metals.
- Some physical properties of group 2 such as melting point and densities of these elements vary down the group.
- The variations in melting points and densities are related to differences in the packing of metal atoms.

**Check Understanding!**

Q.1 The general electronic configuration of Group II elements is:
(A) $ns^1$ (B) $ns^2$
(C) $ns^2np^1$ (D) $ns^2np^2$

➢ **General Properties:**

**Salient Characteristics of Group 2 (Be-Ba)**

| Property | Beryllium (Be) | Magnesium (Mg) | Calcium (Ca) | Strontium (Sr) | Barium (Ba) |
|---|---|---|---|---|---|
| Atomic Number | 4 | 12 | 20 | 38 | 56 |
| Electron Configuration | [He] $2s^2$ | [Ne] $3s^2$ | [Ar] $4s^2$ | [Kr] $5s^2$ | [Xe] $6s^2$ |
| Metallic Radius (pm) | 112 | 160 | 197 | 215 | 222 |
| Ionic, $M^{2+}$ Radius (pm) | 31 | 65 | 99 | 113 | 135 |
| 1st Ionization Energy (kJ $mol^{-1}$) | 900 | 738 | 590 | 550 | 503 |
| 2nd Ionization Energy (kJ $mol^{-1}$) | 1757 | 1451 | 1145 | 1064 | 965 |
| Electronegativity | 1.5 | 1.2 | 1.0 | 1.0 | 0.9 |
| Melting Point (°C) | 1287 | 650 | 842 | 777 | 727 |
| Density (g $cm^{-3}$) | 1.85 | 1.74 | 1.54 | 2.64 | 3.51 |
| Standard Electrode Potential (E°) V | −1.97 | −2.37 | −2.87 | −2.89 | −2.91 |

**Q.3 Explain the trend in reactivity of Group 2 elements.** L/Q

**Ans. Chemical Reactivity of Group 2 Elements:**

The reactivity of Group 2 elements can be explained on the basis of their electronic configuration.

- All these elements have two electrons in their outermost s-subshells, $ns^2$.
- After losing these two electrons, they form stable ions with a +2 charge i.e., $M^{2+}$. Therefore, they react readily with other substances. e.g.,

$$Mg_{(s)} \longrightarrow Mg^{2+} + 2e^-$$

$$Mg_{(s)} + 2H_2O_{(l)} \longrightarrow Mg(OH)_2 + H_{2(g)}$$

- Thus reactivity increases from Be to Ba **due to an increase in atomic size and shielding effect, and a decrease in ionization energy down the group.**
- This makes the removal of the outermost electrons easier, and reactivity increases.
- The increasing order of reactivity is:

$$Be < Mg < Ca < Sr < Ba$$

- Hence, beryllium is the least reactive and barium is the most reactive element of Group 2.




**Figure: Relative sizes of the atoms of the Group 2 elements**



# CHEMICAL REACTIONS OF GROUP 2 ELEMENTS

**Q.4 Describe the reactions of Group 2 elements with oxygen.** L/Q

**Ans. Reactions with Oxygen:**

All Group 2 metals burn in oxygen to form metal oxides, MO.

$$2M + O_2 \longrightarrow 2MO$$

- **Beryllium:** Beryllium reacts with oxygen at high temperature, above 600 °C, to form beryllium oxide (BeO).

$$2Be_{(s)} + O_{2(g)} \xrightarrow{600^\circ C} 2BeO_{(s)}$$

- A thin **non-porous, strong oxide layer protects beryllium** and makes it less reactive than the other members of the group.
- **Magnesium:** Magnesium burns brightly in air or oxygen to form magnesium oxide, MgO.
- **Calcium:** Calcium reacts more vigorously with oxygen and producing a brick-red flame.
- The oxides of Group 2 elements are generally white solids and basic in nature except BeO.
- Their basic character increases down the group.
- In water, the oxide ion reacts with water to produce hydroxide ions.

$$O^{2-}_{(s)} + H_2O_{(l)} \longrightarrow 2OH^-_{(aq)}$$

**Check Understanding!**

Q.2 Why does beryllium differ from other Group II elements?

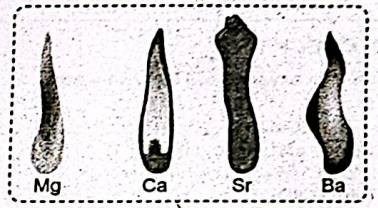



**Figure: Flames of Group 2 Elements**

**Interesting Note**

When Mg burns in air, it forms MgO. Air contains $N_2$, too and hot Mg reacts with it.

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

To avoid its formation, we can use pure $O_2$.

**Q.5 Describe the reactions of Group 2 elements with water.** Exercise D/Q.4

**Ans. Reactions of Group 2 Elements with Water:**

Except beryllium, Group 2 metals react with water to form metal hydroxides, $M(OH)_2$, and hydrogen gas, $H_2$.

- **Beryllium:** Beryllium does not react with water or steam, even on heating, due to its protective beryllium oxide layer.

➢ **Magnesium:**

**Reaction with Cold Water:**

- Magnesium reacts very slowly with cold water to form magnesium hydroxide and hydrogen gas fizzes steadily.

$$Mg_{(s)} + 2H_2O_{(l)} \longrightarrow Mg(OH)_{2(s)} + H_{2(g)}$$

**Reaction with Steam:**

- With steam, magnesium reacts faster to form magnesium oxide and hydrogen gas.

$$Mg_{(s)} + H_2O_{(g)} \longrightarrow MgO_{(s)} + H_{2(g)}$$

➢ **Calcium:**

- Calcium reacts with cold water and steam more quickly than magnesium to form calcium hydroxide and hydrogen gas.
- Calcium hydroxide is sparingly soluble so dissolves very little in water and forms a white precipitate.

$$Ca_{(s)} + 2H_2O_{(l)} \longrightarrow Ca(OH)_{2(s)} + H_{2(g)}$$

- The hydroxides of Group 2 elements are **less basic** than hydroxides of Group 1 elements.
- However, their basic character increases down the group due to increasing solubility.

**Interesting Information**

Milk of magnesia is the common brand name of suspension $Mg(OH)_2$. It is an antacid. It works by neutralizing excess stomach acid ($HC\ell$) provide relief from heart burn and indigestion.

$$Mg(OH)_2 + 2HC\ell \longrightarrow MgC\ell_2 + 2H_2O$$

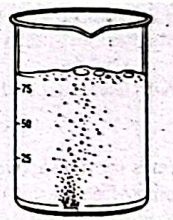


**Figure: Calcium forms a sparingly soluble hydroxide with water**

CamScanner

**Q.6 Describe the reactions of Group 2 elements with dilute acids.** Exercise D/Q.4

**Ans. Reactions with Acids:**

Group 2 metals react with dilute acids to produce a salt and hydrogen gas.

➢ **General Reaction:**

$$M_{(s)} + 2HCl_{(aq)} \longrightarrow MCl_{2(aq)} + H_{2(g)}$$

- The reactivity of Group 2 metals increases down the group.
- **Beryllium** reacts with dilute acids to form beryllium chloride and hydrogen gas. However, its protective oxide layer can slow down the reaction.
- **Magnesium** reacts readily with **dilute hydrochloric acid** and **dilute sulphuric acid** to form magnesium salts and hydrogen gas.

$$Mg_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_{2(g)}$$
$$Mg_{(s)} + H_2SO_{4(aq)} \longrightarrow MgSO_{4(aq)} + H_{2(g)}$$

- **Calcium** reacts quickly with dilute hydrochloric acids to form calcium salts and hydrogen gas.

$$Ca_{(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_{2(g)}$$

- With dilute sulphuric acid, the reaction of calcium can stop early.

**Reason:** Calcium sulphate formed dissolves very little in water (sparingly soluble). It coats the surface of calcium metal and forms a protective layer.

$$Ca_{(s)} + H_2SO_{4(aq)} \longrightarrow CaSO_{4(s)} + H_{2(g)}$$

### ☑ QUICK CHECK 17.1

**a) Write equations for the following reactions: i) Ca with oxygen ii) Ba with water**

**Ans. (i) Calcium** burns in oxygen to form calcium oxide.

$$2Ca_{(s)} + O_{2(g)} \longrightarrow 2CaO_{(s)}$$

**(ii) Barium** reacts with water to form barium hydroxide and hydrogen gas.

$$Ba_{(s)} + 2H_2O_{(l)} \longrightarrow Ba(OH)_{2(aq)} + H_{2(g)}$$

**b) Predict the extent of the reactions of Sr and Ba with $H_2SO_4$.**

**Ans. Sr with $H_2SO_4$:** Reaction of **strontium** with $H_2SO_4$ is a vigorous **redox displacement** reaction to form **bright white** precipitate of strontium sulphate and hydrogen gas.

$$Sr_{(s)} + H_2SO_{4(aq)} \longrightarrow SrSO_{4(s)} + H_{2(g)}$$

The reaction starts readily, but strontium sulphate forms a dense solid coating on the surface of strontium. Therefore, the reaction slows down or stops early.

**Ba with $H_2SO_4$: Barium** reacts with $H_2SO_4$ to form pure white precipitate of barium sulphate and hydrogen gas.

$$Ba_{(s)} + H_2SO_{4(aq)} \longrightarrow BaSO_{4(s)}\downarrow + H_{2(g)}$$

Barium is below strontium in Group 2 and is more reactive. Therefore, it reacts more quickly at first. However, the barium sulphate formed can also coat the metal surface with a protective layer, so this reaction may also stop early.

**c) Explain why Group 2 elements are reactive, based on their electron configuration and ion formation.**

**Ans.** Group 2 elements have two electrons in their outermost s-subshell. Their general outer electronic configuration is $ns^2$. They lose these two electrons to form stable ions with a +2 charge, $M^{2+}$. These ions combine with negative ions of other substances to form compounds. Therefore, Group 2 elements react readily with other substances.

**d) Write a balanced equation for magnesium and barium burning in air and compare their reactivity.**

**Ans.**

- Magnesium and barium burn in oxygen present in air to form their oxides.

$$2Mg_{(s)} + O_{2(g)} \longrightarrow 2MgO_{(s)}$$

- With excess $O_2$ and strong heating at 500-600°C, Barium peroxide ($BaO_2$) is formed.

$$Ba + O_2 \xrightarrow[\text{Barium Per oxide}]{500°C-600°C} BaO_2$$

Barium is more reactive than calcium because it lies lower in Group 2. Its larger atomic size and greater shielding effect result in lower ionization energy. Therefore, barium loses its outermost electrons more easily than calcium.

**e) Predict the density and melting point of the radioactive radium (Ra) following the trend in Group 2.**

**Ans. Density:**

In Group 2 elements, density generally increases from top to bottom.



**Reason:** Because among group 2 element, down the group atomic mass increases much faster than atomic volume. Since **radium is below barium**, its density is expected to be higher (Predicted density = 5.5 g $cm^{-3}$) than that density of barium (3.51 g $cm^{-3}$).

**Trend:** The melting points of Group 2 elements **generally decrease** down the group (Be: 1287°C to Ba = 727°C). As atomic radius increases, the valence electrons are farther from the positively charged nuclei. This weakens metallic bonding. Therefore, radium has a lower melting point (≈ 700°C).

## COMPARISON OF GROUP 2 ELEMENTS WITH GROUP 1 ELEMENTS

**Q.7 Compare the reactivity of Group 1 and Group 2 elements.**

**Ans.** Group 1 and Group 2 elements are highly reactive metals. However, Group 1 metals are more reactive than Group 2 metals counter parts in the same period.

- Group 1 metals have one electron in their outermost shell. They lose this electron easily to form a +1 ion, $M^+$. Therefore, they react readily.
- Group 2 metals have two electrons in their outermost shell. They lose two electrons to form a +2 ion, $M^{2+}$. The removal of two electrons requires more energy; therefore, they are generally less reactive than Group 1 metals.
- In both groups, reactivity increases down the group due to increasing atomic size and decreasing ionization energy.

**Check Understanding!**

**Q.3 Which Group II element does not react with cold water?**

(A) Calcium (B) Strontium
(C) Barium (D) Beryllium

**Comparison of Group 1 elements with Group 2 elements**

| Feature | Group 1 (Alkali Metals) | Group 2 (Alkaline Earth Metals) |
|---|---|---|
| Valence Electrons | 1 ($ns^1$) | 2 ($ns^2$) |
| Ion Formation | Forms +1 ions ($M^+$) e.g., $Na^+$ | Forms +2 ions ($M^{2+}$) e.g., $Mg^{2+}$ |
| Reactivity | More reactive than group 2 elements. | Less reactive (compared to Group 1 elements in the same period). |
| Reason for Reactivity | Lowest ionization energies. | Higher ionization energies. |
| Hardness | Very soft (can be cut with a knife). | Harder than Group 1 metals. |
| Density | Low densities e.g., $d_{Li}$ = 0.53 g/$cm^3$ | Higher densities than Group 1 metals e.g., $d_{Be}$ = 1.85 g/$cm^3$ |
| Melting/Boiling Points | Lower melting/boiling points than group 2. | Higher melting/boiling points. |
| Reaction with Water | Very vigorous, often explosive (e.g., Na with water). | Less vigorous (e.g., Ca with water, Mg with steam). |
| Oxides | Form $M_2O$ (e.g., $Na_2O$); highly basic. | Form MO (e.g., CaO); less basic than Group 1 oxides. |
| Hydroxides | Highly soluble, strong bases. | Less soluble than Group 1, but solubility increases down the group. Less basic than Group 1 hydroxides. |

## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Which electron configuration is common to all Group 2 elements?**
   (A) $ns^1$ (B) $ns^2$ (C) $ns^2np^1$ (D) $ns^2np^2$
2. **The increasing order of reactivity of Group 2 elements is:**
   (A) Ba < Sr < Ca < Mg < Be (B) Be < Mg < Ca < Sr < Ba
   (C) Mg < Be < Ca < Ba < Sr (D) Be < Ca < Mg < Sr < Ba
3. **The reactivity of Group 2 elements increases down the group mainly because:**
   (A) Atomic radius decreases (B) Ionization energy increases
   (C) Ionization energy decreases (D) Electronegativity increases
4. **Which Group 2 element is least reactive?**
   (A) Magnesium (B) Calcium (C) Beryllium (D) Barium
5. **On burning in oxygen, Group 2 metals generally form:**
   (A) Peroxides (B) Superoxides (C) Metal oxides (D) Hydroxides

CamScanner

6. Which Group 2 element reacts with oxygen only at high temperature due to a protective oxide layer?
(A) Calcium (B) Magnesium (C) Barium (D) Beryllium
7. The basic character of Group 2 oxides:
(A) Decreases down the group (B) Remains constant
(C) Increases down the group (D) First increases then decreases
8. Which Group 2 metal does NOT react with water or steam?
(A) Magnesium (B) Calcium (C) Barium (D) Beryllium
9. Magnesium reacts rapidly with to produce $H_2$:
(A) Cold water (B) Steam (C) Ice (D) Dilute nitric acid only
10. Calcium reacts with cold water to produce:
(A) $CaO + H_2$ (B) $Ca(OH)_2 + H_2$ (C) $CaH_2 + O_2$ (D) $CaO_2 + H_2$
11. Calcium hydroxide formed with water is:
(A) Highly soluble (B) Insoluble (C) Sparingly soluble (D) Volatile
12. Group 2 metals react with dilute hydrochloric acid to produce:
(A) Metal oxide and hydrogen (B) Metal chloride and oxygen
(C) Metal chloride and hydrogen (D) Metal hydroxide and chlorine
13. Which reaction slows because of the formation of a protective $CaSO_4$ layer?
(A) $Ca + HCl$ (B) $Mg + HCl$ (C) $Ca + H_2SO_4$ (D) $Mg + H_2SO_4$
14. Group 2 elements generally form ions of charge:
(A) +1 (B) +2 (C) +3 (D) +4
15. Compared with Group 1 metals, Group 2 metals are generally:
(A) Softer (B) More reactive (C) Harder (D) Less dense
16. Group 2 hydroxides are generally:
(A) More basic than Group 1 hydroxides (B) Neutral
(C) Less basic than Group 1 hydroxides (D) Acidic
17. Which Group 2 metal is an essential part of chlorophyll?
(A) Calcium (B) Magnesium (C) Strontium (D) Barium
18. Which property generally increases down Group 2?
(A) Electronegativity (B) First ionization energy (C) Metallic radius (D) Melting point
19. Group 2 metals lose _____ electrons to attain noble gas configuration.
(A) One (B) Two (C) Three (D) Four
20. Which statement correctly compares Group 1 and Group 2 metals?
(A) Group 2 metals are more reactive than Group 1.
(B) Group 1 metals form +2 ions.
(C) Group 2 metals have higher ionization energies than Group 1 metals.
(D) Both groups have identical chemical properties.

## THERMAL DECOMPOSITION OF CARBONATES AND NITRATES

**Q.8 Explain the thermal decomposition of carbonates and nitrates of Group 2 elements. Give reason and relative order of the ease of thermal stability.** Exercise Q10

**Ans.** Thermal decomposition is a chemical reaction in which a single compound breaks down into two or more simpler substances on heating.

- This process usually requires energy (endothermic) to break the chemical bonds within the compound.
- On heating, Group 2 carbonates decompose to form a metal oxide (MO) and carbon dioxide gas.

**General Reaction:**

$$MCO_{3(s)} \longrightarrow MO_{(s)} + CO_{2(g)}$$

**Examples:**

$$MgCO_{3(s)} \xrightarrow{heat} MgO_{(s)} + CO_{2(g)}$$
$$CaCO_{3(s)} \xrightarrow{heat} CaO_{(s)} + CO_{2(g)}$$

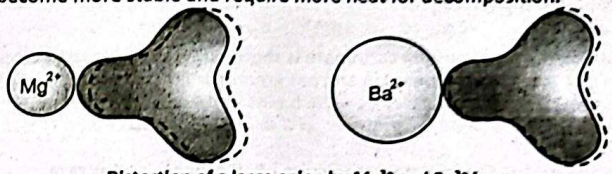
- The thermal stability of Group 2 carbonates increases down the group. Thus, $BeCO_3$ decomposes at the lowest temperature, whereas $BaCO_3$ requires the highest temperature for decomposition.

**Check Understanding!**
Q.4 How quicklime is prepared from $CaCO_3$.

In group 2 carbonates, ease of decomposition decreases down the group.



- This trend is due to the size of the $M^{2+}$ ion. Smaller and highly charged cations ($Mg^{2+}$) have greater "polarizing power".
- They distort the $CO_3^{2-}$ ion more strongly, weaken its bonds, and make it easier to decompose on heating.
- Down the group, the metal ions become larger and their polarizing power decreases. Therefore, the carbonates become more stable and require more heat for decomposition.




**Distortion of a large anion by $Mg^{2+}$ and $Ba^{2+}$ ions**
**$Mg^{2+}$ causes greater polarization than $Ba^{2+}$**

The figure shows the polarizing power of Group 2 metal ions on a large negative ion.
- $Mg^{2+}$ is smaller than $Ba^{2+}$ and has a higher charge density. Therefore, it attracts and distorts the electron cloud of the nearby anion more strongly. In the left diagram, the difference between the dashed outline and the shape represents this greater distortion.
- $Ba^{2+}$ is larger and has lower charge density. Its polarizing power is weaker, so it causes much less distortion of the anion. In the right diagram, the shape is closer to the dashed outline.

➢ **Thermal decomposition and thermal stability of Group 2 nitrates:**

On heating, Group 2 nitrates decompose to form a metal oxide, brown nitrogen dioxide gas, and oxygen gas.

$$2Ca(NO_3)_{2(s)} \xrightarrow{heat} 2CaO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

- The thermal stability of Group 2 nitrates increases down the group.
- $Be(NO_3)_2$ is the least stable, whereas $Ba(NO_3)_2$ is the most stable nitrate of the group.
- The trend is due to the polarizing power of the $M^{2+}$ ions. Smaller ions at the top of the group (e.g. $Be^{2+}$, $Mg^{2+}$) distort the $NO_3^-$ ion more strongly. This makes the nitrate easier to decompose at a lower temperature.
- Down the group, the $M^{2+}$ ions become larger and their polarizing power decreases. Therefore, the nitrates become more stable and need more heat for decomposition.

➢ **Thermal decomposition help in identifying Group 2 carbonates and nitrates:**

The temperature at which Group 2 carbonates or nitrates decompose can help to identify unknown compounds and confirm the presence of specific elements.

- The decomposition pattern helps to understand the relationship between ionic size, charge density, and thermal stability.
- The thermal stability of Group 2 carbonates increases down the group.
- Example: $BeCO_3$ decomposes at 100°C, whereas $BaCO_3$ decomposes at 1360°C. Thus, a higher decomposition temperature indicates a more thermally stable carbonate.
- The temperatures at which Group 2 carbonates decompose are given in the following Table.

**Table: Temperatures of Decomposition of the Group 2 Carbonates at 1 atm**

| Metal Carbonate | Temperature (°C) |
|---|---|
| $BeCO_3$ | ~ 100 |
| $MgCO_3$ | ~ 540 |
| $CaCO_3$ | ~ 900 |
| $SrCO_3$ | ~ 1150 |
| $BaCO_3$ | ~ 1360 |

### QUICK CHECK 17.2

**a) State two physical differences between Group 1 and Group 2 metals.**

**Ans. Differences:**

I. Group 1 metals are very soft and can be cut with a knife, whereas Group 2 metals are harder.
II. Group 1 metals have low densities, whereas Group 2 metals have higher densities.

CamScanner

**b) State the general formula for a Group 1 oxide and a Group 2 oxide.**

i. Group 1 metals form +1 ions, so the general formula of their oxides is $M_2O$.

ii. Group 2 metals form +2 ions, so the general formula of their oxides is MO.

**c) Write the balanced equation for the thermal decomposition of $SrCO_3$.**

**Ans.** On heating, strontium carbonate decomposes to form strontium oxide and carbon dioxide.
The balanced equation is given below:

$$SrCO_{3(s)} \xrightarrow{1150^\circ C} SrO_{(s)} + CO_{2(g)}$$

**d) Explain qualitatively why magnesium carbonate is thermally less stable than calcium carbonate.**

**Ans.** Magnesium ion is smaller than calcium ion and has greater polarizing power. Magnesium ion distorts the carbonate ion more strongly, which weakens the bonds in the carbonate ion.
Therefore, magnesium carbonate decomposes at a lower temperature and is less thermally stable than calcium carbonate.

**e) Write the equation for the thermal decomposition of: i) Magnesium nitrate. ii) Barium nitrate. Which of these decomposes at a lower temperature?**

**Ans. i) Magnesium Nitrate:** On heating, magnesium nitrate decomposes to form magnesium oxide, brown nitrogen dioxide gas and oxygen gas.
The balanced equation is given below:

$$2Mg(NO_3)_{2(s)} \xrightarrow{Heat} 2MgO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

**(ii) Barium Nitrate:** On heating, barium nitrate decomposes to form barium oxide, brown nitrogen dioxide gas and oxygen gas.
The balanced equation is given below:

$$2Ba(NO_3)_{2(s)} \xrightarrow{Heat} 2BaO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

**Decomposes at a Lower Temperature:**
Magnesium nitrate decomposes at a lower temperature (330°C-400°C) than **barium nitrate** (592°C).

$$2Mg(NO_3)_2 \longrightarrow 2MgO + 4NO_2 + O_2$$

**Reason:** Magnesium ion is smaller and has greater **polarizing power** than barium ion. Magnesium ion distorts the nitrate ion more strongly, so magnesium nitrate is less thermally stable and decomposes more easily on heating.

## SOLUBILITY OF GROUP 2 SULPHATES AND HYDROXIDES

**Q.9 Explain the energy changes involved when an ionic compound dissolves in water.** L/Q

**Ans.** The solubility of an ionic compound in water depends on the balance between hydration enthalpy and lattice enthalpy.

**i. Enthalpy of hydration, $\Delta H^\circ_{hyd}$**

**Definition:** It is the energy released when gaseous ions are surrounded and attracted by water molecules (and become hydrated).

- It is always exothermic.
- Stronger attraction between ions and water molecules means a more negative $\Delta H^\circ_{hyd}$.
- Smaller ions with higher charge density attract water molecules more strongly and have a more negative (larger magnitude) hydration enthalpy.
- Down a group, ions become larger; therefore, $\Delta H^\circ_{hyd}$ becomes less negative (less energy released).

**Check Understanding!**
**Q.5 Which group 2 ion has the most exothermic enthalpy of hydration?**
(A) $Ba^{2+}$ (B) $Sr^{2+}$
(C) $Mg^{2+}$ (D) $Be^{2+}$

**ii. Lattice enthalpy, $\Delta H^\circ_{lattice}$**

**Definition:** The energy required to break one mole of a solid ionic compound into gaseous ions is called lattice enthalpy.

- It is always endothermic.
- Stronger forces between ions in the crystal lattice result in higher lattice enthalpy.
- **Factors:** It depends on the charges and sizes of the ions. As the sizes of the cation and the anion are comparable, the attractive forces become stronger and the lattice energy is higher.
- When one of the ions is larger and the other much smaller, the forces become weaker and the compound will have lower lattice energy.



**iii. Enthalpy of solution, $\Delta H^\circ_{soln}$**

- The enthalpy of solution is the overall energy change when an ionic solid dissolves in water.
- It is related to lattice enthalpy and hydration enthalpy as:

$$\Delta H^\circ_{soln} = \Delta H^\circ_{lattice} + \Delta H^\circ_{hyd}$$

- $\Delta H^\circ_{lattice}$ is positive because energy is needed to separate the ions in the solid lattice.
- $\Delta H^\circ_{hyd}$ is negative because energy is released when water molecules surround and hydrate the ions.
- Thus, a compound dissolves more easily when the **negative** hydration **enthalpy** is large enough to balance or exceed the **positive lattice enthalpy.**
- A more negative or less positive value of $\Delta H^\circ_{soln}$ generally means greater solubility.

**Check Understanding!**
**Q.6 Why is $CaSO_4$ sparingly soluble but $BaSO_4$ is insoluble in water?**

**Q.10 Explain the solubility trends of Group 2 hydroxides and sulphates.** Exercise D/Q.6

**Ans.** The solubility of Group 2 hydroxides increases down the group.

- **Example:** $Mg(OH)_2$ dissolves very little in water, whereas $Ba(OH)_2$ is quite soluble.
- **Reason:** Down Group 2, both hydration enthalpy and lattice enthalpy decrease. However, in the hydroxides, the decrease in lattice enthalpy is more significant than the decrease in hydration enthalpy. Therefore, the hydroxides become more soluble down the group.
  The solubility of Group 2 sulphates decreases down the group.
- **For example,** $MgSO_4$ is soluble, whereas $BaSO_4$ is insoluble.
- **Reason:** The sulphate ion, $SO_4^{2-}$, is relatively large. Down Group 2, both hydration enthalpy and lattice enthalpy decrease. But, for a large anion like sulphate, the decrease in hydration enthalpy is more significant than the decrease in lattice enthalpy. Therefore, the sulphates become less soluble down the group.

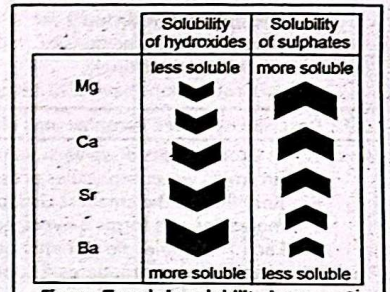


**Figure: Trends in solubility in group 2 hydroxides and sulphates**

**Table: Solubility of Group 2 hydroxides and sulphates**

| Group 2 Hydroxides | Solubility at 298 K ($\frac{mol}{100\ g}$ of water) | Group 2 Sulphates | Solubility at 298 K ($\frac{mol}{100\ g}$ of water) |
|---|---|---|---|
| $Mg(OH)_2$ | $2 \times 10^{-5}$ | $MgSO_4$ | $1.83 \times 10^{-1}$ |
| $Ca(OH)_2$ | $1.5 \times 10^{-3}$ | $CaSO_4$ | $4.66 \times 10^{-3}$ |
| $Sr(OH)_2$ | $3.4 \times 10^{-3}$ | $SrSO_4$ | $7.11 \times 10^{-5}$ |
| $Ba(OH)_2$ | $1.5 \times 10^{-2}$ | $BaSO_4$ | $9.43 \times 10^{-7}$ |

## COMPLEX ION FORMATION

**Q.11 What is a complex ion? Explain the formation of complex ions by Group 2 metal ions.** L/Q

**Ans. Complex Ion:**
A complex ion is an ion in which a central metal ion is bonded to a number of surrounding electron-donating species.
OR
A complex ion is a charged species consisting of a central metal cation bonded to one or more ligands by coordinate covalent bonds.

➢ **Formation of Complex Ions**

- In the formation of complex ions, the central metal ion acts as a Lewis acid because it accepts electron pairs.

**Check Understanding!**
**Q.7 The complexes of group 2 metals are mostly:**
(A) Covalent, low spin and colored.
(B) Ionic, inert and colored.
(C) Covalent, inert and paramagnetic.
(D) Ionic, labile and colorless.

CamScanner

➢ **Role of Central Metal Atom and Ligands:**

- **Ligands-Lewis bases:** Any specie that donates electron pairs to the central metal ion and form coordinate bonds. Molecules or ions having lone pairs of electrons, such as $H_2O$, $NH_3$, $Cl^-$ and $OH^-$, act as Lewis bases.

➢ **Coordination Number:**

- The number of **coordinate bonds** formed between the central metal ion and the electron donors is called **the coordination number.** Common coordination numbers are 2, 4 and 6.
  **Example:** In $[Be(H_2O_4)]^{2+}$, the coordination no. of Be = 4.

➢ **Complex Formation by Group 2 Vs Transition Elements:**

- Complex ion formation is more typical for transition metals because they have available **d-orbitals** for bonding.
- However, Group 2 elements can also form complex ions, especially the elements present at the top of the group.
- Their tendency to form complexes is far less pronounced than that of transition metals.
- The ability of a Group 2 metal ion to form a complex ion depends on its size and charge. Smaller ions have higher charge density, that is, a high charge-to-size ratio. Therefore, they attract electron-donating species more strongly.
- All Group 2 ions have a +2 charge, which provides electrostatic attraction for electron-pair donors.

**Q.12 Describe hydrated complex ions of Group 2 elements.** L/Q

**Ans.** When Group 2 salts dissolve in water, their metal ions become hydrated. These **hydrated ions are complex ions** in which water molecules act as electron-pair donors.

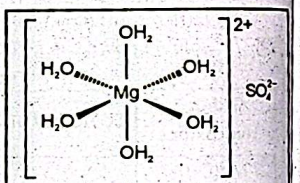
- **Beryllium** is the smallest Group 2 ion and has high charge density. Therefore, it strongly attracts water molecules and forms a hydrated ion.
- Each $H_2O$ molecule donates one electron pair and forms one coordinate bond with $Be^{2+}$. Beryllium generally accommodates 4 donor atoms. Since four $H_2O$ molecules are attached to $Be^{2+}$, its coordination number is 4.

$$[Be(H_2O)_4]^{2+}$$

- Magnesium ions are larger and usually form hexahydrate complexes with coordination number 6 $[Mg(H_2O)_6]^{2+}$.
- Larger ions, such as $Ca^{2+}$, $Sr^{2+}$ and $Ba^{2+}$, also form hydrated ions, mostly with coordination number 6, although the strength of interaction decreases down the group.
- Group 2 ions, especially the smaller ones, can form stable complexes with donors having more than one donatable electron pair. These donors can form more than one coordinate bond to the same metal ion and produce a ring-like structure.
- Calcium ion forms a complex ring structure with EDTA (ethylenediaminetetraacetic acid), which is a six-electron-pair donor.

$$Ca^{2+}_{(aq)} + EDTA^{4-}_{(aq)} \longrightarrow [Ca(EDTA)]^{2-}_{(aq)}$$

- EDTA is hexadenate. It binds to a central atom using **six donor** site at once.

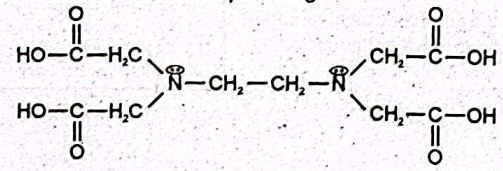


Hydrated magnesium ion, $[Mg(H_2O)_6]^{2+}$, showing coordination number 6

EDTA is added to certain canned foods to remove transition metal ions that can catalyze the deterioration of food.

➢ **Uses of EDTA:**

- The Ca-EDTA complex is used in water softening, where EDTA removes $Ca^{2+}$ and $Mg^{2+}$ ions from hard water.
- EDTA can be used in **chelation therapy** to remove toxic metal ions, including $Ca^{2+}$ when its level is too high, from the body.
- EDTA is used to treat lead poisoning.





Ca-EDTA complex is used in medicines to remove metal ions from the body



**QUICK CHECK 17.3**

**a) Why does $MgSO_4$ dissolve easily as compared to $BaSO_4$?**

**Ans.** The enthalpy of solution, $\Delta H_{sol}$, is the overall energy change when an ionic compound dissolves in water. For a salt to dissolve, hydration energy must overcome lattice energy.
$Mg^{2+}$ is small and has high charge density so it attracts water molecules strongly and $MgSO_4$ dissolves quickly. While $Ba^{2+}$ is large and has low charge density, so weak hydration energy cannot overcome lattice energy. So $BaSO_4$ is almost insoluble.

**b) How does lattice enthalpy affect the solubility of Group 2 sulphates?**

**Ans.**
- A high lattice enthalpy means that more energy is required to separate the ions in the crystal lattice. This increases the enthalpy of solution and generally reduces solubility.
- In Group 2 sulphates, lattice enthalpy decreases down the group. However, hydration enthalpy decreases more significantly.
- Therefore, the enthalpy of solution increases and the solubility of sulphates decreases down the group.

$$\text{Lattice energy} \propto \frac{1}{r^+ + r^-}$$

As size of $Sr^{2+} > Ca^{2+}$, lattice energy decreases more than hydration energy.

**c) Which hydroxide is more soluble, $Ca(OH)_2$ or $Sr(OH)_2$? Give reason.**

**Ans.** $Sr(OH)_2$ is more soluble than $Ca(OH)_2$.
**Reasons:** In Group 2 hydroxides, both hydration enthalpy and lattice enthalpy decrease down the group. However, the decrease in lattice enthalpy is more significant than the decrease in hydration enthalpy.
- Therefore, the enthalpy of solution decreases down the group 2.
- $Sr(OH)_2$ has a lower enthalpy of solution than $Ca(OH)_2$ and therefore dissolves more easily.

## EXTRACTION AND PURIFICATION OF GROUP 2 ELEMENTS AND THEIR COMPOUNDS

**Q.13 Explain the extraction of magnesium from seawater by the Dow Process.** Exercise D/Q.7

**Ans. Dow Process for the Mg production from Sea Water:**
The Dow Process is a multi-step **chemical and electrochemical process** used to extract magnesium metal from the magnesium ions ($Mg^{2+}$) present in seawater.

- It is an industrial process for obtaining magnesium metal from sea water which is a vast reservoir of magnesium.
- In this process, seawater is treated with calcium hydroxide, which is obtained from limestone or oyster shells.
- Calcium hydroxide precipitates magnesium ions as insoluble magnesium hydroxide.

$$Mg^{2+}_{(aq)} + Ca(OH)_{2(s)} \longrightarrow Mg(OH)_{2(s)} + Ca^{2+}_{(aq)}$$

- The precipitated magnesium hydroxide is filtered and then reacted with hydrochloric acid to form magnesium chloride.

$$Mg(OH)_{2(s)} + 2HC\ell_{(aq)} \longrightarrow MgC\ell_{2(aq)} + 2H_2O_{(\ell)}$$

- The magnesium chloride ($MgC\ell_2$) solution is concentrated and dried.
- The molten magnesium chloride is then subjected to electrolysis in large electrolytic cells.

**Check Understanding!**
**Q.8 Why is Dow process used for Mg extraction instead of direct electrolysis of aqueous solution?**

➢ **Electrolysis Products:**

$$Mg^{2+}_{(\ell)} + 2C\ell^-_{(\ell)} \longrightarrow Mg_{(\ell)} + C\ell_{2(g)}$$

- **At cathode:** Pure magnesium metal

$$Mg^{2+}_{(\ell)} + 2e^- \longrightarrow Mg_{(\ell)}$$

- **At anode:** chlorine gas

$$2C\ell^-_{(\ell)} \longrightarrow C\ell_{2(g)} + 2e^-$$

➢ **Significance:**

- The Dow Process revolutionized magnesium production by extracting a valuable metal from seawater on a massive industrial scale.

CamScanner

## ➲ Production of Quicklime (CaO) from Limestone ($CaCO_3$)

**Q.14 Describe the production of quicklime from limestone.** L/Q

**Ans.** **Quicklime is calcium oxide,** CaO. It is produced from calcium carbonate, which occurs naturally as limestone, processes involving a Group 2 compound.

- The production of quicklime from limestone is one of the oldest and most fundamental industrial
- Quicklime is an important chemical used in construction for cement and mortar, in agriculture for soil treatment, in metallurgy, and in various chemical industries.
- Limestone is a naturally found in sedimentary rock composed primarily of calcium carbonate.
- Limestone is heated in a high temperature furnace called a **lime kiln** at about 900 to 1000°C. This process is called **calcination** or **thermal decomposition.**

$$CaCO_{3(s)} \xrightarrow{900-1000^\circ C} CaO_{(s)} + CO_{2(g)}$$

- In modern lime kilns, the ingredients are heated by circulating hot gases at the reaction temperature.
- The reaction is reversible in a closed container. Continuous removal of carbon dioxide makes the reaction occur faster.
- Removal of carbon dioxide shifts the equilibrium to the right and results in faster production of a large amount of quicklime.

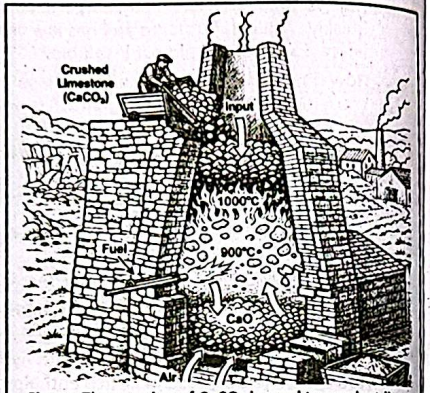



**Figure: The reaction of $CaCO_3$ is used to product lime (CaO), which has many applications**

## USES OF GROUP 2 COMPOUNDS

**Q.15 State the uses of Group 2 compounds in construction and the environment.** S/Q

**Ans.** Group 2 compounds have diverse uses in industries and everyday life because of their basic nature and varying solubility.

### ➲ Role of Group 2 Compounds in industry and Everyday Life

**i. Use in Construction:**

- Calcium carbonate $CaCO_3$ occurs as limestone, marble, and chalk and is widely used as a building material, in cement and concrete, and as a filler in paper and plastics.
- Calcium oxide CaO or quicklime and calcium hydroxide $Ca(OH)_2$ or slaked lime are used in making cement, mortar, and plaster.
- Quicklime is used in steel production to remove impurities.
- Calcium sulphate $CaSO_4 \cdot 2H_2O$ or gypsum is used to make plasterboard or **drywall** and plaster of Paris (POP) $CaSO_4 \cdot \frac{1}{2}H_2O$.

**ii. Use in Environment:**

- Calcium oxide CaO and calcium carbonate $CaCO_3$ are used in flue gas desulphurization or wet scrubbing to remove acidic sulphur dioxide $SO_2$ from power plant emissions and prevent acid rain.
- Magnesium oxide MgO is used as a refractory material for lining furnaces because of its high melting point.

**Check Understanding!**

**Q.9 Which property of $Mg(OH)_2$ makes it useful as an antacid?**

(A) It is acidic
(B) It is a strong base that corrodes stomach lining.
(C) Mild base, neutralizes excess HCl in stomach
(D) It is insoluble in water

**Did You Know?**

Magnesium (metal) is used in lightweight alloys (e.g., aerospace, automotive), fireworks, and flares due to its bright burning. Strontium compounds are used to produce red colour in fireworks and flares. Beryllium is used in alloys to increase strength (e.g., in springs, aerospace components) and in X-ray tubes as it is transparent to X-rays.

**Q.16 State the medical uses of Group 2 compounds.** S

**Ans.** **Medical Uses of Group 2 Compounds:**

Magnesium hydroxide $Mg(OH)_2$ or Milk of Magnesia is used as Antacid i.e. neutralizes excess stomach ac $(Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O)$ and as a mild laxative (a substance that promote bowel movemen and its low solubility makes it safe to use.



- Calcium carbonate $CaCO_3$ is used in **indigestion** tablets as an **antacid.**
- Calcium compounds such as calcium carbonate and calcium citrate are essential for strong bones and teeth and are widely used as dietary calcium supplements to prevent **osteoporosis.**
- Magnesium compounds such as magnesium sulphate and magnesium citrate are important for **muscle** and **nerve function** and are used to treat magnesium deficiencies.
- **Epsom salts $MgSO_4 \cdot 7H_2O$** are used as a **laxative** and in baths.
- Barium sulphate $BaSO_4$ is used in barium meals for **X ray imaging** of the digestive system because it is opaque to X rays and is safe as it is highly insoluble and passes through the body without being absorbed.




**Milk of Magnesia containing magnesium hydroxide $Mg(OH)_2$**

**Q.17 State the agricultural uses of Group 2 compounds.** S/Q

**Ans.** **Agricultural Uses of Group 2 Compounds:**

Calcium carbonate $CaCO_3$ and calcium hydroxide $Ca(OH)_2$ are added to acidic soils to increase pH and neutralize acidity, making the soil more suitable for crop growth.

- Calcium and magnesium are essential plant nutrients.
- Calcium is crucial for cell wall development and magnesium is a central atom in chlorophyll that is essential for photosynthesis.
- Calcium nitrate and magnesium sulphate or Epsom salts can be used as fertilizers.

### ☑ QUICK CHECK 17.4

**a) Write the balanced equation for the electrolysis step in the Dow Process.**

**Ans.** In the Dow Process, molten magnesium chloride is subjected to electrolysis in large electrolytic cells.

- **At the cathode:** Pure magnesium metal

$$Mg^{2+}_{(\ell)} + 2e^- \longrightarrow Mg_{(\ell)}$$

- **At the anode:** Chlorine gas

$$2Cl^-_{(\ell)} \longrightarrow Cl_{2(g)} + 2e^-$$

- **The balanced equation for the electrolysis step is:**

$$Mg^{2+}_{(\ell)} + 2Cl^-_{(\ell)} \longrightarrow Mg_{(\ell)} + Cl_{2(g)}$$

**b) Write the balanced equation for producing quicklime, CaO, from limestone.**

**Ans.** Limestone, $CaCO_3$, is heated in a high-temperature lime kiln.

- This process is called calcination or thermal decomposition.
- The calcium oxide formed is called quicklime.
- The balanced equation for producing quicklime is:

$$CaCO_{3(s)} \xrightarrow{900-1000^\circ C} CaO_{(s)} + CO_{2(g)}$$

**c) State one agricultural use of $CaCO_3$ and the chemical principle involved.**

**Ans.** **Chemical Principle:**

- The primary chemical principle involved in using $CaCO_3$ agriculture is acid neutralization.

**Agricultural Use:**

- Calcium carbonate is added to acidic soils to make the soil more suitable for crop growth.
- It increases the pH of the soil by neutralizing its acidity.
- The chemical principle involved: An acid-base neutralization.

## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **On heating, Group 2 carbonates generally decompose into:**
   (A) Metal + $CO_2$ (B) Metal oxide + $CO_2$ (C) Metal hydroxide + $CO_2$ (D) Metal oxide + CO
2. **Which Group 2 carbonate is the least thermally stable?**
   (A) $BaCO_3$ (B) $SrCO_3$ (C) $MgCO_3$ (D) $BeCO_3$
3. **Thermal stability of Group 2 carbonates:**
   (A) Decreases down the group (B) Remains constant
   (C) Increases down the group (D) First increases then decreases
4. **Which carbonate requires the highest temperature for decomposition?**
   (A) $MgCO_3$ (B) $CaCO_3$ (C) $SrCO_3$ (D) $BaCO_3$

CamScanner

5. Heating calcium nitrate produces:
(A) $Ca + NO_2$ (B) $CaO + NO_2 + O_2$ (C) $CaO + N_2$ (D) $Ca(NO_2)_2$

6. Brown fumes evolved during decomposition of Group 2 nitrates are:
(A) $CO_2$ (B) NO (C) $NO_2$ (D) $SO_2$

7. Which nitrate is the most thermally stable?
(A) $Be(NO_3)_2$ (B) $Mg(NO_3)_2$ (C) $Ca(NO_3)_2$ (D) $Ba(NO_3)_2$

8. The thermal stability of Group 2 nitrates increases because:
(A) Polarizing power decreases down the group. (B) Atomic size decreases.
(C) Ionization energy increases. (D) Electronegativity increases.

9. The solubility of Group 2 hydroxides:
(A) Decreases down the group (B) Increases down the group
(C) Remains constant (D) First decreases then increases

10. Which hydroxide is most soluble in water?
(A) $Mg(OH)_2$ (B) $Ca(OH)_2$ (C) $Sr(OH)_2$ (D) $Ba(OH)_2$

11. The solubility of Group 2 sulphates:
(A) Increases down the group (B) Remains constant
(C) Decreases down the group (D) Doubles down the group

12. Which sulphate is least soluble?
(A) $MgSO_4$ (B) $CaSO_4$ (C) $SrSO_4$ (D) $BaSO_4$

13. The central metal ion in a complex ion behaves as a:
(A) Lewis base (B) Bronsted acid (C) Lewis acid (D) Reducing agent

14. The usual coordination number of hydrated magnesium ion is:
(A) 2 (B) 4 (C) 6 (D) 8

15. EDTA is commonly used to:
(A) Produce oxygen (B) Remove $Ca^{2+}$ and $Mg^{2+}$ ions from hard water
(C) Produce lime (D) Extract magnesium from limestone

16. In the Dow Process, magnesium is extracted from:
(A) Dolomite (B) Limestone (C) Seawater (D) Bauxite

17. During electrolysis of molten $MgCl_2$, magnesium is produced at the:
(A) Anode (B) Cathode (C) Salt bridge (D) Electrolyte surface

18. Quicklime is chemically known as:
(A) $CaCO_3$ (B) $Ca(OH)_2$ (C) CaO (D) $CaSO_4$

19. Limestone is converted into quicklime by:
(A) Neutralization (B) Calcination (C) Electrolysis (D) Reduction

20. Which compound is used as a contrast medium for X-ray imaging of the digestive system?
(A) $MgSO_4$ (B) $CaCO_3$ (C) $BaSO_4$ (D) $SrSO_4$

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

**BLOCK # 01**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. C | 4. C | 5. C | 6. D | 7. C | 8. D | 9. B | 10. B | 11. C | 12. C | 13. C | 14. B | 15. C |
| 16. C | 17. B | 18. C | 19. B | 20. C | | | | | | | | | | |

**BLOCK # 02**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. D | 3. C | 4. D | 5. B | 6. C | 7. D | 8. A | 9. B | 10. D | 11. C | 12. D | 13. C | 14. C | 15. B |
| 16. C | 17. B | 18. C | 19. B | 20. C | | | | | | | | | | |

## CHECK UNDERSTANDING (SOLUTIONS)

| Q. # | Option | Hint/Explanation |
|---|---|---|
| 1. | (B) | Group II members like Be, Mg have $ns^2$ electronic configuration. |
| 2. | S/Q | Beryllium differs from the other Group II elements because of its very small atomic size, high ionization energy ($1^{st}$ I.E. of Be = 900 kJ $mol^{-1}$) and high polarizing power. As a result, it forms mainly covalent compounds and shows amphoteric behaviour. |
| 3. | (D) | Be metal surface is covered by a very thin, hard layer of BeO. This layer stops water from reaching the fresh Be metal underneath. |
| 4. | S/Q | $CaCO_3 \rightarrow CaO + CO_2$. CaO is called quicklime, used in cement and steel industry. |
| 5. | (D) | $Be^{2+}$ is smallest with highest charge density. Strongest attraction to water gives most –ve $\Delta H^\circ_{hyd}$ |



| | | |
|---|---|---|
| 6. | S/Q | $CaSO_4$ is sparingly soluble because $Ca^{2+}$ has fairly high hydration energy, but lattice energy is also high. If forms gypsum $CaSO_4.2H_2O$ |
| 7. | (D) | Group 2 bonding is mainly electrostatic. Complex are ionic, readily exchange ligands = labile, and no d–electrons = colourless. |
| 8. | S/Q | It is because in aqueous solution, $H_2O$ would be reduced at cathode instead of $Mg^{2+}$ due to lower discharge potential. Also hydrated $MgCl_2$ on heating gives MgO. So fused anhydrous $MgCl_2$ is electrolyzed at –700°C. |
| 9. | (C) | $Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$. |

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I) Which Group 2 oxide forms the most alkaline solution in water?
a) Beryllium oxide b) Magnesium oxide c) Calcium oxide d) Strontium oxide

II) Which Group 2 element does not react with water or steam?
a) Beryllium (Be) b) Magnesium(Mg) c) Calcium(Ca) d) Strontium (Sr)

III) What are the products when magnesium reacts with steam?
a) $Mg(OH)_2$ and $H_2$ b) MgO and $H_2$ c) $Mg(OH)_2$ only d) MgO and $H_2O$

IV) The species formed when a Group 2 basic oxide such as CaO reacts with water is
a) A salt and hydrogen b) A metal hydroxide c) A metal carbonated) A salt and water

V) Which Group 2 carbonate is the most thermally stable?
a) $BeCO_3$ b) $MgCO_3$ c) $CaCO_3$ d) $BaCO_3$

VI) What are the products of heating a Group 2 nitrate (e.g., $Ca(NO_3)_2$)?
a) Metal oxide, $CO_2$, $O_2$ b) Metal oxide, $NO_2$, $O_2$ c) Metal hydroxide, $N_2$, $O_2$ d) Metal, $NO_2$, $H_2O$

VII) The reason for the increasing thermal stability of Group 2 nitrates down the group is:
a) Smaller cations, higher polarizing power b) Larger cations, lower polarizing power
c) Larger size of the nitrate ion ($NO_3^-$) d) Decrease in the charge on the cation

VIII) Which Group 2 sulphate is the least soluble in water?
a) $MgSO_4$ b) $BaSO_4$ c) $CaSO_4$ d) $BeSO_4$

IX) Which of the following hydroxides is the least soluble in water?
a) $Mg(OH)_2$ b) $Ba(OH)_2$ c) $Ca(OH)_2$ d) $Sr(OH)_2$

X) Why does $Be^{2+}$ form complexes more easily than $Ba^{2+}$?
a) Larger size b) Lower charge density c) Higher charge density d) Smaller atomic radius

## ANSWERS KEY WITH EXPLANATION

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | d | Strontium oxide | The basic character of Group 2 oxides increases down the group. Therefore, SrO (which is at the bottom in the given options) forms the most alkaline solution among the given oxides. |
| II. | a | Beryllium (Be) | Beryllium does not react with water or steam because it has a protective oxide layer. |
| III. | b | MgO and $H_2$ | Magnesium reacts with steam to form magnesium oxide and hydrogen gas. |
| IV. | b | A metal hydroxide | A Group 2 basic oxide reacts with water to form the corresponding metal hydroxide. |
| V. | d | $BaCO_3$ | The thermal stability of Group 2 carbonates increases down the group. Therefore, $BaCO_3$ (which is at the bottom in the given options) is the most thermally stable. |
| VI. | b | Metal oxide, $NO_2$, $O_2$ | On heating, a Group 2 nitrate forms a metal oxide, nitrogen dioxide and oxygen gas. |
| VII. | b | Larger cations, lower polarizing power | Down Group 2, metal ions become larger and have lower polarizing power. They distort nitrate ions less, so nitrates become more stable. |

CamScanner

| | | | |
|---|---|---|---|
| VIII. | b | $BaSO_4$ | $K_{sp}$ of $BaSO_4 = 1.1 \times 10^{-10}$ |
| IX. | a | $Mg(OH)_2$ | $Mg(OH)_2$ has the lowest solubility among the given compounds. If solubility = 0.009 g/100 mL (Practically insoluble) $Mg^{2+}$ is very small with high charge density and it holds $OH^-$ very tightly. Other ions are larger and dissolve more than $Mg(OH)_2$. |
| X. | c | Higher charge density | $Be^{2+}$ is much smaller than $Ba^{2+}$. Its higher charge density enables it to attract electron-pair donors more strongly and form complexes more easily. |

## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) Exactly 0.1 moles of calcium hydroxide and barium hydroxide are added to separate beakers containing 100 $cm^3$ of water and stirred to form saturated solutions. Explain which solution has the higher pH value.**

Ans. Barium hydroxide solution has the higher pH value. The solubility of Group 2 hydroxides increases down the group. $Ba(OH)_2$ is more soluble than $Ca(OH)_2$. So, has a higher pH value.

**b) The size of dichromate ion is larger than the sulphate ion. Following the pattern for the solubilities of Group 2 sulphates, predict which of calcium dichromate and strontium dichromate is more soluble in water.**

Ans. $Ca(Cr_2O_7)_2$ Calcium dichromate is more soluble than strontium dichromate. Dichromate ion is larger than sulphate ion. For large anions, the decrease in hydration enthalpy down Group 2 is more significant than the decrease in lattice enthalpy. Therefore, solubility is expected to decrease from calcium dichromate to strontium dichromate.

**c) Write the balanced equation for the reaction of barium with cold water.**

Ans. Barium reacts vigorously with cold water to form barium hydroxide and hydrogen gas.

$$Ba_{(s)} + 2H_2O_{(\ell)} \longrightarrow Ba(OH)_{2(aq)} + H_{2(g)}$$

**d) Why does beryllium metal form a protective layer on reacting with air while other Group 2 metals do not? Explain in terms of the strength of bonding between $Be^{2+}$ and oxide ion.**

Ans. Beryllium forms a thin, strong non-porous oxide layer (BeO) on reacting with air.
**Reason:** $Be^{2+}$ is very small and has high charge density. Therefore, $Be^{2+}$ has strong attraction for oxide ions $O^{2-}$, and forms (shows) strong bonding in BeO. This strong oxide layer protects beryllium and makes it less reactive than other Group 2 metals.

**e) Predict the products of the thermal decomposition of strontium nitrate. Write the chemical equation.**

Ans. On heating, strontium (Sr) nitrate decomposes to form barium oxide, nitrogen dioxide and oxygen.

$$2Sr(NO_3)_{2(s)} \xrightarrow{Heat} 2SrO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

**f) Why does the solubility of Group 2 hydroxides increase down the group in terms of $\Delta H°_{hyd}$ and $\Delta H°_{lattice}$?**

Ans. Solubility depends on

$$\Delta H_{solution} = \Delta H_{lattice} + \Delta H_{hyd.}$$

Down Group 2, both $\Delta H_{hyd}$ and $\Delta H_{lattice}$ decrease.

- In Group 2 hydroxides, the decrease in lattice enthalpy is more significant and rapid than the decrease in hydration enthalpy.
- Therefore, the enthalpy of solution becomes more negative (exothermic) down the group and the solubility of hydroxides increases.

**g) In the Dow Process, write the balanced equation for the precipitation of magnesium ions from seawater.**

Ans. In the Dow Process, seawater is treated with calcium hydroxide to precipitate magnesium hydroxide.

$$Mg^{2+}_{(aq)} + Ca(OH)_{2(s)} \longrightarrow Mg(OH)_{2(s)} + Ca^{2+}_{(aq)}$$

- Magnesium hydroxide is insoluble and is removed by filtration.

**h) State one medical use of $BaSO_4$ and $Mg(OH)_2$ each.**

Ans. **Medical Use of $BaSO_4$:**
Barium sulphate is used in barium meals for X-ray imaging of the digestive system.

- $BaSO_4$ is opaque to X-rays.
- It is safe (non-toxic) because it is highly insoluble and passes through the body without being absorbed



**Medical Use of $Mg(OH)_2$:**

- Magnesium hydroxide, known as **Milk of Magnesia**, is used to neutralize excess stomach acid.
- It may also be used as a **mild laxative**.
- Its low solubility makes it safe to use.

## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**) Why are the melting point and density of Be higher than Mg and Ca?**

Ans. Beryllium has a much smallest atomic radius and high charge density as compared to Mg and Ca. Its valence electrons form a compact, strongly bonded metallic lattice, so more energy is required to melt it. Its small atomic volume also gives Be a relatively high density compared with Mg and Ca.

Be < Mg < ca

Be has smallest size. Be has highest melting point of 1287°C than Mg(650°C) and Ca(842°C) the density trend is

| Be | > | Mg | > | Ca |
|---|---|---|---|---|
| 1.85 ($g/cm^3$) | | 1.74 ($g/cm^3$) | | 1.54 ($g/cm^3$) |

**) Compare the reactivities of Group 1 and Group 2 metals in the same period?**

ns. In the same period, a Group 1 metal is more reactive than the corresponding Group 2 metal because Group 1 loses only one valence electron and has lower ionization energy. Group 2 must remove two electrons, so more energy is required. In both groups, reactivity generally increases down the group as atomic size and shielding increase. e.g., In period 3, Na is more reactive than Mg. Na reacts with cold water while Mg reacts only with steam (For further details see table in text book Q.7).

**Explain why calcium hydroxide is used in agriculture.**

ns. Calcium hydroxide is added to acidic soils.
**Reasons:**
i) Calcium hydroxide is a base, so it neutralizes excess $H^+$ ions and thus soil acidity and increases the pH of the soil. This makes the soil more suitable for crop growth.
ii) It provides calcium nutrient which is essential for root growth.

## DESCRIPTIVE QUESTIONS DQs

**4 Describe the reactivity of Group 2 elements with water and dilute hydrochloric acid. Provide relevant chemical equations and differences in their reactivity.**

s. See Question No. 5 & 6

**5 Explain the thermal decomposition of carbonates and nitrates of Group 2 elements. Give reason and relative order of the ease of thermal stability.**

s. See Question No. 8

**6 Explain the solubility of sulphates and hydroxides of Group 2 elements, and discuss the trend in their solubility down the group with appropriate examples.**

s. See Question No. 10

**7 Explain the process of extraction of Mg through Dow's method.**

s. See Question No. 13

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**1 Why are Group II elements called alkaline earth metals?**

s. Group II elements are called alkaline earth metals because their oxides and hydroxides are alkaline in nature. These elements occur naturally in the earth's crust in the form of minerals and ores, which were historically known as "earths."

**2 Write the electronic configuration of Group II elements and explain their valency.**

s. The general electronic configuration of Group II elements is $ns^2$. They lose two valence electrons to attain the stable electronic configuration of the nearest noble gas and therefore exhibit a valency of +2.
**For example:**

Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$

CamScanner

**Q.3 Why does reactivity increase down Group II?**

**Ans.** The reactivity of Group II elements increases down the group because atomic size increases and ionization energy decreases. As a result, removal of valence electrons becomes easier and metals lose electrons more readily.

**Q.4 Explain the reaction of magnesium with oxygen.**

**Ans.** Magnesium reacts vigorously with oxygen on heating to form magnesium oxide. Magnesium burns with a brilliant white flame and produces a white powder of magnesium oxide.
**Equation:**

$$2Mg + O_2 \longrightarrow 2MgO_2$$

**Q.5 Describe the reaction of calcium with water.**

**Ans.** Calcium reacts readily with cold water to form calcium hydroxide and hydrogen gas. The reaction is more vigorous than that of magnesium due to the greater reactivity of calcium.
**Equation:**

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

**Observation:** Effervescence due to hydrogen gas is observed.

**Q.6 Explain the reaction of magnesium with steam.**

**Ans.** Magnesium does not react appreciably with cold water but reacts with steam at high temperature t produce magnesium oxide and hydrogen gas.
**Equation:**

$$Mg + H_2O_{(g)} \longrightarrow MgO + H_2$$

**Q.7 Describe the reaction of magnesium with dilute hydrochloric acid.**

**Ans.** Magnesium reacts rapidly with dilute hydrochloric acid to produce magnesium chloride and hydrogen ga The reaction demonstrates the reducing nature of magnesium.
**Equation:**

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

**Q.8 What is meant by reactivity series?**

**Ans.** The reactivity series is the arrangement of metals in decreasing order of their reactivity. It is used to predi displacement reactions and the products formed during chemical reactions.

**Q.9 What is meant by thermal decomposition?**

**Ans.** Thermal decomposition is the breakdown of a compound into simpler substances by heating. Group carbonates and nitrates commonly undergo thermal decomposition reactions.

**Q.10 Explain the thermal decomposition of magnesium carbonate.**

**Ans.** Magnesium carbonate decomposes on heating to form magnesium oxide and carbon dioxide gas. T reaction is an example of thermal decomposition.
**Equation:**

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

**Q.11 Explain the thermal decomposition of magnesium nitrate.**

**Ans.** Magnesium nitrate decomposes on strong heating to produce magnesium oxide, nitrogen dioxide a oxygen gas. The reaction is accompanied by the evolution of brown fumes of nitrogen dioxide.
**Equation:**

$$2Mg(NO_3)_2 \xrightarrow{\Delta} 2MgO + 4NO_2 + O_2$$

**Observation:** Brown fumes of $NO_2$ gas are evolved.

**Q.12 Why does the thermal stability of Group II carbonates increase down the group?**

**Ans.** The thermal stability of Group II carbonates increases from magnesium carbonate to barium carbon because the size of the metal ion increases down the group. Larger cations possess lower polarizing po and therefore distort the carbonate ion less effectively.
Hence, higher temperatures are required for decomposition.



**Q.13 Why does the thermal stability of Group II nitrates increase down the group?**

**Ans.** The thermal stability of Group II nitrates increases down the group because larger cations have lower charge density and weaker polarizing power. As a result, the nitrate ion experiences less distortion and becomes more stable towards heat.
Therefore, barium nitrate is more thermally stable than magnesium nitrate.

**Q.14 Explain the trend in solubility of Group II hydroxides.**

**Ans.** The solubility of Group II hydroxides increases down the group from magnesium hydroxide to barium hydroxide. This is because the decrease in lattice enthalpy is greater than the decrease in hydration enthalpy. Consequently, the enthalpy of solution becomes more favorable and solubility increases.

**Q.15 Explain the trend in solubility of Group II sulphates.**

**Ans.** The solubility of Group II sulphates decreases down the group from magnesium sulphate to barium sulphate. In this case, hydration enthalpy decreases more rapidly than lattice enthalpy.
As a result, dissolution becomes less favorable and solubility decreases.

**Q.16 What is meant by polarizing power?**

**Ans.** Polarizing power is the ability of a cation to distort the electron cloud of a nearby anion. Small and highly charged cations possess greater polarizing power than large cations.
In Group II, $Be^{2+}$ has the highest polarizing power because of its small size.

**Q.17 Explain the effect of ionic radius on the stability of carbonates and nitrates.**

**Ans.** As ionic radius increases down Group II, the polarizing power of the cation decreases. Consequently, the carbonate and nitrate ions experience less distortion and become more stable.
Therefore, thermal stability increases from magnesium to barium compounds.

**Q.18 What is meant by a complex ion?**

**Ans.** A complex ion is an ion consisting of a central metal ion surrounded by molecules or ions called ligands which donate lone pairs of electrons to the metal ion.
Complex ions are formed through coordinate covalent bonding.

**Q.19 Explain complex formation by Group II elements.**

**Ans.** Group II elements generally have a lower tendency to form complexes than transition metals because they lack partially filled d-orbitals. However, small ions such as $Be^{2+}$ can form complexes due to their high charge density and small size.
**For example:** $[BeF_4]^{2-}$ is a stable complex ion of beryllium.

**Q.20 Explain the extraction of magnesium.**

**Ans.** Magnesium is extracted commercially by electrolysis of molten magnesium chloride. During electrolysis, magnesium ions are reduced at the cathode while chloride ions are oxidized at the anode.
**Cathode Reaction:**

$$Mg^{2+} + 2e^- \longrightarrow Mg$$

**Anode Reaction:**

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

**Q.21 Why is magnesium used in fireworks and flares?**

**Ans.** Magnesium burns with an intense dazzling white flame and releases a large amount of heat energy. Due to this property, it is widely used in fireworks, signal flares and photographic flash bulbs.
**Equation:**

$$2Mg + O_2 \longrightarrow 2MgO_2$$

**Q.22 State the uses of magnesium hydroxide.**

**Ans.** Magnesium hydroxide is commonly known as milk of magnesia and is used as an antacid to neutralize excess stomach acid. It is also used as a mild laxative in medicine.
**Neutralization Reaction:**

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$$

CamScanner

**Q.23 State the uses of calcium carbonate.**

**Ans.** Calcium carbonate is widely used in the manufacture of cement, glass and lime. It is also used in agriculture to neutralize acidic soils and improve soil fertility.
**Reaction:**

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

**Q.24 State the uses of barium sulphate.**

**Ans.** Barium sulphate is used as a contrast medium in X-ray examination of the digestive system because it strongly absorbs X-rays. It is preferred because of its very low solubility and non-toxic nature.

**Q.25 Compare the reactivity of Group I and Group II elements.**

**Ans.** Group I metals are generally more reactive than Group II metals in the same period because they lose only one electron to attain stability. Group II elements must lose two electrons and therefore require more energy. Hence, sodium is more reactive than magnesium.

**Q.26 Explain why Group II oxides are basic in nature.**

**Ans.** Group II oxides are basic because they react with acids to form salts and water. Their basic character arises due to the presence of oxide ions which readily accept protons.
**Equation:**

$$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$$

**Q.27 Why is BeO amphoteric while other Group II oxides are basic?**

**Ans.** Beryllium oxide is amphoteric because it reacts with both acids and alkalis. This behavior is due to the small size and high polarizing power of the $Be^{2+}$ ion.
**Examples:**

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$
$$BeO + 2NaOH \longrightarrow Na2BeO_2 + H_2O$$

**Q.28 Explain the role of Group II compounds in agriculture.**

**Ans.** Group II compounds such as calcium carbonate are used to reduce soil acidity and improve crop growth. Magnesium compounds are also used in fertilizers because magnesium is an essential component of chlorophyll.

**Q.29 Explain the role of Group II compounds in medicine.**

**Ans.** Several Group II compounds have important medical applications. Magnesium hydroxide is used as an antacid, while barium sulphate is used as an X-ray contrast agent for imaging the digestive tract. These compounds play an important role in diagnosis and treatment in medicine.



## SELF-ASSESSMENT

Total Mark: 30

**Q.1 Encircle the correct option.** (1 × 6 = 6)

(I) **The increasing order of reactivity of Group 2 elements is:**
(A) Ba < Sr < Ca < Mg < Be (B) Be < Mg < Ca < Sr < Ba
(C) Mg < Be < Ca < Ba < Sr (D) Be < Ca < Mg < Sr < Ba

(II) **Which Group 2 element is least reactive?**
(A) Magnesium (B) Calcium (C) Beryllium (D) Barium

(III) **Which sulphate is least soluble?**
(A) $MgSO_4$ (B) $CaSO_4$ (C) $SrSO_4$ (D) $BaSO_4$

(Iv) **Why does $Be^{2+}$ form complexes more easily than $Ba^{2+}$?**
(A) Larger size (B) Lower charge density (C) Higher charge density (D) Smaller atomic radius

(v) **The species formed when a Group 2 basic oxide such as CaO reacts with water is**
(A) A salt and hydrogen (B) A metal hydroxide (C) A metal carbonate (D) A salt and water

(vi) **The reason for the increasing thermal stability of Group 2 nitrates down the group is:**
(A) Smaller cations, higher polarizing power (B) Larger cations, lower polarizing power
(C) Larger size of the nitrate ion ($NO_3^-$) (D) Decrease in the charge on the cation

**Q.2 Write short answers of the following questions.** (2 × 8 = 16)

(i) Write equations for the following reactions: i) Ca with oxygen ii) Ba with water
(ii) Why does $MgSO_4$ dissolve easily as compared to $BaSO_4$?
(iii) Write the balanced equation for the reaction of barium with cold water.
(iv) Predict the products of the thermal decomposition of strontium nitrate. Write the chemical equation.
(v) State one medical use of $BaSO_4$ and $Mg(OH)_2$ each.
(vi) Why are the melting point and density of Be higher than Mg and Ca?
(vii) Compare the reactivities of Group 1 and Group 2 metals in the same period?
(viii) Why does the thermal stability of Group II nitrates increase down the group?

**Q.3 Extensive Questions.** (4 + 4 = 8)

(a) Describe the reactivity of Group 2 elements with water and dilute hydrochloric acid. Provide relevant chemical equations and differences in their reactivity.
(b) Explain the process of extraction of Mg through Dow's method.

## ENTRANCE TEST MCQs

1. **Which of the following sulphates is not soluble in water?** (UHS 2010)
(A) Sodium sulphate (B) Potassium sulphate (C) Barium sulphate (D) Zinc sulphate

2. **When elements of group 2 (alkaline earth metals) are exposed to air, they quickly become coated with a layer of oxide. What is the purpose of this oxide layer?** (UHS 2011)
(A) The oxide layer exposes the metal of atmospheric attack
(B) The oxide layer increases the reactivity of metal
(C) The oxide layer protects the metal from further atmospheric attack
(D) The oxide layer gives the metal a shiny silvery appearance

3. **Alkaline earth metal hydroxides decompose on heating. Which of the following reactions is a correct representation of this decomposition?** (UHS 2012)
(A) $M(OH)_{2(s)} \longrightarrow MO_{(s)} + H_2O_{(l)}$ (B) $2MOH_{2(s)} \longrightarrow 2MO_{(s)} + H_{2(l)}$
(C) $MOH_{(s)} \longrightarrow M_2O_{(s)} + H_2O_{(l)}$ (D) $4MOH_{(s)} \longrightarrow 4M_{(s)} + 2H_2O_{(l)} + O_2$

4. **Alkaline earth metal oxides react with water to give hydroxides. The solubility of alkaline earth metal oxides in water increases as we move from top to bottom in a group. Which of the following alkaline earth metal oxides is least soluble in water?** (UHS 2013)
(A) MgO (B) BaO (C) CaO (D) SrO

CamScanner

5. The important use of Lime in agriculture is: (ECAT 2017)
(A) For chlorophyll development (B) As fertilizer
(C) For neutralizing acidic soils (D) To increase fruit production

6. Equal moles of Mg and Ca react with excess HCl. How do their $H_2$ amounts compare?
(A) Ca produces twice as much $H_2$ (B) Mg produces twice as much $H_2$
(C) Both produce the same moles of $H_2$ (D) Neither produces $H_2$

7. Which observation would indicate a Group 2 metal lies below Mg?.
(A) It forms a stable 2 ion (B) It reacts even more slowly with water than Mg
(C) It produces no oxide in oxygen (D) Reacts readily with cold water, forming $M(OH)_2$ and $H_2$

8. Equal masses of Mg and Ca react with excess HCl. Why are the $H_2$ amounts different?
(A) Equal masses contain different moles of Mg and Ca
(B) Mg forms $Mg^+$ only
(C) Ca does not form $H_2$
(D) Equal masses always contain equal moles

9. Compared with cold water, how does Mg behave with steam?
(A) Both give MgO at the same rate (B) Cold water gives $MgCl_2$; steam gives $MgSO_4$
(C) Steam prevents any reaction (D) Cold water gives $Mg(OH)_2$ slowly; steam gives MgO faster

10. Why is "reactivity increases down Group 2" more accurate than "all reactions become explosive"?
(A) Reaction vigour depends only on the metal's colour
(B) Vigour also depends on conditions and surface
(C) Reactivity cannot be compared experimentally
(D) Every Group 2 metal reacts at the same rate

11. The carbonate ion is the same in all Group 2 carbonates. What actually changes down the group?
(A) Carbonate has no electrons (B) The cation changes; $CO_3^{2-}$ remains the same
(C) All ions have the same ionic radius (D) The metal changes into carbon

Why do Group 2 hydroxide and sulphate solubility trends differ?
(A) Different anion sizes alter the lattice-hydration balance
(B) Hydroxide has no charge
(C) The metal ion charges reverse in sulphates
(D) The composition of water changes between the experiments

13. Why do Group 2 ions form fewer complexes than transition-metal ions?
(A) Transition metals cannot accept lone pairs
(B) Group 2 ions have no charge
(C) They lack accessible d orbitals and variable bonding
(D) Water cannot coordinate to Group 2 ions

14. Which pairing of compound and use is chemically justified?
(A) $CaCO_3$ - acidifying soil
(B) $BaSO_4$ - highly soluble barium supplement
(C) $Mg(OH)_2$ - producing chlorine gas in the stomach
(D) MgO - furnace lining because of high melting point

**Answers Key**

| 1. C | 2. C | 3. A | 4. A | 5. C | 6. C | 7. D | 8. A | 9. D | 10. B | 11. B | 12. A | 13. C | 14. D |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|



18 CHAPTER

# TRANSITION METALS

## Student Learning Outcomes (SLOs)

[C-12- B-16 to C-12-B-47]

- Define a transition element as a d-block element which forms one or more stable ions with incomplete d orbitals.
- Identify the general physical and chemical properties of the first row of transition elements, titanium to copper.
- Identify the properties of transition elements (Some examples include:
  a) they have variable oxidation states
  b) they behave as catalysts
  c) they form complex ions
  d) they form coloured compounds
- Explain why transition elements have variable oxidation states in terms of the similarity in energy of the 3d and the 4s subshells.
- Explain why transition elements form complex ions in terms of vacant d orbitals that are energetically accessible.
- Explain why transition elements behave as catalysts in terms of having more than one stable oxidation state, and vacant d orbitals that are energetically accessible and can form dative bonds with ligands.
- Define the term complex as a molecule or ion formed by a central metal atom/ion surrounded by one or more ligands.
- Define the term ligand as a species that contains a lone pair of electrons that forms a dative covalent bond to a central metal atom/ion.
- State what is meant by coordination number.
- Use the term monodentate ligand including as examples $H_2O$, $NH_3$, $Cl^-$ and $CN^-$.
- Use the term bidentate ligand including as examples 1,2-diaminoethane, $H_2NCH_2CH_2NH_2$ and the ethanedioate ion, $C_2O_4^{2-}$ ; polydentate ligand including as an example EDTA.
- Describe the geometry (shape and bond angles) of transition element complexes which are linear, square planar, tetrahedral or octahedral.
- Predict the formula and charge of a complex ion, given the metal ion, its charge or oxidation state, the ligand and its coordination number or geometry.
- Use the terms degenerate and non-degenerate d orbitals.
- Describe the splitting of degenerate d orbitals into two non-degenerate sets of d orbitals of higher energy, and use of $\Delta E$ in:
- a) Octahedral complexes, two higher E and three lower E d orbitals
- b) Tetrahedral complexes, three higher E and two lower E d orbitals
- Explain why transition elements form coloured compounds in terms of the frequency of light absorbed as an electron is promoted between two non-degenerate orbitals.
- Describe, in qualitative terms, the effects of different ligands on $\Delta E$, frequency of light absorbed, and hence the complementary colour that is observed.
- Sketch the shape of a $3d_{xy}$ orbital and $3d_{z^2}$ orbital.
- Explain the reactions of transition elements with ligands to form complexes, including the complexes of copper(II) and cobalt(II) ions with water and ammonia molecules and hydroxide and chloride ions.

CamScanner

- Explain qualitatively that ligand exchange can occur, including the complexes of copper(II) ions and cobalt(II) ions with water and ammonia molecules and hydroxide and chloride ions.
- Use the complexes of copper(II) ions and cobalt(II) ions with water and ammonia molecules and hydroxide, chloride ions as examples of ligand exchange affecting the colour observed.
- Define the stability constant, $K_{stab}$, of a complex as the equilibrium constant for the formation of the complex ion in a solvent (from its constituent ions or molecules).
- Write an expression for a $K_{stab}$ of a complex [$H_2O$] should not be included).
- Use $K_{stab}$ expressions to perform calculations.
- Explain ligand exchanges in terms of $K_{stab}$ values and understand that a large $K_{stab}$ is due to the formation of a stable complex ion."
- Describe the types of stereoisomerism shown by complexes, including those associated with bidentate ligands.
- Geometrical (cis-trans) isomerism, e.g., square planar such as $[Pt(NH_3)_2Cl_2]$ and octahedral such as $[Co(NH_3)_4(H_2O)_2]^{3+}$ and $[Ni(H_2NCH_2CH_2NH_2)_2(H_2O)_2]^{2+}$.
- Deduce the overall polarity of complexes.
- Optical isomerism, e.g. $[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}$ and $[Ni(H_2NCH_2CH_2NH_2)(H_2O)_2]^{2+}$.
- Predict, using $E^\circ$ values, the feasibility of redox reactions involving transition elements and their ions
- Analyse reactions involving $MnO_4^-/C_2O_4^{2-}$ in acid solution given suitable data (including describing the reaction and doing calculations).
- Analyse reactions involving $MnO_4^-/Fe^{2+}$ in acid solution given suitable data (including describing the reaction and doing calculations).
- Analyse reactions involving $Cu^{2+}$ / $I^-$ given suitable data (including describing the reaction and doing calculations).
- Perform calculations involving other redox systems given suitable data.

## Transition Metals

Transition metals, found in d and f blocks of the modern periodic table, are characterized by their high dens conductivity, and ability to form colourful compounds. Iron stands as the backbone of human civilization; it played a key role in the industrial revolution for the creation of durable tools and modern steel infrastructu

### Use:

Copper, silver and gold are well known since ancient ages as symbols of wealth and prestige. They have b historically used for coinage and jewellery; they remain essential today in high-end electronics and denti due to their exceptional corrosion resistance and conductivity. From the steel in our cars to the gold in smartphones, transition metals are highly valuable for our modern life.

### Classification:

The transition metals can be classified on the basis of their electronic configuration into
(i) d-block (if their outermost electrons are being filled in d-orbitals) or outer transition elements.
(ii) f-block (if their outermost electrons are being filled in f-orbitals) or inner transition elements.
However, as the d-block transition elements are more common in our daily life usage, and among them row transition elements i.e., 3 d-series, have a key role in human civilization and development.

## FIRST ROW TRANSITION ELEMENTS (3d)

**Q.1 Discuss the first row (3d series) of transition elements with same examples of electronic configuratio these metals and their ions.**

**Ans. 3d-series Transition Elements (Sc to Zn):**

First row transition elements are the elements found in the d block of the Periodic Table, having partially filled 3d-orbitals in any of their stable oxidation state. They are called transition elements because they show transitions between variable oxidation states.

**Check Understanding!**
Q.1 [Ar] $3d^6 4s^2$ is electronic configuration of:
(A) $Fe^{3+}$ (B) $Fe^{2+}$
(C) $Fe^{1+}$ (D) Fe

### Sc and Zn:

Although d-block elements are composed of groups 3 to 12, however, zinc and scandium cannot be clas as transition elements.



- Zn forms only one ion ($Zn^{2+}$), which has a complete 3d subshell.
- The electronic configuration of $Zn^{2+}$ = [Ar]$3d^{10}s^0$.

## Electronic Configuration of Transition Metals and their Ions

The first row of transition elements includes the metals from titanium to copper. Electronic configuration of the transition elements usually follows Aufbau principle.

- **Exception of chromium (Cr) and copper (Cu):** These two elements of 3d-series show anomalous behaviour due to acquiring stability of half-filled (chromium; 3 $d^5$) and completely filled (copper; $3d^{10}$) d-subshell. This stabilizing factor makes the electron cloud of these two elements more symmetrical and provides a better shielding effect to nucleus.
- The electronic configuration of first row of transition elements in their neutral ($M^0$), dipositive ($M^{2+}$) and tripositive ($M^{3+}$) oxidation states are given in the following Table.

**Table: Electronic Configurations of First Row Transition Elements**

| Element | Symbol | Atomic Number | Electronic Configuration | | |
|---|---|---|---|---|---|
| | | | ($M^0$) | ($M^{2+}$) | ($M^{3+}$) |
| Titanium | Ti | 22 | [Ar] $3d^2 4s^2$ | [Ar] $3d^2 4s^0$ | [Ar] $3d^1 4s^0$ |
| Vanadium | V | 23 | [Ar] $3d^3 4s^2$ | [Ar] $3d^3 4s^0$ | [Ar] $3d^2 4s^0$ |
| Chromium | Cr | 24 | [Ar] $3d^5 4s^1$ | [Ar] $3d^4 4s^0$ | [Ar] $3d^3 4s^0$ |
| Manganese | Mn | 25 | [Ar] $3d^5 4s^2$ | [Ar] $3d^5 4s^0$ | [Ar] $3d^4 4s^0$ |
| Iron | Fe | 26 | [Ar] $3d^6 4s^2$ | [Ar] $3d^6 4s^0$ | [Ar] $3d^5 4s^0$ |
| Cobalt | Co | 27 | [Ar] $3d^7 4s^2$ | [Ar] $3d^7 4s^0$ | [Ar] $3d^6 4s^0$ |
| Nickel | Ni | 28 | [Ar] $3d^8 4s^2$ | [Ar] $3d^8 4s^0$ | [Ar] $3d^7 4s^0$ |
| Copper | Cu | 29 | [Ar] $3d^{10} 4s^1$ | [Ar] $3d^9 4s^0$ | ——— |

## PROPERTIES OF TRANSITION ELEMENTS

**Q.2 Discuss some physical and chemical properties of 3d-series elements in brief.** LQ

**Ans.** The common physical and chemical properties arising due to their partially filled 3d orbitals are given as under.

## Physical Properties of 3d-series Transition Elements

i. The transition metals exist as hard and rigid solids.
ii. Except copper, which is reddish brown, others occur as silvery or grey lustrous metals.
iii. Their atomic radius usually decreases from left to right, however, at the end it increases a little. This increase may be associated to the stability acquired by copper due to its completely filled d-subshell.
iv. They have **high melting and boiling points**. The melting and boiling points of these elements show a variable trend from left to right (as shown in Figure).
v. They are good conductors of electricity and heat.
vi. They have high densities that generally increase across the row from titanium to copper. This is due to a regular build-up of nuclear charge and atomic size shrinkage.
vii. They possess a shiny surface, and are malleable (can be hammered into thin sheets), and ductile (can be drawn into wires).
viii. Most of them and their compounds are paramagnetic due to the presence of unpaired d electrons.
ix. They form coloured ions and complexes due to the transition of electrons from lower energy to higher energy level as a result of absorption of light.

## Chemical Properties of 3d-Transition Elements

- Transition metals have variable oxidation states as they can lose varying number of electrons to form stable ions (e.g., $Fe^{2+}$ and $Fe^{3+}$).
- They have a high tendency to form coordination compounds (complexes) by accepting lone pairs of electrons from ligands into vacant d-orbitals.
- These metals and their compounds behave as catalysts in organic and inorganic reactions.

**Check Understanding!**
Q.2 Write common of oxidation states of Mn?

CamScanner

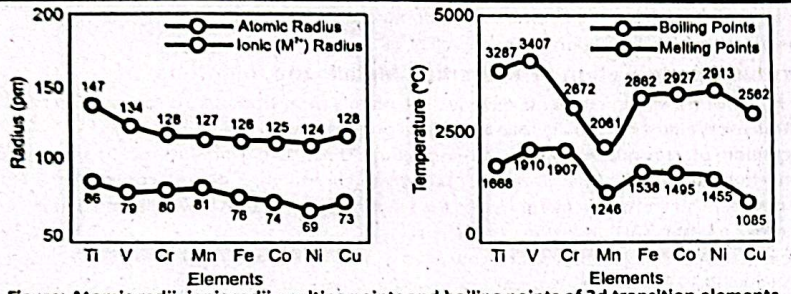



**Figure: Atomic radii, ionic radii, melting points and boiling points of 3d transition elements**

## ➲ Variable Oxidation States

**Q.3 Discuss the variable oxidation states in 3d series of transition elements.** LQ

**Ans.** First row transition elements show variable oxidation states because the 3d and 4s subshells have comparable (very similar) energy. The energy difference between the inner 3d subshell and the outermost 4s subshell is very small. Thus, like 4s electrons, the 3d electrons can also easily be lost. This means that not only the electrons in the outermost 4s subshell, but also the electrons in the partially filled 3d subshell are involved in chemical bonding.

**A 3d Metal Atom Can Lose:**

- Only the 4s electrons, usually giving the common +2 oxidation state.
- The 4s electrons plus a variable number of 3 d electrons, giving the higher oxidation states.

Among 3d series metals, $_{25}$Mn has the maximum oxidation state of +7. The oxidation state of transition elements varies in parabolic trend from left to right within d-block. The various oxidation states of 3d elements are provided in Table.

**Table: Common oxidation states of 3d elements**

| Ti | V | Cr | Mn | Fe | Co | Ni | Cu |
|---|---|---|---|---|---|---|---|
| | | | +7 | | | | |
| | | +6 | +6 | +6 | | | |
| | +5 | +5 | +5 | +5 | +5 | | |
| +4 | +4 | +4 | +4 | +4 | +4 | +4 | |
| +3 | +3 | +3 | +3 | +3 | +3 | +3 | +3 |
| +2 | +2 | +2 | +2 | +2 | +2 | +2 | +2 |
| | | | +1 | +1 | | | +1 |

### ☑ QUICK CHECK 18.1

**a) Write down electronic configuration of $Co^{2+}$ and $Co^{3+}$, and find the number of unpaired electrons in d-orbitals.**

**Ans.** **Electronic Configuration of:**

$Co^{2+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^7, 4s^0$, No. of unpaired electrons in d-orbital = 7

$Co^{3+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^0$, No. of unpaired electrons in d-orbital = 6

**b) Why are the density and melting points of transition metals much higher than Group 1 metals?**

**Ans.** Density and Melting points of transition metals are greater than group 1 metals (Alkali metals):

**Reasons:**

i. Transition metals have unpaired d-electrons plus s-electrons that participate in metallic bonding. They have stronger bonding and tight packing. While alkali metals have only one electron to participate in bonding e.g., Melting point of Fe = 1538°C, Melting point of sodium = 98°C.

ii. Transition metals have greater nuclear charge as compared to group 1 metals. As a result transition metals have more density e.g., Density of Fe = 7.87 g/cm$^3$, Density of sodium = 0.97 g/cm$^3$.



**c) The electronic configuration of $Sc^{3+}$ ion is $[Ar]3d^04s^0$. Why is scandium not classified as a transition element?**

**Ans.** $Sc^{3+} = [Ar]3d^04s^0$, (Sc atom = $[Ar]3d^14s^2$)

Scandium is not classified as transition metal. Sc in its compounds almost always forms $Sc^{3+}$ ion.

$$Sc \longrightarrow Sc^{3+} + 3e^-$$

$Sc^{3+}$ has no d-electrons left, so its compounds are colourless and diamagnetic. Thus by strict definition, Scandium is not a transition metal.

## ➲ Transition Metals as Catalysts

**Q.4 Discuss the transition metals as catalysts.** LQ

**Ans.** Transition elements act as effective catalysts to carry out various chemical reactions.

**Reasons:**

i. **Variable Oxidation States:** They can easily switch between their different stable oxidation states (e.g., $Fe^{2+} \rightleftharpoons Fe^{3+}$). This allows the metal ion to form an unstable intermediate compound with a reactant molecule. The intermediate then quickly reacts to form the final product and regenerates the catalyst back to its original oxidation state, providing a reaction pathway with lower activation energy. This process usually occurs in homogeneous catalysis.

**Example:** Nickel salts are used in the preparation of acrylic acid from acetylene, involving the oxidation states of Ni(0) and Ni(II).

**Check Understanding!**

**Q.3 Common transition metals catalysts used in heterogeneous catalysis for formation of ammonia in the Haber process is:**

(A) Li (B) Be

(C) B (D) Fe

ii. **Vacant d-Orbital:** Another characteristic of transition metals is their vacant d-orbitals that are energetically accessible. Reactant molecules attach with the catalyst surface and form a temporary activated complex on the surface, which holds the reactants in the correct orientation, lowering the activation energy required for the reaction to occur. After the reaction, the products desorb, and the catalyst is ready for the next cycle. This process is generally observed in heterogeneous catalysis.

**Example:** A classic example of heterogeneous catalysis is the use of **solid iron** to accelerate the reaction between nitrogen and hydrogen gases to form ammonia in the Haber process.

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{Fe_{(s)}} 2NH_{3(g)}$$

### ☑ QUICK CHECK 18.2

**a) How Vanadium can show the range of oxidation states from +2 to +5?**

**Ans.** Vanadium can exhibit multiple oxidation states because the energy levels of its 4s and 3d orbitals are very close. This allows it to lose or share electrons from both the outer 4s subshell and the inner 3d subshell. By utilizing different numbers of these electrons, it can form stable states ranging from +2 to +5.

**b) Why transition metals use both 4s and 3d electrons in bonding, unlike s-block elements.**

**Ans.** Transition metals use both because the 4s and 3d electrons are energetically similar (close in energy), making both available for chemical bonding. In contrast, s-block elements have a large energy gap between their outermost s-electrons and the inner shell electrons, so they only use their valence s-electrons.

**c) Write the electronic configuration for $Fe^{3+}$.**

**Ans.** The electronic configuration for $_{26}Fe = [Ar]3d^64s^2$ (or) $_{26}Fe = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6, 4s^2$

When it loses three electrons it becomes $Fe^{3+}$ with configuration = $[Ar]3d^5$ (or) $Fe^{3+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5$

**d) Which properties of transition metals enable them to be used as heterogeneous catalysts and homogeneous catalysts?**

**Ans.** Transition metals are effective catalysts due to:

- **Variable Oxidation States:** They can easily gain or lose electrons to form unstable intermediates with reactants/ligands.
- **Vacant d-orbitals:** These provide "space" or sites for reactant molecules to attach to the metal surface (in heterogeneous catalysis) or to accept electron pairs from ligands (in homogeneous catalysis).
- **Surface Adsorption:** Their ability to adsorb reactant molecules by forming weak bonds on their surface lowers the activation energy and increase rate of the reaction.

**(Note:** Heterogeneous catalyst works mainly due to surface adsorption and homogeneous works mainly due to variable oxidation state + complex formation).

CamScanner

## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **A transition element is defined as an element that has:**
   (A) A completely filled d-subshell in all oxidation states
   (B) A partially filled d-subshell in at least one stable oxidation state
   (C) Only s-electrons in the outermost shell
   (D) A filled f-subshell
2. **Which of the following is NOT considered a transition element?**
   (A) Titanium (B) Iron (C) Zinc (D) Chromium
3. **Chromium shows an exceptional electronic configuration because of:**
   (A) Large atomic size (B) Completely filled 4s orbital
   (C) Stability of half-filled 3d subshell (D) High electronegativity
4. **Copper has the electronic configuration:**
   (A) [Ar] $3d^9 4s^2$ (B) [Ar] $3d^{10} 4s^1$ (C) [Ar] $3d^9 4s^2$ (D) [Ar] $3d^{10} 4s^2$
5. **Which property is common to most transition metals?**
   (A) Low density (B) Low melting point (C) High electrical conductivity (D) Soft nature
6. **Except copper, transition metals generally appear:**
   (A) Black (B) Yellow (C) Silvery-grey (D) Blue
7. **The high density of transition metals is mainly due to:**
   (A) Large atomic size (B) Regular increase in nuclear charge with shrinking atomic radiu
   (C) Presence of p-orbitals (D) Low atomic mass
8. **Transition metals are generally:**
   (A) Brittle and non-conducting (B) Soft and low melting
   (C) Hard, malleable and ductile (D) Gaseous at room temperature
9. **Most transition metal compounds are paramagnetic because they contain:**
   (A) Filled d-orbitals (B) Unpaired d-electrons (C) Paired s-electrons (D) Filled p-orbitals
10. **Variable oxidation states arise because:**
    (A) 3d and 4s orbitals have comparable energies (B) 4p orbitals are empty
    (C) The nucleus is unstable (D) They possess f-orbitals
11. **Which transition element exhibits the highest oxidation state (+7)?**
    (A) Iron (B) Cobalt (C) Chromium (D) Manganese
12. **The most common oxidation state of transition metals formed by losing only 4s electrons is:**
    (A) +1 (B) +2 (C) +3 (D) +4
13. **Transition metals readily form complexes because they possess:**
    (A) Filled p-orbitals (B) Vacant accessible d-orbitals
    (C) Only s-electrons (D) Weak metallic bonds
14. **Transition metal ions are coloured mainly due to:**
    (A) Nuclear transitions (B) d–d electronic transitions
    (C) Ionization (D) Radioactivity
15. **Transition metals behave as catalysts because they:**
    (A) Have low melting points (B) Easily change oxidation states
    (C) Are chemically inert (D) Form only one oxidation state
16. **Which catalyst property lowers the activation energy of a reaction?**
    (A) High density (B) Formation of unstable intermediates
    (C) High boiling point (D) High electronegativity
17. **Which transition metal is reddish-brown in colour?**
    (A) Iron (B) Nickel (C) Copper (D) Titanium
18. **Which pair correctly represents variable oxidation states?**
    (A) $Na^+ / Na^{2+}$ (B) $Fe^{2+} / Fe^{3+}$ (C) $Mg^{2+} / Mg^{3+}$ (D) $Ca^+ / Ca^{2+}$
19. **Which statement is correct regarding transition metals?**
    (A) They are poor conductors of electricity. (B) They generally have high melting and boiling points.
    (C) They are less dense than alkali metals. (D) They cannot form coloured compounds.
20. **Nickel salts are industrially used as catalysts in the preparation of:**
    (A) Methanol (B) Acrylic acid from acetylene (C) Sulphuric acid (D) Ammonia

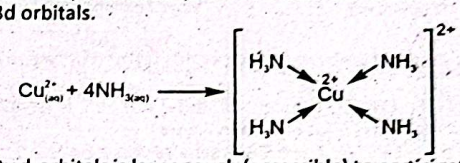


# TRANSITION METAL COMPLEXES

**Q.5 What are Transition metal compounds? Explain the terms: (a) Metal Complex (b) Ligand (c) Coordination number (d) Coordination sphere (e) Charge on coordination sphere** UQ

**OR Draw the structure of EDTA ligand and label its electron pair donating sites.** Exercise C/Q.3.(ii)

**Ans.** Transition elements form complexes and compounds because they have vacant (empty) d orbitals that are energetically accessible to accept electron pairs. The central transition metal ion e.g., $Fe^{3+}$ or $Cu^{2+}$ has partially filled or empty 3d orbitals.




The energy of these empty d-orbitals is low enough (accessible) to participate in bond formation. The vacant d-orbitals on the metal ion accept the lone pairs of electrons donated by the ligands, forming coordinate covalent bonds (or dative bonds).

The electron pair donor species (molecules or ions, like $H_2O$, $NH_3$ or $Cl^-$) are called ligands. This donation and acceptance of electron pairs create a stable complex ion (or coordination compound).

**Check Understanding!**
**Q.4 Give on example each of bidentate and hexa dentate ligands.**

### (a) Metal Complex:

A metal complex (or coordination compound) is a molecule or ion that forms when a central metal atom or ion is surrounded by a number of electron donor species (molecules or ions). A transition element acts as a Lewis acid (electron pair acceptor) in complex formation.

### (b) Ligand and Their Types:

A ligand is a molecule or ion (for example, $H_2O$, $NH_3$ or $Cl^-$) that possesses at least one lone pair of electrons and forms a coordinate covalent bond (dative bond) to the central metal atom or ion in a complex.

**Origin of 'Ligand':** The word "ligand" originates from the Latin "ligare", meaning "to bind". It acts as a Lewis base because it donates an electron pair.

Ligands can be classified into different categories.

i. **Anionic Ligands:** The negatively charged electron pair donor species are called anionic ligands. Their names usually end at "-o", e.g., chloride becomes "chloro" and cyanide becomes "cyano" etc. The most common examples are $Cl^-$, $CN^-$, $OH^-$, $C_2O_4^{2-}$ etc.

ii. **Neutral Ligands:** The neutral molecular species which are able to donate pair of electrons to form the transition metal complexes are called neutral ligands. **Examples:** $H_2O$ (Aqua), $NH_3$ (Ammine), CO (Carboxyl), NO (Nitrosyl) etc. Their names usually remain the same, though some have special names like $H_2O$ (aqua), $NH_3$ (ammine) and CO (carbonyl).

iii. **Cationic Ligands:** The positively charged electron pair donating species are called cationic ligands. They are rare and their names often ends at "-ium". **Examples:** $NO^+$ (nitrosonium), $NH_2—NH_3^+$ (hydrazinium) etc.

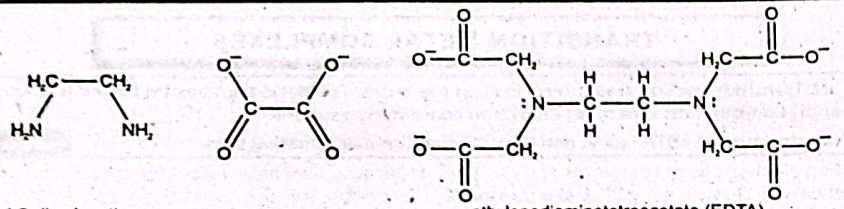
### Types of Ligands on the Basis of Number of Electron Pair Donation:

i. **Monodentate Ligand:** Types on the basis of number of electron pair donation. A monodentate ligand is a species that can donate only one pair of electrons to the central metal atom or ion. Some examples are $H_2O$, $NH_3$, CO, $Cl^-$, $OH^-$ and $CN^-$ etc. In each case, only a single atom on the ligand forms the dative covalent bond to the metal.

ii. **Bidentate Ligands:** Bidentate ligands can donate two electron pairs to the central metal atom/ion. Typical examples are 1,2-diaminoethane (also known as ethylenediamine) and ethanedioate (or oxalate) ion. In 1,2-diaminoethane ($H_2NCH_2CH_2NH_2$, abbreviated as en), each of the two nitrogen (N) atoms donate a lone pair to the metal. In the ethanedioate ion ($C_2O_4^{2-}$), two oxygen (O) atoms, one from each carboxyl group, donate electron pairs.

iii. **Polydentate Ligand:** A polydentate ligand is ligand that forms more than two dative bonds to a single central metal atom/ion.
**Example:** Ethylenediaminetetracetate ion **(EDTA)** is a common example of a **hexadentate ligand.** EDTA can attach to a metal ion using six donor atoms (four oxygen and two nitrogen atoms).

CamScanner



1,2-diaminoethane ethanedioate ethylenediaminetetraacetate (EDTA)

**(c) Coordination Number:**

The coordination number is the total number of dative bonds formed between ligands and the central metal atom or ion in a complex.

**Examples:** In the complex ion $[Fe(CN)_6]^{4-}$, the central metal ion $Fe^{2+}$ is bonded to six $CN^-$ ligands, so the coordination number of the metal ion is 6 (as shown in Figure).

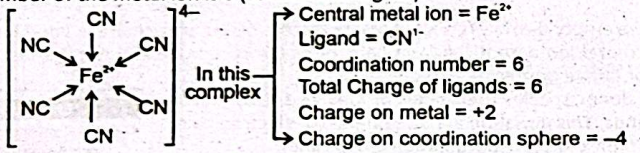



**Figure: Hexacyanoferrate (II) complex and its components**

In $[Cu(NH_3)_4]SO_4$, the coordination number of copper is 4.

**(d) Coordination Sphere:**

A coordination sphere is the central metal atom or ion and the directly bonded ligands (molecules or ions) surrounding it within a coordination compound. It defines the immediate chemical environment, is usually written inside square brackets [Complex]. It may be anionic, cationic or neutral.

In $K_4[Fe(CN)_6]^{-4}$, in this complex compound, $[Fe(CN)_6]^{-4}$ is the anionic coordination sphere.

**(e) Charge on Coordination Sphere:**

The charge on coordination sphere is the arithmetic sum of the charges of central metal atom or ion and ligands. Whereas, the charge on the metal atom or ion will be the difference of the charge on sphere and total charge of ligands. In $[Fe(CN)_6]^{-4}$, charge on Fe = +2, Total charge on six $CN^{-1}$ ions = −6.

Charge on the coordination sphere = −6 + 2 = −4.

## PREDICTING FORMULA AND CHARGE OF A COMPLEX ION

**Q.6 Using the examples $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$, demonstrate how to predict the formula and overall charge of a complex ion. Clearly explain the role of the central metal ion charge, ligand charge, and coordination number in determining the final result for both examples.**

**Ans.** The formula and charge of a complex ion are determined by combining the central metal ion, its oxidation state, and the ligands along with their charges. The general structure of a complex ion is $[M(L)_x]^{\pm y}$.

Where, M is the central metal ion.

L is the ligand, x is the number of ligand (determined by the coordination number) and ±y is the overall charge of the complex ion.

**Check Understanding!**

**Q.5** Example of anionic ligand is:

(A) $NH_3$ (B) $CN^-$

(C) CO (D) $H_2O$

**Table: Predicting formula and charge of a complex ion**

| Complex type | Cationic Complex | Anionic Complex | Neutral Complex |
|---|---|---|---|
| Metal Ion | Co | Fe | Ni |
| Oxidation state of metal | +3 | +2 | 0 |
| Ligand | $NH_3$ (Ammine) | $CN^-$ (cyano/cyanido) | CO (Carbonyl) |
| Ligand type and charge | Neutral, 0 | Anionic, −1 | Neutral, 0 |
| Coordination number | 6 | 6 | 4 |
| Determination of formula | Place Metal (Co) first, then Ligand ($NH_3$) with its number as a subscript (6), all inside square brackets [ ]. | Place Metal (Fe) first, then Ligand (CN) with its number as a subscript (6), inside brackets [ ]. | Place Metal (Ni) first, then Ligand (CO) with its number as a subscript (4), inside brackets [ ]. |
| Calculate the charge | (+3) + [6 × (0)] = +3 | (+2) + [6 × (−1)] = −4 | (0) + [4 × (0)] = 0 |
| Explanation of charge calculation of complex | Metal charge (+3) + (Number of ligands × Ligand charge). A positive sum. | Metal charge (+2) + (Number of ligands × Ligand charge). A negative sum. | Metal charge (0) + (Number of ligands × Ligand charge). A zero sum. |
| Final form and charge | $[Co(NH_3)_6]^{3+}$ | $[Fe(CN)_6]^{4}$ | $[Ni(CO)_4]$ |



## GEOMETRY OF TRANSITION METAL COMPLEXES

**Q.7 Explain the factors that determine the specific geometry (shape) of a transition metal complex.** Exercise D/Q. 4

**Ans.** Transition metal complexes show (exhibit) specific geometries (shapes) depending upon:

i) The electronic configuration.
ii) Coordination number (number of donor atoms attached) of the metal).
iii) The nature of the ligands.

➢ **Common Geometries in Transition Metal Complexes:**

i. **Linear Geometry:** In this geometry, the two ligands are attached on opposite sides of the central metal ion at an angle of 180°.
**Typical examples of linear complexes:** $[Ag(NH_3)_2]Cl$, $K[Ag(CN)_2]$.

**Check Understanding!**

**Q.6** Discuss linear geometry of transition metal complexes.

ii. **Square planar Geometry:** In square planar shape, the central metal ion and the four ligands lie in the same plane, at the corners of a square with bond angle 90°.
**Examples:** This geometry is characteristic of $d^8$ metal ions (e.g., $Ni^{2+}$ and $Pt^{2+}$) with ligands like, $NH_3$ and $CN^-$).
**Examples:** $[Ni(CN)_4]^{2-}$, $[Pt(NH_3)_4]^{2+}$.

iii. **Tetrahedral Geometry:** In tetrahedral complexes, four ligands are present at the corners of a tetrahedron with bond angle of 109.5°. Tetrahedral geometry is common with bulky/weak ligands such as $Cl^-$ e.g., $[CoCl_4]^{2-}$ ($d^7$) and $[MnCl_4]^{2-}$ ($d^5$).

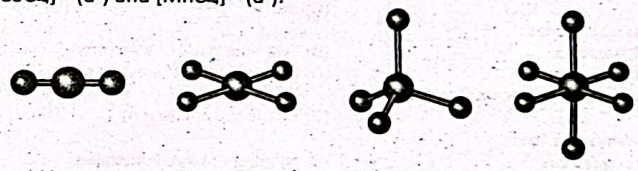



**Figure: Shapes of Transition Metal complexes**

iv. **Octahedral Geometry:** In this geometry, the central metal ion is surrounded by **six ligands**, coming along the x, y and z axes. **Four ligands** form a **square plane** with an angle of 90°, and the other two are positioned above and below this plane at an angle of 180°. Octahedral geometry is the most common geometry for transition metal complexes.
**Examples:** $[Cr(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Fe(CN)_6]$.

### QUICK CHECK 18.3

**a) How does Lewis acid base concept explains the transition metal complex formation?**

**Ans.**
- **Ligands:** Act as Lewis bases by donating lone pairs.
- **Metal Ions:** Act as Lewis acids by accepting lone pairs into vacant d-orbitals.
- **Bonding:** Forms coordinate covalent bonds.

**b) Determine the overall charge of a complex ion formed from $Cr^{3+}$ metal ion with six neutral $H_2O$ ligands and a coordination number of 6. Show your calculation.**

**Ans. Formula:** Overall Charge = (+3) + [6 × (0)]

CamScanner

Result: Overall Charge = +3
Complex: $[Cr(H_2O)_6]^{3+}$

c) **Predict the likely geometry for the complex ion $[MnCl_4]^{2-}$, given that the central metal ion has a $d^5$ electron configuration and a coordination number of 4.**

Ans. **Geometry:** Tetrahedral (As $Cl^-$ is a weak field ligand).
**Reason:** Coordination number 4 with a $d^5$ configuration (is $Mn^{2+}$) preferentially forms tetrahedral shapes.

d) **EDTA is described as a hexadentate ligand. Explain what "hexadentate" means in terms of coordinate covalent bonds formed with a single metal ion.**

Ans. **Definition:** It binds using six donor atoms.
**Bonds:** Formulates exactly six coordinate covalent bonds with a single metal ion.

e) **Identify the two essential features of a transition metal ion that enable it to form complex ions.**

Ans. i. Small size and high charge density of transition elements creates a strong electrostatic force of attraction for ligands to donate electron pairs to the metal ions.
ii. Presence of vacant d orbitals to accept lone pair of electrons from ligands to form coordinate covalent bonds.

f) **What is the role of a ligand in forming a complex ion, and what type of bond is formed?**

Ans. A ligand donates a lone pair of electrons to the central metal ion. It act as a Lewis base and stabilizes the complex ion by forming coordinate covalent bonds around the metal ion. Thus the bond formed is a coordinate covalent (dative covalent) bond in which both bonding electrons are supplied by the ligand.

## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **A transition metal complex consists of a central metal atom/ion surrounded by:**
(A) Metal ions only (B) Ligands (C) Neutral molecules only (D) Metal oxides
2. **In a coordination compound, the central transition metal acts as a:**
(A) Lewis base (B) Bronsted acid (C) Lewis acid (D) Reducing agent
3. **A ligand behaves as a:**
(A) Lewis acid (B) Lewis base (C) Bronsted acid (D) Catalyst
4. **Which of the following is an anionic ligand?**
(A) $NH_3$ (B) $H_2O$ (C) $Cl^-$ (D) CO
5. **Which of the following is a neutral ligand?**
(A) $CN^-$ (B) $Cl^-$ (C) $NH_3$ (D) $OH^-$
6. **Which ligand is hexadentate?**
(A) $NH_3$ (B) $H_2O$ (C) EDTA (D) CO
7. **A monodentate ligand donates:**
(A) One lone pair of electrons (B) Two lone pairs of electrons
(C) Three lone pairs of electrons (D) Six lone pairs of electrons
8. **Which of the following is a bidentate ligand?**
(A) $NH_3$ (B) $H_2O$ (C) Ethylenediamine (en) (D) $Cl^-$
9. **The coordination number is the:**
(A) Charge on the complex ion (B) Number of oxidation states
(C) Number of coordinate bonds formed with the central metal
(D) Number of unpaired electrons
10. **What is the coordination number of Fe in $[Fe(CN)_6]^{4-}$?**
(A) 2 (B) 4 (C) 6 (D) 8
11. **The coordination sphere includes:**
(A) Only the ligands (B) Only the metal ion
(C) The central metal ion and directly attached ligands (D) All ions present in solution
12. **Which complex is electrically neutral?**
(A) $[Co(NH_3)_6]^{3+}$ (B) $[Fe(CN)_6]^{4-}$ (C) $[Ni(CO)_4]$ (D) $[Cu(H_2O)_6]^{2+}$
13. **The overall charge on $[Co(NH_3)_6]^{3+}$ is:**
(A) +1 (B) +2 (C) +3 (D) 0
14. **Which geometry is commonly associated with coordination number 2?**
(A) Octahedral (B) Linear (C) Square planar (D) Tetrahedral
15. **Which geometry is commonly shown by $[Ni(CN)_4]^{2-}$?**
(A) Tetrahedral (B) Linear (C) Square planar (D) Octahedral
16. **The bond angle in a tetrahedral complex is approximately:**
(A) 90° (B) 109.5° (C) 120° (D) 180°
17. **The most common geometry for coordination number 6 is:**
(A) Linear (B) Square planar (C) Tetrahedral (D) Octahedral



18. **The complex $[Cr(NH_3)_6]^{3+}$ is:**
(A) Linear (B) Square planar (C) Octahedral (D) Tetrahedral
19. **The coordinate covalent bond is formed by:**
(A) Equal sharing of electrons by both atoms (B) Donation of an electron pair from ligand to metal ion
(C) Transfer of electrons (D) Metallic bonding
20. **Which property mainly enables transition metals to form complex ions?**
(A) High melting point (B) Presence of vacant accessible d-orbitals
(C) Large atomic size (D) Low ionization energy

## COLOUR OF COMPLEXES

**Q.8 Describe the splitting of d-orbitals and colour formation in octahedral and tetrahedral complexes.**
Exercise D/Q. 5

Ans. The d-orbitals have a characteristic cloverleaf shape, generally resembling four lobes ($d_{xy}, d_{xz}, d_{yz}, d_{x^2-z^2}$) or two dumbbells in a plane ($d_{z^2}$), with five distinct orbitals $d_{xy}, d_{xz}, d_{yz}, d_{x^2-z^2}$ and $d_{z^2}$. In an isolated atom, all five d orbitals have the same energy (degenerate), but their different shapes lead to different energies in complex ions (non-degenerate). Their spatial (in space) arrangements and energy levels decide the bonding, colour, and magnetic properties of transition metals.
When ligands approach the metal ion to form an octahedral or a tetrahedral complex, they create an electric field that causes the five d orbitals to split into two groups with different energies, making them non-degenerate. The energy difference is related to the extent of splitting between the two sets of orbitals and is represented by Δ.

**Check Understanding!**
**Q.7 What is the initial and final colour of $Cu^{2+}$ ions before and after addition of conc. $NH_3$ solution?**
(A) Blue to yellow green.
(B) Pink to yellow.
(C) Blue to deep blue.
(D) Pink to blue.

### Octahedral Complexes

In octahedral complexes (with six ligands), like $[Ti(H_2O)_6]^{3+}$, the five d orbitals split into two sets; three lower-energy orbitals including, $d_{xy}$, $d_{xz}$, $d_{yz}$ and two higher-energy orbitals; $d_{x^2-y^2}$, $d_{z^2}$ (Figure).

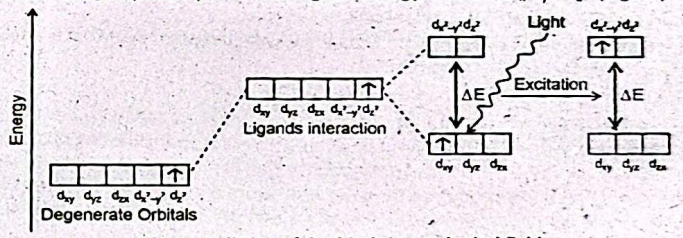



**Figure: Splitting of d orbitals in octahedral field**

### Tetrahedral Complexes

In tetrahedral complexes (with four ligands), like $[CuCl_4]^{2-}$, the d-orbital splitting is inverted with three higher-energy orbitals $d_{xy}$, $d_{xz}$, $d_{yz}$ and two lower-energy orbitals $d_{x^2-y^2}$, $d_{z^2}$. The magnitude of splitting in tetrahedral complexes is smaller than that in octahedral complexes i.e., almost 44% of octahedral splitting (Figure).

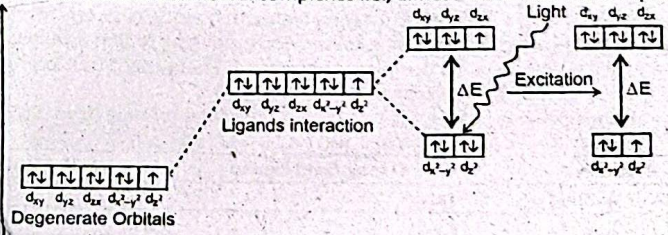



**Figure: Splitting of d orbitals in tetrahedral field**

CamScanner

| Property | Octahedral | Tetrahedral |
|---|---|---|
| High energy | $d_{x^2-y^2}$, $d_{z^2}$ | $d_{xy}$, $d_{xz}$, $d_{yz}$ |
| Lower energy | $d_{xy}$, $d_{xz}$, $d_{yz}$ | $d_{x^2-y^2}$, $d_{z^2}$ |
| Spin | High spin and low spin possible. | Always high spin. |

## Colour Formation

The electrons in a lower-energy d orbital absorb light and are promoted (excited) to a higher-energy orbital. The light energy involved in the transition of electron is responsible for showing definite colour to the complex. The unabsorbed light is transmitted and it decides the nature of the colour. This process is called a d-d transition. The energy required for a d-d transition, corresponds to a specific frequency ($\upsilon$) and wavelength ($\lambda$) of visible light according to the Planck's equation, $\Delta E = h\upsilon = hc/\lambda$ (h is Planck's constant and c is speed of light).

When white light falls on the compound, it may get absorbed completely, and the complex appears black. The compound may reflect or transmit the whole light, and appears to be white. The compound may absorb some of the light and reflect the remaining part, then complex shows different colours depending upon colour of the light reflected. The colour is produced in the substances due to absorption and emission of light in the visible region of the spectrum according the following colour scheme (Figure).

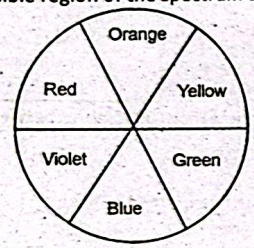



**Figure: Colour wheel showing complementary colours**

**Interesting Information**

**Factors Affecting ΔE:**

- **Nature of Ligand**
  Strong field ligands, larger ΔE.
- **Oxidation State of Metal**
  Higher oxidation state or charge on metal ion larger ΔE.
- **Nature of Metal**
  5d > 4d > 3d
  5d metals have lasser ΔE than 4d and 3d.

The colour we see is the complementary colour frequency/wavelength of light that is absorbed. For example if a complex absorbs yellow light, it appears violet.

### d-d Transition:

The electrons in a lower-energy d-orbital absorb light and are promoted (excited) to a higher-energy orbital. The light energy involved in the transition of electron is responsible for showing definite colour the complex. The unabsorbed light is transmitted and it decides the nature of the colour. This process called a d-d transition. The energy required for a d-d transition, corresponds to a specific frequency ($\upsilon$) wavelength ($\lambda$) of visible light according to the Planck's equation, $\Delta E = h\upsilon = hc/\lambda$ (h is Planck's constant c is speed of light).

### Effect of Different Ligands on ΔE and Colour:

The **nature of the ligand** affects the magnitude of the splitting, ΔE.

**Strong field Ligands:**

Some ligands like $NH_3$, $CN^-$ cause larger splitting, increasing the energy gap (ΔE). Ligands like $C\ell^-$, $I^-$ small splitting i.e. ΔE is smaller. A larger ΔE means a higher frequency, (shorter wavelength) of light must absorbed that is in the region of violet or blue colour. Corresponding to that a yellow light is reflected by the compound a yellow colour. Some complexes absorb low-energy light (red/orange) and appear green according to the complementary colour scheme.

Ligands can be arranged in order of their ability to cause d-orbital splitting (from high ΔE to low ΔE)

$$CN^- > en > NH_3 > H_2O > OH^- > C\ell^- > Br^- > I^-$$

| Property | Strong Field Ligand | Weak Field Ligands |
|---|---|---|
| Magnitude of splitting | Large | Small |
| Spin | Low | High |
| Pairing | Electrons pair in $t_{2g}$. | Electrons stay unpaired. |
| Examples | Co, $CN^-$, $NH_3$, en | $I^-$, $Br^-$, $C\ell^-$, $F^-$, $H_2O$ |



18. The complex $[Cr(NH_3)_6]^{3+}$ is:
(A) Linear (B) Square planar (C) Octahedral (D) Tetrahedral

19. The coordinate covalent bond is formed by:
(A) Equal sharing of electrons by both atoms (B) Donation of an electron pair from ligand to metal ion
(C) Transfer of electrons (D) Metallic bonding

20. Which property mainly enables transition metals to form complex ions?
(A) High melting point (B) Presence of vacant accessible d-orbitals
(C) Large atomic size (D) Low ionization energy

# COLOUR OF COMPLEXES

**Q.8 Describe the splitting of d-orbitals and colour formation in octahedral and tetrahedral complexes.**

Exercise D/O. 5

**Ans.** The d-orbitals have a characteristic cloverleaf shape, generally resembling four lobes ($d_{xy}$, $d_{xz}$, $d_{yz}$, $d_{x^2-y^2}$) or two dumbbells in a plane ($d_{z^2}$), with five distinct orbitals $d_{xy}$, $d_{xz}$, $d_{yz}$, $d_{x^2-y^2}$ and $d_{z^2}$. In an isolated atom, all five d orbitals have the same energy (degenerate), but their different shapes lead to different energies in complex ions (non-degenerate). Their spatial (in space) arrangements and energy levels decide the bonding, colour, and magnetic properties of transition metals.

When ligands approach the metal ion to form an octahedral or a tetrahedral complex, they create an electric field that causes the five d orbitals to split into two groups with different energies, making them non-degenerate. The energy difference is related to the extent of splitting between the two sets of orbitals and is represented by Δ.

**Check Understanding!**

**Q.7 What is the initial and final colour of $Cu^{2+}$ ions before and after addition of conc. $NH_3$ solution?**
(A) Blue to yellow green.
(B) Pink to yellow.
(C) Blue to deep blue.
(D) Pink to blue.

## Octahedral Complexes

In octahedral complexes (with six ligands), like $[Ti(H_2O)_6]^{3+}$, the five d orbitals split into two sets; three lower-energy orbitals including, $d_{xy}$, $d_{xz}$, $d_{yz}$ and two higher-energy orbitals; $d_{x^2-y^2}$, $d_{z^2}$ (Figure).

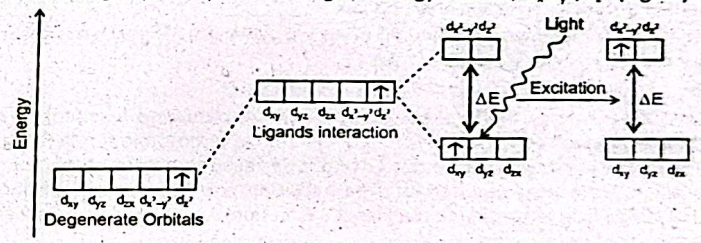



**Figure: Splitting of d orbitals in octahedral field**

## Tetrahedral Complexes

In tetrahedral complexes (with four ligands), like $[CuC\ell_4]^{2-}$, the d-orbital splitting is inverted with three higher-energy orbitals $d_{xy}$, $d_{xz}$, $d_{yz}$ and two lower-energy orbitals $d_{x^2-y^2}$, $d_{z^2}$. The magnitude of splitting in tetrahedral complexes is smaller than that in octahedral complexes i.e., almost 44% of octahedral splitting (Figure).

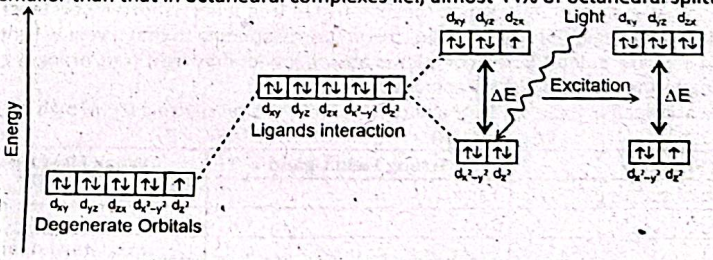



**Figure: Splitting of d orbitals in tetrahedral field**

CamScanner

| Property | Octahedral | Tetrahedral |
|---|---|---|
| High energy | $d_{x^2-y^2}, d_{z^2}$ | $d_{xy}, d_{xz}, d_{yz}$ |
| Lower energy | $d_{xy}, d_{xz}, d_{yz}$ | $d_{x^2-y^2}, d_{z^2}$ |
| Spin | High spin and low spin possible. | Always high spin. |

## Colour Formation

The electrons in a lower-energy d orbital absorb light and are promoted (excited) to a higher-energy orbital. The light energy involved in the transition of electron is responsible for showing definite colour the complex. The unabsorbed light is transmitted and it decides the nature of the colour. This process called a d-d transition. The energy required for a d-d transition, corresponds to a specific frequency (υ) a wavelength (λ) of visible light according to the Planck's equation, $\Delta E = h\upsilon = hc/\lambda$ (h is Planck's constant a c is speed of light).

When white light falls on the compound, it may get absorbed completely, and the complex appears bla The compound may reflect or transmit the whole light, and appears to be white. The compound may abso some of the light and reflect the remaining part, then complex shows different colours depending up colour of the light reflected. The colour is produced in the substances due to absorption and emission light in the visible region of the spectrum according the following colour scheme (Figure).

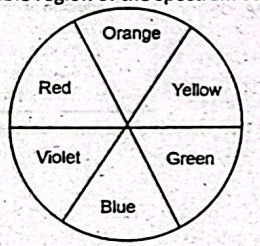



**Figure: Colour wheel showing complementary colours**

**Interesting Information**

Factors Affecting ΔE:

- Nature of Ligand
  Strong field ligands, larger ΔE.
- Oxidation State of Metal
  Higher oxidation state or charge on metal l larger ΔE.
- Nature of Metal
  5d > 4d > 3d
  5d metals have lasser ΔE than 4d and 3d.

The colour we see is the complementary colour frequency/wavelength of light that is absorbed. For exam if a complex absorbs yellow light, it appears violet.

## d-d Transition:

The electrons in a lower-energy d-orbital absorb light and are promoted (excited) to a higher-energ orbital. The light energy involved in the transition of electron is responsible for showing definite colou the complex. The unabsorbed light is transmitted and it decides the nature of the colour. This proces called a d-d transition. The energy required for a d-d transition, corresponds to a specific frequency (υ) a wavelength (λ) of visible light according to the Planck's equation, $\Delta E = h\upsilon = hc/\lambda$ (h is Planck's constant c is speed of light).

## Effect of Different Ligands on ΔE and Colour:

The nature of the ligand affects the magnitude of the splitting, ΔE.

**Strong field Ligands:**

Some ligands like $NH_3$, $CN^-$ cause larger splitting, increasing the energy gap (ΔE). Ligands like $Cl^-$, $I^-$ c small splitting i.e. ΔE is smaller. A larger ΔE means a higher frequency, (shorter wavelength) of light mus absorbed that is in the region of violet or blue colour. Corresponding to that a yellow light is reflected g the compound a yellow colour. Some complexes absorb low-energy light (red/orange) and appear blu green according to the complementary colour scheme.

Ligands can be arranged in order of their ability to cause d-orbital splitting (from high ΔE to low ΔE):

$$CN^- > en > NH_3 > H_2O > OH^- > Cl^- > Br^- > I^-$$

| Property | Strong Field Ligand | Weak Field Ligands |
|---|---|---|
| Magnitude of splitting | Large | Small |
| Spin | Low | High |
| Pairing | Electrons pair in $t_2g$. | Electrons stay unpaired. |
| Examples | Co, $CN^-$, $NH_3$, en | $I^-$, $Br^-$, $Cl^-$, $F^-$, $H_2O$ |



## QUICK CHECK 18.4

**a) How does the presence of ligands affect the degeneracy of d-orbitals in a complexion?**

Ans.
- **Field creation:** Approaching negative or polar ligands generate an uneven electrostatic field.
- **Degeneracy removal:** This asymmetric field destroys the equal energy status of the five d-orbitals.
- **Spatial splitting:** Repulsion forces the orbitals to split into separate, distinct energy levels.

**b) Describe the key difference in d-orbital splitting patterns between octahedral complexes and tetrahedral complexes.**

Ans.
- **Octahedral approach Six:** Ligands attack directly along the x, y, z axes.
- **Octahedral energy:** Octahedral splitting energy $\Delta_o$ is large. The 5d-Orbitals split into 2 high energy e.g., orbital $d_{x^2-y^2}, d_{z^2}$ and 3 lower energy $t_{2g}$ orbitals i.e. $d_{xy}, d_{yz}, d_{xz}$.
- **Tetrahedral approach:** Four ligands attack (approach) in between the axes.
- **Tetrahedral energy:** Reverses the pattern by raising three orbitals ($t_2$) and lowering two (e).

$\Delta t$ = Tetrahedral splitting energy is much smaller than $\Delta_o$ $\left(\Delta t \approx \frac{4}{9}\Delta_o\right)$

**c) Explain the relationship between the absorbed light energy (ΔE) and the observed colour of a transition metal complex. Reference Planck's equation ($\Delta E = h\nu = hc/\lambda$).**

Ans. According to Planck's equation, the energy split (ΔE) is inversely proportional to the wavelength (λ) of light. When a complex absorbs a specific wavelength to excite an electron across this energy gap, that specific colour is removed from white light, and the compound reflects the remaining wavelengths, which appear as the complementary colour.

**d) If a complex containing the ligand $Cl^-$ absorbs light in the red/orange region of the spectrum, what general colour range would you expect the complex to appear?**

Ans. According to the provided colour wheel, the direct complementary opposites of red and orange are green and blue. Therefore, if the complex absorbs low-energy light in the red/orange region, the remaining transmitted light will cause the complex to appear in the blue/green colour range.

**e) Explain the phenomenon (d-d transitions) responsible for the colour of transition metal compounds.**

Ans. A d-d transition occurs when an electron residing in a lower-energy split d-orbital absorbs a photon of visible light matching the energy gap (ΔE). This energy promotes the electron to a vacant, higher-energy split d-orbital, and the resulting removal of that specific wavelength leaves behind the complementary colour we see.

## LIGAND EXCHANGE REACTIONS OF COMPLEXES

If new complex to be formed is more stable then substitution of ligands occurs and it will change the properties of the new complex, like colour, structure and reactivity. The complexes of copper(II) and cobalt(II) ions can be used to show ligand substitution reactions.

**Q.9 Compare the reactions of conc. HCl with aqueous $Cu^{2+}$ and aqueous $Co^{2+}$. Include equations, colour/geometry changes, and the reason for different colours.** Exercise D/Q.6

### (a) Ligand Exchange Reactions of Copper (II) Complexes

Whenever, we write $Cu^{2+}_{(aq)}$, we actually refer to the complex ion $[Cu(H_2O)_6]^{2+}$. This ion gives blue colour to the solution of a copper(II) salt, for example, copper sulphate. On adding sodium hydroxide to a copper(II) solution, a light blue precipitate is formed. Two water ligands are replaced by two hydroxide ions in this reaction.

$[Fe^{3+}(CN)_6^{-1\times6}]^{3-}$

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow [Cu(H_2O)_4(OH)_2]_{(s)} + 2H_2O_{(\ell)}$$

blue solution — light blue precipitate

If concentrated ammonia solution is added, the light blue precipitate dissolves resulting in a dark blue solution.

The structure of $[Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)}$ is shown in Figure.

**Check Understanding!**

**Q.8 What is the initial and final colour of $Co^{2+}$ ions before and after addition of conc. $NH_3$ solution?**

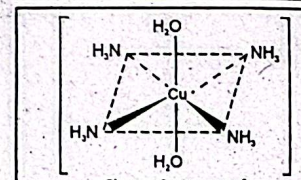



**Figure: Structure of $[Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)}$ ion**

CamScanner

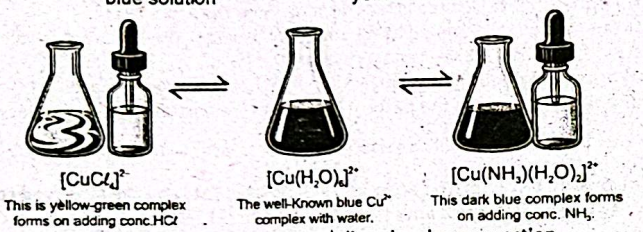
Water ligands in $[Cu(H_2O)_6]^{2+}$ can also be exchanged directly with ammonia by replacing four water molecules. For simplicity, $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is usually written as $[Cu(NH_3)_4]^{2+}$.

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)} + 4H_2O_{(l)}$$

The chloride ions can also replace water ligands in $[Cu(H_2O)_6]^{2+}$ on addition of concentrated hydrochloric acid drop by drop. A yellow-green solution is obtained that contains the complex ion $[CuCl_4]^{2-}$ (Figure) as follows.

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \longrightarrow [CuCl_4]^{2-} + 6H_2O$$

blue solution yellow solution



$[CuCl_4]^{2-}$ — This is yellow-green complex forms on adding conc.HCl

$[Cu(H_2O)_6]^{2+}$ — The well-Known blue $Cu^{2+}$ complex with water.

$[Cu(NH_3)(H_2O)_2]^{2+}$ — This dark blue complex forms on adding conc. $NH_3$.

**Figure: Colour changes as a result ligand exchange reaction**

## (b) Ligand Exchange Reactions of Cobalt(II) Complexes

Cobalt(II) salts also form complex ions in aqueous solution. In the case of copper(II), a $Co^{2+}_{(aq)}$ ion refers to the complex ion $[Co(H_2O)_6]^{2+}$. This ion gives a pink colour to the aqueous solution of cobalt(II) sulphate. On adding sodium hydroxide solution, a blue precipitate of cobalt(II) hydroxide is observed, which may turn pink on standing.

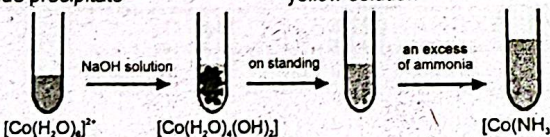
$$[Co(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow [Co(H_2O)_4(OH)_2]_{(s)} + 2H_2O_{(l)}$$

pink solution blue precipitate

When excess ammonia solution is added to the cobalt(II) hydroxide precipitate, a ligand exchange reaction takes place. The ammonia molecules (ligand) replace the water and hydroxide ions, forming a soluble ammine complex, hexaamminecobalt(II). The colour of the solution turns yellow (Figure).

$$[Co(H_2O)_4(OH)_2]_{(s)} + 6NH_{3(aq)} \longrightarrow [Co(NH_3)_6]^{2+}_{(aq)} + 4H_2O_{(l)} + 2OH^-_{(aq)}$$

blue precipitate yellow solution




$[Co(H_2O)_6]^{2+}$ $[Co(H_2O)_4(OH)_2]$ $[Co(NH_3)_6]^{2}$

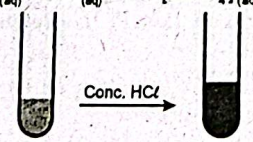
**Figure: Colour changes in $[Co(H_2O)_6]^{2+}$ on addition of hydroxide and $NH_3$**

Water ligands in $[Co(H_2O)_6]^{2+}$ can also be exchanged directly with ammonia ligands by adding concentrated ammonia solution.

$$[Co(H_2O)_6]^{2+}_{(aq)} + 6NH_{3(aq)} \longrightarrow [Co(NH_3)_6]^{2+}_{(aq)} + 6H_2O_{(l)}$$

The addition of concentrated hydrochloric acid drop by drop to an aqueous solution of cobalt(II) ions results in the formation of a blue solution containing the tetrahedral complex $[CoCl_4]^{2-}_{(aq)}$ (Figure).

$$[Co(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \longrightarrow [CoCl_4]^{2-}_{(aq)} + 6H_2O_{(l)}$$




$[Co(H_2O)_6]^{2+}$ $[CoCl_4]^{2-}$

**Figure: Exchange of water molecules by chloride ions in a Co (II) complex**

Aqueous cobalt(II) ions usually form tetrahedral complexes with monodentate anionic ligands such as $OH^-$ and $SCN^-$.



### QUICK CHECK 18.4

**a) How does the presence of ligands affect the degeneracy of d-orbitals in a complexion?**

Ans.
- **Field creation:** Approaching negative or polar ligands generate an uneven electrostatic field.
- **Degeneracy removal:** This asymmetric field destroys the equal energy status of the five d-orbitals.
- **Spatial splitting:** Repulsion forces the orbitals to split into separate, distinct energy levels.

**b) Describe the key difference in d-orbital splitting patterns between octahedral complexes and tetrahedral complexes.**

Ans.
- **Octahedral approach Six:** Ligands attack directly along the x, y, z axes.
- **Octahedral energy:** Octahedral splitting energy $\Delta_o$ is large. The 5d-Orbitals split into 2 high energy e.g., orbital $d_{x^2-y^2}$, $d_{z^2}$ and 3 lower energy $t_{2g}$ orbitals i.e. $d_{xy}$, $d_{yz}$, $d_{xz}$.
- **Tetrahedral approach:** Four ligands attack (approach) in between the axes.
- **Tetrahedral energy:** Reverses the pattern by raising three orbitals ($t_2$) and lowering two (e).

$\Delta t$ = Tetrahedral splitting energy is much smaller than $\Delta_o$ ($\Delta t \approx \frac{4}{9}\Delta_o$)

**c) Explain the relationship between the absorbed light energy ($\Delta E$) and the observed colour of a transition metal complex. Reference Planck's equation ($\Delta E = hv = hc/\lambda$).**

Ans. According to Planck's equation, the energy split ($\Delta E$) is inversely proportional to the wavelength ($\lambda$) of light. When a complex absorbs a specific wavelength to excite an electron across this energy gap, that specific colour is removed from white light, and the compound reflects the remaining wavelengths, which appear as the complementary colour.

**d) If a complex containing the ligand $Cl^-$ absorbs light in the red/orange region of the spectrum, what general colour range would you expect the complex to appear?**

Ans. According to the provided colour wheel, the direct complementary opposites of red and orange are green and blue. Therefore, if the complex absorbs low-energy light in the red/orange region, the remaining transmitted light will cause the complex to appear in the blue/green colour range.

**e) Explain the phenomenon (d-d transitions) responsible for the colour of transition metal compounds.**

Ans. A d-d transition occurs when an electron residing in a lower-energy split d-orbital absorbs a photon of visible light matching the energy gap ($\Delta E$). This energy promotes the electron to a vacant, higher-energy split d-orbital, and the resulting removal of that specific wavelength leaves behind the complementary colour we see.

## LIGAND EXCHANGE REACTIONS OF COMPLEXES

If new complex to be formed is more stable then substitution of ligands occurs and it will change the properties of the new complex, like colour, structure and reactivity. The complexes of copper(II) and cobalt(II) ions can be used to show ligand substitution reactions.

**Q.9 Compare the reactions of conc. HCl with aqueous $Cu^{2+}$ and aqueous $Co^{2+}$. Include equations, colour/geometry changes, and the reason for different colours.** Exercise D/Q.6

### (a) Ligand Exchange Reactions of Copper (II) Complexes

Whenever, we write $Cu^{2+}_{(aq)}$, we actually refer to the complex ion $[Cu(H_2O)_6]^{2+}$. This ion gives blue colour to the solution of a copper(II) salt, for example, copper sulphate. On adding sodium hydroxide to a copper(II) solution, a light blue precipitate is formed. Two water ligands are replaced by two hydroxide ions in this reaction. $[Fe^{3+}(CN)_6^{-1\times6}]^{3-}$

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow [Cu(H_2O)_4(OH)_2]_{(s)} + 2H_2O_{(l)}$$

blue solution light blue precipitate

If concentrated ammonia solution is added, the light blue precipitate dissolves resulting in a dark blue solution.

The structure of $[Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)}$ is shown in Figure.

**Check Understanding!**

**Q.8 What is the initial and final colour of $Co^{2+}$ ions before and after addition of conc. $NH_3$ solution?**

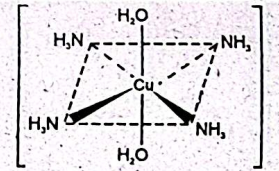



**Figure: Structure of $[Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)}$ ion**

CamScanner

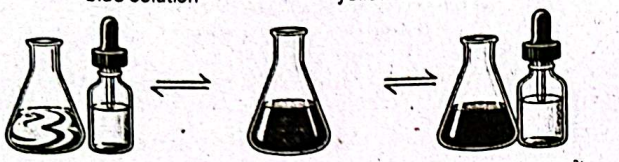
Water ligands in $[Cu(H_2O)_6]^{2+}$ can also be exchanged directly with ammonia by replacing four water molecules. For simplicity, $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is usually written as $[Cu(NH_3)_4]^{2+}$.

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)} + 4H_2O_{(l)}$$

The chloride ions can also replace water ligands in $[Cu(H_2O)_6]^{2+}$ on addition of concentrated hydrochloric acid drop by drop. A yellow-green solution is obtained that contains the complex ion $[CuCl_4]^{2-}$ (Figure) as follows.

$$[Cu(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \longrightarrow [CuCl_4]^{2-} + 6H_2O$$

blue solution → yellow solution



$[CuCl_4]^{2-}$ — This is yellow-green complex forms on adding conc HCl

$[Cu(H_2O)_6]^{2+}$ — The well-Known blue $Cu^{2+}$ complex with water.

$[Cu(NH_3)(H_2O)_2]^{2+}$ — This dark blue complex forms on adding conc. $NH_3$.

**Figure: Colour changes as a result ligand exchange reaction**

## (b) Ligand Exchange Reactions of Cobalt(II) Complexes

Cobalt(II) salts also form complex ions in aqueous solution. In the case of copper(II), a $Co^{2+}_{(aq)}$ ion refers to the complex ion $[Co(H_2O)_6]^{2+}$. This ion gives a pink colour to the aqueous solution of cobalt(II) sulphate. On adding sodium hydroxide solution, a blue precipitate of cobalt(II) hydroxide is observed, which may turn pink on standing.

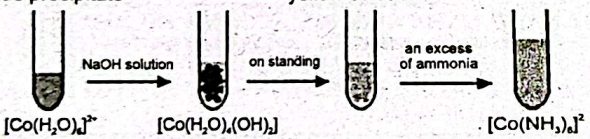
$$[Co(H_2O)_6]^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow [Co(H_2O)_4(OH)_2]_{(s)} + 2H_2O_{(l)}$$

pink solution → blue precipitate

When excess ammonia solution is added to the cobalt(II) hydroxide precipitate, a ligand exchange reaction takes place. The ammonia molecules (ligand) replace the water and hydroxide ions, forming a soluble ammine complex, hexaamminecobalt(II). The colour of the solution turns yellow (Figure).

$$[Co(H_2O)_4(OH)_2]_{(s)} + 6NH_{3(aq)} \longrightarrow [Co(NH_3)_6]^{2+}_{(aq)} + 4H_2O_{(l)} + 2OH^-_{(aq)}$$

blue precipitate → yellow solution




$[Co(H_2O)_6]^{2+}$ $[Co(H_2O)_4(OH)_2]$ $[Co(NH_3)_6]^{2+}$

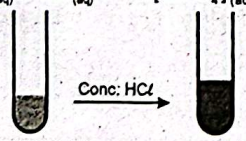
**Figure: Colour changes in $[Co(H_2O)_6]^{2+}$ on addition of hydroxide and $NH_3$**

Water ligands in $[Co(H_2O)_6]^{2+}$ can also be exchanged directly with ammonia ligands by adding concentrated ammonia solution.

$$[Co(H_2O)_6]^{2+}_{(aq)} + 6NH_{3(aq)} \longrightarrow [Co(NH_3)_6]^{2+}_{(aq)} + 6H_2O_{(l)}$$

The addition of concentrated hydrochloric acid drop by drop to an aqueous solution of cobalt(II) ions results in the formation of a blue solution containing the tetrahedral complex $[CoCl_4]^{2-}_{(aq)}$ (Figure).

$$[Co(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \longrightarrow [CoCl_4]^{2-}_{(aq)} + 6H_2O_{(l)}$$




$[Co(H_2O)_6]^{2+}$ $[CoCl_4]^{2-}$

**Figure: Exchange of water molecules by chloride ions in a Co (II) complex**

Aqueous cobalt(II) ions usually form tetrahedral complexes with monodentate anionic ligands such as $OH^-$ and $SCN^-$.



### Effect of Ligand Exchange on the Colour of Complexes

The exchange of ligands in a complex changes the magnitude of splitting for the metal ion. As a result, the frequency of absorbed light also changes, leading to a change in the observed colour. In each case, the new complex has a different $\Delta E$ because the new ligands ($NH_3$ or $Cl^-$) makes more stable complex than the original $H_2O$ ligands. It leads to a different absorbed frequency and a different observed colour.

**Table: Ligand Exchange and Colour Change**

| Metal Ion | Initial Colour of Complex | Ligand Exchange Reaction | Final Colour of Complex |
|---|---|---|---|
| $Cu^{2+}$ | $[Cu(H_2O)_6]^{2+}$ (Blue) | Add conc. $NH_3$ solution | $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (Deep Blue) |
| $Cu^{2+}$ | $[Cu(H_2O)_6]^{2+}$ (Blue) | Add conc. HCl solution | $[CuCl_4]^{2-}$(Yellow-Green) |
| $Co^{2+}$ | $[Co(H_2O)_6]^{2+}$ (Pink) | Add conc. $NH_3$ solution | $[Co(NH_3)_6]^{2+}$ (Yellow) |
| $Co^{2+}$ | $[Co(H_2O)_6]^{2+}$ (Pink) | Add conc. HCl solution | $[CoCl_4]^{2-}$ (Blue) |

### QUICK CHECK 18.5

**a) Write the equation for the reaction, where $[Cu(H_2O)_4(OH)_2]_{(s)}$ dissolves in excess ammonia.**

**Ans. Reaction with Excess Ammonia:**

When the neutral copper (II) hydroxide complex dissolves in excess ammonia, it forms a deep blue solution of the tetraamminediaquacopper (II) ion.

**Equation:**

$$[Cu(H_2O)_4(OH)_2]_{(s)} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}_{(aq)} + 2OH^-_{(aq)} + 2H_2O_{(l)}$$

**b) Pink $[Co(H_2O)_6]^{2+}$ turns blue with conc. HCl. Explain this colour change using d-orbital splitting.**

**Ans. Colour change and d-orbital Splitting:**

The change from pink to blue is due to a change in geometry and the resulting magnitude of d-orbital splitting ($\Delta$):

- **Octahedral Complex:** $[Co(H_2O)_6]^{2+}$ is octahedral. The crystal fielding splitting ($\Delta_o$) is relatively large, resulting in the absorption of light that makes the complex appear pink.
- **Tetrahedral Complex:** Adding conc. HCl froms $[CoCl_4]^{2-}$, which is tetrahedral. In tetrahedral fields, the splitting energy ($\Delta_t$) is much smaller than in octahedral fields ($\Delta_t \approx \frac{4}{9}\Delta_o$).
- **Energy Gap:** Because the energy gap ($\Delta$) is smaller in the tetrahedral complex, it absorbs lower-energy light (longer wavelengths), causing the observed color to shift to blue.

**c) For the reaction: $[Co(H_2O)_6]^{2+} + 4Cl^- \longrightarrow [CoCl_4]^{2-} + 6H_2O$, identify the coordination number and geometry of the product complex.**

**Ans. For the Reaction:**

$$[Co(H_2O)_6]^{2+} + 4Cl^- \longrightarrow [CoCl_4]^{2-} + 6H_2O$$

- **Coordination Number:** 4 (There are four chloride ligands attached to the cobalt center).
- **Geometry:** Tetrahedral (Typical for cobalt (II) complexes with four bulky or weak field ligands like $Cl^-$)

## STABILITY OF COMPLEXES AND STABILITY CONSTANT, $K_{stab}$

**Q.10 Discuss the stability of complexes and stability constant, $K_{stab}$.**

**Ans.** The stability constant ($K_{stab}$) is an equilibrium constant ($K_c$) for the formation of a complex ion. In aqueous solutions, water is the initial ligand. When we add a new ligand, it competes with water to bind with the metal ion.

**Example:**

Let us take the example of the complexation reaction with its $K_{stab}$ expression;

$$[Cu(H_2O)_6]^{2+} + 4Cl^-_{(aq)} \rightleftharpoons [CuCl_4]^{2-}_{(aq)} + 6H_2O_{(l)}$$

$$K_{stab} = \frac{[CuCl_4]^{2-}}{[Cu(H_2O)_6]^{2+}\,[Cl^-]^4}$$

**Check Understanding!**

**Q.9 What is the value of $\log_{10} K_{stab}$ of $[CuCl_4]^{2-}$:**

(A) 5.6 (B) 13.1
(C) 18.8 (D) 20.2

CamScanner

Concentration of water [$H_2O$] being solvent (remains constant) is omitted from the $K_{stab}$ expression. Stability constants are usually provided on a $\log_{10}$ scale. This makes it easier to compare very large numbers.

$$K_{stab} \propto \text{stability}$$

Higher the $\log_{10} K_{stab}$, more stable will be the complex and the equilibrium lies far to the right. And lower the $\log_{10} K_{stab}$, the complex is less stable, and the ligands can be easily displaced. The stability constant values ($\log_{10} K_{stab}$) of some copper (II) complexes are given Table.

**Table: Stability constants of some Cu (II) complexes**

| Complex | $\text{Log}_{10} K_{stab}$ |
|---|---|
| $[CuCl_4]^{2-}$ | 5.6 |
| $[Cu(NH_3)_6]^{2-}$ | 13.1 |
| $[Cu(EDTA)]^{2-}$ | 18.8<br>Most stable among there |

The data shows that complexes with polydentate ligands have higher stability constant values than those with monodentate ligands. This is called chelating effect of the ligands.

$$[Cu(H_2O)_{6(aq)}] + 3en \longrightarrow [Cu(en)_3]^{2+} + 6H_2O_{(l)}$$

A ligand with a higher $K_{stab}$ can displace a ligand with a lower $K_{stab}$. For example, adding ammonia to a chloride complex will turn the solution blue because the ammonia complex is significantly more stable.

$$[CuCl_{4(aq)}]^{2-} + 4NH_{3(aq)} \longrightarrow [Cu(NH_3)_4]^{2+} + 4Cl^-_{(aq)}$$

Similarly, if a stable complex is diluted with a huge (massive) amount of water, the equilibrium can be forced back to the left, re-forming the original hydrated ion.

### QUICK CHECK 18.6

**a) Write the $K_{stab}$ equilibrium expression for the formation of $[Cu(NH_3)_4]^{2+}$ from $[Cu(H_2O)_6]^{2+}$ and $NH_3$.**

**Ans.** The stability constant ($K_{stab}$) represents the equilibrium constant for the formation of the complex ion in water.

$$K_{stab} = \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(H_2O)_6]^{2+}][NH_3]^4}$$

**b) Explain why polydentate ligands form more stable complexes using $K_{stab}$ data ($\log_{10} K_{stab}$) data for $[CuCl_4]^{2-}$ (5.6) and $[Cu(EDTA)]^{2-}$ (18.8).**

**Ans.** Polydentate ligands like EDTA from significantly more stable complexes than monodentate ligands (like $Cl^-$) due to the chelate effect.

- **The Data:** The log $K_{stab}$ for $[Cu(EDTA)]^{2-}$ (18.8) is much higher than for $[CuCl_4]^{2-}$ (5.6), indicating that the EDTA complex is roughly $10^{13}$ times more stable.
- **Entropy:** When a polydentate ligand binds, it displaces multiple water molecules. For example, one EDTA molecule displaces six water molecules. This results in a large increase in entropy ($\Delta S > 0$) because the total number of independent particles in the system increases.
- **Stability:** Since $\Delta G = \Delta H - T\Delta S$, a highly positive entropy change results in a more negative Gibbs free energy, making the formation of the chelate complex much more favorable and stable.

**c) Write the balanced equation for the first step of the stepwise substitution of water ligands by ammonia in $[Cu(H_2O)_6]^{2+}$.**

**Ans. Equation:** $[Cu(H_2O)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(H_2O)_5]^{2+} + H_2O$

## STEREOISOMERISM IN TRANSITION METAL COMPLEXES

**Q.11 Discuss the two types of stereoisomerism found in transition metal complexes. Use the example $[Pt(NH_3)_2Cl_2]$ (square planar) and $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ (octahedral) to illustrate the key structural differences that give rise to geometrical and optical isomerism, respectively.** Exercise C/Q.3, Exercise D/Q.

**OR Explain the stereoisomerism with its types in transition metal complexes.**

**Ans.** The compounds that have the same chemical formula and bonds but differ with respect to the arrangement of ligands in space are called stereoisomers.

There are two types of stereoisomerism:

(i) geometrical (cis-trans) isomerism (ii) optical isomerism.



### (i) Cis-Trans Isomerism

In cis-trans isomers, identical ligands are present at either adjacent (90° angle, cis) or opposite (180° angle, trans) positions. This is common in square planar (e.g., $[Pt(NH_3)_2Cl_2]$) and octahedral complexes (e.g., $[Co(NH_3)_4Cl_2]$).

**Check Understanding!**
**Q.10 Draw cisplatin and Transplatin.**

➢ **Explanation:**

**Example 1:**

The cis and trans isomers of $[Pt(NH_3)_2Cl_2]$ are shown in Figure.

- **Cis-Form:** In cis-$[Pt(NH_3)_2Cl_2]$ (cisplatin), the chlorine atoms are adjacent to each other at the angle of 90° in the square complex (i.e., $2Cl^-$ ligands on one side and $2NH_3$ ligands on the other side).
- **Trans-Form:** In trans-$[Pt(NH_3)_2Cl_2]$ (transplatin), they are opposite to each other at an angle of 180°. The properties of these geometrical isomers are different. It is interesting to know that the polarity of cisplatin helps it interact with water and with DNA and thus cisplatin is used as an anti-cancer drug, while transplatin does not show such property.

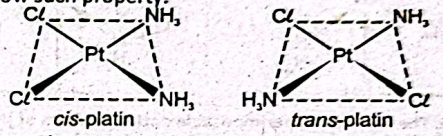



**Figure: The geometrical isomers, cisplatin and transplatin**

- **In transplatin,** the individual bond dipoles of the identical ligands are pointed in opposite direction and cancel each other, making the molecule nonpolar ($\mu$=0). **In cisplatin,** the similar individual bond moments do not cancel out, resulting in a non-zero dipole moment that makes it polar ($\mu \approx$ 15-16 D).
- **Note:** Cisplatin is water soluble and biologically active.

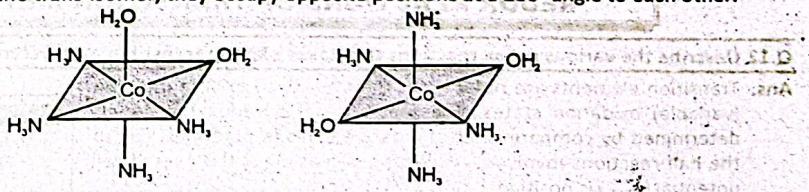
**Interesting Information**

Cisplatin, or cis-diamminedichloroplatinum(II), is a landmark inorganic anticancer drug. Its discovery was accidental, found when platinum electrodes inhibited bacterial cell division. It specifically targets rapidly dividing cancer cells by entering the cell and undergoing ligand exchange, where water replaces its chloride ions. The "activated" drug then binds to guanine bases in DNA, creating cross-links that kink the double helix. This structural damage prevents DNA replication, triggering programmed cell death (apoptosis).

**Example 2:**

$[Co(NH_3)_4(H_2O)_2]^{3+}$ is an $[MA_4B_2]$ type octahedral complex. The cis and trans isomers of $[Co(NH_3)_4(H_2O)_2]^{3+}$ are shown in Figure.

- **Cis-Isomer:** In the cis isomer, the two $H_2O$ ligands occupy adjacent positions at a 90° angle with respect to each other.
- **Trans-Isomer:** In the trans-isomer, they occupy opposite positions at a 180° angle to each other.




**(i) Cis (Adjacent, 90°)** **(ii) Trans (Angle 180°)**

**Figure: The geometrical isomers, $[Co(NH_3)_4(H_2O)_2]^{3+}$**

### (ii) Optical Isomerism

Optical isomers are non-superimposable mirror images of each other. Optical isomerism is commonly shown by octahedral complexes with bidentate ligands. The condition for it is that the complex must be chiral (no plane of symmetry).

- **en (ethylenediammine) nickel (II) ion:** An example is the nickel (II) complex containing 1,2-diaminoethane ($NH_2CH_2CH_2NH_2$) as the bidentate ligand (Figure).

CamScanner

- The two of en (ethylenediammine) nickel (II) ion isomers are optical isomers because the two di... molecules are mirror images of each other and condition is that they cannot be superimposed ... pairs of molecules are called enantiomers.

The optical isomers rotate the plane of polarized light in opposite directions.

- **Dextrorotatory (+):** The isomer that rotates the plane of polarized light in right hand direction is ... dextrorotatory " + ".
- **Laevorotatory (–):** The isomer that rotates the plane of polarized light in left hand direction is ... laevorotatory "—".

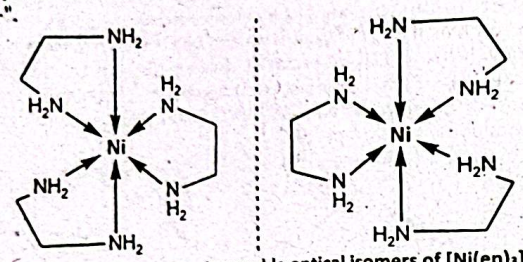



**Figure: The two non-superimposable optical isomers of $[Ni(en)_3]^{2+}$**

### QUICK CHECK 18.7

**a) Which type of geometries shows cis-trans isomerism?**

**Ans.** Cis-trans isomerism is primarily exhibited by square planar and octahedral geometries. These must ... two or more different ligands.

**b) What type of ligand is most often required for a complex to show optical isomerism?**

**Ans.** **Bidentate** (or chelating) ligands are most commonly required to create the chiral structure necessa... optical isomerism.

**c) For the complex $[Ni(en)_3]^{2+}$, state the coordination number and the type of ligand.**

**Ans.** **Type of Ligand:** Bidentate (ethylenediamine).
**Coordination Number:** 6 (Since each of the 3 ligands forms two bonds).
**(Note:** It shows octahedral geometry).

**d) Identify the type of isomerism displayed by the complex $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$, and describe how two different isomers interact with plane-polarized light.**

**Ans.** **Type of isomerism:** Optical isomerism.
**Interaction with Light:** One isomer the dextrorotatory form (+) rotates plane-polarized light to the ... while the other the levorotatory form (–) rotates it to the left.

## REDOX REACTIONS OF TRANSITION METALS

**Q.12 Describe the various redox reactions that takes place in transition metal complex ions.** Exercis...

**Ans.** Transition elements are notable for their ability to exist in multiple (variable) oxidation states. The feasibility of a redox reaction is determined by comparing the standard electrode potentials (E°) of the half-reactions involved. A reaction is feasible if the overall cell potential ($E^\circ_{cell}$) is positive.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

Generally, in practice the species with the more positive E° value will be reduced (gain electrons). The species with the more negative (less positive) value will be oxidized (lose electrons).

**Check Understanding!**
Q.11 $E^\circ_{Cell}$ = ?
(A) $E^\circ_{cathode} - E^\circ_{anode}$
(B) $E^\circ_{cathode} - E^\circ_{anode}$
(C) $E^\circ_{cathode}$ only
(D) $E^\circ_{anode}$ only

### ➲ Reaction of Acidified Manganate (VII) Ions ($MnO_4^-$) with Ethanedioate Ions ($C_2$...

Take the example of the reaction between acidified $MnO_4^-$ and $C_2O_4^{2-}$, we compare the standard re... potentials of the two half-reactions. The half-reaction with the more positive E° value is more ... undergo reduction (to proceed to the right).



### (I) Cis-Trans Isomerism

In cis-trans isomers, identical ligands are present at either adjacent (90° angle, cis) or opposite (180° angle, trans) positions. This is common in square planar (e.g., $[Pt(NH_3)_2Cl_2]$) and octahedral complexes (e.g., $[Co(NH_3)_4Cl_2]$).

➢ **Explanation:**

**Check Understanding!**
Q.10 Draw cisplatin and Transplatin.

**Example 1:**

The cis and trans isomers of $[Pt(NH_3)_2Cl_2]$ are shown in Figure.

- **Cis-Form:** In cis-$[Pt(NH_3)_2Cl_2]$ (cisplatin), the chlorine atoms are adjacent to each other at the angle of 90° in the square complex (i.e., $2Cl^-$ ligands on one side and $2NH_3$ ligands on the other side).
- **Trans-Form:** In trans-$[Pt(NH_3)_2Cl_2]$ (transplatin), they are opposite to each other at an angle of 180°. The properties of these geometrical isomers are different. It is interesting to know that the polarity of cisplatin helps it interact with water and with DNA and thus cisplatin is used as an anti-cancer drug, while transplatin does not show such property.

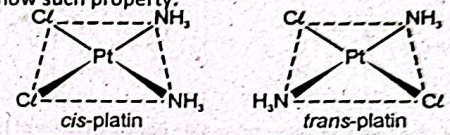



**Figure: The geometrical isomers, cisplatin and transplatin**

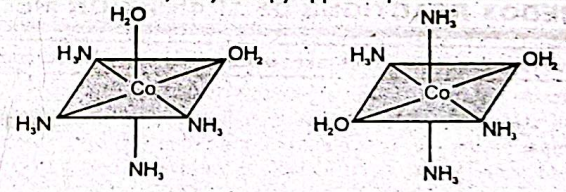
- **In transplatin,** the individual bond dipoles of the identical ligands are pointed in opposite direction and cancel each other, making the molecule nonpolar ($\mu$=0). **In cisplatin,** the similar individual bond moments do not cancel out, resulting in a non-zero dipole moment that makes it polar ($\mu \approx$ 15-16 D).
- **Note:** Cisplatin is water soluble and biologically active.

**Interesting Information**
Cisplatin, or cis-diamminedichloroplatinum(II), is a landmark inorganic anticancer drug. Its discovery was accidental, found when platinum electrodes inhibited bacterial cell division. It specifically targets rapidly dividing cancer cells by entering the cell and undergoing ligand exchange, where water replaces its chloride ions. The "activated" drug then binds to guanine bases in DNA, creating cross-links that link the double helix. This structural damage prevents DNA replication, triggering programmed cell death (apoptosis).

**Example 2:**

$[Co(NH_3)_4(H_2O)_2]^{3+}$ is an $[MA_4B_2]$ type octahedral complex. The cis and trans isomers of $[Co(NH_3)_4(H_2O)_2]^{3+}$ are shown in Figure.

- **Cis-Isomer:** In the cis isomer, the two $H_2O$ ligands occupy adjacent positions at a 90° angle with respect to each other.
- **Trans-Isomer:** In the trans-isomer, they occupy opposite positions at a 180° angle to each other.




**(i) Cis (Adjacent, 90°)** **(ii) Trans (Angle 180°)**

**Figure: The geometrical isomers, $[Co(NH_3)_4(H_2O)_2]^{3+}$**

### (ii) Optical Isomerism

Optical isomers are non-superimposable mirror images of each other. Optical isomerism is commonly shown by octahedral complexes with bidentate ligands. The condition for it is that the complex must be chiral (no plane of symmetry).

- **en (ethylenediammine) nickel (II) ion:** An example is the nickel (II) complex containing 1,2-diaminoethane ($NH_2CH_2CH_2NH_2$) as the bidentate ligand (Figure).

CamScanner

- The two of **en (ethylenediammine) nickel (II) ion** isomers are optical isomers because the two different molecules are mirror images of each other and condition is that they cannot be superimposed. Such pairs of molecules are called enantiomers.

The optical isomers rotate the plane of polarized light in opposite directions.

- **Dextrorotatory (+):** The isomer that rotates the plane of polarized light in right hand direction is called dextrorotatory "+".
- **Laevorotatory (–):** The isomer that rotates the plane of polarized light in left hand direction is called laevorotatory "–".

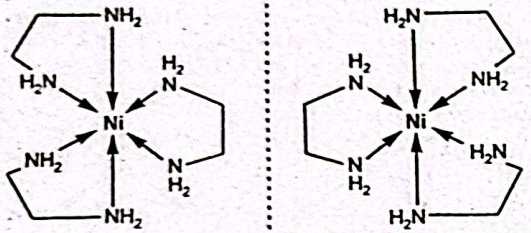


Figure: The two non-superimposable optical isomers of $[Ni(en)_3]^{2+}$

## QUICK CHECK 18.7

**a) Which type of geometries shows cis-trans isomerism?**

**Ans.** Cis-trans isomerism is primarily exhibited by square planar and octahedral geometries. These must have two or more different ligands.

**b) What type of ligand is most often required for a complex to show optical isomerism?**

**Ans.** **Bidentate** (or chelating) ligands are most commonly required to create the chiral structure necessary for optical isomerism.

**c) For the complex $[Ni(en)_3]^{2+}$, state the coordination number and the type of ligand.**

**Ans.** **Type of Ligand:** Bidentate (ethylenediamine).
**Coordination Number:** 6 (Since each of the 3 ligands forms two bonds).
**(Note:** It shows octahedral geometry).

**d) Identify the type of isomerism displayed by the complex $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$, and describe how the two different isomers interact with plane-polarized light.**

**Ans.** **Type of isomerism:** Optical isomerism.
**Interaction with Light:** One isomer the dextrorotatory form (+) rotates plane-polarized light to the right while the other the levorotatory form (–) rotates it to the left.

# REDOX REACTIONS OF TRANSITION METALS

**Q.12 Describe the various redox reactions that takes place in transition metal complex ions.** Exercise D

**Ans.** Transition elements are notable for their ability to exist in multiple (variable) oxidation states. The feasibility of a redox reaction is determined by comparing the standard electrode potentials ($E^\circ$) of the half-reactions involved. A reaction is feasible if the overall cell potential ($E^\circ_{cell}$) is positive.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

Generally, in practice the species with the more positive $E^\circ$ value will be reduced (gain electrons). The species with the more negative (less positive) value will be oxidized (lose electrons).

**Check Understanding!**
Q.11 $E^\circ_{Cell}$ = ?
(A) $E^\circ_{cathode} - E^\circ_{anode}$
(B) $E^\circ_{cathode} - E^\circ_{anode}$
(C) $E^\circ_{cathode}$ only
(D) $E^\circ_{anode}$ only

## ➲ Reaction of Acidified Manganate (VII) Ions ($MnO_4^-$) with Ethanedioate Ions ($C_2O_4^{2-}$)

Take the example of the reaction between acidified $MnO_4^-$ and $C_2O_4^{2-}$, we compare the standard reduction potentials of the two half-reactions. The half-reaction with the more positive $E^\circ$ value is more likely to undergo reduction (to proceed to the right).



Based on the $E^\circ$ values, the $MnO_4^-$ ion is more likely to be reduced to $Mn^{2+}$ (acting as the oxidizing agent), and the Ethanedioate ($C_2O_4^{2-}$) ion must be oxidized to $CO_2$ (acting as the reducing agent).

$$2CO_{2(g)} + 2e^- \longrightarrow C_2O^{2-}_{4(aq)} \qquad E^\circ = -0.49\ V$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O_{(\ell)} \qquad E^\circ = +1.52\ V$$

The reaction with higher reduction potential is likely to occur and proceed to the right and vice versa. The given reduction potential values indicate that Mn (VII) ion should be reduced to Mn (II) acting as an oxidizing agent while oxalate ($C_2O_4^{2-}$) must be oxidized to $CO_2$ and behave as reducing agent.
The number of electrons lost must be equal to number of electrons gained. It is done by multiplying the two half reactions with different coefficients. Here, oxidation half equation is multiplied by by 5 and reduction half equation by 2.

$2\times[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O_{(\ell)}]$ $E^\circ = +1.52\ V$
$5\times[C_2O^{2-}_{4(aq)} \longrightarrow 2CO_{2(g)} + 2e^-]$ (The reaction and $E^\circ$ value written in opposite way) $E^\circ = +0.49\ V$
$2MnO_4^- + 5C_2O^{2-}_{4(aq)} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_{2(g)} + 8H_2O_{(\ell)}$ $E^\circ_{cell} = +2.01\ V$

**Note:** The large positive net $E^\circ$ value (+1.03 V) indicates that the forward reaction is feasible.

## ➲ Reaction of Manganate (VII) Ion ($MnO_4^-$) with Iron(II) Ion ($Fe^{2+}$)

This redox reaction involves the reduction of $MnO_4^-$ and the oxidation of $Fe^{2+}$ as indicated by the potential values. The relevant half-reactions (in reduction form) are:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O_{(\ell)} \qquad E^\circ = +1.52\ V$$
$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad E^\circ = +0.77\ V$$

Combine and balance the two equations and sum up their standard electrode potentials so that we can check feasibility of the overall reaction.

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O_{(\ell)}$ $E^\circ = +1.52\ V$
$5\times[Fe^{2+} \longrightarrow Fe^{3+} + e^-]$ $E^\circ = -0.77\ V$
$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{2+} + 4H_2O_{(\ell)}$ $E^\circ_{cell} = +0.75\ V$

The positive value of the standard electrode potential indicates that this reaction will proceed to the right, making this reaction feasible.

## ➲ Reaction Between Copper(II) Ion ($Cu^{2+}$) and Iodide Ion ($I^-$)

**Q.13 The reaction between $Cu^{2+}$ and $I^-$ results in a solid precipitate of CuI and aqueous $I_2$.** Exercise C/Q.3(i, iii)
**a) Write down the two relevant reduction half-equations and their $E^\circ$ values (provided in the text).**
**b) Explain why comparing only the $E^\circ$ values suggests the reaction is not feasible as written.**
**c) Use Le Chatelier's principle to explain why the reaction proceeds forward in practice.**

**(a)** When an excess of potassium iodide is added to an aqueous solution of copper(II) sulphate, the following reaction occurs:

$$2Cu^{2+}_{(aq)} + 4I^-_{(aq)} \longrightarrow 2CuI_{(s)} + I_{2(aq)}$$

**(b)** The reaction splits into the following half-equations:

$$\frac{1}{2}I_{2(aq)} + e^- \longrightarrow I^-_{(aq)} \qquad E^\circ = +0.54\ V$$
$$Cu^{2+}_{(aq)} + e^- \longrightarrow Cu^+_{(aq)} \qquad E^\circ = +0.15\ V$$

Typically, the $I_2/I^-$ couple, with the higher $E^\circ$ value, would be more likely to undergo reduction. The $Cu^{2+}/Cu^+$ couple has a lower $E^\circ$, suggesting $Cu^+$ is a better reducing agent than $I^-$.
However, the overall reaction proceeds forward despite a calculated negative net standard potential.

**(c) Reaction proceeds forward according to Le-chatelier's Principle:**
The reaction is driven forward because CuI formed is continuously precipitating out of the solution, which effectively removes the $Cu^+$ product and shifts the equilibrium to the right (Le Chatelier's principle). The amount of $I_2$ formed in this reaction can be quantified by titrating it with a thiosulfate solution.

CamScanner

## ☑ QUICK CHECK 18.8

**a) State the principle used to determine the feasibility of a redox reaction using standard electrode potentials ($E^\circ$).**

**Ans.** The feasibility of a redox reaction is determined by the total standard electrode potential ($E^\circ_{cell}$). A reaction is considered feasible (will proceed to the right) if the sum of the standard electrode potentials results in a positive value.

**b) For the reaction between $MnO_4^-$ and $Fe^{2+}$, the relevant reduction potentials are $MnO_4^-/Mn^{2+}$ ($E^\circ$ = + 1.52 V) and $Fe^{3+}/Fe^{2+}$ ($E^\circ$ = +0.77 V). Identify the oxidizing agent and the reducing agent in this specific feasible reaction.**

**Ans.** Oxidizing Agent: $MnO_4^-$ (It is reduced as it has the more positive $E^\circ$ value).
Reducing Agent: $Fe^{2+}$ (It is oxidized to $Fe^{3+}$).

**c) Explain why water is omitted when calculating the $E^\circ_{cell}$ for the reaction between $MnO_4^-$ and $C_2O_4^{2-}$ ions, even though it appears in the overall balanced equation.**

**Ans.** Water is omitted from $E^\circ$ calculation because it does not undergo a change in oxidation state during the redox process. The $E^\circ_{cell}$ calculation only accounts for the specific half-reactions where electrons are transferred (reduction and oxidation). Since water acts as a medium or a byproduct of the oxygen/hydrogen balance rather than an active redox couple in this context. It has no standard reduction potential for the overall cell calculation. Water is a spectator in terms of electron transfer.

## BLOCK # 03 MULTIPLE CHOICE QUESTIONS (MCQs)

**1. The colour of transition metal complexes is mainly due to:**
(A) Nuclear transitions (B) d–d electronic transitions
(C) Ionization of ligands (D) Metallic bonding

**2. In an isolated transition metal ion, the five d-orbitals are:**
(A) Split into two energy levels (B) Degenerate (equal in energy)
(C) Filled completely (D) Empty

**3. d-Orbital splitting occurs when:**
(A) The metal is heated (B) Ligands approach the metal ion
(C) The complex is dissolved in water (D) Electrons are removed

**4. In an octahedral complex, the coordination number is:**
(A) 2 (B) 4 (C) 6 (D) 8

**5. Compared with octahedral complexes, tetrahedral complexes generally have:**
(A) Greater d-orbital splitting (B) Smaller d-orbital splitting
(C) No splitting (D) Equal splitting

**6. The energy difference between split d-orbitals is represented by:**
(A) λ (B) ν (C) ΔE (Δ) (D) h

**7. If a complex absorbs yellow light, it appears:**
(A) Yellow (B) Green (C) Violet (D) Red

**8. Which ligand causes the greatest d-orbital splitting?**
(A) $I^-$ (B) $Cl^-$ (C) $H_2O$ (D) $CN^-$

**9. Which ligand produces the smallest value of Δ?**
(A) $NH_3$ (B) $CN^-$ (C) $I^-$ (D) en

**10. In aqueous solution, $Cu^{2+}$ mainly exists as:**
(A) $[CuCl_4]^{2-}$ (B) $[Cu(NH_3)_4]^{2+}$ (C) $[Cu(H_2O)_6]^{2+}$ (D) CuO

**11. Adding concentrated $NH_3$ to $Cu^{2+}$ solution finally produces:**
(A) Yellow solution (B) Dark blue solution (C) Pink solution (D) Green solution

**12. Addition of concentrated HCl to aqueous copper(II) solution forms:**
(A) $[Cu(H_2O)_6]^{2+}$ (B) $[CuCl_4]^{2-}$ (C) $[Cu(NH_3)_4]^{2+}$ (D) $Cu(OH)_2$

**13. The aqueous complex $[Co(H_2O)_6]^{2+}$ is:**
(A) Blue (B) Yellow (C) Pink (D) Green

**14. Which ligand forms the most stable Cu(II) complex?**
(A) $Cl^-$ (B) $H_2O$ (C) $NH_3$ (D) EDTA

**15. A higher value of $K_{stab}$ indicates:**
(A) Lower stability (B) Greater stability of the complex
(C) Faster reaction only (D) Lower coordination number



Based on the $E^\circ$ values, the $MnO_4^-$ ion is more likely to be reduced to $Mn^{2+}$ (acting as the oxidizing agent), and the Ethanedioate ($C_2O_4^{2-}$) ion must be oxidized to $CO_2$ (acting as the reducing agent).

$$2CO_{2(g)} + 2e^- \longrightarrow C_2O_{4(aq)}^{2-} \qquad E^\circ = -0.49\ V$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O_{(\ell)} \qquad E^\circ = +1.52\ V$$

The reaction with higher reduction potential is likely to occur and proceed to the right and vice versa. The given reduction potential values indicate that Mn (VII) ion should be reduced to Mn (II) acting as an oxidizing agent while oxalate ($C_2O_4^{2-}$) must be oxidized to $CO_2$ and behave as reducing agent.
The number of electrons lost must be equal to number of electrons gained. It is done by multiplying the two half reactions with different coefficients. Here, oxidation half equation is multiplied by by 5 and reduction half equation by 2.

$2\times[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O_{(\ell)}]$ $E^\circ = +1.52\ V$
$5\times[C_2O_{4(aq)}^{2-} \longrightarrow 2CO_{2(g)} + 2e^-]$ (The reaction and $E^\circ$ value written in opposite way) $E^\circ = +0.49\ V$
$2MnO_4^- + 5C_2O_{4(aq)}^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_{2(g)} + 8H_2O_{(\ell)}$ $E^\circ_{cell} = +2.01\ V$

Note: The large positive net $E^\circ$ value (+1.03 V) indicates that the forward reaction is feasible.

### ➲ Reaction of Manganate (VII) Ion ($MnO_4^-$) with Iron(II) Ion ($Fe^{2+}$)

This redox reaction involves the reduction of $MnO_4^-$ and the oxidation of $Fe^{2+}$ as indicated by the potential values. The relevant half-reactions (in reduction form) are:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O_{(\ell)} \qquad E^\circ = +1.52\ V$$
$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \qquad E^\circ = +0.77\ V$$

Combine and balance the two equations and sum up their standard electrode potentials so that we can check feasibility of the overall reaction.

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O_{(\ell)}$ $E^\circ = +1.52\ V$
$5\times[Fe^{2+} \longrightarrow Fe^{3+} + e^-]$ $E^\circ = -0.77\ V$
$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{2+} + 4H_2O_{(\ell)}$ $E^\circ_{cell} = +0.75\ V$

The positive value of the standard electrode potential indicates that this reaction will proceed to the right, making this reaction feasible.

### ➲ Reaction Between Copper(II) Ion ($Cu^{2+}$) and Iodide Ion ($I^-$)

**Q.13 The reaction between $Cu^{2+}$ and $I^-$ results in a solid precipitate of CuI and aqueous $I_2$.** Exercise C/Q.3(i, iii)

**a) Write down the two relevant reduction half-equations and their $E^\circ$ values (provided in the text).**
**b) Explain why comparing only the $E^\circ$ values suggests the reaction is not feasible as written.**
**c) Use Le Chatelier's principle to explain why the reaction proceeds forward in practice.**

**(a)** When an excess of potassium iodide is added to an aqueous solution of copper(II) sulphate, the following reaction occurs:

$$2Cu_{(aq)}^{2+} + 4I_{(aq)}^- \longrightarrow 2CuI_{(s)} + I_{2(aq)}$$

**(b)** The reaction splits into the following half-equations:

$$\frac{1}{2}I_{2(aq)} + e^- \longrightarrow I_{(aq)}^- \qquad E^\circ = +0.54\ V$$
$$Cu_{(aq)}^{2+} + e^- \longrightarrow Cu_{(aq)}^+ \qquad E^\circ = +0.15\ V$$

Typically, the $I_2/I^-$ couple, with the higher $E^\circ$ value, would be more likely to undergo reduction. The $Cu^{2+}/Cu^+$ couple has a lower $E^\circ$, suggesting $Cu^+$ is a better reducing agent than $I^-$.
However, the overall reaction proceeds forward despite a calculated negative net standard potential.

**(c) Reaction proceeds forward according to Le-chatelier's Principle:**
The reaction is driven forward because CuI formed is continuously precipitating out of the solution, which effectively removes the $Cu^+$ product and shifts the equilibrium to the right (Le Chatelier's principle). The amount of $I_2$ formed in this reaction can be quantified by titrating it with a thiosulfate solution.

CamScanner

## QUICK CHECK 18.8

a) State the principle used to determine the feasibility of a redox reaction using standard electrode potentials ($E^\circ$).

Ans. The feasibility of a redox reaction is determined by the total standard electrode potential ($E^\circ_{cell}$). A reaction is considered feasible (will proceed to the right) if the sum of the standard electrode potentials results in a positive value.

b) For the reaction between $MnO_4^-$ and $Fe^{2+}$, the relevant reduction potentials are $MnO_4^-/Mn^{2+}$ ($E^\circ$ = + 1.52 V) and $Fe^{3+}/Fe^{2+}$ ($E^\circ$ = +0.77 V). Identify the oxidizing agent and the reducing agent in this specific feasible reaction.

Ans. Oxidizing Agent: $MnO_4^-$ (It is reduced as it has the more positive $E^\circ$ value).
Reducing Agent: $Fe^{2+}$ (It is oxidized to $Fe^{3+}$).

c) Explain why water is omitted when calculating the $E^\circ_{cell}$ for the reaction between $MnO_4^-$ and $C_2O_4^{2-}$ ions, even though it appears in the overall balanced equation.

Ans. Water is omitted from $E^\circ$ calculation because it does not undergo a change in oxidation state during the redox process. The $E^\circ_{cell}$ calculation only accounts for the specific half-reactions where electrons are transferred (reduction and oxidation). Since water acts as a medium or a byproduct of the oxygen/hydrogen balance rather than an active redox couple in this context. It has no standard reduction potential for the overall cell calculation. Water is a spectator in terms of electron transfer.

## BLOCK # 03 MULTIPLE CHOICE QUESTIONS (MCQs)

1. The colour of transition metal complexes is mainly due to:
(A) Nuclear transitions (B) d–d electronic transitions
(C) Ionization of ligands (D) Metallic bonding

2. In an isolated transition metal ion, the five d-orbitals are:
(A) Split into two energy levels (B) Degenerate (equal in energy)
(C) Filled completely (D) Empty

3. d-Orbital splitting occurs when:
(A) The metal is heated (B) Ligands approach the metal ion
(C) The complex is dissolved in water (D) Electrons are removed

4. In an octahedral complex, the coordination number is:
(A) 2 (B) 4 (C) 6 (D) 8

5. Compared with octahedral complexes, tetrahedral complexes generally have:
(A) Greater d-orbital splitting (B) Smaller d-orbital splitting
(C) No splitting (D) Equal splitting

6. The energy difference between split d-orbitals is represented by:
(A) λ (B) ν (C) ΔE (Δ) (D) h

7. If a complex absorbs yellow light, it appears:
(A) Yellow (B) Green (C) Violet (D) Red

8. Which ligand causes the greatest d-orbital splitting?
(A) $I^-$ (B) $Cl^-$ (C) $H_2O$ (D) $CN^-$

9. Which ligand produces the smallest value of Δ?
(A) $NH_3$ (B) $CN^-$ (C) $I^-$ (D) en

10. In aqueous solution, $Cu^{2+}$ mainly exists as:
(A) $[CuCl_4]^{2-}$ (B) $[Cu(NH_3)_4]^{2+}$ (C) $[Cu(H_2O)_6]^{2+}$ (D) CuO

11. Adding concentrated $NH_3$ to $Cu^{2+}$ solution finally produces:
(A) Yellow solution (B) Dark blue solution (C) Pink solution (D) Green solution

12. Addition of concentrated HCl to aqueous copper(II) solution forms:
(A) $[Cu(H_2O)_4]^{2+}$ (B) $[CuCl_4]^{2-}$ (C) $[Cu(NH_3)_4]^{2+}$ (D) $Cu(OH)_2$

13. The aqueous complex $[Co(H_2O)_6]^{2+}$ is:
(A) Blue (B) Yellow (C) Pink (D) Green

14. Which ligand forms the most stable Cu(II) complex?
(A) $Cl^-$ (B) $H_2O$ (C) $NH_3$ (D) EDTA

15. A higher value of $K_{stab}$ indicates:
(A) Lower stability (B) Greater stability of the complex
(C) Faster reaction only (D) Lower coordination number



16. The increased stability of complexes containing EDTA is called the:
(A) Inductive effect (B) Common ion effect (C) Chelating effect (D) Resonance effect

17. Cis-trans isomerism is commonly shown by:
(A) Square planar and octahedral complexes (B) Linear complexes only
(C) Tetrahedral complexes only (D) Trigonal planar complexes

18. Optical isomerism is commonly observed in complexes containing:
(A) Monodentate ligands only (B) Bidentate ligands
(C) Halide ions only (D) Water molecules only

19. In the reaction between acidified $MnO_4^-$ and $C_2O_4^{2-}$ ions, $MnO_4^-$ acts as the:
(A) Reducing agent (B) Catalyst (C) Oxidizing agent (D) Ligand

20. Under standard conditions, a redox reaction is feasible when:
(A) $E^\circ cell = 0$ (B) $E^\circ cell$ is negative (C) $E^\circ cell$ is positive (D) The oxidation potential is zero

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

**BLOCK # 01**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. C | 4. B | 5. C | 6. C | 7. B | 8. C | 9. B | 10. A | 11. D | 12. B | 13. B | 14. B | 15. B |
| 16. B | 17. C | 18. B | 19. B | 20. B | | | | | | | | | | |

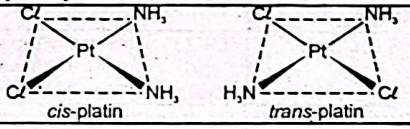
**BLOCK # 02**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. B | 4. C | 5. C | 6. C | 7. A | 8. C | 9. C | 10. C | 11. C | 12. C | 13. C | 14. B | 15. C |
| 16. B | 17. D | 18. C | 19. B | 20. B | | | | | | | | | | |

**BLOCK # 03**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. B | 4. C | 5. B | 6. C | 7. C | 8. D | 9. C | 10. C | 11. B | 12. B | 13. C | 14. D | 15. B |
| 16. C | 17. A | 18. B | 19. C | 20. C | | | | | | | | | | |

## CHECK UNDERSTANDING (SOLUTIONS)

| Q. # | Option | Hint/Explanation |
|---|---|---|
| 1. | (D) | $_{26}Fe$ = [Ar] $3d^6 4s^2$ |
| 2. | S/Q | +1,+2,+3,+4,+5,+6,+7 |
| 3. | (D) | Solid iron to accelerate the reaction between nitrogen and hydrogen to from ammonia. |
| 4. | S/Q | Bidentate = 1, 2–diamioethane, Hexa dentate = EDTA |
| 5. | (B) | CN– is anionic ligand while all other options are neutral ligands. |
| 6. | S/Q | In linear geometry, the two ligands are attached on opposite sides of the central metal ion at an angle of 180°. |
| 7. | (C) | $[Cu(H_2O)_6]^{2+}$ (Blue) ⟶ $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (Deep Blue) |
| 8. | S/Q | $[Co(H_2O)_6]^{2+}$ (Pink) ⟶ $[Co(NH_3)_6]^{2+}$ (Yellow) |
| 9. | (A) | The value of $\log_{10} K_{stab}$ of $[CuCl_4]^{2-}$ 5.6. |
| 10. | S/Q |   |
| 11. | (A) | $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ |

## EXERCISE

### Q 1. MULTIPLE CHOICE QUESTIONS MCQs

1. Which statement about the general physical properties of the first-row transition elements (titanium to copper) is incorrect?
a) They generally have high densities. b) They are typically soft solids at room temperature.
c) They are good conductors of heat and electricity. d) They possess high melting and boiling points.

CamScanner

II. What is the reason for variable oxidation states in 3d transition metals?
a) Incomplete 3d orbitals. b) Stable, filled 4s subshell.
c) Comparable energy of 3d and 4s subshells. d) Both a and c.

III. Which ionic configuration represents a metal that lost only its 4s electrons?
a) $Ti^{4+}$([Ar]) b) $V^{5+}$([Ar]) c) $Fe^{2+}$([Ar]$3d^6$) d) $Sc^{3+}$([Ar])

IV. In the complex ion, $[Fe(CN)_6]^{4-}$, what is coordination number of central metal ion?
a) 2 b) 4 c) 6 d) 8

V. The colour displayed by a transition metal complex is a result of electrons moving between d-orbitals. This process is called a:
a) p-p transition b) d-d transition c) s-p transition d) Ligand-to-metal charge transfer

VI. Adding excess ammonia to pink $[Co(H_2O)_6]^{2+}$ gives a yellow solution. What other changes occur besides colour change?
a) Coordination number changes from 6 to 4 b) Oxidation state of Co changes form +2 to +3
c) d-orbital splitting magnitude (ΔE) changes d) Complex becomes a precipitate

VII. Which one of the following complex has different geometry than others?
a) $[CuCl_4]^{2-}$ b) $[Cu(H_2O)_4(OH)_2]$ c) $[Cu(H_2O)_6]^{2+}$ d) $[Cu(NH_3)_4(H_2O)_2]^{2+}$

VIII. What geometry is typical when $Co^{2+}_{(aq)}$ reacts with six monodentate anionic ligands?
a) Octahedral b) Square Planar c) Linear d) Tetrahedral

IX. Optical isomers are characterized by their ability to rotate plane-polarized light. The isomer that rotates light to the right is called:
a) Laevorotatory (–) b) Superimposable c) Dextrorotatory (+) d) Achiral

## ANSWERS KEY WITH EXPLANATIONS

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | b | They are typically soft solids at room temperature. | First-row transition metals are generally hard, dense metals rather than typically soft solids. |
| II. | d | Both a and c. | Variable oxidation states arise because 3d is incomplete and 3d/4s levels are close enough for different numbers of electrons to be used/lost. |
| III. | c | $Fe^{2+}$ ([Ar]$3d^6$) | Fe forms $Fe^{2+}$ by losing the two 4s electrons first while retaining its 3d electrons. |
| IV. | c | 6. | Six monodentate $CN^-$ ligands are directly bonded to Fe, so the coordination number is 6. |
| V. | b | d-d transition. | Absorption promotes an electron between split d orbitals; the complementary transmitted colour is observed. |
| VI. | c | d-orbital splitting magnitude (ΔE) changes. | Replacing $H_2O$ by $NH_3$ changes ligand-field strength and therefore changes ΔE and the absorbed wavelength. |
| VII. | a | $[CuCl_4]^{2-}$. | $[CuCl_4]^{2-}$ is normally tetrahedral, whereas in the other options b, c, Cu(II) complexes have coordination number 6 and show octahedral/distorted octahedral geometry. |
| VIII. | a | Octahedral. | Six monodentate ligands give coordination number 6, for which octahedral geometry is typical. |
| IX. | c | Dextrorotatory (+). | A dextrorotatory enantiomer rotates plane-polarized light to the right (clockwise). |

## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) Why is zinc not included in the transition metals, although it shows electronic configuration with d-orbitals?**

**Ans.** Zinc is a d-block element because its last electron enters the 3d subshell. However, it is not a transition metal because neither zinc nor its common ion, $Zn^{2+}$, contains an incomplete d-orbital.

Electronic Configuration of Zn = [Ar] $3d^{10}4s^2$ , $Zn^{2+}$ = [Ar] $3d^{10}$



16. The increased stability of complexes containing EDTA is called the:
(A) Inductive effect (B) Common ion effect (C) Chelating effect (D) Resonance effect

17. Cis-trans isomerism is commonly shown by:
(A) Square planar and octahedral complexes (B) Linear complexes only
(C) Tetrahedral complexes only (D) Trigonal planar complexes

18. Optical isomerism is commonly observed in complexes containing:
(A) Monodentate ligands only (B) Bidentate ligands
(C) Halide ions only (D) Water molecules only

19. In the reaction between acidified $MnO_4^-$ and $C_2O_4^{2-}$ ions, $MnO_4^-$ acts as the:
(A) Reducing agent (B) Catalyst (C) Oxidizing agent (D) Ligand

20. Under standard conditions, a redox reaction is feasible when:
(A) E°cell = 0 (B) E°cell is negative (C) E°cell is positive (D) The oxidation potential is zero

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

**BLOCK # 01**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. C | 4. B | 5. C | 6. C | 7. B | 8. C | 9. B | 10. A | 11. D | 12. B | 13. B | 14. B | 15. B |
| 16. B | 17. C | 18. B | 19. B | 20. B | | | | | | | | | | |

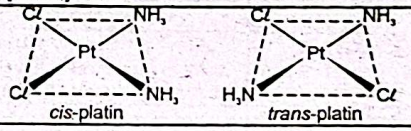
**BLOCK # 02**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. B | 4. C | 5. C | 6. C | 7. A | 8. C | 9. C | 10. C | 11. C | 12. C | 13. C | 14. B | 15. C |
| 16. B | 17. D | 18. C | 19. B | 20. B | | | | | | | | | | |

**BLOCK # 03**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. B | 4. C | 5. B | 6. C | 7. C | 8. D | 9. C | 10. C | 11. B | 12. B | 13. C | 14. D | 15. B |
| 16. C | 17. A | 18. B | 19. C | 20. C | | | | | | | | | | |

## CHECK UNDERSTANDING (SOLUTIONS)

| Q. # | Option | Hint/Explanation |
|---|---|---|
| 1. | (D) | $_{26}Fe$ = [Ar] $3d^64s^2$ |
| 2. | S/Q | +1,+2,+3,+4,+5,+6,+7 |
| 3. | (D) | Solid iron to accelerate the reaction between nitrogen and hydrogen to from ammonia. |
| 4. | S/Q | Bidentate = 1, 2–diamioethane, Hexa dentate = EDTA |
| 5. | (B) | CN– is anionic ligand while all other options are neutral ligands. |
| 6. | S/Q | In linear geometry, the two ligands are attached on opposite sides of the central metal ion at an angle of 180°. |
| 7. | (C) | $[Cu(H_2O)_6]^{2+}$ (Blue) ⟶ $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (Deep Blue) |
| 8. | S/Q | $[Co(H_2O)_6]^{2+}$ (Pink) ⟶ $[Co(NH_3)_6]^{2+}$ (Yellow) |
| 9. | (A) | The value of $\log_{10} K_{stab}$ of $[CuCl_4]^{2-}$ 5.6. |
| 10. | S/Q |   *cis*-platin *trans*-platin |
| 11. | (A) | $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$ |

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. Which statement about the general physical properties of the first-row transition elements (titanium to copper) is incorrect?
a) They generally have high densities. b) They are typically soft solids at room temperature.
c) They are good conductors of heat and electricity. d) They possess high melting and boiling points.

CamScanner

II. What is the reason for variable oxidation states in 3d transition metals?
a) Incomplete 3d orbitals. b) Stable, filled 4s subshell.
c) Comparable energy of 3d and 4s subshells. d) Both a and c.

III. Which ionic configuration represents a metal that lost only its 4s electrons?
a) $Ti^{4+}$([Ar]) b) $V^{5+}$([Ar]) c) $Fe^{2+}$([Ar]$3d^6$) d) $Sc^{3+}$([Ar])

IV. In the complex ion, $[Fe(CN)_6]^{4-}$, what is coordination number of central metal ion?
a) 2 b) 4 c) 6 d) 8

V. The colour displayed by a transition metal complex is a result of electrons moving between d-orbitals. This process is called a:
a) p-p transition b) d-d transition c) s-p transition d) Ligand-to-metal charge transfer

VI. Adding excess ammonia to pink $[Co(H_2O)_6]^{2+}$ gives a yellow solution. What other changes occur besides colour change?
a) Coordination number changes from 6 to 4 b) Oxidation state of Co changes form +2 to +3
c) d-orbital splitting magnitude (ΔE) changes d) Complex becomes a precipitate

VII. Which one of the following complex has different geometry than others?
a) $[CuCl_4]^{2-}$ b) $[Cu(H_2O)_4(OH)_2]$ c) $[Cu(H_2O)_6]^{2+}$ d) $[Cu(NH_3)_4(H_2O)_2]^{2+}$

VIII. What geometry is typical when $Co^{2+}_{(aq)}$ reacts with six monodentate anionic ligands?
a) Octahedral b) Square Planar c) Linear d) Tetrahedral

IX. Optical isomers are characterized by their ability to rotate plane-polarized light. The isomer that rotates light to the right is called:
a) Laevorotatory (–) b) Superimposable c) Dextrorotatory (+) d) Achiral

## ANSWERS KEY WITH EXPLANATIONS

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | b | They are typically soft solids at room temperature. | First-row transition metals are generally hard, dense metals rather than typically soft solids. |
| II. | d | Both a and c. | Variable oxidation states arise because 3d is incomplete and 3d/4s levels are close enough for different numbers of electrons to be used/lost. |
| III. | c | $Fe^{2+}$ ([Ar]$3d^6$) | Fe forms $Fe^{2+}$ by losing the two 4s electrons first while retaining its 3d electrons. |
| IV. | c | 6. | Six monodentate $CN^-$ ligands are directly bonded to Fe, so the coordination number is 6. |
| V. | b | d-d transition. | Absorption promotes an electron between split d orbitals; the complementary transmitted colour is observed. |
| VI. | c | d-orbital splitting magnitude (ΔE) changes. | Replacing $H_2O$ by $NH_3$ changes ligand-field strength and therefore changes ΔE and the absorbed wavelength. |
| VII. | a | $[CuCl_4]^{2-}$. | $[CuCl_4]^{2-}$ is normally tetrahedral, whereas in the other options b, c, Cu(II) complexes have coordination number 6 and show octahedral/distorted octahedral geometry. |
| VIII. | a | Octahedral. | Six monodentate ligands give coordination number 6, for which octahedral geometry is typical. |
| IX. | c | Dextrorotatory (+). | A dextrorotatory enantiomer rotates plane-polarized light to the right (clockwise). |

## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) Why is zinc not included in the transition metals, although it shows electronic configuration with d-orbitals?**

**Ans.** Zinc is a d-block element because its last electron enters the 3d subshell. However, it is not a transition metal because neither zinc nor its common ion, $Zn^{2+}$, contains an incomplete d-orbital.

Electronic Configuration of Zn = [Ar] $3d^{10}4s^2$, $Zn^{2+}$ = [Ar] $3d^{10}$



Since the d-subshell remains completely filled, zinc does not exhibit the characteristic properties of transition metals such as variable oxidation states and coloured ions.

**b) What is the correlation between the variable oxidation states of transition elements and their electronic configuration?**

**Ans.** Transition elements exhibit variable oxidation states because the energies of the ns and (n–1)d orbitals are very similar. Therefore, electrons can be removed from both orbitals during bonding.

**Example:** Fe = [Ar]$3d^6 4s^2$

Iron commonly shows +2 and +3 oxidation states because it can lose two 4s electrons or two 4s and one 3d electron.

**c) How do transition metals function as effective catalysts? Give examples.**

**Ans.** Transition metals act as catalysts because they possess variable oxidation states and vacant d-orbitals, allowing them to form temporary complexes with reactants. This provides an alternative reaction pathway with lower activation energy.

**Examples:**
- Iron (Fe) in the Haber process.
- Vanadium (V) oxide ($V_2O_5$) in the Contact process.
- Nickel (Ni) in hydrogenation of alkenes.

**d) Why is the complex $[Cr(en)_3]^{3+}$ more stable than $[Cr(H_2O)_6]_{3+}$?**

**Ans.** The ethane-1,2-diamine (en) ligand is bidentate, forming two coordinate bonds with the chromium ion. This produces stable chelate rings, making the complex more stable than the water complex, which contains monodentate ligands. This increased stability is known as the chelate effect.

**e) What is the coordination number? Give its value for $[Fe(CN)_6]^{4-}$.**

**Ans.** The coordination number is the number of coordinate bonds formed between the central metal ion and the surrounding ligands.
In $[Fe(CN)_6]^{4-}$ there are six cyanide ligands attached to iron.
Coordination number = 6

**f) Define a bidentate ligand and state how many bonds it forms to the central ion.**

**Ans.** **Bidentate Ligand:** A bidentate ligand is a ligand that contains two donor atoms and donates two lone pairs of electrons to the central metal ion.
Therefore, one bidentate ligand forms two coordinate bonds.
**Examples:** Ethane-1,2-diamine (en), Oxalate ion ($C_2O_4^{2-}$)

**(g) Explain why comparing only the E° values suggests the reaction is not feasible as written.**

**Ans.** The reaction splits into the following half-equations:

$$\frac{1}{2}I_{2(aq)} + e^- \longrightarrow I^-_{(aq)} \qquad E^\circ = +0.54\ V$$

$$Cu^{2+}_{(aq)} + e^- \longrightarrow Cu^+_{(aq)} \qquad E^\circ = +0.15\ V$$

Typically, the $I_2/I^-$ couple, with the higher E° value, would be more likely to undergo reduction. The $Cu^{2+}/Cu^+$ couple has a lower E°, suggesting $Cu^+$ is a better reducing agent than $I^-$.
However, the overall reaction proceeds forward despite a calculated negative net standard potential.

**h) Define $K_{stab}$. How does it reflect the stability of coordination complexes?**

**Ans.** The stability constant ($K_{stab}$) is the equilibrium constant for the formation of a coordination complex from a metal ion and its ligands.

**Example:**

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

$$K_{stab} = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4}$$

A large value of $K_{stab}$ indicates that the complex is highly stable, while a small value indicates lower stability.

CamScanner

**i) Why does coordination number 4 have two possible geometries: tetrahedral and square planar? Explain it.**

**Ans.** Coordination number 4 may have either tetrahedral or square planar geometry depending on the electronic configuration of the metal ion and the strength of the ligands. Weak ligands generally produce tetrahedral complexes, whereas strong ligands often produce square planar complexes.

**Examples:**

$[ZnCl_4]^{2-} \longrightarrow$ Tetrahedral

$[Pt(NH_3)_2Cl_2 \longrightarrow$ Square planar

**j) Illustrate the type of isomerism shown by $[Pt(NH_3)_2Cl_2]$.**

**Ans.** $[Pt(NH_3)_2Cl_2]$ is a square planar complex that exhibits geometrical (cis-trans) isomerism.

- **Cis-isomer:** Similar ligands are adjacent (90°).
- **Trans-isomer:** Similar ligands are opposite each other (180°).

This type of isomerism arises due to the fixed arrangement of ligands in square planar complexes.

**k) Give the medicinal importance of cis-platin.**

**Ans.** Cis-platin is an important anticancer drug used in chemotherapy. It binds to DNA in cancer cells, preventing DNA replication and cell division, which ultimately destroys the cancer cells.
It is commonly used in the treatment of testicular, ovarian and bladder cancers.

**l) What happens when excess ammonia solution is added to cobalt(II) hydroxide precipitate?**

**Ans.** Cobalt(II) hydroxide dissolves in excess aqueous ammonia due to the formation of a soluble ammine complex.

$$Co(OH)_2 + 6NH_3 \longrightarrow [Co(NH_3)_6]^{2+} + 2OH^-$$

On standing in air, this complex is oxidized to the more stable cobalt(III) complex.

**m) Is there any effect of excessive dilution of complexes? If yes then justify how does dilution affect the position of equilibrium in ligand ion exchange reactions?**

**Ans.** Yes. Excessive dilution decreases the concentration of ligands in solution. According to Le-Chatelier's principle, the equilibrium shifts towards dissociation of the complex ion, reducing its stability.

**For example:** $[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$

Dilution shifts the equilibrium to the left, causing partial decomposition of the complex.

## Q 3. CONSTRUCTED RESPONSE QUESTIONS (CRQs)

**a) Discuss the two types of stereoisomerism found in transition metal complexes. Use the example $[Pt(NH_3)_2Cl_2]$ (square planar) and $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ (octahedral) to illustrate the key structural differences that give rise to geometrical and optical isomerism, respectively.**

**Ans.** See Question No. 11

**b) The reaction between $Cu^{2+}$ and $I^-$ results in a solid precipitate of CuI and aqueous $I_2$.**

**(i) Write down the two relevant reduction half-equations and their E° values (provided in the text).**
**(ii) Draw the structure of EDTA ligand and label its electron pair donating sites.**
**(iii) Use Le Chatelier's principle to explain why the reaction proceeds forward in practice.**

**Ans.** (i) and (iii) See Question No. 13
(ii) See Question No. 5(b) Example EDTA

**c) Using the examples $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$, demonstrate how to predict the formula and overall charge of a complex ion. Clearly explain the role of the central metal ion charge, ligand charge, and coordination number in determining the final result for both examples.**

**Ans.**

| Example 1: $[Co(NH_3)_6]^{3+}$ | Example 2: $[Fe^{3+}(CN)_6^{-1\times6}]^{3-}$ |
|---|---|
| In Hexamine cobalt (III) ion, | In Hexacyanoferrate (III) ion, |
| Overall charge on complex ion = +3 | Overall charge on complex ion = −3 |
| Charge on central metal cobalt ion = +3 | Charge on central metal 'Fe' ion = +3 |
| Neutral Ligand ($NH_3$) charge = zero | Anionic Ligand ($CN^-$) charge = −1 |
| Coordination Number = 6 | Coordination Number = 6 |



Since the d-subshell remains completely filled, zinc does not exhibit the characteristic properties of transition metals such as variable oxidation states and coloured ions.

**b) What is the correlation between the variable oxidation states of transition elements and their electronic configuration?**

**Ans.** Transition elements exhibit variable oxidation states because the energies of the ns and (n−1)d orbitals are very similar. Therefore, electrons can be removed from both orbitals during bonding.

**Example:** Fe = $[Ar]3d^64s^2$

Iron commonly shows +2 and +3 oxidation states because it can lose two 4s electrons or two 4s and one 3d electron.

**c) How do transition metals function as effective catalysts? Give examples.**

**Ans.** Transition metals act as catalysts because they possess variable oxidation states and vacant d-orbitals, allowing them to form temporary complexes with reactants. This provides an alternative reaction pathway with lower activation energy.

**Examples:**

- Iron (Fe) in the Haber process.
- Vanadium (V) oxide ($V_2O_5$) in the Contact process.
- Nickel (Ni) in hydrogenation of alkenes.

**d) Why is the complex $[Cr(en)_3]^{3+}$ more stable than $[Cr(H_2O)_6]_{3+}$?**

**Ans.** The ethane-1,2-diamine (en) ligand is bidentate, forming two coordinate bonds with the chromium ion. This produces stable chelate rings, making the complex more stable than the water complex, which contains monodentate ligands. This increased stability is known as the chelate effect.

**e) What is the coordination number? Give its value for $[Fe(CN)_6]^{4-}$.**

**Ans.** The coordination number is the number of coordinate bonds formed between the central metal ion and the surrounding ligands.
In $[Fe(CN)_6]^{4-}$ there are six cyanide ligands attached to iron.
Coordination number = 6

**f) Define a bidentate ligand and state how many bonds it forms to the central ion.**

**Ans.** **Bidentate Ligand:** A bidentate ligand is a ligand that contains two donor atoms and donates two lone pairs of electrons to the central metal ion.
Therefore, one bidentate ligand forms two coordinate bonds.
**Examples:** Ethane-1,2-diamine (en), Oxalate ion ($C_2O_4^{2-}$)

**(g) Explain why comparing only the E° values suggests the reaction is not feasible as written.**

**Ans.** The reaction splits into the following half-equations:

$$\frac{1}{2}I_{2(aq)} + e^- \longrightarrow I^-_{(aq)} \qquad E° = +0.54\ V$$

$$Cu^{2+}_{(aq)} + e^- \longrightarrow Cu^+_{(aq)} \qquad E° = +0.15\ V$$

Typically, the $I_2/I^-$ couple, with the higher E° value, would be more likely to undergo reduction. The $Cu^{2+}/Cu^+$ couple has a lower E°, suggesting $Cu^+$ is a better reducing agent than $I^-$.
However, the overall reaction proceeds forward despite a calculated negative net standard potential.

**h) Define $K_{stab}$. How does it reflect the stability of coordination complexes?**

**Ans.** The stability constant ($K_{stab}$) is the equilibrium constant for the formation of a coordination complex from a metal ion and its ligands.

**Example:**

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

$$K_{stab} = \frac{[Cu(NH_3)_4^{2+}]}{[Cu^{2+}][NH_3]^4}$$

A large value of $K_{stab}$ indicates that the complex is highly stable, while a small value indicates lower stability.

CamScanner

**i) Why does coordination number 4 have two possible geometries: tetrahedral and square planar? Explain it.**

**Ans.** Coordination number 4 may have either tetrahedral or square planar geometry depending on the electronic configuration of the metal ion and the strength of the ligands. Weak ligands generally produce tetrahedral complexes, whereas strong ligands often produce square planar complexes.

**Examples:**

$[ZnCl_4]^{2-} \longrightarrow$ Tetrahedral

$[Pt(NH_3)_2Cl_2 \longrightarrow$ Square planar

**j) Illustrate the type of isomerism shown by $[Pt(NH_3)_2Cl_2]$.**

**Ans.** $[Pt(NH_3)_2Cl_2]$ is a square planar complex that exhibits geometrical (cis-trans) isomerism.

- **Cis-isomer:** Similar ligands are adjacent (90°).
- **Trans-isomer:** Similar ligands are opposite each other (180°).

This type of isomerism arises due to the fixed arrangement of ligands in square planar complexes.

**k) Give the medicinal importance of cis-platin.**

**Ans.** Cis-platin is an important anticancer drug used in chemotherapy. It binds to DNA in cancer cells, preventing DNA replication and cell division, which ultimately destroys the cancer cells.
It is commonly used in the treatment of testicular, ovarian and bladder cancers.

**l) What happens when excess ammonia solution is added to cobalt(II) hydroxide precipitate?**

**Ans.** Cobalt(II) hydroxide dissolves in excess aqueous ammonia due to the formation of a soluble ammine complex.

$$Co(OH)_2 + 6NH_3 \longrightarrow [Co(NH_3)_6]^{2+} + 2OH^-$$

On standing in air, this complex is oxidized to the more stable cobalt(III) complex.

**m) Is there any effect of excessive dilution of complexes? If yes then justify how does dilution affect the position of equilibrium in ligand ion exchange reactions?**

**Ans.** Yes. Excessive dilution decreases the concentration of ligands in solution. According to Le-Chatelier principle, the equilibrium shifts towards dissociation of the complex ion, reducing its stability.

**For example:** $[Cu(NH_3)_4]^{2+} \rightleftharpoons Cu^{2+} + 4NH_3$

Dilution shifts the equilibrium to the left, causing partial decomposition of the complex.

## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) Discuss the two types of stereoisomerism found in transition metal complexes. Use the example $[Pt(NH_3)_2Cl_2]$ (square planar) and $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ (octahedral) to illustrate the key structural differences that give rise to geometrical and optical isomerism, respectively.**

**Ans.** See Question No. 11

**b) The reaction between $Cu^{2+}$ and $I^-$ results in a solid precipitate of CuI and aqueous $I_2$.**

**i) Write down the two relevant reduction half-equations and their $E^\circ$ values (provided in the text).**
**ii) Draw the structure of EDTA ligand and label its electron pair donating sites.**
**iii) Use Le Chatelier's principle to explain why the reaction proceeds forward in practice.**

**Ans.** (i) and (iii) See Question No. 13
(ii) See Question No. 5(b) Example EDTA

**c) Using the examples $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$, demonstrate how to predict the formula and overall charge of a complex ion. Clearly explain the role of the central metal ion charge, ligand charge, and coordination number in determining the final result for both examples.**

**Ans.**

| Example 1: | Example 2: |
|---|---|
| $[Co(NH_3)_6]^{3+}$ | $[Fe^{3+}(CN)_6^{-1\times6}]^{3-}$ |
| In Hexamine cobalt (III) ion, | In Hexacyanoferrate (III) ion, |
| Overall charge on complex ion = +3 | Overall charge on complex ion = −3 |
| Charge on central metal cobalt ion = +3 | Charge on central metal 'Fe' ion = +3 |
| Neutral Ligand ($NH_3$) charge = zero | Anionic Ligand ($CN^-$) charge = −1 |
| Coordination Number = 6 | Coordination Number = 6 |



## DESCRIPTIVE QUESTIONS DQs

**Q.4 Explain the factors that determine the specific geometry (shape) of a transition metal complex.**

**Ans.** See Question No. 7

**Q.5 Describe the splitting of d-orbitals and colour formation in octahedral and tetrahedral complexes.**

**Ans.** See Question No. 8

**Q.6 Compare the reactions of conc. HCl with aqueous $Cu^{2+}$ and aqueous $Co^{2+}$. Include equations, colour/geometry changes, and the reason for different colours.**

**Ans.** See Question No. 9

**Q.7 Describe the various redox reactions that takes place in transition metal complex ions.**

**Ans.** See Question No. 12

**Q.8 Explain the stereoisomerism with its types in transition metal complexes.**

**Ans.** See Question No. 11

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 What is a d-block transition element?**

**Ans.** A transition element is a d-block element that forms one or more stable ions with an incomplete d-subshell. **For example,** $Fe^{2+}$ has the configuration [Ar] $3d^6$.

**Q.2 Why do transition metals show variable oxidation states?**

**Ans.** The 3d and 4s subshells have very similar energies. Therefore, a transition-metal atom can lose the 4s electrons and, in higher oxidation states, a variable number of 3d electrons as well. This gives more than one stable oxidation state. **Examples:** $Fe^{2+}$, $Fe^{3+}$

**Q.3 Why do transition metals form coloured compounds?**

**Ans.** In a complex, ligands split the five degenerate d-orbitals into two non-degenerate energy sets. An electron can absorb visible light and move from a lower-energy d-orbital to a higher-energy d-orbital (a d-d transition). The unabsorbed light is observed as the characteristic, complementary colour of the complex.

**Q.4 Define a ligand with examples.**

**Ans.** A ligand is an ion or molecule which contains at least one lone pair of electrons and donates it to a metal ion to form a coordinate covalent bond. **Examples:** $H_2O$, $NH_3$, $Cl^-$, $CN^-$

**Q.5 What is meant by coordination number?**

**Ans.** The coordination number is the total number of dative bonds formed between the ligands and the central metal atom/ion. In $[Fe(CN)_6]^{4-}$, six $CN^-$ ligands are directly bonded to $Fe^{2+}$, so the coordination number is 6.

**Q.6 Differentiate between monodentate and bidentate ligands.**

**Ans.** A monodentate ligand donates one electron pair and forms one dative bond to the central metal, whereas a bidentate ligand donates two electron pairs through two donor atoms and forms two dative bonds. **Example:** $H_2O$, $NH_3$ and $Cl^-$ are monodentate; 1,2-diaminoethane (en) and ethanedioate are bidentate.

**Q.7 Explain tetrahedral splitting of d-orbitals.**

**Ans.** In a tetrahedral complex, four ligands split the five d-orbitals in the opposite pattern to an octahedral complex: dxy, dxz and dyz are the three higher-energy orbitals, while $dx^2 - y^2$ and $dz^2$ are the two lower-energy orbitals. The magnitude of ΔE is smaller than in an octahedral complex.

**Q.8 Explain the formation of colour in transition metal complexes.**

**Ans.** A lower-energy d-electron absorbs a specific amount of visible-light energy and is promoted to a higher-energy d-orbital. This d-d transition requires an energy ΔE that is related to the absorbed light by $\Delta E = h\nu = hc/\lambda$. The light that is not absorbed determines the observed colour.

CamScanner

**Q.9 What is meant by complementary colour?**

**Ans.** The observed colour of a complex is complementary to the colour of light it absorbs. For example, if a complex absorbs yellow light, it appears violet.

**Q.10 Describe ligand exchange in hexaaquacopper(II) ion with ammonia.**

**Ans.** Ammonia replaces four water ligands in the hydrated copper(II) complex:
**Equation:** $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$
**Observation:** The pale blue solution changes to deep blue.

**Q.11 Describe ligand exchange in hexaaquacopper(II) ion with chloride ions.**

**Ans.** When concentrated hydrochloric acid is added to hexaaquacopper(II) ions, chloride ions replace water ligands to form tetrachlorocuprate(II) ions.
**Equation:** $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$
**Observation:** The blue solution changes to yellow-green.

**Q.12 Describe ligand exchange in hexaaquacobalt(II) ion with chloride ions.**

**Ans.** Chloride ions replace water ligands in hexaaquacobalt(II) ions to form tetrachlorocobaltate(II) ions.
**Equation:** $[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$
**Observation:** The pink solution changes to blue.

**Q.13 Define the stability constant ($K_{stab}$).**

**Ans.** The stability constant, Kstab, is the equilibrium constant for the formation of a complex ion in a solvent from its constituent ions or molecules.

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O,$$

Water is omitted from the expression because it is the solvent: $K_{stab} = [CuCl_4^{2-}] / ([Cu(H_2O)_6^{2+}][Cl^-]^4)$.

**Q.14 What is the significance of a large value of $K_{stab}$?**

**Ans.** A large $K_{stab}$ (or large $\log_{10}K_{stab}$) means the complex is more stable and the formation equilibrium lies farther to the right. A ligand forming the complex with the larger $K_{stab}$ can displace a ligand associated with a smaller $K_{stab}$.

**Q.15 Explain geometrical isomerism in square planar complexes.**

**Ans.** Square-planar complexes can show cis-trans isomerism when identical ligands occupy either adjacent positions (cis, 90°) or opposite positions (trans, 180°). $[Pt(NH_3)_2Cl_2]$ occurs as cisplatin and transplatin.

**Q.16 Explain geometrical isomerism in octahedral complexes.**

**Ans.** Octahedral complexes can also show cis-trans isomerism. In $[Co(NH_3)_4(H_2O)_2]^{3+}$, the two $H_2O$ ligands are adjacent at 90° in the cis isomer and opposite at 180° in the trans isomer.

**Q.17 What is optical isomerism? Explain optical isomerism in transition metal complexes.**

**Ans.** Optical isomers are non-superimposable mirror images (enantiomers). They rotate plane-polarized light in opposite directions: the dextrorotatory (+) form rotates it to the right and the laevorotatory (–) form to the left. Optical isomerism is commonly shown by octahedral complexes containing bidentate ligands. The chapter uses $[Ni(en)_3]^{2+}$ as an example; its two forms are non-superimposable mirror images and rotate plane-polarized light in opposite directions.

**Q.18 Explain the reduction of acidified manganate(VII) ions.**

**Ans.** In acidic solution, $MnO_4^-$ is reduced from Mn(VII) to Mn(II):

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

In the chapter's redox examples, acidified $MnO_4^-$ acts as an oxidizing agent.

**Q.19 Describe the reaction between copper(II) ions and iodide ions.**

**Ans.** When excess iodide is added to aqueous $Cu^{2+}$
**Equation:** $2Cu^{2+} + 4I^- \longrightarrow 2CuI_{(s)} + I_{2(aq)}$
**Observation:** A white precipitate of CuI and a red-brown iodine solution are formed. The precipitation of CuI removes product from solution and helps drive the reaction forward.



## DESCRIPTIVE QUESTIONS DQs

**Q.4 Explain the factors that determine the specific geometry (shape) of a transition metal complex.**

**Ans.** See Question No. 7

**Q.5 Describe the splitting of d-orbitals and colour formation in octahedral and tetrahedral complexes.**

**Ans.** See Question No. 8

**Q.6 Compare the reactions of conc. HCl with aqueous $Cu^{2+}$ and aqueous $Co^{2+}$. Include equations, colour/geometry changes, and the reason for different colours.**

**Ans.** See Question No. 9

**Q.7 Describe the various redox reactions that takes place in transition metal complex ions.**

**Ans.** See Question No. 12

**Q.8 Explain the stereoisomerism with its types in transition metal complexes.**

**Ans.** See Question No. 11

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 What is a d-block transition element?**

**Ans.** A transition element is a d-block element that forms one or more stable ions with an incomplete d-subshell. For example, $Fe^{2+}$ has the configuration [Ar] $3d^6$.

**Q.2 Why do transition metals show variable oxidation states?**

**Ans.** The 3d and 4s subshells have very similar energies. Therefore, a transition-metal atom can lose the 4s electrons and, in higher oxidation states, a variable number of 3d electrons as well. This gives more than one stable oxidation state. **Examples:** $Fe^{2+}$, $Fe^{3+}$

**Q.3 Why do transition metals form coloured compounds?**

**Ans.** In a complex, ligands split the five degenerate d-orbitals into two non-degenerate energy sets. An electron can absorb visible light and move from a lower-energy d-orbital to a higher-energy d-orbital (a d-d transition). The unabsorbed light is observed as the characteristic, complementary colour of the complex.

**Q.4 Define a ligand with examples.**

**Ans.** A ligand is an ion or molecule which contains at least one lone pair of electrons and donates it to a metal ion to form a coordinate covalent bond. **Examples:** $H_2O$, $NH_3$, $Cl^-$, $CN^-$

**Q.5 What is meant by coordination number?**

**Ans.** The coordination number is the total number of dative bonds formed between the ligands and the central metal atom/ion. In $[Fe(CN)_6]^{4-}$, six $CN^-$ ligands are directly bonded to $Fe^{2+}$, so the coordination number is 6.

**Q.6 Differentiate between monodentate and bidentate ligands.**

**Ans.** A monodentate ligand donates one electron pair and forms one dative bond to the central metal, whereas a bidentate ligand donates two electron pairs through two donor atoms and forms two dative bonds. **Example:** $H_2O$, $NH_3$ and $Cl^-$ are monodentate; 1,2-diaminoethane (en) and ethanedioate are bidentate.

**Q.7 Explain tetrahedral splitting of d-orbitals.**

**Ans.** In a tetrahedral complex, four ligands split the five d-orbitals in the opposite pattern to an octahedral complex: dxy, dxz and dyz are the three higher-energy orbitals, while $dx^2 - y^2$ and $dz^2$ are the two lower-energy orbitals. The magnitude of $\Delta E$ is smaller than in an octahedral complex.

**Q.8 Explain the formation of colour in transition metal complexes.**

**Ans.** A lower-energy d-electron absorbs a specific amount of visible-light energy and is promoted to a higher-energy d-orbital. This d-d transition requires an energy $\Delta E$ that is related to the absorbed light by $\Delta E = h\nu = hc/\lambda$. The light that is not absorbed determines the observed colour.

CamScanner

**Q.9 What is meant by complementary colour?**

**Ans.** The observed colour of a complex is complementary to the colour of light it absorbs. For example, if a complex absorbs yellow light, it appears violet.

**Q.10 Describe ligand exchange in hexaaquacopper(II) ion with ammonia.**

**Ans.** Ammonia replaces four water ligands in the hydrated copper(II) complex:
**Equation:** $[Cu(H_2O)_6]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + 4H_2O$
**Observation:** The pale blue solution changes to deep blue.

**Q.11 Describe ligand exchange in hexaaquacopper(II) ion with chloride ions.**

**Ans.** When concentrated hydrochloric acid is added to hexaaquacopper(II) ions, chloride ions replace water ligands to form tetrachlorocuprate(II) ions.
**Equation:** $[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$
**Observation:** The blue solution changes to yellow-green.

**Q.12 Describe ligand exchange in hexaaquacobalt(II) ion with chloride ions.**

**Ans.** Chloride ions replace water ligands in hexaaquacobalt(II) ions to form tetrachlorocobaltate(II) ions.
**Equation:** $[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$
**Observation:** The pink solution changes to blue.

**Q.13 Define the stability constant ($K_{stab}$).**

**Ans.** The stability constant, Kstab, is the equilibrium constant for the formation of a complex ion in a solvent from its constituent ions or molecules.

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O,$$

Water is omitted from the expression because it is the solvent: $K_{stab} = [CuCl_4^{2-}] / ([Cu(H_2O)_6^{2+}][Cl^-]^4)$.

**Q.14 What is the significance of a large value of $K_{stab}$?**

**Ans.** A large $K_{stab}$ (or large $\log_{10}K_{stab}$) means the complex is more stable and the formation equilibrium lies farther to the right. A ligand forming the complex with the larger $K_{stab}$ can displace a ligand associated with a smaller $K_{stab}$.

**Q.15 Explain geometrical isomerism in square planar complexes.**

**Ans.** Square-planar complexes can show cis-trans isomerism when identical ligands occupy either adjacent positions (cis, 90°) or opposite positions (trans, 180°). $[Pt(NH_3)_2Cl_2]$ occurs as cisplatin and transplatin.

**Q.16 Explain geometrical isomerism in octahedral complexes.**

**Ans.** Octahedral complexes can also show cis-trans isomerism. In $[Co(NH_3)_4(H_2O)_2]^{3+}$, the two $H_2O$ ligands are adjacent at 90° in the cis isomer and opposite at 180° in the trans isomer.

**Q.17 What is optical isomerism? Explain optical isomerism in transition metal complexes.**

**Ans.** Optical isomers are non-superimposable mirror images (enantiomers). They rotate plane-polarized light in opposite directions: the dextrorotatory (+) form rotates it to the right and the laevorotatory (–) form to the left. Optical isomerism is commonly shown by octahedral complexes containing bidentate ligands. The chapter uses $[Ni(en)_3]^{2+}$ as an example; its two forms are non-superimposable mirror images and rotate plane-polarized light in opposite directions.

**Q.18 Explain the reduction of acidified manganate(VII) ions.**

**Ans.** In acidic solution, $MnO_4^-$ is reduced from Mn(VII) to Mn(II):

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

In the chapter's redox examples, acidified $MnO_4^-$ acts as an oxidizing agent.

**Q.19 Describe the reaction between copper(II) ions and iodide ions.**

**Ans.** When excess iodide is added to aqueous $Cu^{2+}$
**Equation:** $2Cu^{2+} + 4I^- \longrightarrow 2CuI_{(s)} + I_{2(aq)}$
**Observation:** A white precipitate of CuI and a red-brown iodine solution are formed. The precipitation of CuI removes product from solution and helps drive the reaction forward.



**Q.20 Define a complex and the nature of the bond between its components.**

**Ans.** A complex (coordination compound) is a molecule or ion in which a central metal ion is surrounded by one or more ligands. The bond between the metal ion and ligand is a coordinate (dative covalent) bond, in which both electrons are donated by the ligand. **Example:** $[Cu(NH_3)_4]^{2+}$

**Q.21 Draw the colour wheel used to predict the colour of transition metal complexes. Also pair the complementary colours.**

**Ans.** Transition metal complexes absorb one colour of visible light and appear in its complementary colour.

| Absorbed Colour | Observed (Complementary) Colour |
|---|---|
| Red | Green |
| Orange | Blue |
| Yellow | Violet |
| Green | Red |
| Blue | Orange |
| Violet | Yellow |

The observed colour is always the complementary colour of the absorbed light.

## SELF-ASSESSMENT

**Total Mark: 30**

**Q.1 Encircle the correct option.** **(1 × 6 = 6)**

**(i)** **Chromium shows an exceptional electronic configuration because of:**
(A) Large atomic size (B) Completely filled 4s orbital
(C) Stability of half-filled 3d subshell (D) High electronegativity

**(ii)** **Which of the following is NOT considered a transition element?**
(A) Titanium (B) Iron (C) Zinc (D) Chromium

**(iii)** **What is the coordination number of Fe in $[Fe(CN)_6]^{4-}$?**
(A) 2 (B) 4 (C) 6 (D) 8

**(iv)** **Which complex is electrically neutral?**
(A) $[Co(NH_3)_6]^{3+}$ (B) $[Fe(CN)_6]^{4-}$ (C) $[Ni(CO)_4]$ (D) $[Cu(H_2O)_6]^{2+}$

**(v)** **The most common geometry for coordination number 6 is:**
(A) Linear (B) Square planar (C) Tetrahedral (D) Octahedral

**(vi)** **Adding excess ammonia to pink $[Co(H_2O)_6]^{2+}$ gives a yellow solution. What other changes occur besides colour change?**
(A) Coordination number changes from 6 to 4 (B) Oxidation state of Co changes form +2 to +3
(C) d-orbital splitting magnitude (ΔE) changes (D) Complex becomes a precipitate

**Q.2 Write short answers of the following questions.** **(2 × 8 = 16)**

(i) Why is zinc not included in the transition metals, although it shows electronic configuration with d-orbitals?
(ii) Why is the complex $[Cr(en)_3]^{3+}$ more stable than $[Cr(H_2O)_6]_{3+}$?
(iii) Illustrate the type of isomerism shown by $[Pt(NH_3)_2Cl_2]$.
(iv) Explain the phenomenon (d-d transitions) responsible for the colour of transition metal compounds.
(v) How does Lewis acid base concept explains the transition metal complex formation?
(vi) The $Sc^{3+}$ ion is $[Ar]3d^04s^0$. Why is scandium not classified as a transition element?
(vii) How does Lewis acid base concept explains the transition metal complex formation?
(viii) EDTA is described as a hexadentate ligand. Explain what "hexadentate" means in terms of coordinate covalent bonds formed with a single metal ion.

**Q.3 Extensive Questions.** **(4 + 4 = 8)**

(a) Describe the splitting of d-orbitals and colour formation in octahedral and tetrahedral complexes.
(b) Explain the stereoisomerism with its types in transition metal complexes.

CamScanner

## ENTRANCE TEST MCQs

1. The geometry of the complexes depends upon the type of _____ taking place in the valence shell of the central metal atom: (UHS 2010)
(A) Hybridization (B) Protonation (C) Deprotonation (D) Dissociation
2. Which one pair has the same oxidation state of 'Fe'? (UHS 2013)
(A) $FeSO_4$ and $FeCl_3$ (B) $FeSO_4$ and $FeCl_2$ (C) $FeCl_2$ and $FeCl_3$ (D) $Fe_2(SO_4)_3$ and $FeSO_4$
3. Which pair of transition elements shows abnormal electronic configuration? (UHS 2012)
(A) Sc and Zn (B) Zn and Cu (C) Cu and Sc (D) Cu and Cr
4. Electronic configuration of Manganese ($_{25}Mn$) is: (UHS 2014)
(A) $[Ar]3d^4 4s^2$ (B) $[Ar]3d^4 4s^1$ (C) $[Ar]3d^5 4s^2$ (D) $[Ar]3d^5 4s^1$
5. Oxidation state of 'Fe' in $K_3[Fe(CN)_6]$ is: (UHS 2013)
(A) +2 (B) –6 (C) +3 (D) –3
6. Ligands donating two lone pair of electrons to the central transition metal ion are known as: (UHS 2018)
(A) Polydentate ligands (B) Monodentate ligands (C) Bidentate ligands (D) Hexadentate ligands
7. The shape of $[Co(NH_3)_6]^{3+}$ complex is: (UHS 2018)
(A) Linear (B) Tetrahedral (C) Square planar (D) Octahedral
8. Zn is not classified as a transition element because:
(A) Neutral Zn has no d electrons (B) Zn is a non-metal
(C) $Zn^{2+}$ has a completely filled $3d^{10}$ subshell (D) Zn never forms ions
9. Sc is excluded from the transition elements because:
(A) Its atomic number is greater than zinc (B) Its stable $Sc^{3+}$ ion has the configuration [Ar] $3d^0$
(C) Its atom contains no 4s electrons (D) It forms only covalent compounds
10. How many unpaired d electrons are present in a free $Fe^{3+}$ ion according to Hund's rule?
(A) Three (B) Five (C) Zero (D) Two
11. Which ion satisfies the transition-element criterion?
(A) $Ti^{3+}$ with an incomplete $3d^1$ subshell (B) $Zn^{2+}$ with $3d^{10}$
(C) $Sc^{3+}$ with $3d^0$ (D) $Ca^{2+}$ with no d electrons
12. Why does the maximum oxidation state rise toward manganese and then generally fall?
(A) The 4s subshell disappears after manganese
(B) All later metals become non-metals
(C) Valence electrons increase, then high charges destabilize
(D) Atomic numbers decrease after manganese
13. Why do transition metals often have higher densities and melting points than Group 1 metals?
(A) Compact atoms form stronger metallic bonds
(B) Transition metals exist as simple molecular substances
(C) Group 1 metals have stronger d-electron bonding
(D) Transition metals have no metallic bonding
14. What is the coordination number of Ni in $[Ni(CO)_4]$?
(A) 8 (B) 4 (C) 0 (D) 2
15. What is the geometry of $[Pt(NH_3)_4]^{2+}$?
(A) Square planar (B) Tetrahedral (C) Octahedral (D) Linear

**Answers Key**

| 1. A | 2. B | 3. D | 4. D | 5. C | 6. C | 7. D | 8. C | 9. B | 10. B | 11. A | 12. C | 13. A | 14. B | 15. A |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|



19 CHAPTER

# BASICS OF ORGANIC CHEMISTRY

### Student Learning Outcomes (SLOs)

[C-12-D-01 to C-12-D-20]

- Define catenation and explain its importance in organic chemistry.
- Recognize that hydrocarbons are compounds made up of C and H atoms only.
- Describe the shape of benzene and other aromatic molecules, including $sp^2$ hybridization, in terms of $\sigma$ bonds and a delocalized $\pi$ system.
- Recognize that compounds contain a functional group which dictates their physical and chemical properties.
- Recognize that alkanes are simple hydrocarbons with no functional group.
- Describe the use of systematic nomenclature of simple aliphatic organic molecules with functional groups.
- Interpret the general, structural, displayed and skeletal formulae of the classes of compounds.
- Deduce the molecular and / or empirical formula of a compound, given its structural, displayed or skeletal formula.
- Apply the term 'planar' when describing the arrangement of atoms in organic molecules.
- Describe terminology associated with the types of organic compounds and reactions (some examples include: Homologous series, saturated and unsaturated, homolytic and heterolytic fission, free radical, initiation, propagation, termination, nucleophile, electrophile, nucleophilic, electrophilic addition, substitution, elimination, hydrolysis, condensation, oxidation and reduction).
- Describe terminology associated with types of organic mechanisms (Some examples include: Freeradical substitution, electrophilic addition, nucleophilic substitution, nucleophilic addition).
- Draw the mechanism of a chemical reaction using curly arrows to represent the movement of a pair of electrons in at least three different types of reactions, including nucleophilic substitution, electrophilic addition, and elimination reactions.
- Describe structural isomerism (in the context of organic molecules) in its division into chain, positional, functional group isomerism, metamerism and tautomerism.
- Explain stereoisomerism and its division into cis-trans (cis/trans) and optical isomerism.
- Describe the effect of two optical isomers of a single substance on a plane polarised light.
- Explain what is meant by a chiral center and that such a center gives rise to two optical isomers (enantiomers).
- Describe that enantiomers have identical physical and chemical properties except for their ability to rotate plane-polarised light and potential biological activity.
- Apply the terms optically active, racemic mixture and mesocompounds on given structure.
- Describe cis-trans (cis/trans) isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of $\pi$ bonds.
- Explain the significance of chirality in the synthetic preparation of drug molecules, including the potential different biological activity of enantiomers, the need to separate racemic mixtures, and the use of chiral catalysts to produce a single pure optical isomer using thalidomide as an example.

CamScanner

We are familiar with more than 20 million carbon-containing compounds, most of these are studied in organic chemistry.

**Q.1 What is organic Chemistry?** S/Q

**Ans.** Organic chemistry is defined by the **IUPAC** as:

*"The study of compounds containing carbon, where carbon is bonded to itself, hydrogen, or other elements excluding some simple compounds traditionally classed as inorganic compounds."*

➢ **Organic Compounds:**

*"The compounds of hydrogen and carbon and their derivate are called organic compounds.* e.g., methane ($CH_4$), benzene ($C_6H_6$) etc.

➢ **Carbon Containing Compounds which are Inorganic:**

- There are some carbon containing compounds which are excluded from organic chemistry.
- Examples of traditional inorganic compounds are carbonates, cyanides (e.g., KCN), $CO_2$, CO, etc.
- Organic compounds can be easily distinguished from inorganic compounds by their unique properties, such as low+ melting point (m.p), boiling point (b.p), low densities and low solubility in water.

**Inorganic Compounds generally**
- Have high M.Pt, B.Pt.
- Are non-flammable
- Are mostly soluble in polar solvents like water
- Show fast reactions
- Occur in non-living things
- Catenation is absent

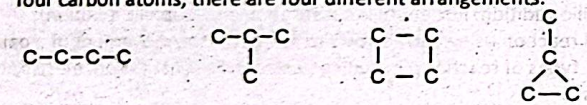
## CATENATION

**Q.2 Define Catenation. Give example.** S/Q

**Ans. Catenation:**

**The ability of self-linkage between the atoms of the same element is known as catenation (from the Latin: Catena-Chain).** Carbon forms long chains and rings through the stable C – C covalent bonds. The self-linking property of carbon atoms has unique importance in organic chemistry.

Tetravalent nature of carbon enables it to have many different ways of arrangements to give a variety of compounds. **For example,** with four carbon atoms, there are four different arrangements.



Catenation explains why organic compounds are complex, having large structures and vast diversity.

**Catenation Order**

C – C > S – S > P – P > Si – Si

More the bond energy, more is the catenation.

**Check Understanding!**

**Q.1 Urea belongs tow which class of compounds?**

(A) Imides (B) Amines

(C) Amides (D) Carboxylic acid

### QUICK CHECK 19.1

**a) Draw the different possible structures containing five carbon atoms.**

**Ans.** Compounds containing five carbon atoms ($C_5H_{12}$) have three structural (chain) isomers.

**1. n-Pentane**

$CH_3 — CH_2 — CH_2 — CH_2 — CH_3$

Pentane

**2. Isopentane**

$CH_3 — CH(CH_3) — CH_2 — CH_3$

2-Methylbutane

**3. Neopentane**

$C(CH_3)_4$

2, 2-Dimethylpropane



**b) Give different open chain structures containing six carbon atoms.**

**Ans.** Compounds containing six carbon atoms ($C_6H_{14}$) have five open-chain structural isomers.

**1. n-Hexane**

$CH_3 — CH_2 — CH_2 — CH_2 — CH_2 — CH_3$

Hexane

**2. 2-Methylpentane**

$CH_3 — CH(CH_3) — CH_2 — CH_2 — CH_3$

**3. 3-Methylpentane**

$CH_3 — CH_2 — CH(CH_3) — CH_2 — CH_3$

**4. 2,2-Dimethylbutane**

$CH_3 — C(CH_3)_2 — CH_2 — CH_3$

**5. 2,3-Dimethylbutane**

$CH_3 — CH(CH_3) — CH(CH_3) — CH_3$

## HYDROCARBONS (COMPOUNDS OF CARBON AND HYDROGEN ONLY)

**Q.3 What are hydrocarbons? How are they classified?** L/Q

**Ans.** ***Compounds containing carbon and hydrogen only in their molecules are called hydrocarbons.***

On the basis of carbon skeleton, hydrocarbons are broadly classified into two types:

**a) Open Chain or Acyclic Hydrocarbons:** Hydrocarbons possessing open chain of carbon atoms are called open chain or acyclic hydrocarbons. These can be further subdivided into saturated hydrocarbons (alkanes) or unsaturated hydrocarbons (alkenes and alkynes).

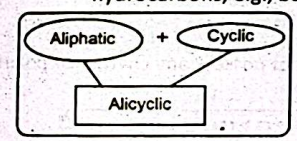
**b) Closed Chain or Cyclic Hydrocarbons:** Hydrocarbons possessing rings of carbon atoms are called closed chain or cyclic hydrocarbons. These can be further divided into two types;

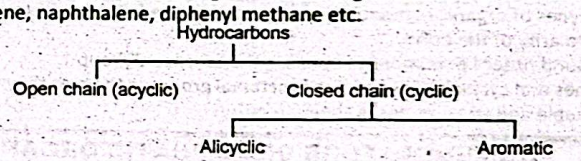
(i) Some cyclic hydrocarbons both saturated and unsaturated, which behave like open chain hydrocarbons, are called alicyclic hydrocarbons **e.g.,** cycloalkanes, cycloalkenes etc. Open chain hydrocarbons and alicyclic compounds are classified as aliphatic hydrocarbons.

(ii) Some cyclic hydrocarbons having benzene ring or resembling structures are called aromatic hydrocarbons, e.g., benzene, naphthalene, diphenyl methane etc.

**Check Understanding!**

**Q.2 Give names of any two aromatic hydrocarbons?**




**Aliphatic hydrocarbons**

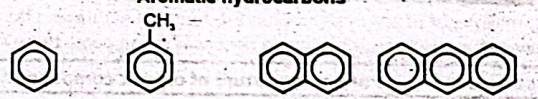
$CH_3 – CH_3$ ethane

$H_2C = CH_2$ ethene

$HC \equiv CH$ ethyne

cyclohexane

**Aromatic hydrocarbons**



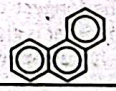

### QUICK CHECK 19.2

**a) Classify the following compounds as an aliphatic, alicyclic or aromatic.**

i) 

ii) 

iii) 

iv) 

v) $CH_3(CH_2)_2CH_3$ vi) $CH_3C(CH_3)_2CH_3$ vii)  viii) 

Ans.

| Compound | Name | Classification | Reason |
|---|---|---|---|
| i) | Methylcyclohexane | Alicyclic | Saturated cyclic compound (non-aromatic). |
| ii) | 5-Methylcyclohexa-1,3-diene | Alicyclic | Cyclic but non-aromatic (does not satisfy aromaticity conditions). |
| iii) | Ethylbenzene | Aromatic | Contains a benzene ring with delocalized π-electrons. |
| iv) | Phenanthrene | Aromatic | Consists of three fused benzene rings at an angle forming a jagged shaped, aromatic. |
| v) | n-Butane | Aliphatic | Open-chain (no ring). |
| vi) | 2,2-dimethylpropane | Aliphatic | Branched open-chain (no ring). |
| vii) | Cyclohexane | Alicyclic | Saturated cyclic hydrocarbon (non-aromatic). |
| viii) | Methylcyclopentane | Alicyclic | Saturated cyclic hydrocarbon (non-aromatic). |

## FUNCTIONAL GROUPS

**Q.4 Define functional groups. What factors dictate the type of organic compound on the basis of their functional groups?** L/Q

**Ans. Functional Group:**

**An atom or group of atoms or presence of double or triple bond which determines the characteristic properties of an organic compound is called functional group.**

Both physical and chemical properties of organic compounds are highly affected by the nature of functional groups they possess. Methanol and ethanol are liquids while methane and ethane are gases. Likewise, m.pt and b.pt of alcohols are higher than their corresponding alkanes. These properties are due to the presence of the hydroxyl functional group (–OH) in alcohols. The alcohol functional group has the ability to form the hydrogen bonding. Alkanes lack this ability as they have no such functional group in their molecules. Similarly, lower alcohols and carboxylic acids, glucose and sucrose etc., are soluble in polar solvents like water due to their polar functional groups.

**Check Understanding!**
Q.3 Functional groups of acid amides is:
(A) –OH (B) $-NH_2$
(C) $-CONH_2$ (D) –COOH

➢ **Factors:**

The types of organic compounds are dictated by the following factors in their functional groups:

i) Polarity of the bond
ii) Bond order i.e. number of bonds in the functional group

Alkanes and cycloalkanes have **no functional groups** in them as they do not possess any charges or polarity or double and triple bonds in their structures.

## NOMENCLATURE OF ALIPHATIC ORGANIC COMPOUNDS

Since, millions of organic compounds are found in nature and hundreds and thousands of new compounds are being synthesized every year, therefore, a need was felt to name these compounds according to their structures.

**Q.5 What are IUPAC rules of nomenclature of organic compound?** L/Q

**Ans.** A set of rules was thus formulated by IUPAC (International Union of Pure and Applied Chemistry) for systematic nomenclature of organic compounds. The systematic or IUPAC name of an organic compound is **based on the parent hydrocarbon.** Each name consists of the components listed below.

**i) Stem or Root:**

It gives the longest continuous carbon chain including the carbon bearing the functional group. Lowest possible number is given to the carbon bearing the functional group. If the carbon atoms are joined in a ring the name is started by "cyclo".



**ii) Suffix:**

**There are two types of suffixes:**

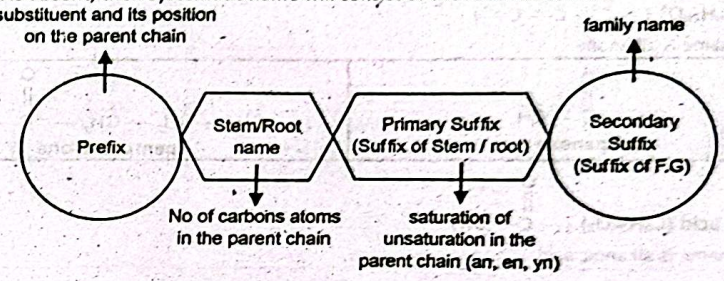
a) Primary suffix, also called suffix of stem or root. It indicates whether the parent chain is saturated or unsaturated.
b) Secondary suffix, also called suffix of the key functional group. It gives family name of the compound.

**Check Understanding!**
Q.4 Name the two types of suffixes used in nomenclature of aliphatic organic compounds.

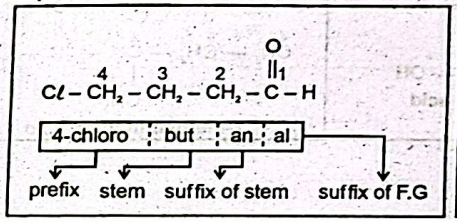
**iii) Prefix:**

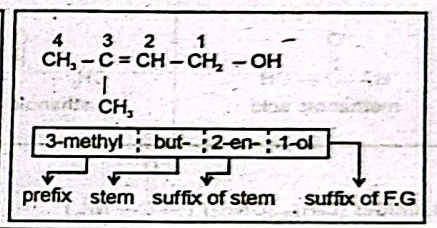
It gives the name of the side chain (alkyl group) or any substituent (e.g., some functional groups like halo, nitro, etc.) along with the number of carbon atoms to which it is attached.

If the prefix is absent, then systematic name will consist of the root and suffix.




➢ **Examples:**




**Q.6 Discuss the simple rule and IUPAC nomenclature of various classes of organic compounds.** L/Q

**Ans.** Keeping in view, the above procedure for giving systematic or IUPAC names to various organic compounds, following different classes will be discussed one by one:

**1. Alkyl halides ($C_nH_{2n+1}X$) (—C—X)**

The IUPAC name is halogenoalkane (more precisely monohaloalkane)

| | | |
|---|---|---|
| $CH_3—C\ell$ **chloromethane** | $CH_3—\overset{2}{C}H(Br)—CH_3$ **2-bromopropane** | $CH_3—\overset{3}{C}H(CH_3)—CH_2—CH_2—I$ **3-methyl-1-iodobutane** |

**2. Alcohols ($C_nH_{2n+2}O$) (—C—OH)**

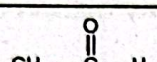
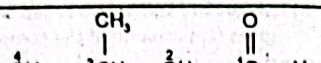
The IUPAC name is alkanol.

| | | |
|---|---|---|
| $CH_3—OH$ **methanol** | $CH_3—CH_2—CH_2—OH$ **propan-1-ol** | $CH_3—C(CH_3)_2—OH$ **2-methylpropan-2-ol** |

CamScanner

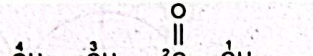
**3. Aldehydes ($C_nH_{2n}O$) ($-\overset{O}{\overset{\|}{C}}-H$)**

The IUPAC name is alkanal.

| | | |
|---|---|---|
|  methanal |  ethanal |  3-methylbutanal |

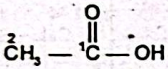
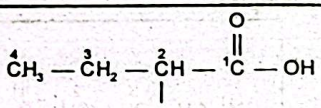
**4. Ketones ($C_nH_{2n}O$) ($-C-C-\overset{O}{\overset{\|}{C}}-$)**

The IUPAC name is alkanone

| | |
|---|---|
|  propanone |  pentpan-2-one |

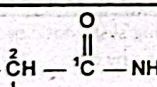
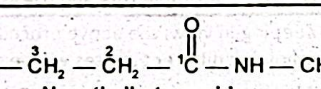
**5. Carboxylic acid ($C_nH_{2n}O_2$) ($-\overset{O}{\overset{\|}{C}}-OH$)**

The IUPAC name is alkanoic acid

| | | |
|---|---|---|
|  methanoic acid |  ethanoic acid |  2-methylbutanoic acid |

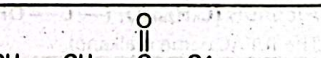
**6. Acid amides ($C_nH_{2n-1}ONH_2$) ($-\overset{O}{\overset{\|}{C}}-NH_2$)**

The IUPAC name is alkanamide.

| | | |
|---|---|---|
|  ethanamide |  2-methylpropanamide |  N-methylbutanamide<br>Any attachment to N-atom is named with an N-prefix. It does not get a number, just "N–" |

**7. Acid halides ($C_nH_{2n-1}OX$) ($-\overset{O}{\overset{\|}{C}}-X$)**

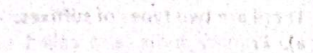
The IUPAC name is alkanoyl halides.

| | |
|---|---|
|  ethanoyl chloride |  propanoyl chloride |

**8. Esters ($C_nH_{2n}O_2$) ($-\overset{O}{\overset{\|}{C}}-O-C$)**

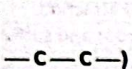
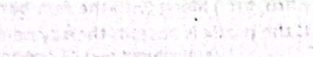
The IUPAC name is alkyl alkanoate.



| | | |
|---|---|---|
|  methyl ethanoate |  ethyl ethanoate |  propyl propanoate |

**9. Acid anhydrides ($-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$)**

The IUPAC name is alkanoic anhydride.

| | |
|---|---|
|  ethanoic anhydride |  ethanoic propanoic anhydride |

**10. Ethers ($C_nH_{2n+2}O$) ($-C-O-C-$)**

The IUPAC name is alkoxyalkane.

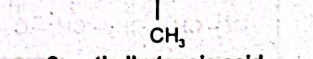
| | | |
|---|---|---|
| $CH_3-O-CH_3$ methoxymethane | $CH_3-O-CH_2-CH_3$ methoxyethane | $CH_3-CH_2-O-CH_2-CH_3$ Ethoxyethane |
|  1-methoxy-2-methylpropane | | |

**11. Amines ($C_nH_{2n+1}NH_2$)**

There are three types of amines.

**a) Primary Amines ($-C-NH_2$)**

The IUPAC name is Alkanamine.

| | | |
|---|---|---|
| $CH_3-CH_2-NH_2$ ethanamine |  propan-1-amine |  propan-2-amine |

**b) Secondary Amines ($-C-NH-R$)**

The IUPAC name is N-Alkylalkanamine

| | |
|---|---|
|  N-methylpropan-1-amine |  N-methylpropan-2-amine |

**c) Tertiary amines ($-C-\underset{\underset{R}{|}}{N}-R$)**

The IUPAC name may be (R = R) N, N - Dialkylakanamine or (R≠R)N - alkyl - N - alkyalkanamine.

| | |
|---|---|
|  N, N-dimethylpropan-1-amine |  N-ethyl-N-methylpropan-1-amine |

**12. Alkyl Cyanides ($C_nH_{2n-1}N$) ($-C\equiv N$)**

The IUPAC name is alkanenitrile. Here C of —CN is counted in main chain.

| | |
|---|---|
| $CH_3-CN$ ethanenitrile |  2-methylpropanenitrile |

CamScanner

**13. Nitroalkanes ($C_nH_{2n+1}NO_2$) (—C—$NO_2$)**

The IUPAC name is nitroalkane

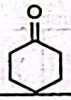
| | | |
|---|---|---|
| $CH_3—NO_2$ nitromethane | $\overset{3}{C}H_3—\overset{2}{C}H_2—\overset{1}{C}H_2—NO_2$ 1-nitropropane | $\overset{1}{C}H_3—\overset{2}{C}H(NO_2)—\overset{3}{C}H_3$ 2-nitropropane |

## QUICK CHECK 19.3

**a) What are the systematic names of the following?**

| | |
|---|---|
| i) $(CH_3)_3COH$ | ii) $CH_3CCl_3$ |
| Ans. Systematic Name: 2-Methylpropan-2-ol | Ans. Systematic Name: 1,1,1-Trichloroethane |
| iii) $CH_3-CH_2-CH_2-OH$ | iv) $CH_3COC_6H_5$ |
| Ans. Systematic Name: Propan-1-ol | Ans. Systematic Name: 1-Phenylethan-1-one |
| v) $CH_3-CH(CH_3)COOCH_3$ | |
| Ans. Systematic Name: Methyl 2-methylpropanoate | |

**b) Draw the structures of the following.**

| | |
|---|---|
| i) 2-methylbutanal: | ii) ethylpropanoate: |
| Ans. Structure: $CH_3-CH_2-CH(CH_3)-CHO$ | Ans. Structure: $H_3C—CH_2—C(=O)—O—CH_2—CH_3$ |
| iii) Phenylethanoic acid: | iv) Cyclohexanone: |
| Ans. Structure: $C_6H_5-CH_2-COOH$ | Ans. Structure:  |
| v) 3-Methylpentanal: | |
| Ans. Structure: $CH_3-CH_2-CH(CH_3)-CH_2-CHO$ | |

## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. According to IUPAC, organic chemistry is the study of:
   (A) All carbon-containing compounds (B) Only natural compounds
   (C) Only hydrocarbons (D) Hydrocarbons and their derivatives
2. Which one of the following is considered an inorganic carbon compound?
   (A) Ethanol (B) Benzene (C) Carbon dioxide (D) Methane
3. The ability of carbon atoms to link with one another is called:
   (A) Polymerization (B) Catenation (C) Hybridization (D) Isomerism
4. The unique diversity of carbon compounds is mainly due to:
   (A) High electronegativity (B) Tetravalency and catenation
   (C) Metallic character (D) Low ionization energy
5. Hydrocarbons are compounds containing only:
   (A) Carbon and oxygen (B) Carbon and nitrogen (C) Carbon and hydrogen (D) Carbon and sulphur
6. Open-chain hydrocarbons are also called:
   (A) Aromatic hydrocarbons (B) Alicyclic hydrocarbons (C) Aliphatic hydrocarbons (D) Heterocyclic hydrocarbons
7. Which of the following is a saturated hydrocarbon?
   (A) Ethene (B) Ethyne (C) Propene (D) Ethane
8. Benzene belongs to the class of:
   (A) Aliphatic hydrocarbons (B) Alicyclic hydrocarbons (C) Aromatic hydrocarbons (D) Saturated hydrocarbons
9. Cyclohexane is classified as:
   (A) Aromatic hydrocarbon (B) Alicyclic hydrocarbon (C) Alkyne (D) Alkene



10. A functional group is responsible mainly for the:
    (A) Characteristic chemical properties of a compound (B) Characteristic physical properties of a compound
    (C) Number of carbon atoms (D) Colour of a compound
11. Which functional group is present in alcohols?
    (A) –COOH (B) –CHO (C) –OH (D) $–NH_2$
12. Alcohols generally have higher boiling points than alkanes because of:
    (A) Ionic bonding (B) Hydrogen bonding (C) Metallic bonding (D) Covalent network bonding
13. In IUPAC nomenclature, the stem (root) indicates the:
    (A) Longest continuous carbon chain (B) Shortest continuous carbon chain
    (C) Side chain (D) Position of substituent
14. The primary suffix in IUPAC nomenclature indicates:
    (A) Functional group (B) Number of substituents
    (C) Saturation or unsaturation of the parent chain (D) Position of the side chain
15. The secondary suffix represents the:
    (A) Parent chain (B) Functional group (C) Number of carbon atoms (D) Alkyl substituent
16. Prefixes in IUPAC names indicate:
    (A) Functional groups only (B) Double bonds only (C) Number of hydrogen atoms (D) Substituents
17. The IUPAC family name for alcohols ends with:
    (A) –al (B) –one (C) –ol (D) –oic acid
18. The IUPAC family name for carboxylic acids ends with:
    (A) –amide (B) –oic acid (C) –al (D) –yl
19. Which functional group is present in aldehydes?
    (A) –COOH (B) –CHO (C) –OH (D) –CN

## REPRESENTING ORGANIC MOLECULES

**Q.7 How different types of formulae represent organic compounds?** LQ

Ans. There are different types of formulae which are used to represent organic compounds.

### 1. Empirical Formula

***The formula which represents the smallest whole number ratio of atoms of each element present in a compound is called empirical formula.***

For example, empirical formula of butane ($C_4H_{10}$) is $C_2H_5$, and for ethanoic acid (acetic acid, $C_2H_4O_2$) is $CH_2O$.

**Check Understanding!**
Q.5 Empirical formula of benzene is:
(A) $C_2H_5$ (B) $CH_2O$
(C) $C_3H_3$ (D) CH

### 2. Molecular Formula

***The formula which represents the actual number of atoms of each element present in a molecule of a compound is called molecular formula.***

For example, molecular formula of butane is $C_4H_{10}$, for acetic acid $C_2H_4O_2$ and that of ethanol is $C_2H_6O$. However, molecular formula gives no information about the sequence in which atoms are linked together as well as the nature of a functional group. That is why two different compounds may have the same molecular formula e.g., ethanol and methoxymethane are represented by same molecular formula i.e., $C_2H_6O$.

### 3. Structural Formula

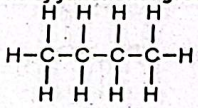
The structural formula not only shows the number of each kind of atom in the molecule but also the sequence in which atoms are joined together.

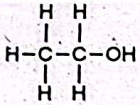
There are different types of structural formulae.

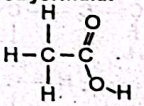
#### (a) Displayed formula (Graphical formula)

This formula is more complete and self-explanatory form of the structural formula.

***The formula which shows all the bonds between different atoms including the type of bonds as well as positions of functional groups in a molecule is called the displayed formula.***


butane


ethanol


ethanoic acid

CamScanner

### (b) Condensed Formula (Linear Formula)

***Displayed formula uses a lot of space, it is very often condensed in to a one - line structure called condensed or linear formula.*** In this kind of formula, single covalent bonds are omitted, however, branches, functional groups, double or triple bonds and separating methylene groups in the middle of the molecule are shown in brackets **e.g.,**

| $CH_3(CH_2)_2CH_3$ | $CH_3CH_2OH$ | $CH_3COOH$ |
|---|---|---|
| Butane | Ethanol | Ethanoic acid |

### (c) Skeletal Formula (Bond-line Formula)

Skeletal formula is the simplified version of displayed formula which can be used to represent more complex organic molecules.

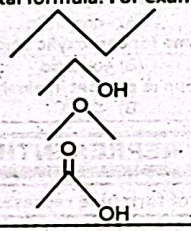
In skeletal formula, all the symbols of carbon and hydrogen atoms as well as the carbon to hydrogen bonds are removed. Bonds between carbon atoms are shown by single lines which meet at an angle. Each carbon is assumed to form enough C — H bonds to make a total of four bonds. Double and triple bonds as well as functional groups are shown in the skeletal formula. **For example:**

i) butane $CH_3 — CH_2 — CH_2 — CH_3$

ii) ethanol $CH_3 — CH_2 — OH$

iii) methoxymethane $CH_3 — O — CH_3$

iv) ethanoic acid $CH_3 — C(=O) — OH$

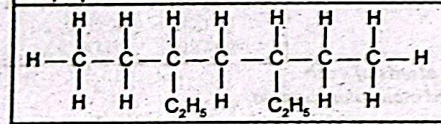
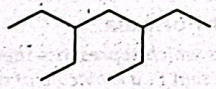



## QUICK CHECK 19.4

**a) Draw the displayed and skeletal formulae of the following:**

**i) 3,5-Diethylheptane**

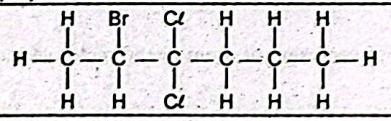
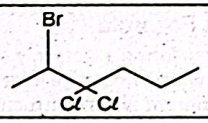
**Ans.**

| Displayed Formula | Skeletal Formula |
|---|---|
|  |  |

(Seven-carbon zigzag chain with ethyl ($-CH_2CH_3$) groups attached at C-3 and C-5.)

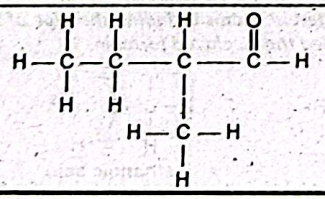
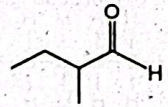
**ii) 2-Bromo-3,3-dichlorohexane**

**Ans.**

| Displayed Formula | Skeletal Formula |
|---|---|
|  |  |

**iii) 2-Methylbutanal**

**Ans.**

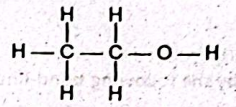
| Displayed Formula | Skeletal Formula |
|---|---|
|  |  |



**b) Draw the displayed and condensed structures of ethanol and methoxy methane, and explain whether they are isomers of the same molecule or not.**

**Ans. (i) Ethanol**

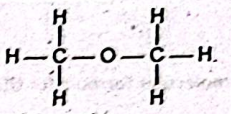
**Displayed Structure:**



**Condensed Formula:** $CH_3CH_2OH$

**(ii) Methoxy Methane (Dimethyl Ether)**

**Displayed Structure:**

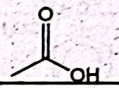


**Condensed Formula:** $CH_3OCH_3$

Yes. Ethanol and methoxy methane have the same molecular formula ($C_2H_6O$) but different functional groups. Ethanol is an alcohol and Methoxy methane is an ether. Therefore, they are functional group isomers.

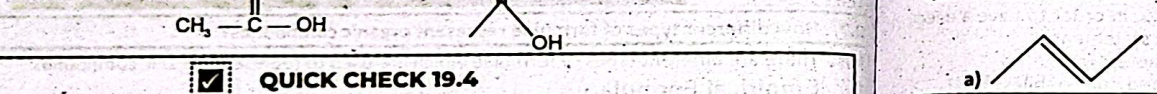
**c) Draw the skeletal formula of ethanoic acid ($CH_3COOH$).**

**Ans. Skeletal Formula of ethanoic acid**

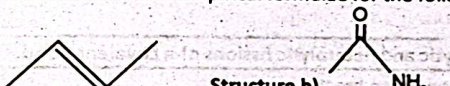



## DETERMINATION OF THE MOLECULAR FORMULA

**Q.8 How molecular and empirical formula of following two compounds are written?** L/Q




**Ans.** Let us write the molecular and empirical formulae for the following compounds.



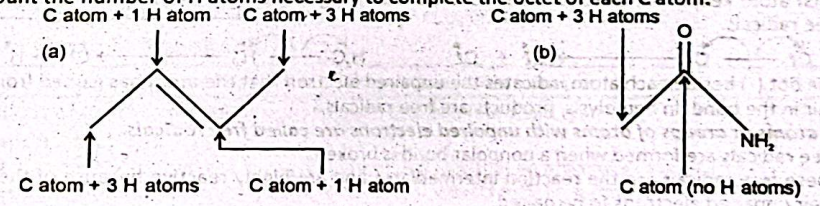

Structure a) Structure b)

**Check Understanding!**

**Q.6 Give molecular formulas of methoxymethane and ethanoic acid.**

Steps to find molecular formula

- Count the C atoms represented and the heteroatoms shown in the skeleton.
- Each line represents a bond and each joint shows a carbon atom. (Double lines represent double bonds). Count one C atom at the end of each line unless another atom is shown there.
- Count the number of H atoms necessary to complete the octet of each C atom:



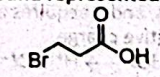

**Solution:**

**Structure a)** Molecular formula: $C_4H_8$: Empirical formula: $CH_2$.

**Structure b)** Molecular formula: $C_2H_5NO$: Empirical formula: $CH_3CONH_2$.

## QUICK CHECK 19.5

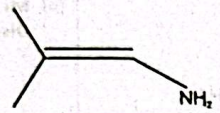
**a) Write molecular formula for the compound represented by the following bond-line structure:**



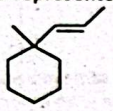

**Ans.** $C_3H_5BrO_2$

b) Draw the skeletal formula for $(CH_3)_2C = CHNH_2$

Ans.

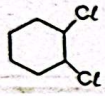



c) Write molecular formula for the compound represented by the following bond-line structure:

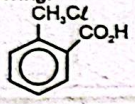


Ans. $C_{11}H_{20}$

d) Give the molecular formulate of the following.




(i)




(ii)

Ans. (i) $C_6H_{10}Cl_2$ (ii) $C_8H_7ClO_2$

## UNDERSTANDING ORGANIC REACTIONS

Since chemical reactions of organic compounds are complex in nature, therefore, in order to have a deep insight into their chemistry, we proceed further by keeping in view the following basic statements:

A. There are two ways in which a covalent bond can break, i.e., homolytic and heterolytic
B. There are basically three types of reagents, i.e., free radicals, electrophiles, and nucleophiles.
C. There are four generally types of organic reactions.

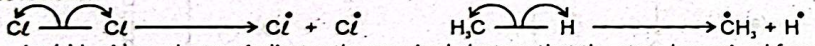
### A. Breaking of Covalent Bonds

**Q.9 Explain the difference between homolytic and heterolytic fissions of a covalent bond.** LQ

Ans. There are two ways in which covalent bonds can break:

**I. Homolytic Fission (Homolysis)**

- Homolytic fission occurs when the breaking bond is nonpolar.
- In this type of fission, the two shared electrons in the bond are distributed equally between the two atoms.
- Each atom keeps one electron from bond pair. So we get two free radicals.



- The dot (·) beside each atom indicates the unpaired electron that the atom has gained from the shared pair in the bond. In hemolysis, products are free radicals.

***These atoms or groups of atoms with unpaired electrons are called free radicals.***

- Free radicals are formed when a nonpolar bond is broken.
- These free radicals are the reaction intermediates and are highly reactive because of the tendency of their unpaired electrons to be paired.
- Free radicals have short life times.

**Check Understanding!**

Q.7 Homolytic fission of $Cl_2$ results in the formation:
(A) Two $Cl^•$ (B) $Cl^• + Cl^+$
(C) $Cl^• + Cl^-$ (D) Two $Cl^-$

**II. Heterolytic Fission (Heterolysis)**

Heterolytic fission occurs when the breaking bond is polar.

- Heterolytic fission occurs when the breaking bond is polar.
- In this type of fission, the two shared electrons in the bond are distributed unequally (unequal split) between the two atoms.
- One of the atoms keeps both electrons, and it acquires a negative charge. The other atom is deficient in one electron and, thus, acquires a positive charge.

$$HCl \longrightarrow H^+ + Cl^-$$

$$(CH_3)_3C - Cl \xrightarrow{Slow} (CH_3)_3C^+ + Cl^-$$

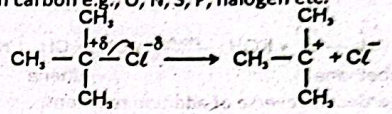


Here both electrons go to chlorine atoms and becomes an anion.

**III. Carbocation Formation**

A species which contains a carbon atom with a positive charge is known as carbocation:
Carbocation is formed when carbon is bonded to a heteroatom whose electronegativity is more than carbon e.g., O, N, S, P, halogen etc.

Carbanion is formed when carbon is bonded to a heteroatom (metal) whose electronegativity is lesser than carbon e.g. Li, Mg, Cd etc.



### B) Types of Reagents

**Q.10 Discuss the type of reagent with examples:** LQ
**I. Free radical ii. Electrophile iii. Nucleophile**

Ans. A chemical reaction between two reactants may be regarded as the attack of one species on the other. In this case, the attacking species is called reagent and the species which is undergoing attack is called the substrate.

**I. Free Radical**

An atom or group of atoms having an unpaired electron are called free radicals.
**Examples:** $Cl^•, H^•, CH_3^•, CH_3COO^•$ etc.

**ii. Electrophile**

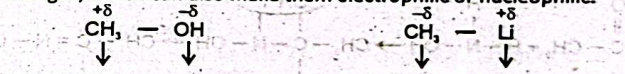
An atom or group of atoms that is able to accept a pair of electrons to form a new bond is called an electrophile. Electrophiles (electron lovers) are either positive ions (including carbocations) or neutral molecules. **Examples:** $CH_3^+, H^+, Br^+, NO_2^+, SO_3, BF_3$ etc.

**iii. Nucleophile**

An atom or group of atoms that is able to donate a pair of electrons to form a new bond is called nucleophile. Nucleophiles (nucleus lovers) are either negative ions (including carbanions) or neutral molecules. π-electron systems like alkenes ($CH_2 = CH_2$), Alkynes ($HC \equiv CH$) also act as nucleophiles.

**Examples:** $CH_3^-, Br^-, OH^-, CN^-, NH_3, H_2\ddot{O}, R\ddot{O}H$ etc.

**Note:** The terms electrophilic and nucleophilic do not apply only to ions. Many organic compounds are polar; they carry partial charges, which can also make them electrophilic or nucleophilic.



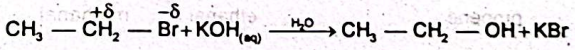

### C. Types of Organic Reactions

**Q.11 Classify the four main types of organic reactions with suitable examples.** LQ

Ans. The reactions of organic compounds can be classified into four main types:

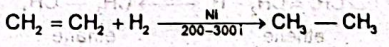
**I. Substitution Reactions**

In substitution reactions, two reactants react in such a way that an atom or group of atoms in one molecule is replaced by another atom or group of atoms. Two products may be formed.
**Example:**




**II. Addition Reactions**

In addition reactions, two reactants react to produce a single product.
**Examples:**




CamScanner

$$CH_2 = CH - CH_3 + \overset{+\delta}{H} - \overset{-\delta}{Br} \longrightarrow CH_3 - CH_2 - CH_2 - Br$$

propene bromopropane

**iii. Elimination Reactions**

In elimination reactions, removal of atoms or groups of atoms from two adjacent atoms in the substrate molecule occurs to form a multiple bond.

**Example:**

$$CH_3 - \overset{+\delta}{CH_2} - \overset{-\delta}{Br} + KOH \xrightarrow{\text{alcohol}} CH_2 = CH_2 + KBr + H_2O$$

bromoethane ethene

Elimination reactions are regarded as reverse of addition reactions.

**iv. Rearrangement Reactions**

In rearrangement reaction, migration of an atom or group of atoms from one site to another within the same molecule takes place and nothing is lost or gained.

$$CH_3 - (CH_2)_6 - CH_3 \xrightarrow[\text{Catalyst}]{\text{Heat}} CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - CH_2 - \underset{CH_3}{CH} - CH_3$$

n-octane 2,2,4 – trimethylpentane (isooctane)

**a) Hydrolysis**

In hydrolysis, a compound breaks into two on reaction with water often helped by $H^+$ or $OH^-$ as catalyst.

**Example:**

$$CH_3 - \overset{O}{\overset{\|}{C}} - O - CH_2 - CH_3 + H_2O \xrightarrow{H^+} CH_3 - \overset{O}{\overset{\|}{C}} - OH + CH_3 - CH_2 - OH$$

ethyl ethanoate ethanoic acid ethanol

**b) Condensation Reactions**

In condensation reactions two molecules combine to form a bigger molecule with or without loss of a small molecule like $H_2O$, $NH_3$, $HCl$ etc.

**Example:**

$$CH_3 - \overset{O}{\overset{\|}{C}} - CH_3 + H - \underset{H}{N} - OH \longrightarrow CH_3 - \underset{CH_3}{\overset{OH\ H}{C}} - N - OH \longrightarrow CH_3 - \underset{CH_3}{C} = N - OH + H_2O$$

propanone hydroxylamine propanoneoxime

**c) Oxidation**

Loss of electron is called oxidation. Moreover, if a molecule gains oxygen or loses hydrogen or there increase in number of bonds of carbon with oxygen or increase in oxidation state of carbon, it is oxidized.

**Example:**

$$CH_3 - CH = CH_2 \xrightarrow[Zn/H_2O]{O_3} CH_3 - \overset{O}{\overset{\|}{C}} - H + H - \overset{O}{\overset{\|}{C}} - H$$

propene ethanal methanal

**d) Reduction**

Reduction is a reaction where gain of electron, loss of oxygen or gain of hydrogen, or a decrease in t number of bonds of carbon with oxygen or decrease in oxidation state of carbon occurs.

**Example:**

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$$

ethene ethane



# MECHANISMS OF CHEMICAL REACTIONS

**Q.12 Describe the two mean types of organic reactions mechanisms.** U/O
**OR Write a note on: (A) free radical mechanism. (B) Ionic or polar mechanism.** U/O

**Ans. Mechanism:**

**A mechanism is the pathway adapted by a reaction showing the breaking and making of bonds in the substrate leading to the formation of the product.**

Depending upon the nature of reagents, reaction mechanisms are divided into two main types.

A. Free radical mechanism B. Ionic or polar mechanism

**Check Understanding!**
**Q.8 Name the three steps involved in free radical mechanism.**

## A) Free Radical Mechanism

It involves homolysis during which free radicals are produced which attack the substrate molecule e.g.

$$CH_4 + 4Cl_2 \xrightarrow{\text{Diffused Sunlight}} CCl_4 + 4HCl$$

This reaction proceeds through the free radical mechanism.

**(i) Initiation Step:** The reaction involves initiation where initial free radicals are produced.

**(ii) Propagation:** These radicals then attack the substrate and generate more radicals in the propagation step.

**(iii) Termination Step:** Finally, the reaction terminates by combining the free radicals of the same or different types.

**Initiation ⟶ Propagation ⟶ Termination**

## B) Ionic or Polar Mechanism

It involves heterolysis, during which electrophiles and nucleophiles are produced, which may attack polar substrate molecules. The polar mechanism is further divided into the following types.

**I. Nucleophilic Substitution Reactions**

In $S_N$ reactions, a nucleophile attacks on a saturated electrophilic carbon and substitutes another nucleophile called leaving group e.g., **In $S_N2$ reaction mechanism:**

$$H - \bar{O}: + \underset{H}{\overset{H}{C}} - \overset{+\delta}{C} - \overset{-\delta}{Br} \longrightarrow \left[ HO \overset{-\delta}{---} \underset{H}{\overset{H}{C}} \overset{+\delta}{---} Br^{-\delta} \right]^{(-)} \longrightarrow H - O - \underset{H}{\overset{H}{C}} + :Br^-$$

nucleophile bromomethane transition state methanol leaving group

**II. Nucleophilic Addition Reactions**

In this type of reactions, a nucleophile attacks on electrophilic carbon of a carbonyl compound to give addition product e.g.,

$$N \equiv \bar{C}: + \overset{O^{-\delta}}{\overset{\|}{C}}{}^{+\delta} \longrightarrow N \equiv C - \underset{CH_3}{\overset{:\bar{O}:}{C}} - H \xrightarrow[H-CN]{+\delta\ -\delta} N \equiv C - \underset{CH_3}{\overset{OH}{C}} - H + :CN^-$$

ethanal 2-hydroxy propanenitrile

**III. Electrophilic Addition Reactions**

In this type of reaction, an electrophile attacks on an electron rich position (nucleophilic) like carbon-carbon double or triple bond e.g.,

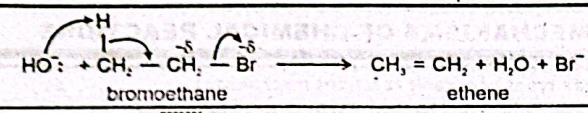
$$H_2C = CH_2 + \overset{+\delta}{H} - \overset{-\delta}{Br} \longrightarrow CH_3 - CH_2 - Br$$

ethene bromoethane

**IV. Elimination Reactions**

In this type of reaction, two atoms or groups are removed from two adjacent carbon atoms in a molecule. The removal results in the formation of a double or a triple bond.

CamScanner




## QUICK CHECK 19.6

**a) Describe each of the following as electrophile, nucleophile or free radical.**

i) $NH_3$ ii) $Br^•$ iii) $H_2O$ iv) $NO_2^⊕$ v) $C\ell^+$

Ans.

| Species | Classification | Reason |
|---|---|---|
| i) $NH_3$ | Nucleophile | It contains a lone pair of electrons and donates an electron pair. |
| ii) $Br^•$ | Free Radical | It has one unpaired electron. |
| iii) $H_2O$ | Nucleophile | Oxygen has two lone pairs of electrons that can be donated. |
| iv) $NO_2^+$ | Electrophile | It is electron-deficient and accepts an electron pair. |
| v) $C\ell^+$ | Electrophile | It is positively charged and seeks electrons. |

**b) Classify each of these reactions as addition, substitution, elimination or rearrangement.**

(i) $CH_3CH = CH_2 + HBr \longrightarrow CH_3CHBrCH_3$

(ii) $CH_4 + Br_2 \longrightarrow CH_3Br + HBr$

(iii) $CH_3CH_2CHC\ell CH_3 \longrightarrow CH_3CH_2CH = CH_2 + HC\ell$

Ans. (i) $CH_3CH = CH_2 + HBr \longrightarrow CH_3CHBrCH_3$ **(Addition Reaction)**
**Reason:** HBr adds across the C=C double bond of propene.

(ii) $CH_4 + Br_2 \longrightarrow CH_3Br + HBr$ **(Substitution Reaction)**
**Reason:** A hydrogen atom of methane is replaced by a bromine atom.

(iii) $CH_3CH_2CHC\ell CH_3 \longrightarrow CH_3CH_2CH = CH_2 + HC\ell$ **(Elimination Reaction)**
**Reason:** $HC\ell$ is removed from the molecule to form an alkene.

**c) Classify the following reactions into one (or more) of the following six categories: Substitution, addition, hydrolysis, reduction, condensation, oxidation.**

(i) $(CH_3)_2C = O + H_2N - NH_2 \longrightarrow (CH_3)_2C = N - NH_2 + H_2O$

(ii) $CH_3CHO + 2[H] \longrightarrow CH_3CH_2OH$

Ans. (i) $(CH_3)_2C = O + H_2N - NH_2 \longrightarrow (CH_3)_2C = N - NH_2 + H_2O$ **(Condensation Reaction)**
**Reason:** Two molecules combine with the elimination of one molecule of water.

(ii) $CH_3CHO + 2[H] \longrightarrow CH_3CH_2OH$ **(Reduction Reaction)**
**Reason:** Ethanal gains hydrogen to form ethanol.

## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **A molecular formula represents:**
(A) The arrangement of atoms only (B) The actual number of atoms of each element in a molecule
(C) The smallest whole-number ratio of atoms (D) Only the carbon atoms present

2. **The empirical formula of a compound shows:**
(A) The exact molecular structure (B) The actual number of atoms
(C) The simplest whole-number ratio of atoms (D) The displayed structure

3. **Which type of formula shows all atoms and all covalent bonds?**
(A) Molecular formula (B) Condensed formula
(C) Displayed (graphical) formula (D) Skeletal formula

4. **In a skeletal formula:**
(A) Every carbon atom is written explicitly. (B) Carbon and hydrogen symbols attached to carbon are omitted.
(C) Oxygen atoms are omitted. (D) Functional groups are omitted.

5. **Which formula gives information about the sequence of atoms joined together?**
(A) Molecular formula (B) Empirical formula (C) Structural formula (D) Atomic formula

6. **During homolytic fission, the shared electron pair is:**
(A) Transferred completely to one atom (B) Shared unequally
(C) Divided equally between both atoms (D) Lost completely

7. **Homolytic fission produces:**
(A) Carbocations (B) Carbanions (C) Free radicals (D) Electrophiles only



8. **Heterolytic fission generally occurs in:**
(A) Non-polar covalent bonds (B) Polar covalent bonds (C) Metallic bonds (D) Ionic bonds

9. **In heterolytic fission, one atom receives:**
(A) No electrons (B) One electron (C) Both bonding electrons (D) Two protons

10. **A carbocation carries:**
(A) A negative charge on carbon (B) A positive charge on carbon
(C) No charge (D) A positive charge on hydrogen

11. **Which species donates an electron pair to form a bond?**
(A) Electrophile (B) Nucleophile (C) Free radical (D) Catalyst

12. **An electrophile is an electron:**
(A) Donor (B) Acceptor (C) Pair (D) Radical

13. **Which of the following is a nucleophile?**
(A) $NO_2^+$ (B) $BF_3$ (C) $OH^-$ (D) $H^+$

14. **Which of the following is an electrophile?**
(A) $CN^-$ (B) $NH_3$ (C) $Br^•$ (D) $OH^-$

15. **In a substitution reaction:**
(A) Two molecules combine into one. (B) One atom or group replaces another.
(C) Water is removed. (D) A double bond is formed only.

16. **Hydrogenation of ethene to ethane is an example of:**
(A) Substitution reaction (B) Addition reaction (C) Elimination reaction (D) Hydrolysis

17. **Elimination reactions generally result in the formation of:**
(A) Saturated compounds (B) Multiple bonds (C) Free radicals only (D) Esters only

18. **Hydrolysis involves reaction with:**
(A) Oxygen (B) Hydrogen (C) Water (D) Chlorine

19. **Which reaction combines two molecules to form a larger molecule with the loss of a small molecule such as $H_2O$?**
(A) Oxidation (B) Hydrolysis (C) Condensation (D) Reduction

20. **Nucleophilic substitution occurs when a nucleophile attacks:**
(A) An aromatic ring only (B) A saturated electrophilic carbon atom
(C) A free radical (D) A carbon-carbon double bond

## ISOMERISM

**Q.13 Define isomerism. What are the two types?** S/Q

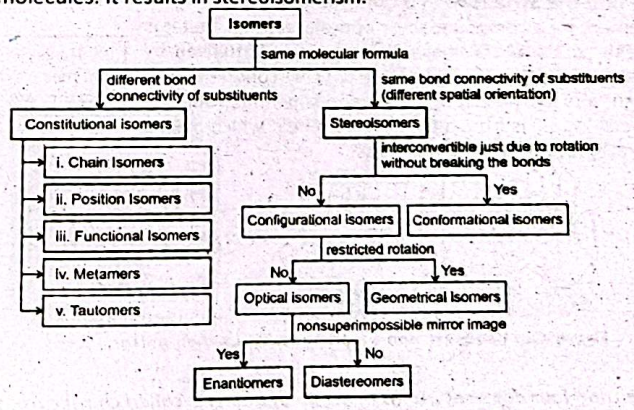
***"Two or more than two compounds which have same molecular formula but different properties are called isomers and the phenomenon is called isomerism."***

The two main types of isomerism of organic compounds.

**Check Understanding!**
**Q.9 Number of isomers of $C_4H_{10}$ is:**
(A) 1 (B) 2
(C) 3 (D) 4

1. **Constitutional Isomerism:** When same atoms or groups are connected at different places in two or more molecules, it results in structural or constitutional isomerism.
(**Note:** This type of isomerism has been discussed earlier in Chemistry 11)

2. **Stereoisomerism:** When the atoms or groups have the same connectivity but different spatial arrangement in two or more molecules. It results in stereoisomerism.




CamScanner

## Stereoisomerism

Stereoisomers are further divided into two types. a) Optical isomers b) Cis-trans isomers

### Optical Isomers:

**Q.14 What are the optical isomers? Who are the measured?** S/Q

**Ans. Optical Isomers:**

- **Optical Isomers are the stereoisomers that differ in their ability to rotate the plane of polarised light.** Such isomers are said to be optically active and this property of these isomers of rotating the plane of polarization is called optical activity.
- **Measurement:** Optical activity is measured by polarimeter. Optical activity of a compound is identified by using plane polarised light (PPL).
- **Rotation of Plane polarized light:** If the compound rotates the plane of polarised light to right (clockwise), it is called dextrorotatory indicated by symbol (+) and if it rotates the plane to left (anticlockwise), it is called levorotatory indicated by the symbol (–).

Enantiomers have same physical properties like m.pt, b.pt, density, solubility in achiral solvents and chemical reactivity with achiral reagents. Enantiomers rotate PPL (Plane Polarised Light) in equal but opposite direction and they may react differently with chiral reagents, enzymes or other biological systems.

**Keep in Mind**

A polarimeter is used to identify and measure quantitively the optical activity of a compound by using PPL. PPL is a monochromatic light having single wavelength which moves only in one plane. A solution of the compound under investigation is placed before PPL. If the compound rotates the PPL, it is optically active and if not, it is optically inactive.

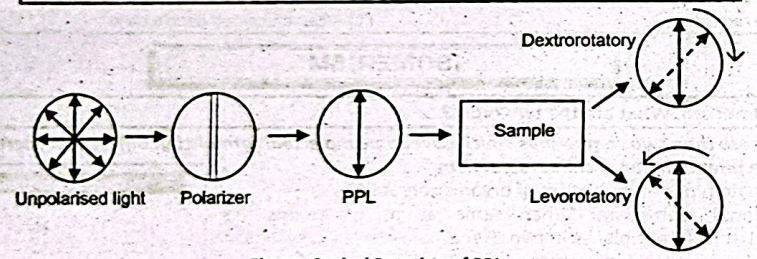



**Figure: Optical Rotation of PPL**

**Q.15 Describe the phenomenon of optical activity. Explain with an example.** Exercise D/Q.6

**Ans. Optical Activity and the Structure of a Compound:**

The basic requirement for a compound to be optically active is that it is non-superimposable on its mirror image. This condition is fulfilled by asymmetric/chiral molecules. It can be understood by considering an analogy of our right and left hands, which are non-superimposable (as in Figure). The word 'chiral' is from a Greek word 'Cheir' which means hand. Hence, chirality is also called handedness.

Molecules which are superimposable on their mirror images are achiral and they are optically inactive.




**Figure: Our hands are non-superimposable on their mirror images.**

### Chiral Carbon:

***A carbon atom bearing four different atoms or group of atoms is called chiral carbon.***

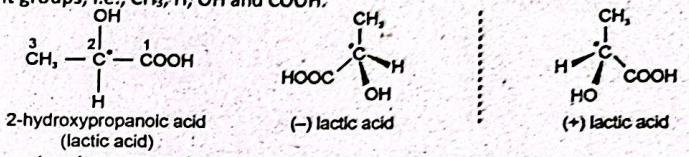


Any organic molecule which is not symmetric and it rotates the plane polarised light is a chiral or asymmetric molecule. If a molecule has only one chiral carbon atom, it is always asymmetric and hence optically active. However, if there are more than one chiral atoms, a molecule may or not be asymmetric and optically active.

### Enantiomers:

If a molecule has only one chiral carbon atom, it is always chiral and hence optically active.

**For example** consider the structure of lactic acid. It has a chiral carbon (indicated by an asterisk) bonded to four different groups, i.e., $CH_3$, H, OH and COOH.

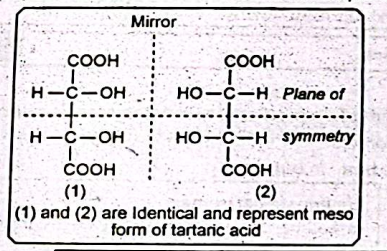



Its three dimensional structure shows that it has two stereoisomers which are non-superimposable mirror image of each other and are called enantiomers ('enantio' means opposite). The enantiomers have identical physical and chemical properties but they rotate the plane of polarised light in opposite directions, with the same extent. One enantiomer is, therefore, dextrorotatory (+) and the other is levorotatory (–). When 50% dextrorotatory and 50% levorotatory enantiomers are present, they form an optically inactive mixture. Such a mixture is called a **racemic mixture**. A racemic mixture is symbolized by placing symbol (±) in front of the name of the compound. Thus, lactic acid exists in two different optically active forms i.e., (+) lactic acid, (–) lactic acid and an inactive racemic mixture (±).

### Meso Isomers

The stereoisomers which contain at least two similar chiral carbon atoms and also possess a plane of symmetry are optically inactive. The plane of symmetry divides the molecule into two equal halves, one half of the molecule being mirror image of the other half. The two halves will rotate the plane of polarised light in opposite direction. As a result, rotation of one half of molecule is internally compensated (cancelled) by the other half and the molecule will become optically inactive. Such stereo isomers are called meso forms.

**Example:** Tartaric acid is the classic example of this phenomenon.




(1) and (2) are Identical and represent meso form of tartaric acid

**Interesting Information**

| Object | Classification | Reason |
|---|---|---|
| Shoe | Chiral | A left shoe and a right shoe are mirror images but cannot be superimposed. |
| Ear | Chiral | Left and right ears are non-superimposable mirror images. |
| Foot | Chiral | Left and right feet are mirror images but not superimposable. |

Maximum number of optical isomers of an optically active compound is given by the formula $2^n$, where 'n' is the number of chiral carbon atoms. This number is reduced, however, if there are two or more similar chiral carbon atoms.

### QUICK CHECK 19.7

**Q1: Classify the following objects as chiral or achiral.**
**i) Pencil ii) Book iii) Cup iv) Spoon**

**Ans.**

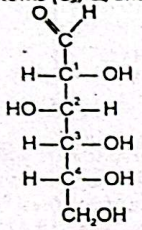
| Object | Classification | Reason |
|---|---|---|
| i) Pencil | Achiral | It has symmetry and is superimposable on its mirror image. |
| ii) Book | Achiral | It possesses a plane of symmetry. |
| iii) Cup | Achiral | Normal cup with one handle is symmetrical and superimposable on its mirror image. |
| iv) Spoon | Achiral | It has a plane of symmetry. |

CamScanner

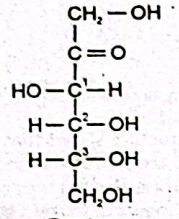
**Q2: Glucose and fructose are two monosaccharides.**
**i. How many chiral carbon atoms are there in glucose and fructose?**
**ii. Calculate the possible number of optical isomers of glucose and fructose.**
**iii. Is there any meso form in glucose or fructose? Give reason.**

**Ans.**

**(i)** **Glucose:** 4 chiral carbon atoms ($C_2$, $C_3$, $C_4$ and $C_5$)
**Fructose:** 3 chiral carbon atoms ($C_3$, $C_4$ and $C_5$)



**Glucose**
**(open chain form)**
**4-Chiral Centres**



**Fructose**
**(open chain form)**
**3-Chiral Centres**

**(ii)** The number of optical isomers is calculated by the formula:
Number of optical isomers = $2^n$, where n = number of chiral carbon atoms.
**Glucose:**
Number of chiral carbons = 4 Possible optical isomers = $2^4 = 16$
**Fructose:**
Number of chiral carbons = 3 Possible optical isomers = $2^3 = 8$

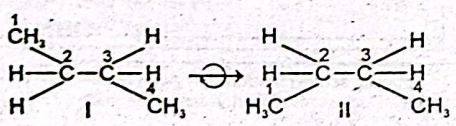
**(iii)** **No, neither glucose nor fructose has a meso form.**
**Reason:** A meso compound must contain two or more chiral carbon atoms and an internal plane of symmetry. Although glucose and fructose have multiple chiral carbon atoms, they do not possess an internal plane of symmetry. Therefore, they do not exhibit meso forms.

**Q.16 Discuss cis-trans isomerism. Explain with two examples.** Exercise D/Q.5

**Ans. Cis-trans Isomerism**

***The stereoisomers having different spatial arrangement of atoms due to restricted rotation about a double bond in open chain compounds are called cis-trans isomers.***

First of all we consider free rotation about C – C single bond in butane.

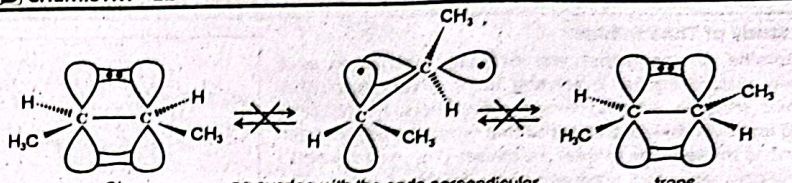


**Confirmational Isomers:**
In butane, forms I or II are called conformational isomers because they are interconvertable into each other due to free rotation of the C – C single bond. They cannot be separated at room temperature.

When the C – C single bond between C – 2 and C – 3 atoms rotates, the methyl groups also rotate and structure I changes in II and II back into I due to this free rotation.

**Example But-2-ene:** Consider but-2-ene, $\overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_3$, in which both carbon atoms 2 and 3 are $sp^2$ hybridized. The C – C double bond consists of a σ bond formed by the linear overlap of $sp^2$ hybrid orbitals and a π bond formed by the parallel overlap of p orbitals. The presence of π bond locks the molecule in one position. The two carbon atoms C – 2 and C – 3 of the double bond and all the groups attached to them lie in the same plane and their position in space is fixed. For free rotation around the C – C double bond, π bond should be broken first. It requires energy equal to 263 kJ/mol, which is not possible at room temperature. The rotation about C – C double bond is therefore restricted. This restriction of rotation about the C – C double bond is responsible for the cis-trans isomerism (Figure).

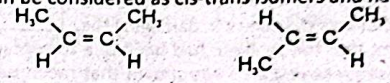




Cis no overlap with the ends perpendicular trans

**Figure: The two isomers of but-2-ene cannot interconvert by rotation about the C–C double bond without breaking the π bond**

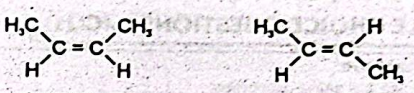
Now the above structures can be considered as cis-trans isomers and named as follows:



Cis-but-2-ene trans-but-2-ene

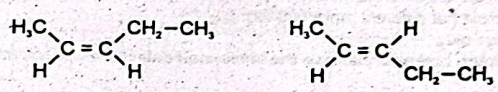
- **cis-Isomer:** The cis isomer is one in which two similar groups are on the same side of the double bond.
- **trans-Isomer:** The trans isomer is that in which two similar groups are on the opposite side of the double bond.

**Example 1:**



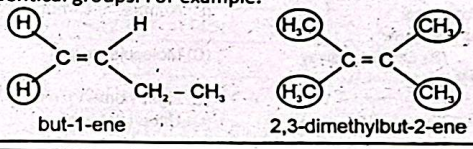
cis-but-2-ene trans-but-2-ene

**Example 2:**



cis-pent-2-ene trans-pent-2-ene

**Note:** It is important to note that cis-trans isomerism will not be possible, if one of the unsaturated carbon atom is bonded to two identical groups. For example:



but-1-ene 2,3-dimethylbut-2-ene

**KEEP IN MIND**
The cis-trans isomers have different physical and chemical properties. The trans isomers are more stable than the corresponding cis isomers and hence differ in chemical reactivity. Similarly, both types of isomers have different physical properties like melting point, boiling point, dipole moment, density, heat of vapourisation etc.

Each of the above two compounds does not show cis-trans isomerism.

➢ **Necessary Condition:**
Thus for an open chain compound the necessary and sufficient condition to show cis-trans isomerism is that, it should have double bond in its molecule and that two different groups must be attached to each of the doubly bonded carbon atoms.

## STEREOCHEMISTRY IN DRUG DEVELOPMENT

**Q.17 Discuss the role of stereochemistry in drug development.** L/Q

**Ans.** In the synthesis of pharmaceutical products chirality is a critical feature to determine safety and efficacy. Because biological systems are composed of chiral building block drug receptors which function as highly specific "chiral locks". As a result, the two enantiomers of a chiral drug often exhibit very different potentials and profiles.

CamScanner

### ➢ Case Study of Thalidomide:

Thalidomide, a tranquilliser was originally distributed as a racemic mixture Figure. It seemed to be a very successful, nontoxic sedative with no known side-effects. In the early 1960s, however, it was discovered that women who had been prescribed the sedative to treat the nausea ('morning sickness') in early pregnancy had produced badly deformed babies. The drug was immediately withdrawn.

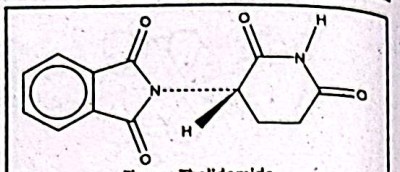


Figure: Thalidomide

**Check Understanding!**

**Q.10 Is Egg chiral orachiral?**

### ➢ Inferences from Reasearch:

Research showed that while the (+) isomer was an effective and safe tranquilliser, the (–) isomer was the culprit in damaging the fetus. Originally it was thought that the problem had been due to contamination by the (–) isomer in some production batches, but subsequent research has shown that racemisation of the pure (+) isomer occurs rapidly as soon as it enters the blood stream. Within 10 minutes racemisation is over 50% complete. Thalidomide will never be marketed again, although analogues, that are chirality stable are being investigated as possible antiinflammatory drugs.

## BLOCK # 03 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Isomers are compounds that have:**
   (A) Different molecular formulae but same properties
   (B) Same molecular formula but different arrangement of atoms
   (C) Same structural formula but different molecular formula
   (D) Same molecular mass only
2. **The phenomenon in which compounds have the same molecular formula but different arrangements of atoms is called:**
   (A) Hybridization (B) Catenation (C) Isomerism (D) Polymerization
3. **Stereoisomers differ in:**
   (A) Molecular formula (B) Bond connectivity
   (C) Spatial arrangement of atoms (D) Number of carbon atoms
4. **A polarimeter is used to measure:**
   (A) Boiling point (B) Optical activity (C) Molecular mass (D) Dipole moment
5. **Plane-polarized light (PPL) is:**
   (A) White light (B) Light vibrating in all planes
   (C) Monochromatic light vibrating in one plane (D) Ultraviolet light
6. **A compound that rotates the plane of polarized light to the right is called:**
   (A) Levorotatory (–) (B) Dextrorotatory (+) (C) Racemic (D) Achiral
7. **A carbon atom attached to four different atoms or groups is called:**
   (A) Carbonyl carbon (B) Aromatic carbon (C) Chiral (asymmetric) carbon (D) Allylic carbon
8. **A molecule that is non-superimposable on its mirror image is:**
   (A) Achiral (B) Symmetrical (C) Chiral (D) Planar
9. **Two mirror-image stereoisomers are known as:**
   (A) Tautomers (B) Diastereomers (C) Enantiomers (D) Metamers
10. **A racemic mixture contains:**
    (A) Only dextrorotatory isomers (B) Only levorotatory isomers
    (C) Equal amounts of (+) and (–) enantiomers (D) Only meso compounds
11. **A meso compound is optically inactive because it possesses:**
    (A) No carbon atoms (B) A plane of symmetry (C) Only one chiral carbon (D) Only double bonds
12. **The maximum number of optical isomers for a molecule containing n chiral carbon atoms is:**
    (A) $n^2$ (B) 2n (C) $2^n$ (D) n!
13. **Cis–trans isomerism arises due to restricted rotation about:**
    (A) C–C single bond (B) C–H bond (C) C=C double bond (D) O–H bond
14. **Which compound can exhibit cis–trans isomerism?**
    (A) But-1-ene (B) Ethane (C) But-2-ene (D) Methane
15. **In the cis isomer, similar groups are located:**
    (A) On opposite sides of the double bond (B) On the same side of the double bond
    (C) At right angles to each other (D) Randomly arranged



16. **The trans isomer generally is:**
    (A) Less stable than the cis isomer (B) More reactive in every reaction
    (C) Optically active only (D) More stable than the cis isomer
17. **Cis–trans isomerism is not possible if:**
    (A) A carbon-carbon double bond is present (B) Each doubly bonded carbon has two different groups
    (C) One doubly bonded carbon has two identical groups (D) The molecule is unsaturated
18. **Which type of isomerism is due to different spatial arrangements of groups without changing bond connectivity?**
    (A) Chain isomerism (B) Functional isomerism (C) Stereoisomerism (D) Position isomerism
19. **Chirality is especially important in pharmaceuticals because:**
    (A) All enantiomers have identical biological effects, so show same biological activities.
    (B) Drug receptors are chiral, so enantiomers may show different biological activities.
    (C) Chiral drugs always have higher melting points, so become significant.
    (D) Only achiral drugs are safe.

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

**BLOCK # 01**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. D | 2. C | 3. B | 4. B | 5. C | 6. C | 7. D | 8. C | 9. B | 10. A | 11. C | 12. B | 13. A | 14. C | 15. B |
| 16. D | 17. C | 18. B | 19. B | | | | | | | | | | | |

**BLOCK # 02**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. C | 4. B | 5. C | 6. C | 7. C | 8. B | 9. C | 10. B | 11. B | 12. B | 13. C | 14. C | 15. B |
| 16. B | 17. B | 18. C | 19. C | 20. B | | | | | | | | | | |

**BLOCK # 03**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. C | 4. B | 5. C | 6. B | 7. C | 8. C | 9. C | 10. C | 11. B | 12. C | 13. C | 14. C | 15. B |
| 16. D | 17. C | 18. C | 19. B | | | | | | | | | | | |

## CHECK UNDERSTANDING (SOLUTIONS)

| Q. # | Option | Hint/Explanation |
|---|---|---|
| 1. | (C) | Amides is the functional group in urea. |
| 2. | S/Q | Benzene and methylbenzene. |
| 3. | (C) | $-CONH_2$ is the functional groups of acid amides (alkanamide) |
| 4. | S/Q | (a) Primary suffix, also called suffix of stem or root.<br>(b) Secondary suffix, also called suffix of the key functional group. |
| 5. | (D) | Molecular formula of benzene = $C_6H_6$ so where n = 6 and its empirical formula becomes CH. |
| 6. | S/Q | Methoxymethane = $C_2H_6O$ and ethanoic acid = $C_2H_4O$ |
| 7. | (A) | $Cl-Cl \longrightarrow Cl^{\bullet} + Cl^{\bullet}$ |
| 8. | S/Q | Initiation ⟶ Propagation ⟶ Termination |
| 9. | (B) | Butane has two chain isomers (constitutional isomers). |
| 10. | S/Q | Egg is Achiral because it has no handedness and is superimposable on its mirror image. |

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. **Which of the following is organic in nature?**
   a) $CO_2$ b) $CS_2$ c) HCN d) $CHCl_3$

II. **The empirical formula of $CH_3CH_2CH = CH_2$ matches with:**
   a) $CH_3CH_3$ b) $CH_2 = CHCH_3$ c) $CH_3CH_2CH_2CH_3$ d) $CH \equiv CH$

CamScanner

III. Compounds having single bonds may undergo reactions:
a) addition only b) elimination only
c) substitution only d) both elimination and substitution

IV. The functional group present in urea ($H_2N-\overset{O}{\overset{\|}{C}}-NH_2$) is:
a) carbonyl b) amino c) amide d) all of these

V. Which molecule is chiral and can rotate the plane polarised light?
a) Pentan-1-ol b) Pentan-2-ol c) 2,2-dimethylpropan-1-ol d) 2-methylbutan-2-ol

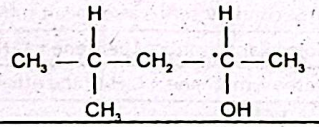
VI. Which carbon in $CH_3CH(CH_3)CH_2CH(OH)CH_3$ is chiral?
a) C – 1 b) C – 2 c) C – 3 d) C – 4

VII. In what ways could two compounds of molecular formula $C_2H_2Br_2$ be related to each other?
a) optical isomers b) cis-trans isomers c) constitutional isomers d) both b and c

VIII. Which of following shows cis-trans isomerism?
a) 1-butene b) propene c) 2-butene d) 1,1-dichloro ethene

IX. Which one of the following pairs do the isomers have identical boiling points?
a) cis and trans isomers b) (+) and (–) enantiomers
c) cis-trans and optical isomers d) structural isomers

## Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | d | $CHCl_3$ | Chloroform, ($CHCl_3$) (trichloromethane) is an organic halogen compound, (Haloalkane) whereas $CO_2$, $CS_2$ and HCN are considered inorganic carbon compounds. |
| II. | b | $CH_2 = CHCH_3$ | $CH_3CH_2CH=CH_2$ has molecular formula $C_4H_8$ and empirical formula $CH_2$. Propene ($C_3H_6$) also has empirical formula $CH_2$. |
| III. | c | Substitution only | Saturated compounds containing only single bonds, such as alkanes, undergo substitution reactions. |
| IV. | d | All of these | Urea contains a carbonyl group (C=O), amino groups ($-NH_2$), and an amide linkage ($-CONH_2$). |
| V. | b | Pentan-2-ol | Carbon-2 in pentan-2-ol is attached to four different groups, making it a chiral carbon and therefore optically active. |
| VI. | d | C–2 | Carbon-2 is attached to –OH, –H, $-CH_3$ and a different alkyl group, so it is the chiral carbon.  |
| VII. | d | Both b and c | Compounds with formula $C_2H_2Br_2$ can exist as structural isomers and also as cis-trans isomers. |
| VIII. | c | 2-Butene | In 2-butene, each carbon of the double bond has two different groups attached, so it exhibits cis-trans isomerism. |
| IX. | b | (+) and (–) enantiomers) | Enantiomers have identical physical properties such as melting and boiling points; they differ only in the direction of rotation of plane-polarized light. |

## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) Define enantiomers. Give enantiomers of 2-methylbutan-2-ol.**

**Ans.** Enantiomers are stereoisomers that are non-superimposable mirror images of each other.
**Enantiomers of 2-methylbutan-2-ol:**
2-Methylbutan-2-ol does not have a chiral carbon atom; therefore, it does not exist as enantiomers.
**Reason:** The carbon carrying the –OH group is attached to two identical $CH_3$ groups, so it is not asymmetric



**b) Alkanes have no functional group. Justify.**

**Ans.** Alkanes contain only C–C and C–H single bonds and do not possess any atom or group of atoms responsible for characteristic chemical reactions. Therefore, alkanes are said to have no functional group.

**c) Deduce the empirical and molecular formulae of the following compounds.**
a)  b)  c) 

| Ans. | a) | Cyclohexane<br>Molecular formula = $C_6H_{12}$<br>Empirical formula = $CH_2$ | b) | 1,3-Butadiene<br>Molecular formula = $C_4H_6$<br>Empirical formula = $C_2H_3$ | c) | Cyclobutadiene<br>Molecular formula = $C_4H_4$<br>Empirical formula = CH |
|---|---|---|---|---|---|---|

**d) Give systematic names of the following compounds.**
i) $CH_3-CH_2-CN$ ii) $CH_3COCH_2CH_2-CH_3$ iii) $CH_3CH_2COOCH_3$

| Ans. | i) | $CH_3-CH_2-CN$<br>Propanenitrile | ii) | $CH_3COCH_2CH_2-CH_3$<br>Pentan-2-one | iii) | $CH_3CH_2COOCH_3$<br>Methyl propanoate |
|---|---|---|---|---|---|---|

**e) Define electrophile and nucleophile with two examples each.**

**Ans. Electrophile:**
An electrophile is an electron-deficient species that accepts an electron pair. **Examples:** $H^+$, $NO_2^+$.
**Nucleophile:**
A nucleophile is an electron-rich species that donates an electron pair. **Examples:** $OH^-$, $CN^-$.

**f) Pent-2-ene shows cis-trans isomerism but pent-1-ene does not. Give reason.**

**Ans.** In **pent-2-ene**, each carbon atom of the double bond is attached to two different groups; therefore, it exhibits **cis-trans isomerism.**
In **pent-1-ene**, one carbon of the double bond is attached to two identical hydrogen atoms. Hence, cis-trans isomerism is not possible.

**g) Define: i) Constitutional isomerism ii) Stereoisomerism**

**Ans. (i) Constitutional Isomerism:**
The phenomenon in which compounds have the same molecular formula but different structural formulae is called constitutional isomerism.
**(ii) Stereoisomerism:**
The phenomenon in which compounds have the same molecular formula and the same structural formula but differ in the spatial arrangement of atoms is called stereoisomerism.

**h) Define: i) racemic mixture ii) Optical activity**

**Ans. (i) Racemic Mixture:**
An equimolar mixture of two enantiomers that does not rotate plane-polarized light is called a racemic mixture.
**(ii) Optical Activity:**
The ability of a substance to rotate the plane of plane-polarized light is called optical activity.

**i) Explain why meso tartaric acid is optically inactive although it has two chiral carbon atoms.**

**Ans.** Meso tartaric acid contains two chiral carbon atoms, but it possesses an **internal plane of symmetry.** The optical rotation produced by one chiral carbon is exactly cancelled by the rotation produced by the other chiral carbon in the opposite direction. Therefore, meso tartaric acid is **optically inactive due to internal compensation.**

## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

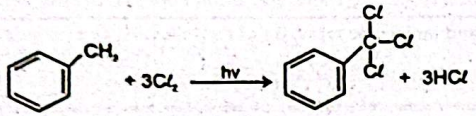
**a) A compound $C_6H_5CH_3$ reacts with $Cl_2$ in the presence of sunlight to form the product $C_6H_5CCl_3$ Name the mechanism of the reaction. Give its different steps.**

**Ans. Name of the Mechanism:**
The reaction proceeds through a Free Radical Substitution Mechanism (Photochemical Chlorination).

CamScanner

In the presence of sunlight (hv), the hydrogen atoms of the methyl group of toluene are successively replaced by chlorine atoms to form benzotrichloride ($C_6H_5CCl_3$).

**Overall Reaction:**



➢ **Steps of Free Radical Substitution Mechanisms**

1. **Initiation Step:**
Sunlight causes the homolytic cleavage of chlorine molecules, producing chlorine free radicals.

$$Cl_2 \xrightarrow{hv} Cl^{\cdot} + Cl^{\cdot}$$

2. **Propagation Steps:**
**Step 1:** A chlorine radical removes a hydrogen atom from the methyl group of toluene.

$$C_6H_5CH_3 + Cl^{\cdot} \longrightarrow C_6H_5CH_2^{\cdot} + HCl$$

**Step 2:** The benzyl radical reacts with another chlorine molecule.

$$C_6H_5CH_2^{\cdot} + Cl_2 \longrightarrow C_6H_5CH_2Cl + Cl^{\cdot}$$

The newly formed chlorine radical continues the chain reaction.
Further chlorination occurs:

$$C_6H_5CH_2Cl + Cl_2 \xrightarrow{hv} C_6H_5CHCl_2 + HCl$$

3. **Termination Steps:**
The reaction stops when free radicals combine together.
**Examples:**

$$Cl^{\cdot} + Cl^{\cdot} \longrightarrow Cl_2$$

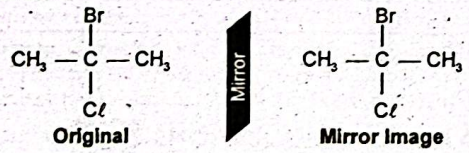
$$C_6H_5CH_2^{\cdot} + Cl^{\cdot} \longrightarrow C_6H_5CH_2Cl$$

**Conclusion:**
The conversion of toluene ($C_6H_5CH_3$) into benzotrichloride ($C_6H_5CCl_3$) in the presence of chlorine and sunlight occurs through a free radical substitution mechanism, which involves initiation, propagation, and termination steps.

**b) Draw the mirror image of each of the following compounds. Label each molecule as chiral or achiral.**
**i) 2-bromo-2-chloropropane ii) 1-bromo-1-chloroethane**
**iii) ethoxyethane iv) 2-aminopropanoic acid**

**Ans.**

**(i) 2-Bromo-2-chloropropane**
**Structure:** The central carbon is attached to: — Br, — Cl, — $CH_3$, — $CH_3$
**Mirror Image Representation:**




Original Mirror Image

Since it has **two identical methyl groups**, it does **not** have four different groups attached. Its mirror image is superimposable on the original molecule.
**Chirality Label:** Achiral

**(ii) 1-Bromo-1-chloroethane**
**Structure:** The carbon attached to Br and Cl is bonded to: — Br, — Cl, — H, — $CH_3$



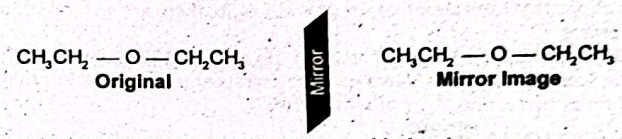
**Mirror Images Representation:**




Original Mirror Image

These are **four different groups**, so this carbon is a **chiral carbon**. These two structures are non-superimposable mirror images (enantiomers).
**Chirality Label:** Chiral

**(iii) Ethoxyethane (Diethyl ether)**
**Structure:**




Original Mirror Image

The molecule has a plane of symmetry and contains **no chiral carbon atom.**
**Label:** Achiral
Its mirror image is superimposable on the original molecule.

**(iv) 2-Aminopropanoic acid (Alanine)**
**Structure:** The central carbon is attached to: — H, — $NH_2$, — COOH, — $CH_3$
**Mirror Images Representation:**




Original Mirror Image

These are **four different groups**, so it is a **chiral carbon**. The two structures are non-superimposable mirror images.
**Label:** Chiral

**c) What is the alkane of lowest relative molecular mass that contains a chiral centre? Give its systematic name and molecular formula. Also draw mirror image of this compound.**

**Ans.** The alkane of lowest relative molecular mass containing a chiral centre is 3-methylhexane.
**Systematic Name:** 3-Methylhexane
**Molecular Formula:** $C_7H_{16}$
**Reason:**
A chiral carbon must be attached to four different groups. In 3-methylhexane, carbon-3 is attached to: — H, — $CH_3$, — $C_2H_5$ (ethyl), — $C_3H_7$ (propyl)
Since these four groups are different, carbon-3 is a chiral centre.
**Mirror Images (Enantiomers)**

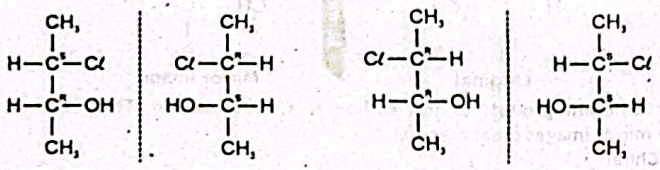



These two structures are non-superimposable mirror images (enantiomers).

CamScanner

**d) 3-chlorobutan-2-ol is an optically active compound. Draw all its possible optical isomers. Is there any meso form of this compound? Give reason.**

**Ans.**




This compound contains two chiral carbon atoms: C-2 (bearing – OH) , C-3 (bearing – Cl)
Hence, the number of possible optical isomers is: $2^n = 2^2 = 4$. So, there are 4 chiral centres.
**The Four Optical Isomers**
The pairs are: (2R, 3R) and (2S, 3S) = Enantiomers , (2R, 3S) and (2S, 3R) = Enantiomers
**Reason:** A meso compound must possess two or more chiral centres, and an internal plane of symmetry. There is no meso form as there is no plane of symmetry.

## DESCRIPTIVE QUESTIONS DQs

**Q.4 Explain the difference between homolytic and heterolytic fissions of a covalent bond.**

**Ans.** The breaking of a covalent bond can occur in two ways: homolytic fission and heterolytic fission.

| Homolytic Fission | Heterolytic Fission |
|---|---|
| The cleavage of a covalent bond in such a way that each atom takes away one electron from the shared pair is called homolytic fission. | The cleavage of a covalent bond in such a way that one atom takes both bonding electrons is called heterolytic fission. |
| The covalent bond breaks symmetrically. | The covalent bond breaks asymmetrically. |
| Each bonded atom takes one electron from the shared pair. | One atom takes both bonding electrons. |
| Free radicals are produced. | Ions (a cation and an anion) are produced. |
| Represented by single-headed (fish-hook) arrows. | Represented by double-headed arrows. |
| Usually occurs in non-polar solvents and in the presence of heat or light. | Usually occurs in polar solvents. |
| Example: $Cl_2 \xrightarrow{h\nu} Cl^{\bullet} + Cl^{\bullet}$ Two chlorine free radicals are produced. | Example: $CH_3Cl \longrightarrow CH_3^+ + Cl^-$ A methyl cation and a chloride anion are formed. |

**Q.5 Discuss cis-trans isomerism. Explain with two examples.**

**Ans.** See Question No. 16

**Q.6 Describe the phenomenon of optical activity. Explain with an example.**

**Ans.** See Question No. 15

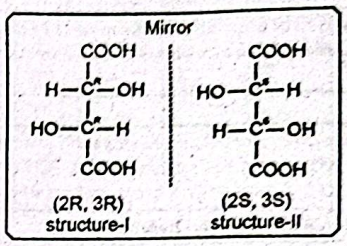
**Q.7 What is the difference between racemic mixture and meso compound? Draw the structures of enantiomers and meso form of tartaric acid.**

**Ans.** **Difference between Racemic Mixture and Meso Compound**

| Racemic Mixture | Meso Compound |
|---|---|
| An equimolar mixture of two enantiomers [(+) and (–)]. | A single compound containing two or more chiral centres. |
| Optically inactive due to external compensation. | Optically inactive due to internal compensation. |
| Contains two different molecules (enantiomers). | Consists of only one molecule. |
| Does not possess a plane of symmetry. | Possesses an internal plane of symmetry. |
| Can be separated into enantiomers. | Cannot be separated into enantiomers because it is a single compound. |

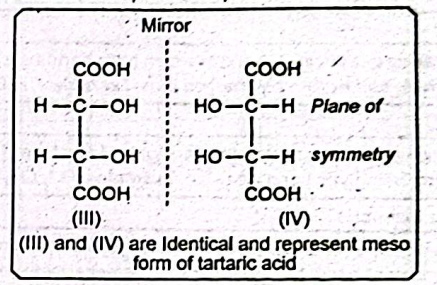


**Enantiomers of Tartaric acid:**




Tartaric acid has two chiral center i.e., the second and third carbon. (2R, 3R) and (2S, 3S)-tartaric acid are enantiomers because they are non-superimposable mirror images. These isomers of tartaric acid have opposite configurations at both the chiral centers.

**Example:** Tartaric acid is the classic example of this phenomenon.




The stereoisomers which contain at least two similar chiral carbon atoms and also possess a plane of symmetry are optically inactive. The plane of symmetry divides the molecule into two equal halves, one half of the molecule being mirror image of the other half. The two halves will rotate the plane of polarised light in opposite direction. As a result, rotation of one half of molecule is internally compensated (cancelled) by the other half and the molecule will become optically inactive. Such stereo isomers are called meso forms.

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 What is catenation? Why is it important in organic chemistry?**

**Ans.** Catenation is the ability of carbon atoms to bond with one another to form long chains, branched chains and rings. Carbon shows strong self-linkage through stable C-C covalent bonds. Together with tetravalency, this property is responsible for the enormous diversity of organic compounds.

**Q.2 Why is carbon capable of forming a large number of compounds?**

**Ans.** Carbon forms a large number of compounds because it exhibits catenation and tetravalency. It can form stable covalent bonds with itself as well as with many other elements such as hydrogen, oxygen and nitrogen. Therefore, carbon can produce chains, branches and cyclic structures.

**Q.3 Describe the structure of benzene.**

**Ans.** Benzene is a planar cyclic molecule consisting of six carbon atoms arranged in a hexagonal ring. Each carbon atom is $sp^2$ hybridized and forms three sigma bonds. The unhybridized p orbitals overlap to produce a delocalized pi-electron system above and below the plane of the ring.

**Q.4 Why is benzene planar?**

**Ans.** Each carbon atom in benzene is $sp^2$ hybridized and has trigonal-planar geometry. The carbon atoms and the atoms directly attached to them lie in one plane, which allows effective sideways overlap of the p orbitals and formation of the delocalized pi system.

CamScanner

**Q.5 What is a functional group? Give examples.**

**Ans.** A functional group is an atom or group of atoms that determines the physical and chemical properties of an organic compound. **Examples include** –OH in alcohols, –CHO in aldehydes, –COOH in carboxylic acids and –$NH_2$ in amines.

**Q.6 What is a homologous series?**

**Ans.** A homologous series is a family of organic compounds having the same functional group and similar chemical properties. Successive members differ from each other by one $–CH_2–$ unit and show a gradual change in physical properties. **For example,** $CH_4$, $C_2H_6$ and $C_3H_8$ are members of the alkane series.

**Q.7 Differentiate between saturated and unsaturated hydrocarbons.**

**Ans.** Saturated hydrocarbons contain only single carbon-carbon bonds, whereas unsaturated hydrocarbons contain at least one C = C or C ≡ C bond. Alkanes are saturated; alkenes and alkynes are unsaturated. Unsaturated hydrocarbons commonly undergo addition reactions.

**Examples:** • **Saturated:** Ethane ($C_2H_6$) • **Unsaturated:** Ethene ($C_2H_4$)

**Q.8 What is heterolytic fission?**

**Ans.** Heterolytic fission is the breaking of a covalent bond in which both bonding electrons are taken by one atom. This process produces positively and negatively charged ions. **Example:** $CH_3Br \longrightarrow CH^{3+} + Br^-$

**Q.9 What is a free radical?**

**Ans.** A free radical is an atom or group of atoms containing an unpaired electron. These species are highly reactive and are usually formed during homolytic bond cleavage. **Examples:** $C\ell^\bullet$, $CH_3^\bullet$

**Q.10 What is a nucleophile? Give examples.**

**Ans.** A nucleophile is an electron-rich species that contains a lone pair of electrons and donates it to an electron-deficient species to form a covalent bond. Nucleophiles may be negatively charged ions or neutral molecules with lone pairs. **Examples:** $OH^-$, $CN^-$, $NH_3$, $H_2O$

**Q.11 What is an electrophile? Give examples.**

**Ans.** An electrophile is an electron-deficient species that accepts an electron pair to form a new covalent bond. Electrophiles may be positive ions or neutral electron-deficient molecules. **Examples:** $H^+$, $NO_2^+$, $BF_3$

**Q.12 Differentiate between nucleophiles and electrophiles.**

**Ans.** Nucleophiles are electron-pair donors and attack electron-deficient centres. Electrophiles are electron-pair acceptors and attack electron-rich centres. **Examples:** • **Nucleophile:** $OH^-$, $CN^-$ • **Electrophile:** $H^+$, $NO_2^+$

**Q.13 What is meant by substitution reaction?**

**Ans.** A substitution reaction is a reaction in which one atom or group in a molecule is replaced by another atom or group. **Example:** $CH_4 + C\ell_2 \xrightarrow{UV} CH_3C\ell + HC\ell$

**Q.14 What is an elimination reaction?**

**Ans.** An elimination reaction removes atoms or groups from two adjacent atoms in a substrate, resulting in formation of a multiple bond. Elimination is regarded as the reverse of addition.

**Example:** $CH_3CH_2Br + KOH_{(alc.)} \longrightarrow CH_2 = CH_2 + KBr + H_2O$

**Q.15 What is hydrolysis?**

**Ans.** Hydrolysis is a reaction in which a compound reacts with water and undergoes bond cleavage to form new products. Acid or base may assist the process. **Example:** $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

**Q.16 What is reduction in organic chemistry?**

**Ans.** Reduction in organic chemistry involves gain of electrons, gain of hydrogen, loss of oxygen, a decrease in the number of carbon-oxygen bonds, or a decrease in the oxidation state of carbon.

**Example:** $CH_3CHO + 2[H] \longrightarrow CH_3CH_2OH$



**Q.17 What is structural isomerism?**

**Ans.** Structural isomerism is the phenomenon in which compounds have the same molecular formula but different structural arrangements of atoms. Such compounds are called structural or constitutional isomers. **Example:** Both butane and 2-methylpropane have the molecular formula, $C_4H_{10}$

**Q.18 Explain chain isomerism with an example.**

**Ans.** Chain isomerism occurs when compounds with the same molecular formula have different carbon skeletons, such as a straight chain and a branched chain.

**Example:** $CH_3CH_2CH_2CH_3$ and $(CH_3)_3CH$ are chain isomers of $C_4H_{10}$.

**Q.19 Explain positional isomerism with an example.**

**Ans.** Positional isomerism occurs when compounds have the same molecular formula and functional group but differ in the position of a substituent, functional group, or multiple bond.

**Example:** $CH_3CH_2CH_2OH$ and $CH_3CHOHCH_3$ are positional isomers of $C_3H_8O$.

**Q.20 Explain functional group isomerism with an example.**

**Ans.** Functional group isomerism occurs when compounds have the same molecular formula but different functional groups, so they belong to different organic families.

**Example:** $CH_3CH_2OH$ and $CH_3OCH_3$ are functional group isomers with molecular formula $C_2H_6O$.

**Q.21 Explain metamerism with an example.**

**Ans.** Metamerism is a type of structural isomerism in which compounds have the same molecular formula and the same functional group but different distributions of alkyl groups on either side of a polyvalent atom or group.

**Example:** $CH_3OCH_2CH_2CH_3$ and $CH_3CH_2OCH_2CH_3$ are metamers.

**Q.22 What is tautomerism?**

**Ans.** Tautomerism is a dynamic equilibrium between two structural isomers that differ mainly in the position of a proton and a double bond. The two forms are called tautomers.

**Example:** • **Keto form:** $CH_3COCH_3$ • **Enol form:** $CH_2 = C(OH)CH_3$

**Q.23 Explain cis-trans isomerism.**

**Ans.** Cis-trans isomerism is a type of stereoisomerism caused by restricted rotation about a carbon-carbon double bond. In the cis isomer, similar groups lie on the same side of the double bond; in the trans isomer, they lie on opposite sides. **Example:** Cis-but-2-ene and trans-but-2-ene.

**Q.24 What is a chiral carbon atom?**

**Ans.** A chiral carbon atom is a carbon atom attached to four different atoms or groups. The presence of a chiral centre gives rise to optical isomerism. **Example:** The second carbon atom in 2-bromobutane is chiral.

**Q.25 What are enantiomers?**

**Ans.** Enantiomers are non-superimposable mirror-image stereoisomers. In an achiral environment they have identical physical and chemical properties except for their action on plane-polarized light; they rotate it by equal amounts in opposite directions.

**Q.26 What is a racemic mixture?**

**Ans.** A racemic mixture is an equimolar mixture of two enantiomers. Since the optical rotations of the two isomers cancel each other, the mixture is optically inactive.

CamScanner

## SELF-ASSESSMENT

Total Mark: 30

**Q.1 Encircle the correct option.** (1 × 6 = 6)

**(i) Cyclohexane is classified as:**
(A) Aromatic hydrocarbon (B) Alicyclic hydrocarbon
(C) Alkyne (D) Alkene

**(ii) A functional group is responsible mainly for the:**
(A) Characteristic chemical properties of a compound (B) Characteristic physical properties of a compound
(C) Number of carbon atoms (D) Colour of a compound

**(iii) Homolytic fission produces:**
(A) Carbocations (B) Carbanions (C) Free radicals (D) Electrophiles only

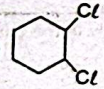
**(iv) Which molecule is chiral and can rotate the plane polarised light?**
(A) Pentan-1-ol (B) Pentan-2-ol (C) 2,2-dimethylpropan-1-ol (D) 2-methylbutan-2-ol

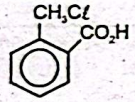
**(v) Which carbon in $CH_3CH(CH_3)CH_2CH(OH)CH_3$ is chiral?**
(A) C – 1 (B) C – 2 (C) C – 3 (D) C – 4

**(vi) Which of following shows cis-trans isomerism?**
(A) 1-butene (B) propene (C) 2-butene (D) 1,1-dichloro ethene

**Q.2 Write short answers of the following questions.** (2 × 8 = 16)

(i) Draw the different possible structures containing five carbon atoms.
(ii) What are the systematic names of the following? i) $(CH_3)_3COH$ ii) $CH_3COC_6H_5$
(iii) Draw the structures of the following. i) Phenylethanoic acid ii) 3-Methylpentanal
(iv) Give the molecular formulate of the following.

i) 


ii) 


(v) Define enantiomers: Give enantiomers of 2-methylbutan-2-ol.
(vi) Define: i) racemic mixture ii) Optical activity
(vii) Describe each of the following as electrophile, nucleophile or free radical.
i) $NH_3$ ii) $Br^-$ iii) $H_2O$ iv) $NO_2^{\oplus}$ v) $Cl^+$
(viii) Define electrophile and nucleophile with suitable examples.

**Q.3 Extensive Questions.** (4 + 4 = 8)

(a) Discuss cis-trans isomerism. Explain with two examples.
(b) Describe the phenomenon of optical activity. Explain with an example.



## ENTRANCE TEST MCQs

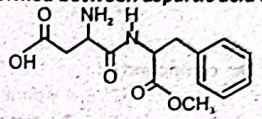
1. **The following is an alcohol:** (ECAT 2016)
(A) $CH_3-CH_2-OH$ (B) $CH_3-O-CH_3$ (C) $CH_3COOH$ (D) $CH_3-CH_2-Br$

2. **Which of the following is the structure of ketone?** (UHS 2013)
(A) $H_3C-\overset{O}{\overset{\|}{C}}-OH$ (B) $H_3C-\overset{O}{\overset{\|}{C}}-CH_3$ (C) $H_3C-\overset{O}{\overset{\|}{C}}-NH_2$ (D) $H_3C-\overset{O}{\overset{\|}{C}}-Cl$

3. **Carbon has the unique ability to form long chains by bonding with other carbon atoms. This property of self-linking in carbon is known as:** (UHS 2012)
(A) Condensation (B) Cyclization (C) Polymerization (D) Catenation

4. **Which one of the following compound is a ketone?** (UHS 2014)
(A) $CH_3-O-CH_2-CH_3$ (B) $CH_3-CO-CH_2-CH_3$ (C) $CH_3COOH$ (D) $CH_3-CH_2CHO$

5. **The skeletal formula of dipeptide formed between aspartic acid and phenylalanine is given below:**

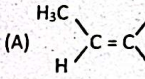
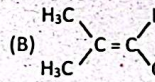
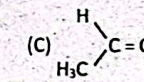
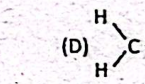



**How many functional groups are present in its formula?** (UHS 2012)
(A) 1 (B) 2 (C) 4 (D) 3

6. **The following functional group is present in both aldehydes and ketones:** (ECAT 2015)
(A) Carbonyl (B) Hydroxyl (C) Oxyboron (D) None of these

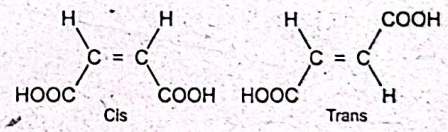
7. **1-chloropropane and 2-chloropropane are isomers of each other, the type of isomerism in these two is called:** (UHS 2011)
(A) Cis-trans isomerism (B) Position isomerism
(C) Chain isomerism (D) Functional group isomerism

8. **Which one of the following pairs can be cis-trans isomer to each other?** (UHS 2016)
(A) $CHCl = CCl_2$ and $CH_2 = CH_2$ (B) $CH_3-CH=CH-CH_3$ and $H_3C-CH=CH-CH_3$
(C) $CHCl = CH_2$ and $CH_2 = CHCl$ (D) $CH_3-CH_3$ and $CH_2 = CH_2$

9. **The cis-isomerism is shown by:** (UHS 2013)
(A) 
(B) 
(C) 
(D) 

10. **Butane molecule can have maximum number of isomers:** (UHS 2018)
(A) 5 (B) 3 (C) 4 (D) 2

11. **Maleic acid and Fumaric acid, both have chemical formula $C_4H_4O_4$. The structure of these acids is shown below:** (UHS 2019)




(A) Position isomers (B) Structural isomers (C) Metamers (D) Cis-trans isomers

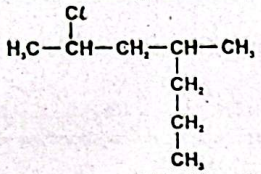
12. **The addition reaction of 2-Butene with HBr produces:** (UHS 2023)
(A) 1-Bromobutane (B) 2, 3-Dibromobutane (C) 1, 3-Dibromobutane (D) 2-Bromobutane

13. **The decreasing stable order of the following carbocation is:** (UHS 2023)
1) $CH_3CH_2CH_2^+$ 2) $(CH_3)_3C^+$ 3) $CH_3CH_2CH^+CH_3$
(A) 1 > 2 > 3 (B) 3 > 2 > 1 (C) 3 > 1 > 2 (D) 2 > 3 > 1

CamScanner

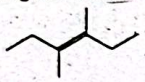
14. Reactions of alkanes with halogens is known as: (UHS 2018)
(A) Addition (B) Free radical substitution (C) Elimination (D) Propagation

15. Which one of the following is the best name according to IUPAC system for the formula given below? (UHS 2017)



(A) 4-methyl-6-chloroheptane (B) 2-chloro-4-methylheptane
(C) 2-chloro-4-n-propylheptane (D) 2-chloro-4-methylpentane

16. Skeletal formula of an organic compound is given below: (UHS 2018)



It is a hydrocarbon, IUPAC name of the compound is:
(A) 3, 3 – dimethyl – 3 – hexene (B) 3, 4 – dimethyl – 3 – hexene
(C) 3 – hexene (D) 2, 3 – dimethyl – 1 – hexene

17. Which product is obtained by the elimination of bromopropane? (UHS 2018)
(A) Propene (B) Butene (C) Ethene (D) Propane

**Answers Key**

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. A | 2. B | 3. D | 4. B | 5. C | 6. A | 7. B | 8. B | 9. C | 10. D | 11. D |
| 12. D | 13. D | 14. B | 15. B | 16. B | 17. A | | | | | |



20 CHAPTER

# AROMATIC HYDROCARBONS

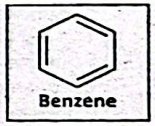
## Student Learning Outcomes (SLOs)

[C-12-D-21 to C-12-D-29]
- Explain the shape of the benzene molecule (molecular orbital aspect).
- Define resonance, resonance energy and relative stability of benzene.
- Compare the reactivity of benzene with alkanes and alkenes.
- Describe the mechanism of substitution reactions with chlorine and bromine, including the formation of ortho, para, and meta isomers, and predict the major product(s) of the reaction.
- Explain the mechanism of nitration, including the formation of a nitronium ion, and predict the major product(s) of the reaction.
- Explain the mechanism of Friedel-Crafts alkylation and acylation, respectively, including the role of the Lewis acid catalyst, and predict the major product(s) of the reaction.
- Explain the mechanism of side chain oxidation, including the formation of benzoic acid, and predict the major product(s) of the reaction.
- Explain the mechanism of hydrogenation, including the role of a metal catalyst, and predict the major product(s) of the reaction, which is cyclohexane.
- Describe the mechanism of electrophilic aromatic substitution, including the role of the electrophile and the formation of a sigma complex, and predict the major product(s) of the reaction based on the directing effects of substituents on the aromatic ring.

Benzene is one of the most important organic compounds with the chemical formula $C_6H_6$. Benzene is the parent compound of various aromatic compound. Benzene is the simplest aromatic hydrocarbon.

**Q.1 What is the origin of the word 'Benzene'?** S/Q

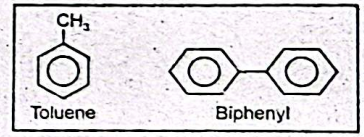
Ans. The work 'Benzene' comes from an aromatic ring **'Gum benzoin'. Benzene derived products are well known to be pleasantly fragrant.** For this reason, organic compounds containing benzene rings were classified as being **"aromatic" (sweet smelling)** amongst scientists in the early 19th century. Many aromatic compounds are sweet/pleasant smelling, such as vanilla.




➢ **Arenes:**

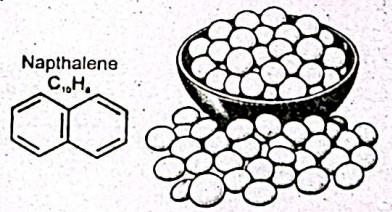
*Organic hydrocarbons containing one or more benzene rings are known as arenes.*

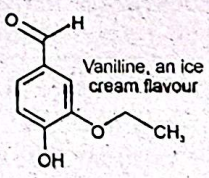
**Note:** The term 'aromatic' continues to be used today in order to designate molecules with benzene and benzene-like rings in their structures that are not good-smelling, rather have foul smells.




**Examples:**

Napthalene $C_{10}H_8$








**For Your Information**

Aromatic compounds follow Huckel rule, according to Huckel rule for a ring to the aromatic, it should have following properties.

- Cyclic
- Completely planar
- Fully conjugated (p-orbitals at every atom in the ring)
- Presence of $(4n + 2)$ π electrons in the ring where n=0 or any positive integer (n=1, 2, 3, ...). This corresponds to totals 2, 6, 10, 14, 18 etc electrons.

**Did You Know?**

Saying that only aromatic compounds smell good and sweet is wrong. Non-aromatic compounds, such as camphor, extracted from the camphor laurel tree, release a strong, minty aroma, yet it lacks the benzene ring in its structure.

## STRUCTURE OF BENZENE

**Q.2 Discuss the structure of benzene by Kekule.** L/Q

**Ans.** After the discovery of benzene, its molecular formula was found to be $C_6H_6$. Following this, many scientists attempted to figure out its structure. Some scientists presented linear structures. But, these were soon rejected as the linear structures (e.g. $CH_2 = CH - CH = CH - CH = CH_2$) could not explain the properties of benzene.

The structure of benzene remained a mystery (problem) until 1865 when a German professor August Kekule illustrated (elucidated) it as a six membered cyclic compound having alternate single and double bonds as below.

**Check Understanding!**

**Q.1** In benzene, the C-C bond length is:

(A) 1.34 Å (B) 1.20 Å

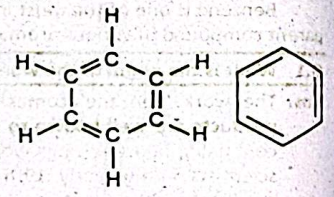
(C) 1.397 Å (D) 1.54 Å

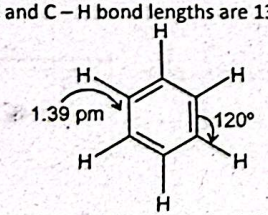
➢ **Kekule Structure of Benzene:**

This structure explained many properties of benzene successfully. There were, however, a number of problems with Kekule's structure in that it didn't fully explain the physical and chemical properties of benzene.

➢ **X-ray Studies of Structure of Benzene:**

X-ray studies of benzene exhibits a planar configuration characterized by a regular hexagonal shape. All six carbon atoms are $sp^2$ hybridized. Each carbon atom is connected to three additional atoms with bond angles of 120° for C – C – C and H – C – C. The length of the C – H bond is 109 pm, while the length of the C – C bond is 139 pm, that lies between the single bond lengths of $sp^3$ hybridized carbons (154 pm) and C = C double bond (133 pm). All C – C and C – H bond lengths are 139 pm and 109 pm.






Bond angles and bond lengths in benzene

**Table: Normal bond lengths of $sp^3$ and $sp^2$ hybridized carbons**

| Bond | Bond Length |
|---|---|
| C – C | 154 pm |
| C = C | 133 pm |

### Thermodynamic Stability of Benzene and Resonance

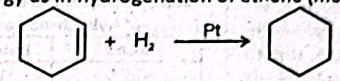
**Q.3 Discuss the thermodynamic stability of benzene and resonance with reference to heat of hydrogenation.** L/Q

**Ans.** Benzene like alkenes appears to have double bonds, however it is much more stable than alkenes. Evidence of the increased stability of benzene is obtained by measuring the heat emitted during the hydrogenation of benzene and cyclic alkenes.



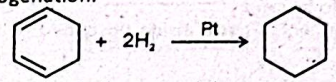
The heat of hydrogenation can be related to the relative thermodynamic stability of a compound. This reaction yields cyclohexane as a common product via catalytic hydrogenation (addition of hydrogen). In the following diagram (Figure), cyclohexane symbolizes a low-energy reference point.

- Let us analyse the heats of hydrogenation of different cyclohexenes.
- The hydrogenation of cyclohexene results in the formation of cyclohexane and releases 120 kJ $mol^{-1}$ of energy as in hydrogenation of ethene (mono-alkene).



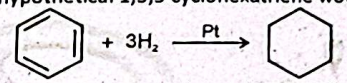

Heat of Hydration ($\Delta H$) = –120 kJ $mol^{-1}$

- From this, we could expect that cyclohexadiene would yield ($2 \times 120 = 240$ kJ $mol^{-1}$) on complete hydrogenation.




Heat of Hydration ($\Delta H$) = $2 \times 120 = -240$ kJ $mol^{-1}$.

- The hypothetical 1,3,5 cyclohexatriene would produce ($3 \times 120 = -360$ kJ $mol^{-1}$) as shown in Figure.



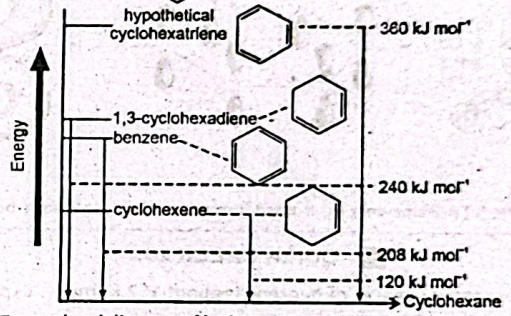




Figure: Energy level diagram of hydrogenation of cyclohexenes and benzene

➢ **Inference:**

- **Expected Heat of Hydrogenation:** Following this, it is expected that heat of hydrogenation of benzene would be much higher if it were a cyclohexene too. Its heat of hydrogenation would be equal to the hypothetical cyclohexatriene i.e. 360 kJ $mol^{-1}$.
- **Actual Heat of Hydrogenation:** Benzene, has much lower heat of hydrogenation (208 kJ $mol^{-1}$) thus exhibiting an exceptional stability. This heat is 152 kJ $mol^{-1}$ lower than expected.
- **Conclusion:** It shows benzene is much more stable than the hypothetical cyclohexatriene. This stability is explained based on the delocalisation of π electrons. According to the modern concept, all the benzene π electrons are delocalised over the ring through the π orbital overlap on all the six carbon atoms.

**Check Understanding!**

**Q.2** What is resonance energy?

➢ **Resonance Energy:**

The actual heat of hydrogenation of benzene is 152 kJ $mol^{-1}$ lower than the theoretical value. This energy is called the resonance energy (delocalisation energy) of benzene.

(**Note:** This concept of delocalisation is explained in the next topic).

### Atomic Orbital Structure of Benzene

**Q.4 Discuss the atomic orbital structure of benzene using hybridization approach.** Exercise Q/Q.4

**Ans.** **Sigma (σ) Framework:**

The hexagonal frame work of benzene ring can be conveniently explained by using hybridization approach. According to this, each carbon atom in benzene is $sp^2$ hybridized.

CamScanner

The three $sp^2$ hybrid orbitals on each carbon are utilized to form three σ-bonds, two with adjacent carbon atoms and one with a hydrogen atom. Since all the $sp^2$ orbitals are in the same plane, therefore, all the carbon and hydrogen atoms of this σ framework are coplanar with bond angles at 120°.

➢ **Pi (π) Electron Cloud:**

The six unhybrid '2 p' orbitals, one from each carbon, are perpendicular to this sigma framework and parallel to each other overlap sideways to form a π electron cloud above and below the plane of the benzene ring making it a conjugated molecule. Due to this overlap six electrons are shared equally among all the six carbons and this is known as delocalization of π electron.

This delocalization causes all the six C – C bond lengths to be same i.e., 139 pm. Benzene is thus represented as a hexagon with a circle inside (inscribed) where the circle represents delocalized π electrons.

**Table: Normal bond length $sp^3$ and $sp^2$ hybridised carbons**

| Bond | Bond Length |
|---|---|
| C – C | 154 pm |
| C = C | 133 pm |

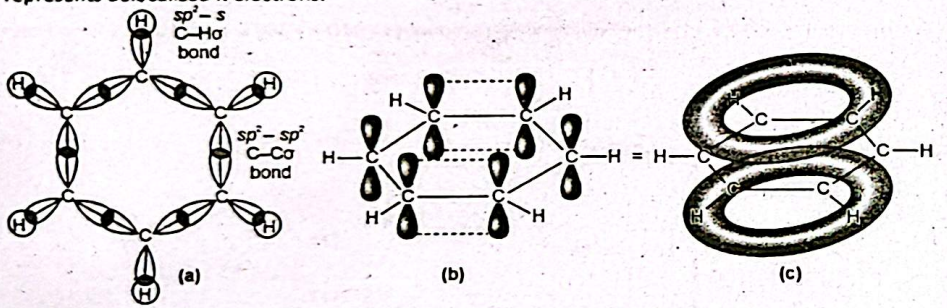



**Figure: (a) σ-framework (b) π-bond formation (c) delocalized π-bond**

## QUICK CHECK 20.1

**a) The delocalization (resonance) energy of benzene is about 152 kJ $mol^{-1}$. Explain what that means and how it affects the reactivity of benzene.**

**Ans.** **Delocalization (resonance) energy** is the extra stability possessed by benzene due to the **delocalization of its six π-electrons** over the entire benzene ring.

The value of **152 kJ $mol^{-1}$** means that benzene is **152 kJ $mol^{-1}$ more stable** than the hypothetical structure having three isolated double bonds (cyclohexatriene).

**Effect on Reactivity**

- Benzene is highly stable because of resonance.
- It resists addition reactions, as addition would destroy the aromatic ring.
- Therefore, benzene mainly undergoes **electrophilic substitution reactions**, which preserve its aromatic character.

**b) The X-ray studies show that benzene has a planar structure. If benzene were not planar, what difference in the reactivity of benzene would be seen?**

**Ans.** The planar structure of benzene allows the **parallel overlap of p-orbitals**, resulting in the **delocalization of π-electrons.**

If benzene were **not planar.**

The p-orbitals would not overlap effectively. Delocalization of π-electrons would not occur. Benzene would lose its aromatic stability. It would become much **more reactive** and would readily undergo **addition reactions**, similar to ordinary alkenes.

**c) Why all the bonds in the benzene ring are of equal bond length?**

**Ans.** In benzene, the **six π-electrons are delocalized** over the entire ring due to resonance.

As a result,



All six carbon-carbon bonds become identical. Each bond has the same bond order (approximately 1.5). Therefore, all C – C bond lengths are equal (about 139 pm), which is intermediate between a single bond (154 pm) and a double bond (134 pm).

**d) How the atomic orbital concept explains the delocalization of π electrons in benzene?**

**Ans.** Each carbon atom in benzene is **$sp^2$ hybridized.**

- Three $sp^2$ hybrid orbitals form **σ-bonds** with two adjacent carbon atoms and one hydrogen atom.
- One **unhybridized p-orbital** remains on each carbon atom.
- These six p-orbitals overlap sideways to form a **continuous π-electron cloud** above and below the plane of the ring.
- The six π-electrons become **delocalized over all six carbon atoms,** making benzene highly stable and aromatic.

# NOMENCLATURE OF MONOSUBSTITUTED BENZENE DERIVED COMPOUNDS

**Q.5 Discuss the nomenclature of monosubstituted benzene derived compounds.** LAQ

**Ans.** Aromatic hydrocarbons that contain only one benzene ring in their structure are known as monocyclic aromatic hydrocarbons.

➢ **Nomenclature of Monocyclic Aromatic Compounds:**

There are two styles of naming benzene derivatives.

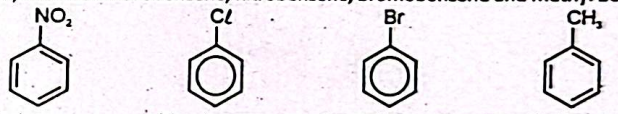
i. In which the compound is named with the suffix 'benzene' and a single substituent as 'Prefix'.
ii. With no benzene i.e., special name.

When a single substituent is present on a benzene, it is a monosubstituted benzene.

**Check Understanding!**

**Q.3 Anisole is:**
(A) methylbenzene
(B) benzenol
(C) methoxybenzene
(D) aniline

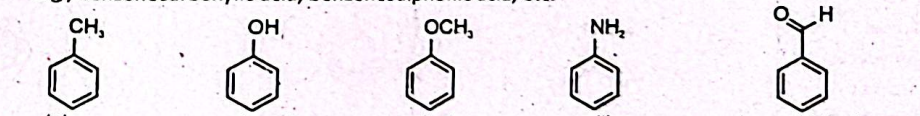
i. Most of the monosubstituted benzenes are named with the base name 'benzene' and using the substituent group as a prefix, such as chlorobenzene, nitrobenzene, bromobenzene and methyl benzene.



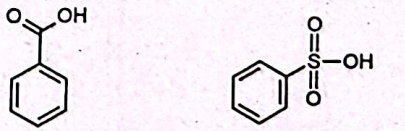

nitrobenzene chlorobenzene bromobenzene methylbenzene

ii. **Common Names of Monosubstituted Benznes:** Many monosubstituted benzenes have common names; some of these names have been included in IUPAC nomenclature as base names for the structure. e.g, phenol, toluene, aniline, etc. Common names in bold face given below are considered to be IUPAC correct base names for structures. The substituent in a monosubstituted benzene is always at C – 1, so there is no need to number its location.

iii. **Special Names:** Some benzene derivatives have special names, which are accepted as IUPAC names, e.g., benzenecarboxylic acid, benzenesulphonic acid, etc.




toluene (methylbenzene) phenol (benzenol) anisole (methoxybenzene) aniline (benzenamine) benzaldehyde (benzenecarbaldehyde)




benzoic acid (benzenecarboxylic acid) benzene sulphonic acid

CamScanner

**Q.6 Discuss the nomenclature of the disubstituted benzene.** S/Q

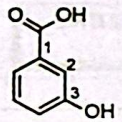
**Ans.** Disubstituted benzenes are compounds when two substituents are present on the benzene ring. They are named according to the following rules.

- **Priority Order of Substituents:** The carbon to which a higher priority substituent is attached is $C_1$. Others are numbered accordingly. The order of priority of substituents (left to right) is:

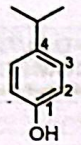
  $$-COOH, -CN, -CHO, -COCH_3, -OH, -NH_2, -OR, -R$$

- If both substituents are the same priority then the carbon having a substituent that comes first alphabetically designated as $C_1$.

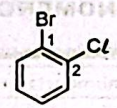
**Examples:**



**3-hydroxybenzoic acid**
(As 'acid' is higher priority than 'alcohol').



**4-isopropylphenol**
(4-(1-methylethyl)-phenol)
(Here the phenol alcohol is C-1)

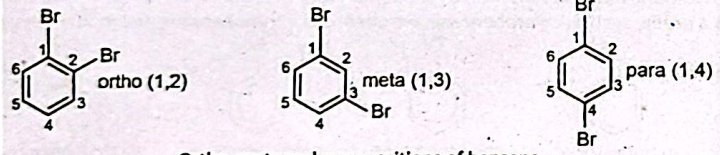


**1-bromo-2-chlorobenzene**
(As bromo comes before chloro in the alphabetic order).

**Names of disubstituted benzenes**

**Did You Know?**

Disubstituted benzenes have common names with reference to the relationship between the two substituents. Instead of using numbers to indicate substituents on a benzene ring, ortho-(o-), meta-(m-), or para(p-) can be used in place of positional markers when there are two substituents on the benzene ring.

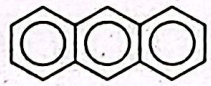
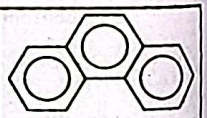
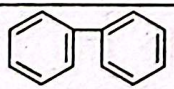
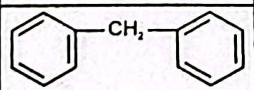



**Ortho, meta and para positions of benzene**

**Q.7 What are polycyclic hydrocarbons? Give examples.** S/Q

**Ans.** Aromatic hydrocarbons that contain two or more benzene rings in their molecules are known as polycyclic aromatic hydrocarbons.

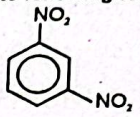
➢ **Example of Polycyclic Benzenes:**

| | | | |
|---|---|---|---|
| **Fused polycyclic aromatic hydrocarbons** |  $C_{10}H_8$ naphthalene |  $C_{14}H_{10}$ Anthracene |  $C_{14}H_{10}$ phenanthrene |
| **Isolated polycyclic aromatic hydrocarbons** |  $C_{12}H_{10}$ Biphenyl |  $C_{14}H_{10}$ Anthracene | |

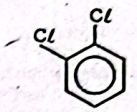


## QUICK CHECK 20.2

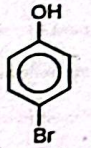
*Give names to following compounds:*

(i) 

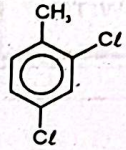
Ans. 1, 3-dinitro benzene

(ii) 

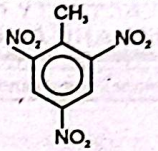
Ans. 1,2-dichloro benzene

(iii) 

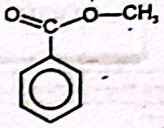
Ans. 4-Bromophenol

(iv) 

Ans. 2,4-dichloro toluene

(v) 

Ans. 2, 4, 6-tri-nitrotoluene

(vi) 

Ans. Methyl benzoate (methyl benzene carboxylate)

## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Benzene is the simplest member of the:**
   (A) Alkynes (B) Aromatic hydrocarbons (C) Cycloalkanes (D) Alcohols
2. **The molecular formula of benzene is:**
   (A) $C_6H_{12}$ (B) $C_6H_6$ (C) $C_7H_8$ (D) $C_6H_{10}$
3. **Aromatic hydrocarbons containing one or more benzene rings are called:**
   (A) Alkenes (B) Arenes (C) Cycloalkanes (D) Alkynes
4. **According to X-ray studies, benzene has:**
   (A) A planar hexagonal structure (B) A tetrahedral structure
   (C) A pyramidal structure (D) A linear structure
5. **Each carbon atom in benzene is:**
   (A) sp hybridized (B) $sp^2$ hybridized (C) $sp^3$ hybridized (D) $dsp^2$ hybridized
6. **The bond angle around each carbon atom in benzene is:**
   (A) 90° (B) 109.5° (C) 120° (D) 180°
7. **The equal C–C bond lengths in benzene are due to:**
   (A) Alternating single and double bonds only (B) Delocalization of π electrons
   (C) Hydrogen bonding (D) Ionic bonding
8. **The resonance (delocalization) energy makes benzene:**
   (A) Less stable than cyclohexene (B) More reactive than alkenes
   (C) More thermodynamically stable (D) Highly polar
9. **The π electrons in benzene are:**
   (A) Localized between two carbon atoms (B) Present only above the ring
   (C) Delocalized over all six carbon atoms (D) Present only below the ring
10. **The modern representation of benzene is:**
    (A) A hexagon with alternating double bonds only (B) A hexagon containing a circle
    (C) A square (D) A triangle
11. **The IUPAC name for methylbenzene is:**
    (A) Phenol (B) Toluene (C) Aniline (D) Benzaldehyde
12. **The IUPAC name for benzenol is:**
    (A) Phenol (B) Toluene (C) Aniline (D) Anisole
13. **The compound $C_6H_5NH_2$ is commonly known as:**
    (A) Phenol (B) Nitrobenzene (C) Aniline (D) Benzoic acid
14. **The compound $C_6H_5NO_2$ is called:**
    (A) Nitrophenol (B) Nitrobenzene (C) Benzamide (D) Benzonitrile
15. **In a monosubstituted benzene, the substituent is assumed to be attached to:**
    (A) Carbon-2 (B) Carbon-3 (C) Carbon-1 (D) Carbon-6

CamScanner

16. The term ortho (o-) represents substitution at positions:
(A) 1,2 (B) 1,3 (C) 1,4 (D) 2,4
17. The term meta (m-) represents substitution at positions:
(A) 1,2 (B) 1,3 (C) 1,4 (D) 2,5
18. The term para (p-) represents substitution at positions:
(A) 1,2 (B) 1,3 (C) 1,4 (D) 1,5
19. Which of the following is a polycyclic aromatic hydrocarbon?
(A) Phenol (B) Toluene (C) Naphthalene (D) Chlorobenzene
20. Which compound contains three fused benzene rings?
(A) Benzene (B) Toluene (C) Anthracene (D) Chlorobenzene

## COMPARISON OF REACTIVITY OF BENZENE WITH ALKANES AND ALKENES

**Q.8 Compare the reactivity of benzene with alkanes and alkenes.** S/Q

**Ans. Alkanes:**

Alkanes are generally an unreactive class of organic compounds due to their non-polar nature and the presence of sigma bond only. However, they undergo **free radical substitution** reactions in the presence of UV light quite easily.

➢ **Alkenes:**

Alkenes are very reactive class of organic compounds due to the presence of π bond and the availability of π electrons for electrophilic reagents. They undergo **electrophilic addition** reactions easily.

**Check Understanding!**
Q.4 Which of the following is least reactive, alkane, alkene and benzene?

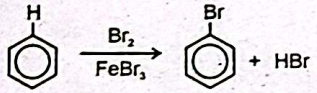
➢ **Benzene:**

Benzene has three π bonds (delocalised) and, as expected, shows some similarities to alkenes in being reactive towards electrophilic species. However, there are two key differences between their reactions with electrophiles:

- Benzene is very stable i.e. less reactive.
- Unlike alkenes, it undergoes the electrophilic substitution and not electrophilic addition reactions:

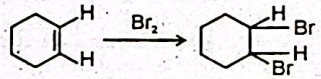
**Example:**

**electrophilic substitution**




The H has been replaced by the Br

**electrophilic addition**




Two Br have been added to the double bond

Bromine in the electrophilic substitution reaction replaces a hydrogen atom. This is due to the stability of the aromatic ring which is due to extensive delocalization of π electrons. Even though the reaction in benzene goes through an intermediate where the aromaticity is broken, it is restored after the completion of the reaction. Therefore, electrophilic substitution does not affect the overall stability of the benzene ring. In electrophilic addition the delocalisation is broken and addition is not favourable.

## ➲ Electrophilic Aromatic Substitution

**Q.9 Discuss the general mechanism of aromatic electrophilic substitution reactions.** L/Q

**Ans.** Regardless of electrophile used, the electrophilic aromatic substitution mechanism can be divided into three main steps.

i. **Generation of Electrophile:** The first step of an electrophilic substitution reaction involves the generation of an electrophile. The electrophile can be a positive ion or the positive end of a polar molecule. Typically, electrophiles cannot simply be added to the reaction mixture. The electrophile is produced in situ, by adding appropriate reagents to the reaction mixture.

**Interesting Information**



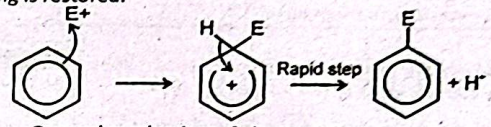
Resonance hybrid

ii. **Electrophilic Attack:** In the second step, the π electrons of benzene attack the electrophile. This forms a sigma bond between one carbon atom of the benzene ring and the electrophile



This disrupts the aromaticity in the ring as there are now only four π electrons and there is a positive charge spread over the five carbon atoms. Because of the new sigma bond formed, this intermediate is a sigma complex called the arenium ion.

iii. **Restoration of Aromaticity:** In the 3rd step, the hydrogen on the $sp^3$-hybridized carbon is removed by a counterion/conjugate base restoring the aromaticity in the ring. This happens by heterolytic cleavage of the C – H bond. This means that the electrons in this bond go into the benzene π bonding system, and the delocalisation in the ring is restored.




**General mechanism of electrophilic substitution**

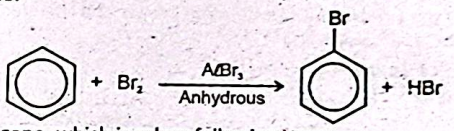
**Examples of electrophilic substitution reactions of arenes are given as follows.**

**Q.10 Discuss the halogenation (Bromination) of benzene.** L/Q

**Ans. Halogenation of Benzene**

Benzene only reacts with bromine and chlorine in the presence of Lewis acids as:
The Lewis acids are usually Aluminum chloride ($AlCl_3$), Ferric (iron) chloride ($FeCl_3$) or Ferric (iron) bromide ($FeBr_3$).

**For Example with Bromine:**



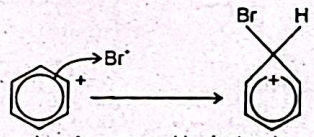

This is bromination of benzene, which involves following steps:



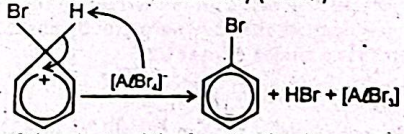

**Step I: Generation of Electrophile:**

**Electrophilic Attack:** Once the electrophile is formed, it follows the same general mechanism as we have discussed earlier.

**Step II: Attack $Br^+$ (Electrophile)**




**Step III:** H-atom of $sp^3$-hybridized carbon in removed by ($AlBr_4^-$)




**With $Cl_2$:** First, the addition of the electrophile, forming the sigma complex which is then deprotonated by $AlBr_4^-$. In the same way, $FeCl_3$ is used as the Lewis acid activator for generating $Cl^+$ (Chloronium ion). The rest of the mechanism is identical to bromination of benzene.

### QUICK CHECK 20.3

a) **Write mechanism of reaction of benzene with chlorine using $AlCl_3$ as catalyst.**
Ans. Please See Short Answer Questions Q.2 (iii)
b) **Although benzene is highly unsaturated yet it does not prefer to undergo addition reactions. Explain.**
Ans. Although benzene is an unsaturated hydrocarbon containing three π-bonds, it does not readily undergo addition reactions because it is an aromatic compound with high resonance stability

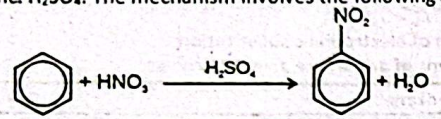
CamScanner

In benzene, the six π-electrons are delocalized over the entire ring. This delocalization gives benzene an extra stability known as **resonance (delocalization) energy**, which is about **152 kJ mol$^{-1}$**.
An **addition reaction** would break the delocalized π-electron cloud and destroy the aromatic nature of benzene. As a result, the molecule would lose its resonance stability, making the process energetically unfavorable.
Therefore, benzene prefers **electrophilic substitution reactions**, in which a hydrogen atom is replaced by another atom or group while the aromatic ring remains intact.

**Q.11 Discuss the nitration of benzene with mechanism.** Exercise D/Q.5

**Ans. Nitration of Benzene**

Nitro group is introduced on benzene, using mixture of conc. $HNO_3$ and conc. $H_2SO_4$. The mechanism involves the following steps:

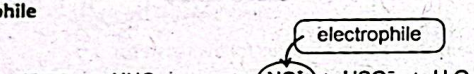


**Step-I:** The electrophile $NO_2^+$ ion is generated by reacting concentrated nitric acid ($HNO_3$) and concentrated sulphuric acid ($H_2SO_4$).
**Step-II:** A pair of electrons from the benzene ring is donated to the $NO_2^+$ electrophile to form a covalent bond causing a loss in aromaticity
**Step-III:** The C – H bond of the substituted carbon atom breaks and the electrons go back into the benzene π bonding system, restoring its aromaticity

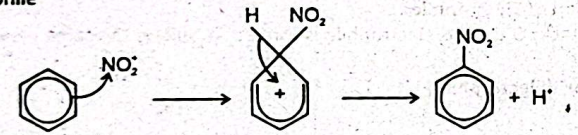
**Check Understanding!**
**Q.5** During nitration of benzene, the active nitrating agent is:
(A) $NO_3^-$ (B) $HNO_3$
(C) $NO_2^-$ (D) $NO_2^+$

➢ **Mechanism of Nitration of Benzene:**

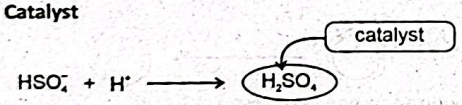
**i. Formation of Electrophile**



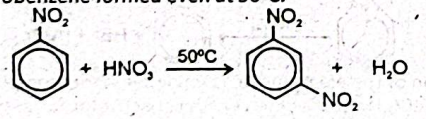
**ii. Attack of Electrophile**



**iii. Regeneration of the Catalyst**



Concentrated sulphuric acid acts as a catalyst so is not written in the equations. At higher temperatures there is a greater chance of getting more than one nitro group substituted onto the ring. Thus we get a certain amount of 1,3-dinitrobenzene formed even at 50°C.



1,3-dinitrobenzene

The substitution of third nitrogroup is not possible.

**QUICK CHECK 20.4**

**Q. Show how the electrophile is produced in the nitration of benzene from sulphuric acid and nitric acid. Which of these two acts as an acid and which acts as a base?**
**Ans. Nitration of Benzene: Reagents:** A 1:1 mixture of conc. $HNO_3$ and conc. $H_2SO_4$ at 50-55°C ($H_2SO_4$ protonates $HNO_3$).



**Electrophile:** Nitronium ion ($NO_2^+$)
**Generation of Electrophile**

$$HONO_2 + H_2SO_4 \xrightleftharpoons{50\text{-}55^\circ C} NO_2^+ + HSO_4^- + H_2O$$

Bronsted-Lowry Acid = $H_2SO_4$, Bronsted-Lowry Base = $HNO_3$

## Friedel-Crafts Alkylation and Acylation

**Q.12 Discuss the Friedel-crafts alkylation and acylation.** Exercise D/Q.6

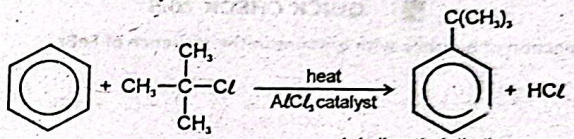
**Ans.** In the Friedel-Crafts alkylation, an alkyl group is substituted into the benzene ring. In the Friedel-Crafts acylation reaction, any acyl group is substituted into the benzene ring in the presence of a Lewis acid catalyst.

An acyl group is the unit $R-\overset{O}{\overset{\|}{C}}-$.

On the other hand, in the Friedel-Crafts alkylation, an alkyl group (e.g., Ethyl) is substituted into the benzene ring.

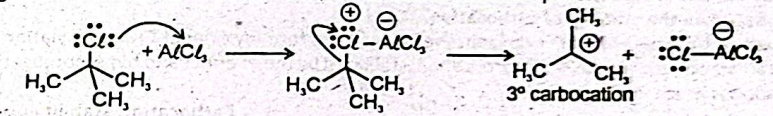
**Check Understanding!**
**Q.6** Show the lewis base and lewis acid in generation of electrophile in friedel–crafts alkylation.

**a) Mechanism of Friedel-Crafts Alkylation:**



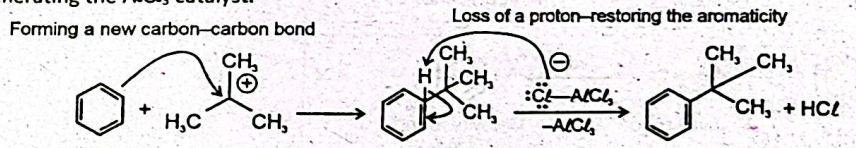
1,1-dimethylethylbenzene

The Friedel-Crafts alkylation reaction proceeds via a three-step mechanism.
**Step I: Generation of Electrophile:** The Lewis acid catalyst ($AlCl_3$) undergoes reaction with the alkyl halide, resulting in the formation of a carbocation, which acts as an electrophile.



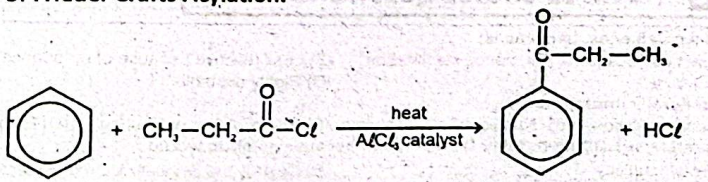
Lewis base Lewis acid electrophile – $E^+$

**Step II: Attack of Electrophile:** The π electrons of aromatic ring attack on electrophilic carbocation, forming an arenium ion as an intermediate. The aromaticity of the arene is temporarily lost due to the disruption of the delocalized π-electron system.
**Step III: Deprotonation:** The deprotonation of the intermediate leads to the reformation of the carbon-carbon double bond, restoring aromaticity to the compound. This proton goes on to form hydrochloric acid, regenerating the $AlCl_3$ catalyst.



Addition of the electrophile resonance structure

**b) Mechanism of Friedel-Crafts Acylation:**

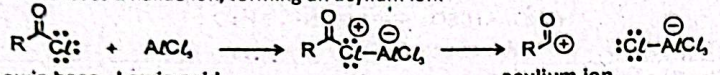


1-phenylpropan-1-one

CamScanner

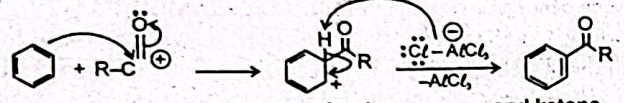
**Friedel-Crafts Acylations Proceed as Follows:**

- A reaction occurs between the Lewis acid catalyst ($AlCl_3$) and the acyl halide. A complex is formed and the acyl halide loses a halide ion, forming an acylium ion.



Lewis base Lewis acid acylium ion

- An electrophilic attack of π electrons of the aromatic ring on the acylium ion ($RCO^+$) takes place.
- The intermediate complex is now deprotonated, restoring the aromaticity to the ring. This proton attaches itself to a chloride ion, forming HCl. The $AlCl_3$ catalyst is regenerated. Thus, the required acyl benzene product is obtained via the Friedel-Crafts acylation reaction.

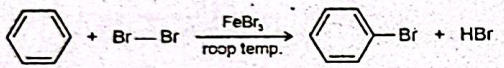


resonance structure aryl ketone

## QUICK CHECK 20.5

**a) Write down the reaction of benzene with bromine in the presence of $FeBr_3$.**

**Ans.**

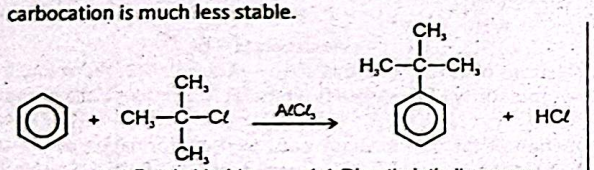


Benzene Bromine Bromobenzene

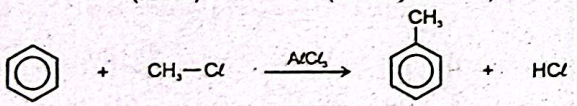
$FeBr_3$ acts as a halogen carrier/Lewis acid and helps generate the electrophile for electrophilic aromatic substitution.

**b) Which of 1,1-dimethyethyllbenzene and methyl benzene is easier to form to Friedel-Craft reaction? Explain based on the stability of carbocation.**

**Ans.** 1,1-Dimethylethylbenzene (tert-butylbenzene) is easier to form by Friedel-Crafts alkylation because the tert-butyl carbocation is a stable 3° carbocation, stabilized by the +I effect and hyperconjugation. A methyl carbocation is much less stable.

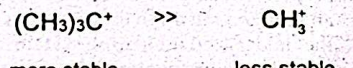


tert-Butyl chloride (t-BuCl) 1,1-Dimethylethylbenzene (tert-Butylbenzene)



Methyl chloride Methylbenzene (Toluene)

**Carbocation Stability Comparison**



more stable 3° Carbocation — less stable Methyl carbocation

## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Compared with alkenes, benzene is:**
   (A) More reactive because of resonance stabilization (B) Less reactive because of resonance stabilization
   (C) Equally reactive (D) Highly unstable
2. **Benzene generally undergoes:**
   (A) Electrophilic addition (B) Nucleophilic substitution (C) Electrophilic substitution (D) Elimination
3. **Benzene prefers substitution rather than addition because addition would:**
   (A) Increase aromaticity (B) Destroy the delocalization of π electrons
   (C) Form stronger σ bonds (D) Increase the delocalization of π electrons



4. **Which type of reagent attacks the electron-rich benzene ring?**
   (A) Nucleophile (B) Electrophile (C) Free radical (D) Base
5. **In electrophilic aromatic substitution, the first step is:**
   (A) Elimination of hydrogen (B) Generation of an electrophile
   (C) Formation of an alkene (D) Oxidation
6. **The intermediate formed during electrophilic substitution is called the:**
   (A) Carbocation (B) Sigma (σ) complex (C) Carbanion (D) Radical intermediate
7. **Aromaticity is restored during electrophilic substitution by:**
   (A) Addition of hydrogen (B) Removal of a proton ($H^+$)
   (C) Oxidation of benzene (D) Cleavage of the benzene ring
8. **Bromination of benzene requires:**
   (A) UV light only (B) $FeBr_3$ or $AlBr_3$ catalyst (C) NaOH solution (D) Nickel catalyst
9. **Chlorination of benzene is commonly carried out in the presence of:**
   (A) NaCl (B) $FeCl_3$ or $AlCl_3$ (C) $KMnO_4$ (D) $H_2O_2$
10. **In bromination of benzene, the Lewis acid catalyst helps by:**
    (A) Destroying the benzene ring (B) Generating a stronger electrophile
    (C) Producing free radicals (D) Reducing bromine
11. **During nitration of benzene, the electrophile produced is:**
    (A) $NO_3^-$ (B) $NO_2^+$ (C) $NH_4^+$ (D) $NO_2^-$
12. **The nitrating mixture consists of:**
    (A) Conc. HCl and conc. $HNO_3$ (B) Conc. $HNO_3$ and conc. $H_2SO_4$
    (C) $H_2SO_4$ and HCl (D) $HNO_3$ and NaOH
13. **In the nitration reaction, concentrated $H_2SO_4$ mainly acts as:**
    (A) A reducing agent (B) An oxidizing agent
    (C) As a base to generate $SO_3$ (D) A catalyst for generating $NO_2^+$
14. **Friedel–Crafts alkylation introduces _____ group into the benzene ring.**
    (A) Acyl (B) Nitro (C) Alkyl (D) Hydroxyl
15. **Friedel–Crafts acylation introduces _____ group into the benzene ring.**
    (A) Alkyl (B) Acyl (C) Amino (D) Halogen
16. **The catalyst commonly used in Friedel-Crafts reactions is:**
    (A) Ni (B) $AlCl_3$ (C) Zn (D) Pt
17. **The electrophile in Friedel-Crafts alkylation is usually a:**
    (A) Carbanion (B) Carbocation (C) Free radical (D) Hydroxide ion
18. **The electrophile in Friedel–Crafts acylation is:**
    (A) Acylium ion ($RCO^+$) (B) Nitronium ion (C) Hydroxide ion (D) Bromide ion
19. **Which reaction introduces a nitro group ($-NO_2$) into benzene?**
    (A) Bromination (B) Sulphonation (C) Nitration (D) Hydrogenation
20. **The major product obtained by bromination of benzene is:**
    (A) Bromocyclohexane (B) Bromobenzene (C) Dibromobenzene (D) Hexabromobenzene

## ORIENTATION IN ELECTROPHILIC SUBSTITUTION REACTIONS

**Q.13 Discuss the orientation in electrophilic substitution reactions.** Exercise D/Q.7

**Ans.** Any group attached with benzene ring affects the electrophilic substitution reaction and determines the orientation of the substitution. There are two ways in which various substituents "direct" electrophilic aromatic substitution of incoming electrophile to benzene ring.

**Check Understanding!**

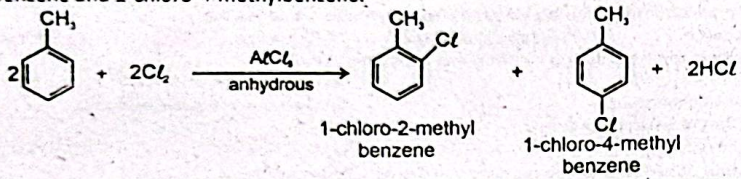
**Q.7 Which of the following is meta directing groups:**
(A) –Cl (B) –OH
(C) –OR (D) $-NO_2$

### Ortho-Para Directing Groups (Activating Groups):

A group that makes the ring more reactive than benzene and influences the incoming electrophile to attach on -ortho and -para positions only, is called an -ortho, -para director. Substituents direct the reaction to give either the "ortho" (1,2) and "para" (1,4) products, with a slight preference for "para". In this pattern, ortho- and para-products dominate, and the meta- product is an extremely minor byproduct. Examples of ortho-, para- directors are –SR, –R,–OH, –OR, $–NR_2$, –SH, –X(–Cl, –Br, –I). Note that these are groups that have the ability to donate electrons to the benzene ring with the exception of the halogen group (–Cl, –Br, –I), which is o,p-directing but deactivating.

CamScanner

The chlorination in the methyl benzene ring takes place in the presence of aluminium chloride (or aluminum bromide if you are using bromine) or iron, and in the absence of UV light. The reactions take place at room temperature. Methyl group is 2,4-directing (o-p directing), which means that incoming groups will tend to go into the 2 or 4 positions on the ring. With chlorine, substitution into the ring gives a mixture of 1-chloro-2-methylbenzene and 1-chloro-4-methylbenzene.



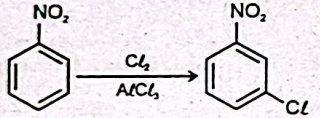

1-chloro-2-methyl benzene

1-chloro-4-methyl benzene

With bromine, you would get the equivalent bromine compounds. Like methyl group on benzene ring, OH group is also ring activator so incoming groups will tend to go into the 2, 4 and 6 positions on the ring.

## ➲ Meta Directing (Deactivating) Groups:

Groups that make the ring less reactive than benzene, and direct the incoming electrophile to attack on meta position mainly are called as-meta directors. Such groups are mostly electron with drawing groups, that destabilize the arenium intermediate. These substituents direct the reaction to give primarily the "meta" (1,3) product. Major product formed in this case is meta substituted. Examples of meta- directors include –CN, C=O, $-NO_2$, $-CO_2-$. Nitrobenzene contains a meta directing group ($NO_2$), its chlorination occurs at the meta position.




*meta*-chloronitrobenzene

### ☑ QUICK CHECK 20.6

**a) Explain why phenol can be nitrated using milder conditions than for benzene.**

**Ans.** Phenol is **more reactive than benzene** towards nitration because the **–OH group is an electron-donating group (+R effect)**. It increases the electron density of the benzene ring, especially at the **ortho** and para positions, making the ring more attractive to electrophiles such as the **nitronium ion ($NO_2^+$)**.

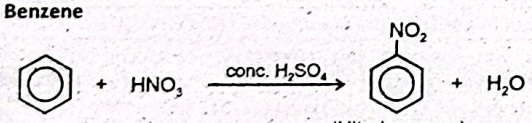
Therefore, Phenol is nitrated under relatively lower temperature. **Phenol** undergoes nitration with dilute nitric acid at room temperature. However, **Benzene** requires a nitrating mixture of concentrated $HNO_3$ and concentrated $H_2SO_4$ along with heating.

Thus, phenol can be nitrated under much **milder conditions** than benzene.

**b) How would you prepare 3-chloronitrobenzene from benzene?**

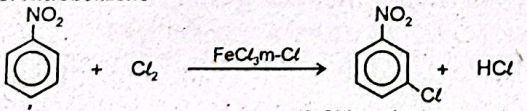
**Ans.** 3-Chloronitrobenzene is prepared by first nitrating benzene and then chlorinating nitrobenzene.

**Step 1: Nitration of Benzene**




(Nitrobenzene)

**Step 2: Chlorination of Nitrobenzene**




(3-Chloronitrobenzene)

**Reason/Explanation:** The $-NO_2$ group is a deactivating, meta-directing group, so chlorine enters the meta position.



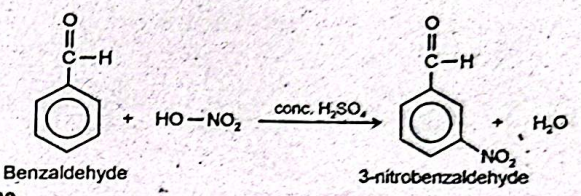
**c) Which products are expected to form in majority when the following are nitrated with conc. nitric acid ($HNO_3$) and sulphuric acid ($H_2SO_4$)? Give reactions**

**i. benzaldehyde ii. Chlorobenzene iii. Phenol iv. Benzene carboxylic acid**

**Ans. (i) Benzaldehyde:** The –CHO group is a meta-directing group.

**Major Product:** 3-Nitrobenzaldehyde (m-Nitrobenzaldehyde)

**Reaction:**




Benzaldehyde

3-nitrobenzaldehyde

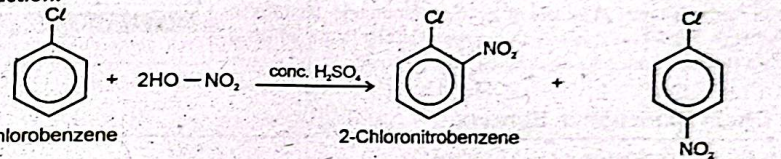
**(ii) Chlorobenzene**

The –Cl group is an ortho-para directing group.

**Major Products:**

- 2-Chloronitrobenzene (ortho)
- 4-Chloronitrobenzene (para) *(major due to less steric hindrance)*

**Reaction:**




Chlorobenzene

2-Chloronitrobenzene

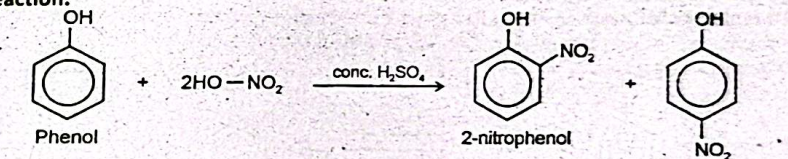
4-Chloronitrobenzene

**(iii) Phenol**

The –OH group is a strong ortho-para directing group.

**Major Products:** 2-Nitrophenol and 4-Nitrophenol

**Reaction:**




Phenol

2-nitrophenol

4-nitrophenol

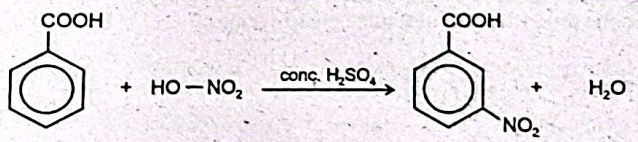
**Note:** Under strongly nitrating conditions (conc. $HNO_3$/conc. $H_2SO_4$), phenol can undergo further nitration to give 2,4,6-trinitrophenol (picric acid). However, if the question asks for the major products of nitration, the expected answer is ortho- and para-nitrophenol.

**(iv) Benzene Carboxylic Acid (Benzoic Acid)**

The –COOH group is a meta-directing group.

**Major Product:** 3-Nitrobenzoic acid (m-Nitrobenzoic acid)

**Reaction:**




Benzene carboxylic acid

3-nitrobenzene carboxylic acid

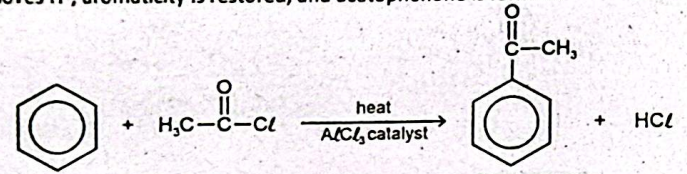
**d) Give a mechanism of the reaction between acetyl chloride and benzene.**

**Ans.** Friedel-Crafts acylation of benzene with acetyl chloride:

CamScanner

$CH_3COCl + AlCl_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}{}^{+} + AlCl_4^-$

i) π-electrons of benzene attack $CH_3CO^+$ to form an arenium (sigma) complex.
ii) $AlCl_4^-$ removes $H^+$, aromaticity is restored, and acetophenone is formed.




Acetophenone

## OTHER REACTIONS OF BENZENE

### ➲ Combustion

**Q.14 Discuss the combustion of benzene.** SQ

**Ans.** When benzene is burnt in excess of air, it is completely oxidized to $CO_2$ and $H_2O$. However, this reaction gives a smoky flame which is used as a test for aromatic compounds.

$$2C_6H_6 + 15O_2 \longrightarrow 12CO_2 + 6H_2O$$

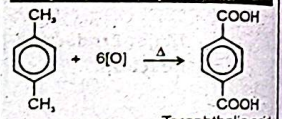
**Check Understanding!**
Q.8 Convert benzene into cyclohexane.

### ➲ Side Chain Oxidation in Benzene

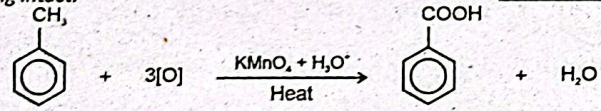
**Q.15 Discuss the side chain oxidation in benzene.** LQ

**Ans.**
- *Oxidation reaction that takes place at an alkyl group directly attached to a benzene ring is termed as side-chain oxidation.*
- *In side chain oxidation reaction, alkyl benzenes are readily oxidized by alkaline $KMnO_4$ or acidic $K_2Cr_2O_7$ or dilute $HNO_3$.*
- *In these kinds of reaction, the alkyl groups are oxidized to the carboxylic acid group, regardless of the size of alkyl group, keeping the benzene ring intact.*

**For Entry Test**

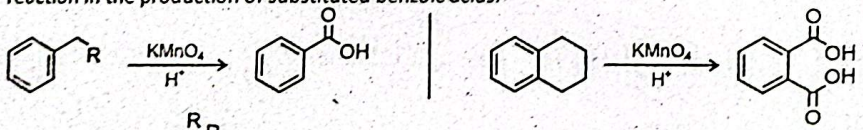


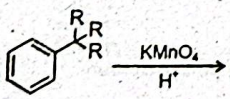

Teraphthalic acid




methylbenzene (toluene) — benzenecarboxylic acid (benzoic acid)

- **Condition for Side Chain Oxidation:** Side-chain oxidation of alkylbenzene takes place when there is at least one benzylic hydrogen attached to the carbon. No reaction occurs in the absence of a benzylic hydrogen. Thus, these reactions have no effect on tertiary carbons attached to an aromatic ring.
- **Length of Alkyl group at One Position:** Whatever the length of an alkyl group may be, it gives only one carboxyl group as a product after oxidation. Following example demonstrates the utilization of oxidation reaction in the production of substituted benzoic acids.




No Reaction because there is no benzylic hydrogen attached to the carbon.



**➢ Important Note:**
Both alkane and benzene are very stable and **insusceptible** to oxidation but when put together, the benzylic carbon which is directly attached to the benzene ring becomes more reactive and more susceptible to oxidation.

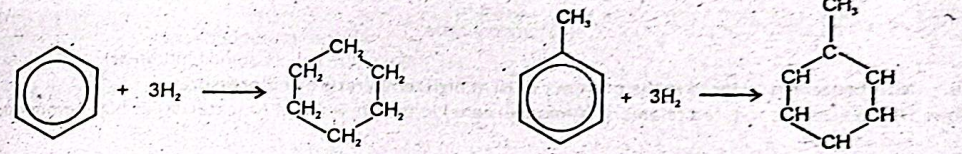
**➢ Significance:**
Oxidation of alkylbenzene containing benzylic protons by $KMnO_4$ is used an **identification test.** Purple colour of $KMnO_4$ solution is discharged, once consumed in the oxidation reaction. Therefore, one can easily differentiate between benzene, benzene containing primary, secondary, and tertiary alkyl groups by a chemical test with $KMnO_4$ solution.

### ➲ Addition Reactions of Benzene

**Q.16 Discuss addition reactions of benzene giving examples of hydrogenation and halogenation of benzene.** LQ

**Ans.** We will examine hydrogenation and halogenation addition reactions of benzene as follows:

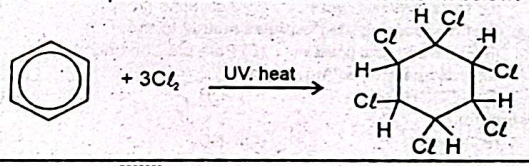
**a) Hydrogenation of Benzene:**
The hydrogenation of benzene and other arenes, involves the addition of 1,2 , or 3 moles of hydrogen to the carbons of benzene. Cyclohexane is produced when benzene is completely hydrogenated. Cyclohexane is a useful solvent and a precursor in the production of other chemicals.




cyclohexane — toluene

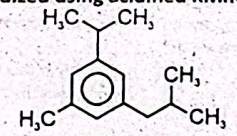
These reactions destroy the electron delocalisation in the original benzene ring, because those electrons are being used to form bonds with the new hydrogen atoms. Although the reactions are exothermic overall, because of the strength of all the new carbon-hydrogen bonds, there is a high activation barrier to the reaction. The reactions are done using the same finely divided nickel catalyst that is used in they hydrogenation of alkenes and at similar temperatures (around 150°C), but a higher pressure is applied.

**b) Addition of Halogens:**
Chlorine and bromine react in the same way in the absence of a catalyst, UV light and heat are sufficient for complete halogenation. The complete chlorination of benzene is shown below:




**☑ QUICK CHECK 20.7**

a) **Predict the product formed when:**
i. **the compound (A) given here is oxidized using acidified $KMnO_4$ or $K_2Cr_2O_7$:**

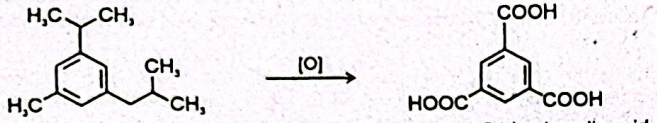



**(A)**

**Ans.** The given compound is **3-ethyl-5-propyltoluene.** All three side chains **(methyl, ethyl and propyl)** contain at least one **benzylic hydrogen atom.** On oxidation with **acidified $KMnO_4$ or $K_2Cr_2O_7$,** each alkyl side chain is completely oxidized to a **carboxyl group (–COOH)** regardless at its length.

CamScanner

**Reaction:**

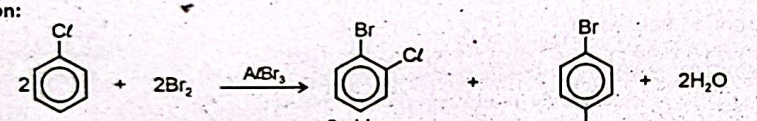



3-Ethyl-5-propyltoluene — Benzene-1,3,5-tricarboxylic acid (Trimesic acid)

**ii. Bromine is added to chlorobenzene in the presence of $AlBr_3$.**

**Ans.** Chlorobenzene undergoes electrophilic aromatic substitution (bromination). The chlorine atom is an ortho-para directing group, so bromine enters the ortho and para positions.

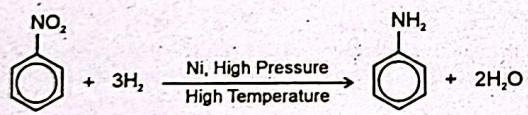
**Reaction:**




2-chloro bromobenzene — 4-chloro bromobenzene (major due to less steric hindrance)

**iii. Nitrobenzene is reduced in the presence of Ni at high temperature and pressure.**

**Ans.** Nitrobenzene is reduced to **aniline (Aminobenzene)** in the presence of Ni (catalyst) at high temperature and pressure.




Aniline (Benzanamine)

## BLOCK # 03 MULTIPLE CHOICE QUESTIONS (MCQs)

1. A group that increases the reactivity of the benzene ring is called:
(A) Deactivating group (B) Meta-directing group (C) Activating group (D) Neutral group
2. The methyl ($-CH_3$) group directs incoming electrophiles mainly to the:
(A) Meta position only (B) Ortho and para positions (C) Para position only (D) Random positions
3. Which of the following is an ortho-para directing group?
(A) $-NO_2$ (B) $-COOH$ (C) $-OH$ (D) $-CN$
4. Which group is a meta director?
(A) $-OH$ (B) $-CH_3$ (C) $-NO_2$ (D) $-NH_2$
5. Meta-directing groups are generally:
(A) Electron-donating (B) Electron-withdrawing (C) Neutral (D) Free radicals
6. Which compound gives meta-chloronitrobenzene on chlorination?
(A) Phenol (B) Toluene (C) Nitrobenzene (D) Aniline
7. Phenol undergoes nitration more easily than benzene because the –OH group is:
(A) Ring deactivating (B) Electron withdrawing (C) Ring activating (D) Meta directing
8. Chlorination of methylbenzene mainly produces:
(A) Meta chlorotoluene only (B) Only ortho-chlorotoluene
(C) Only para-chlorotoluene (D) O- and p-chlorotoluene
9. Benzene burns with a:
(A) Blue non-luminous flame (B) Smoky luminous flame
(C) Green flame (D) Colorless flame
10. Complete combustion of benzene produces:
(A) CO and $H_2$ (B) $CO_2$ and $H_2O$ (C) $CH_4$ and $O_2$ (D) C and $H_2O$
11. Side-chain oxidation of alkylbenzene occurs at the:
(A) Benzene ring (B) Benzylic carbon (C) Double bond (D) Carbonyl carbon



12. Which reagent is commonly used for side-chain oxidation of alkylbenzene?
(A) HCl (B) $KMnO_4$ (C) NaOH (D) $Br_2$
13. Side-chain oxidation occurs only if the alkyl group contains at least:
(A) One benzylic hydrogen (B) One chlorine atom (C) Two methyl groups (D) One double bond
14. Oxidation of toluene with alkaline $KMnO_4$ gives:
(A) Phenol (B) Benzoic acid (C) Benzaldehyde (D) Cyclohexane
15. During oxidation of alkylbenzenes, the benzene ring:
(A) Is destroyed (B) Remains intact
(C) Is converted into cyclohexane (D) Forms an alcohol
16. Hydrogenation of benzene produces:
(A) Cyclohexene (B) Cyclohexane (C) Benzyl alcohol (D) Phenol
17. Hydrogenation of benzene requires:
(A) Ni catalyst at high temp. and P (B) Sulphur catalyst at high temp. and P
(C) UV light (D) $KMnO_4$
18. Complete hydrogenation of one mole of benzene requires:
(A) One mole of $H_2$ (B) Two moles of $H_2$ (C) Three moles of $H_2$ (D) Four moles of $H_2$
19. In the absence of a catalyst, chlorine reacts with benzene under:
(A) Dilute acid (B) UV light and heat (C) Room temperature only (D) Sodium hydroxide

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

**BLOCK # 01**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. B | 4. A | 5. B | 6. C | 7. B | 8. C | 9. C | 10. B | 11. B | 12 A | 13. C | 14. B | 15. C |
| 16. A | 17. B | 18. C | 19. C | 20. C | | | | | | | | | | |

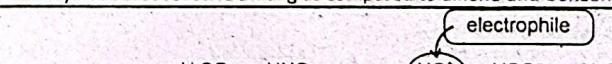
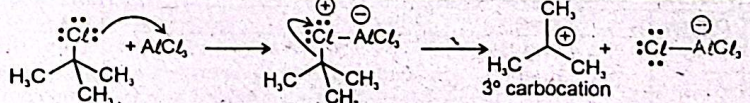
**BLOCK # 02**

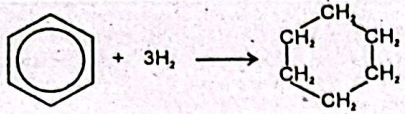
| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. B | 4. B | 5. B | 6. B | 7. B | 8. B | 9. B | 10. B | 11. B | 12. B | 13. D | 14. C | 15. B |
| 16. B | 17. B | 18. A | 19. C | 20. B | | | | | | | | | | |

**BLOCK # 03**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. C | 2. B | 3. C | 4. C | 5. B | 6. C | 7. C | 8. D | 9. B | 10. B | 11. B | 12. B | 13. A | 14. B | 15. B |
| 16. B | 17. A | 18. C | 19. B | | | | | | | | | | | |

## CHECK UNDERSTANDING (SOLUTIONS)

| Q. # | Option | Hint/Explanation |
|---|---|---|
| 1. | (C) | C–C bond length is 1.397Å = 139 pm |
| 2. | S/Q | **Resonance Energy:** The difference of energy between hypothetical compound i.e., (1, 3, 5-Cyclohexatriene) and actual compound i.e. (benzene) is called resonance energy. |
| 3. | (C) | Anisole is methoxybenzene   |
| 4. | S/Q | Alkane are most unreactive organic compounds. They are non–polar and have sigma bond only. So they are least reactive among as compared to alkene and benzene. |
| 5. | (D) |   |
| 6. | S/Q |   Lewis base Lewis acid electrophile – $E^+$ |
| 7. | (D) | $-NO_2$ is meta directing and deactivating group. |

| | | |
|---|---|---|
| 8. | S/Q |  cyclohexane |

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. **Which of the following is the major product when methyl chloride ($CH_3Cl$) reacts with methylbenzene in the presence of $AlCl_3$:**
a) 1,2-dimethyl benzene b) 1,4-dimethyl benzene c) 1,3-dimethyl benzene d) both a and b

II. **Bromine reacts more readily with phenol than with benzene. This is because the:**
a) benzene ring in phenol is more susceptible to nucleophilic attack
b) benzene ring in phenol is deactivated because the oxygen of the OH group is very electronegative
c) lone pair of electrons on the oxygen atom in phenol overlap with the delocalised electrons in the benzene ring
d) lone pair of electrons on the oxygen atom enable phenol to act as an electrophile

III. **Aluminium chloride catalyses the reaction of benzene and ethanoyl chloride. This is because aluminium chloride.**
a) has significant covalent character b) exists as a dimer in non-polar solvents
c) is an electron pair acceptor d) is rapidly hydrolysed

IV. **Benzene is nitrated using a mixture of concentrated nitric and sulphuric acids. Here, sulphuric acid:**
a) acts as a solvent for the benzene and the nitric acid
b) protonates the benzene to speed up the reaction
c) protonates the nitric acid which acts as a base
d) reacts with the benzene to form a benzenesulfonic acid intermediate

V. **In the reaction of benzene with chloromethane, aluminium chloride is added because it reacts with**
a) benzene to produce an electrophile b) benzene to produce a nucleophile
c) chloromethane to produce a nucleophile d) chloromethane to produce an electrophile

VI. **Methylbenzene reacts with a mixture of concentrated nitric acid and concentrated sulphuric acid. What is the name of the mechanism for this reaction?**
a) electrophilic addition b) electrophilic substitution
c) nucleophilic addition d) nucleophilic substitution

VII. **X-ray diffraction provides evidence that benzene molecule has:**
a) delocalised π-electrons b) carbon-carbon bonds that are all the same length
c) lower thermodynamic stability than molecules of 1,3,5-cyclohexatriene
d) greater thermodynamic stability than molecules of 1,3,5-cyclohexatriene

VIII. **Which statement(s) support(s) the delocalised model for the structure of benzene?**
1. **All carbon-carbon bonds have the same length.**
2. **The enthalpy change of hydrogenation of benzene is less exothermic than expected.**
3. **Bromine reacts with benzene less readily than with cyclohexene.**
a) 1,2 and 3 b) Only 1 and 2 c) Only 2 and 3 d) Only 1

IX. **Benzene reacts with an organic reagent in the presence of a halogen carrier to form phenylethanone. Which organic reagent is required?**
a) $CH_3CH_2OH$ b) $CH_3CHO$ c) $CH_3COCl$ d) $CH_3COOH$

### Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | b | 1,4-dimethyl benzene | This reaction is a Friedel-Crafts alkylation. The methyl group ($-CH_3$) already present on methylbenzene is an ortho-para directing group. Therefore, both ortho and para are formed but para (1,4) product has lesser steric hindrance. |
| II. | c | lone pair of electrons on the oxygen atom in phenol overlap with the delocalised electrons in the benzene ring | The oxygen atom of the –OH group donates its lone pair into the benzene ring by resonance (+R effect). This increases the electron density of the ring, making phenol much more reactive towards electrophilic substitution reactions such as bromination. |
| III. | c | is an electron pair acceptor | Aluminium chloride ($AlCl_3$) is a Lewis acid because it accepts an electron pair. It reacts with ethanoyl chloride to generate the electrophile (acylium ion), which attacks the benzene ring during the Friedel-Crafts acylation reaction. |
| IV. | c | protonates the nitric acid which acts as a base | Concentrated sulphuric acid protonates nitric acid to form the nitronium ion ($NO_2^+$), which is the electrophile responsible for the nitration of benzene. |
| V. | d | chloromethane to produce an electrophile | $AlCl_3$ reacts with chloromethane ($CH_3Cl$) to generate the methyl electrophile ($CH_3^+$ or its equivalent). This electrophile attacks the benzene ring during the Friedel-Crafts alkylation reaction. |
| VI. | b | electrophilic substitution | The nitro group replaces a hydrogen atom of methylbenzene while the aromatic ring remains intact. Therefore, the reaction follows an electrophilic substitution mechanism. |
| VII. | b | carbon-carbon bonds that are all the same length | X-ray diffraction studies show that every carbon-carbon bond in benzene has the same bond length (139 pm), confirming the delocalization of π-electrons. |
| VIII. | a | 1,2 and 3 | All three statements support the delocalized model of benzene:<br>All C–C bonds have equal length.<br>The enthalpy of hydrogenation is less exothermic than expected because benzene is resonance stabilized.<br>Benzene reacts less readily with bromine than cyclohexene because addition would destroy aromaticity. |
| IX. | c | $CH_3COCl$ | Phenylethanone (acetophenone) is prepared by Friedel-Crafts acylation of benzene using ethanoyl chloride ($CH_3COCl$) in the presence of $AlCl_3$ catalyst. |

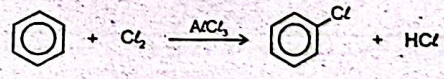


## Q 2. SHORT ANSWER QUESTIONS SAQs

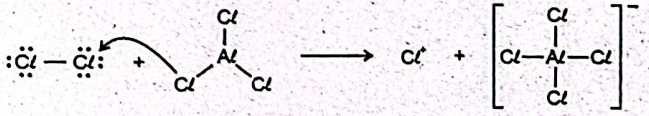
a) **Benzene reacts with chlorine in the presence of a halogen carrier, such as $AlCl_3$.**
i) **Write the equation for the reaction of benzene with chlorine.**
ii) **How does the halogen carrier support the reaction?**
iii) **Outline a mechanism for this reaction. Include curly arrows and relevant dipoles.**
iv) **State the name of this mechanism.**

Ans. i) Benzene reacts with chlorine in the presence of **anhydrous aluminium chloride ($AlCl_3$)** to form **chlorobenzene** and hydrogen chloride.

**Chemical Equation:**



Ans. **ii) Halogen Carrier: $AlCl_3$**
$AlCl_3$ acts as a Lewis-acid halogen carrier. It polarizes $Cl_2$ and generates a strongly electrophilic chlorine species (often represented as $Cl^+$ with $AlCl_4^-$), enabling attack on benzene; $AlCl_3$ is regenerated at the end.
**Polarization of $Cl_2$**



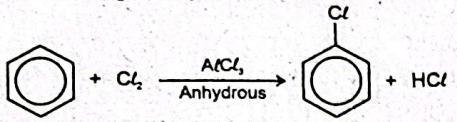
CamScanner

$AlCl_3$ accepts electron density and helps generate the electrophile.

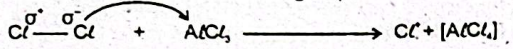
**Ans. iii) Mechanism of Chlorination of Benzene in the presence of $AlCl_3$:**

**Formation of Electrophile:**

$$Cl_2 + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$$



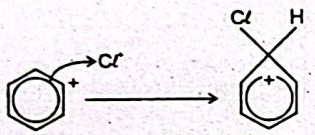

This is chlorination of benzene, which involves following steps:



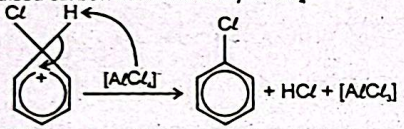

**Step I: Generation of Electrophile:**

**Electrophilic Attack:** Once the electrophile is formed, it π electrons of benzene.

**Step II: Attack $Cl$ (Electrophile)**




**Step III:** H-atom of $sp^3$-hybridized carbon in removed by $AlCl_4^-$

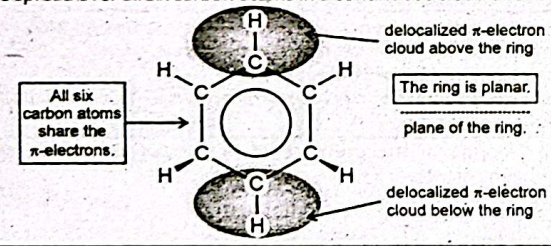



**With $Cl_2$:** In the same way, $FeCl_3$ is used as the Lewis acid activator for generating $Cl^+$ (Chloronium ion). The rest of the mechanism is identical to bromination of benzene.

**Ans. iv)** The reaction proceeds by an Electrophilic Aromatic Substitution mechanism.

**b) Explain what is meant by the term delocalized π-bond electrons.**

**Ans.** Delocalized π-bond electrons are electrons that are not confined between one pair of carbon atoms. In benzene, the six π electrons are spread over all six carbon atoms in a continuous cloud above and below the planar ring.




**c) An acylium ion has the structure R – C = O where R is any alkyl group. In the conversion of benzene into phenylethanone, $C_6H_5COCH_3$, an acylium ion $CH_3CO^+$ reacts with a benzene molecule.**

**i) Write an equation to show the formation of this acylium ion from ethanoyl chloride and one other substance.**

**ii) Name and outline the mechanism of the reaction of this acylium ion with benzene.**

**Ans. i)** The acylium ion is formed by the reaction of ethanoyl chloride with anhydrous aluminium chloride ($AlCl_3$).

**Chemical Equation:**

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \longrightarrow \underset{\text{Acylium ion}}{CH_3-\overset{O}{\overset{\|}{C}}{}^+} + \underset{\text{Tetrachloroaluminate ion}}{AlCl_4^-}$$



Here,

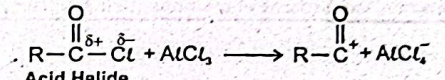
- $CH_3-C\equiv O^+$ = Acylium ion (electrophile)
- $AlCl_4^-$ = Tetrachloroaluminate ion

**ii) Name and Mechanism:**

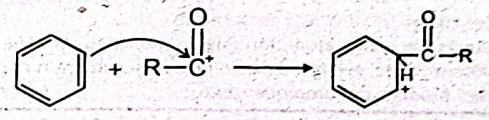
The introduction of an acyl group ($R-\overset{O}{\overset{\|}{C}}-$) in the benzene ring in the presence of an acyl halide and a catalyst $AlCl_3$ is called **Friedel Crafts acylation.**

**Mechanism:**

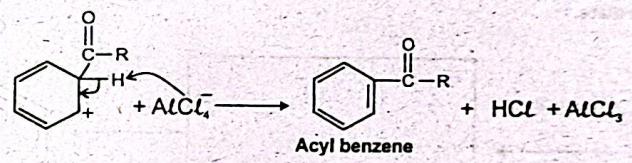
- **Generation of Electrophile:**



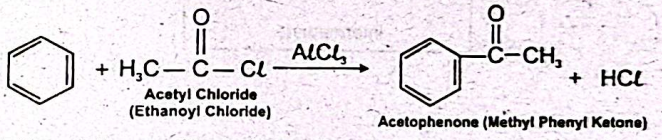

- **Attack of Electrophile:**




- **Deprotonation:**

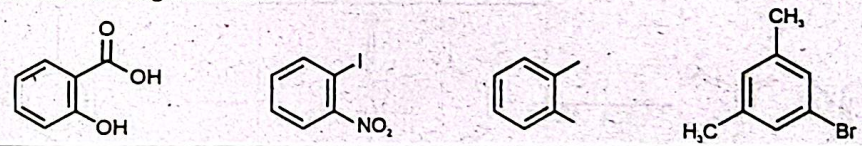



**e.g.,**




**Product:** Phenylethanone (Acetophenone)

**d) Name the following molecules:**

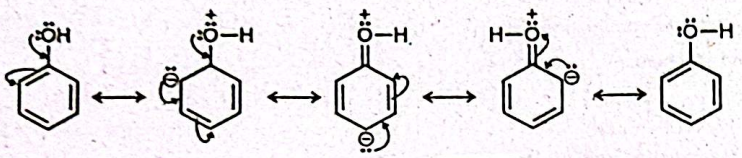



| Ans. | IUPAC Names | Common Names |
|---|---|---|
| (i) | 2-Hydroxybenzoic acid | Salicylic acid |
| (ii) | 1-Iodo-2-nitrobenzene | o-Iodonitrobenzene |
| (iii) | 1,2-Dimethylbenzene | o-Xylene |
| (iv) | 1-Bromo-3,5-dimethylbenzene | 3,5-dimethylbenzene |

CamScanner

**e) Describe, with the aid of a diagram, the bonding in phenol to show delocalization of π electron.**

**Ans.**



## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) The compound iodine monobromide, IBr, also reacts with benzene in an electrophilic reaction. Which compound would be the main product of this reaction, iodobenzene or bromobenzene? Explain your answer.**

**Ans.** The main product is iodobenzene ($C_6H_5I$).

**Explanation:**

Iodine monobromide (IBr) is a polar molecule because bromine is more electronegative than iodine.

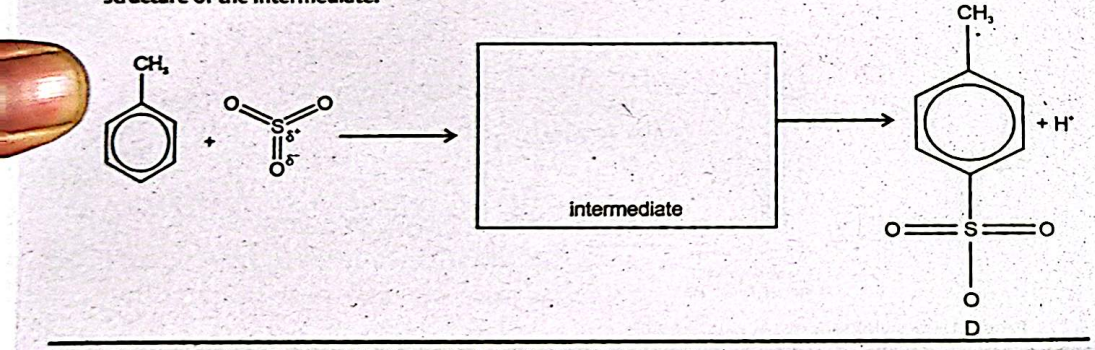
$$I^{\delta+} — Br^{\delta-}$$

The iodine atom carries the partial positive charge ($\delta^+$) and acts as the electrophile.

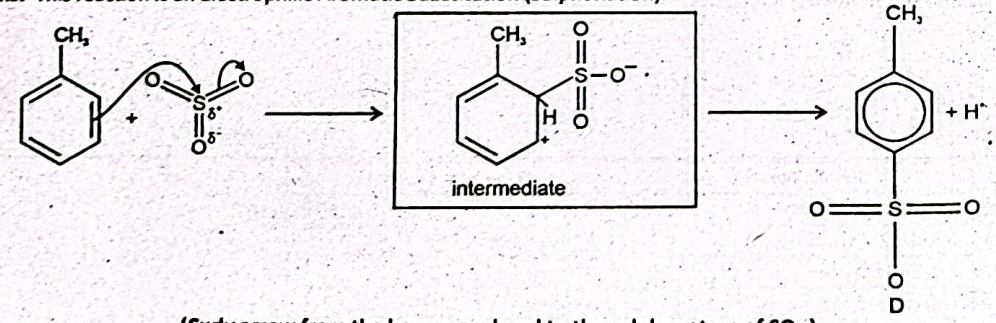
During the reaction, the benzene ring attacks the iodine atom, forming an intermediate. The bromide ion ($Br^-$) then removes the proton from the intermediate, giving iodobenzene as the substitution product.

Therefore, iodobenzene ($C_6H_5I$) is the major product, not bromobenzene.

**b) Methylbenzene reacts with sulphur trioxide, $SO_3$, to form product shown below. The electrophile in this reaction is $SO_3$. Complete the mechanism for the formation of product. Show curly arrows and the structure of the intermediate.**




**Ans.** This reaction is an Electrophilic Aromatic Substitution (Sulphonation).




**(Curly arrow from the benzene π-bond to the sulphur atom of $SO_3$.)**

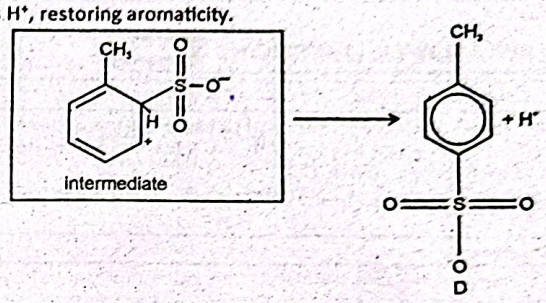


**Step 1: Electrophilic Attack**

The π-electrons of methylbenzene attack the electrophile $SO_3$, producing a σ-complex (arenium ion).

**Step 2: Loss of Proton**

The σ-complex loses $H^+$, restoring aromaticity.




**Product D:** 4-Methylbenzenesulphonic acid (p-Toluenesulphonic acid)

**Name of the Mechanism:** Electrophilic Aromatic Substitution (Sulphonation)

**c) Outline the mechanism for this nitration of benzoic acid. Show how $H_2SO_4$ behaves as a catalyst.**

**Ans.** The reaction proceeds by Electrophilic Aromatic Substitution (Nitration).

**Step 1: Generation of Electrophile**

Sulphuric acid protonates nitric acid to produce the nitronium ion ($NO_2^+$).

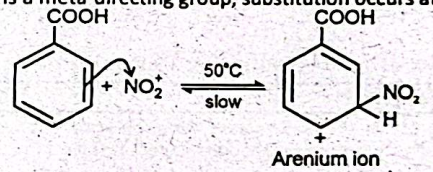
$$HONO_2 + H_2SO_4 \xrightarrow{50\text{-}55°C} NO_2^+ + HSO_4^- + H_2O$$

Here, $H_2SO_4$ acts as a catalyst because it generates the electrophile and is regenerated at the end of the reaction.

**Step 2: Electrophilic Attack**

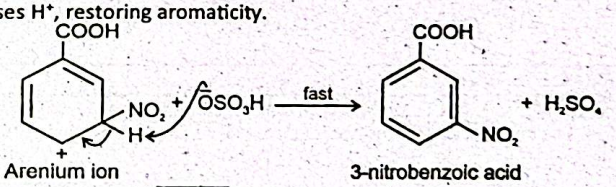
The π-electrons of benzoic acid attack the $NO_2^+$ ion, forming a σ-complex.

Because the –COOH group is a meta-directing group, substitution occurs at the meta position.




**Step 3: Loss of Proton**

The σ-complex loses $H^+$, restoring aromaticity.




## DESCRIPTIVE QUESTIONS DQs

**Q.4 Explain the atomic orbital model for the structure of benzene.**

**Ans.** See Question No. Q.4

**Q.5 Describe the nitration of benzene. Explain its mechanism.**

**Ans.** See Question No. Q.11

CamScanner

**Q.6 Discuss Friedel-Crafts reactions of benzene.**

**Ans.** See Question No. Q.12

**Q.7 Write a note on orientation in electrophilic substitution reactions of benzene.**

**Ans.** See Question No. Q.13

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 Describe the shape of benzene molecule.**

**Ans.** Benzene is a planar hexagonal molecule consisting of six carbon atoms arranged in a ring. Each carbon atom is $sp^2$ hybridized and forms three sigma bonds with two adjacent carbon atoms and one hydrogen atom. The bond angle around each carbon atom is 120°.
The unhybridized p-orbitals overlap sideways to form a delocalized π-electron cloud above and below the plane of the ring.

**Q.2 What is resonance in benzene?**

**Ans.** Resonance is the phenomenon in which a molecule cannot be represented by a single structural formula and is best described by two or more contributing structures. In benzene, the six π-electrons are delocalized over the entire ring rather than being confined between specific carbon atoms.
This delocalization increases the stability of benzene.

**Q.3 What is resonance energy?**

**Ans.** Resonance energy is the extra stability possessed by a molecule due to electron delocalization. It is equal to the difference between the actual energy of the molecule and the energy of its most stable hypothetical structure.
For benzene, the resonance energy is approximately: **152 kJ $mol^{-1}$**

**Q.4 Why is benzene more stable than alkenes?**

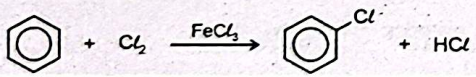
**Ans.** Benzene is more stable because its six π-electrons are delocalized over the entire ring. This delocalization lowers the energy of the molecule and distributes electron density evenly throughout the ring.
Therefore, benzene resists addition reactions and prefers substitution reactions.

**Q.5 Compare the reactivity of benzene with alkenes.**

**Ans.** Alkenes readily undergo electrophilic addition reactions because they contain localized π-bonds. Benzene, however, possesses a delocalized π-electron system and undergoes electrophilic substitution reactions to preserve aromatic stability.
Hence, benzene is less reactive than alkenes towards addition reactions.

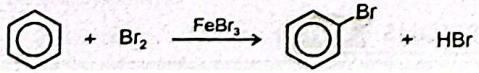
**Q.6 Describe chlorination of benzene.**

**Ans.** Benzene reacts with chlorine in the presence of ferric chloride catalyst to produce chlorobenzene and hydrogen chloride. The reaction proceeds through an electrophilic substitution mechanism.
**Equation:**




**Q.7 Describe bromination of benzene.**

**Ans.** Benzene reacts with bromine in the presence of ferric bromide catalyst to produce bromobenzene and hydrogen bromide. The catalyst generates the electrophile required for substitution.
**Equation:**



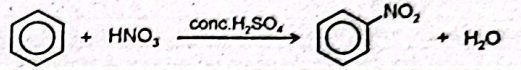

**Q.8 Explain the formation of nitronium ion.**

**Ans.** The nitronium ion ($NO_2^+$) is the electrophile responsible for nitration of benzene. It is generated by the reaction between concentrated nitric acid and concentrated sulfuric acid.
**Equation:** $HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + H_2SO_4^- + H_2O$



**Q.9 Describe nitration of benzene.**

**Ans.** Benzene reacts with concentrated nitric acid in the presence of concentrated sulfuric acid to produce nitrobenzene. The reaction proceeds via electrophilic aromatic substitution.
**Equation:**




**Q.10 What is the role of sulfuric acid in nitration?**

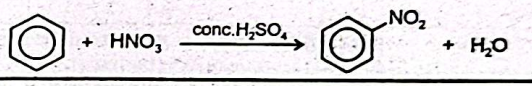
**Ans.** Concentrated sulfuric acid acts as a catalyst and protonating agent in nitration. It converts nitric acid into the nitronium ion ($NO_2^+$), which acts as the electrophile in the reaction.
This electrophile attacks the benzene ring to initiate substitution.

**Q.11 Explain the mechanism of nitration of benzene.**

**Ans.** Nitration of benzene proceeds through an electrophilic aromatic substitution mechanism. First, concentrated sulfuric acid reacts with nitric acid to generate the nitronium ion ($NO_2^+$), which acts as the electrophile. The benzene ring attacks the electrophile to form a sigma complex, which then loses a proton to regenerate aromaticity.
**Step 1: Formation of electrophile**

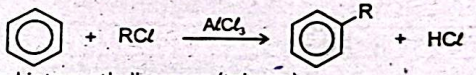
$$HNO_3 + H_2SO_4 \longrightarrow NO_2^+ + HSO_4^- + H_2O$$

**Overall reaction:**




**Q.12 Explain Friedel-Crafts alkylation.**

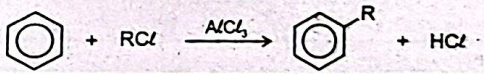
**Ans.** Friedel-Crafts alkylation is an electrophilic substitution reaction in which an alkyl group is introduced into the benzene ring using an alkyl halide and anhydrous aluminium chloride catalyst. The catalyst generates the electrophile required for the reaction.
**Equation:**




Thus, benzene is converted into methylbenzene (toluene).

**Q.13 Explain Friedel-Crafts acylation.**

**Ans.** Friedel-Crafts acylation is a reaction in which an acyl group is introduced into the benzene ring using an acyl chloride and anhydrous aluminium chloride catalyst. The reaction produces aromatic ketones.
**Equation:**




**Q.14 What is the role of aluminium chloride in Friedel-Crafts reactions?**

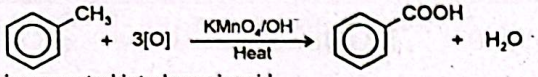
**Ans.** Anhydrous aluminium chloride acts as a Lewis acid catalyst in Friedel-Crafts reactions. It accepts an electron pair from the alkyl halide or acyl chloride and generates a strong electrophile.
**For example:** $CH_3Cl + AlCl_3 \longrightarrow CH_3^+ + AlCl_4^-$
The electrophile then attacks the benzene ring.

**Q.15 Explain side-chain oxidation of alkyl benzene.**

**Ans.** Alkyl benzenes containing at least one benzylic hydrogen atom undergo oxidation of the side chain when heated with hot alkaline potassium permanganate followed by acidification. Regardless of chain length, the final product is benzoic acid.

CamScanner

**Equation:**

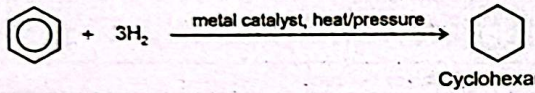



Thus, methylbenzene is converted into benzoic acid.

**Q.16 Explain the hydrogenation of benzene.**

**Ans.** Benzene reacts with hydrogen in the presence of nickel catalyst under high temperature and pressure to form cyclohexane. This reaction is an example of catalytic hydrogenation.

**Equation:**




The product formed is cyclohexane.

**Q.17 What is electrophilic aromatic substitution?**

**Ans.** Electrophilic aromatic substitution is a reaction in which an electrophile replaces a hydrogen atom of the benzene ring while preserving aromaticity. This type of reaction is characteristic of aromatic compounds.

**Examples include:**

- Nitration
- Halogenation
- Sulphonation
- Friedel-Crafts reactions

**Q.18 What is a sigma complex?**

**Ans.** A sigma complex is an unstable intermediate formed when an electrophile attacks the benzene ring during electrophilic substitution. During its formation, aromaticity is temporarily lost.
The sigma complex rapidly loses a proton to regenerate the aromatic system.

**Q.19 Why does benzene prefer substitution reactions instead of addition reactions?**

**Ans.** Benzene undergoes substitution reactions because addition reactions would destroy the delocalized π-electron system and reduce aromatic stability. Substitution reactions preserve the aromatic ring and therefore are energetically more favorable.
Hence, benzene resists addition reactions under ordinary conditions.

**Q.20 What are ortho, meta and para positions in benzene derivatives?**

**Ans.** The relative positions of substituents in a benzene ring are described as ortho, meta and para positions.

- **Ortho (o-)** = positions 1,2
- **Meta (m-)** = positions 1,3
- **Para (p-)** = positions 1,4

These terms are widely used in aromatic substitution reactions.

**Q.21 What are ortho-para directing groups?**

**Ans.** Ortho-para directing groups direct an incoming electrophile mainly to the 2- and 4-positions of a substituted benzene ring. Activating groups discussed in the chapter increase electron density in the ring and favor ortho/para substitution. **Examples include:** $-CH_3$, $-OH$, $-NH_2$, $-Cl$–

**Q.22 What are meta directing groups?**

**Ans.** Meta directing groups are substituents that direct incoming electrophiles to the meta position of the benzene ring. These groups withdraw electron density from the ring and generally deactivate it.

**Examples include:** $-NO_2$, $-COOH$, $-CHO$, $-SO_3H$

**Q.23 Explain nitration of methylbenzene.**

**Ans.** The methyl group activates the aromatic ring and directs nitration mainly to the ortho and para positions. Therefore methylbenzene gives mainly 2-nitromethylbenzene and 4-nitromethylbenzene with the nitrating mixture.

**Q.24 Explain chlorination of methylbenzene.**

**Ans.** The methyl group activates the aromatic ring and directs ring chlorination mainly to the ortho and para positions. Thus methylbenzene gives mainly ortho- and para-chloromethylbenzene under electrophilic substitution conditions.



**Q.25 Why is the methyl group an activating group?**

**Ans.** The methyl group increases the electron density of the benzene ring, so methylbenzene is more reactive than benzene toward electrophilic substitution. It is therefore an activating, ortho-para directing group.

**Q.26 Why is the nitro group a deactivating group?**

**Ans.** The nitro group withdraws electron density from the aromatic ring. This lowers the ring's reactivity toward electrophilic substitution, so $-NO_2$ is a deactivating, meta-directing group.

**Q.27 Predict the major products of nitration of chlorobenzene.**

**Ans.** Although chlorine deactivates the benzene ring, it directs incoming electrophiles to the ortho and para positions due to resonance donation of lone pair electrons.
Therefore, nitration of chlorobenzene mainly produces:

- Ortho-nitrochlorobenzene
- Para-nitrochlorobenzene

**Q.28 Predict the major product of nitration of benzoic acid.**

**Ans.** The carboxyl group is a strong electron-withdrawing and meta-directing group. Therefore, it directs the incoming nitro group to the meta position during nitration.

**Major Product:** • m-nitrobenzoic acid

**Q.29 Why are all carbon-carbon bonds in benzene equal in length?**

**Ans.** In benzene, the six π-electrons are delocalized over the entire ring due to resonance. As a result, all carbon-carbon bonds become identical and possess a bond order intermediate between a single and double bond. The bond length is approximately: 1.39 Å.

## SELF-ASSESSMENT

**Total Mark: 30**

**Q.1 Encircle the correct option.** **(1 × 6 = 6)**

(i) **The bond angle around each carbon atom in benzene is:**
(A) 90° (B) 109.5° (C) 120° (D) 180°

(ii) **Chlorination of methylbenzene mainly produces:**
(A) Meta chlorotoluene only (B) Only ortho-chlorotoluene
(C) Only para-chlorotoluene (D) O- and p-chlorotoluene

(iii) **Side-chain oxidation of alkylbenzene occurs at the:**
(A) Benzene ring (B) Benzylic carbon (C) Double bond (D) Carbonyl carbon

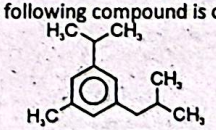
(iv) **Benzene reacts with an organic reagent in the presence of a halogen carrier to form phenylethanone. Which organic reagent is required?**
(A) $CH_3CH_2OH$ (B) $CH_3CHO$ (C) $CH_3COCl$ (D) $CH_3COOH$

(v) **Which of the following is the major product when methyl chloride ($CH_3Cl$) reacts with methylbenzene in the presence of $AlCl_3$:**
(A) 1,2-dimethyl benzene (B) 1,4-dimethyl benzene (C) 1,3-dimethyl benzene (D) both (A) and (B)

(vi) **Methylbenzene reacts with a mixture of concentrated nitric acid and concentrated sulphuric acid. What is the name of the mechanism for this reaction?**
(A) electrophilic addition (B) electrophilic substitution (C) nucleophilic addition (D) nucleophilic substitution

**Q.2 Write short answers of the following questions.** **(2 × 8 = 16)**

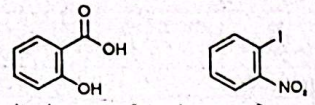
(i) Discuss the mechanism of nitration of benzene.
(ii) Write down the reaction of benzene with bromine in the presence of $FeBr_3$.
(iii) Predict the product formed when the following compound is oxidized using acidified $KMnO_4$ or $K_2Cr_2O_7$.




(iv) What product is formed when bromine is added to chlorobenzene in the presence of $AlBr_3$?
(v) Describe, with the aid of a diagram, the bonding in phenol to show delocalization of π electron.
(vi) The compound iodine monobromide, IBr, also reacts with benzene in an electrophilic reaction. Which compound would be the main product of this reaction, iodobenzene or bromobenzene? Explain your answer.

CamScanner

(vii) Name the following molecules:



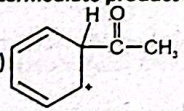
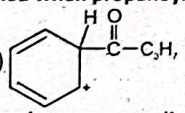
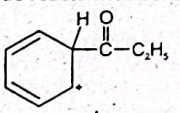
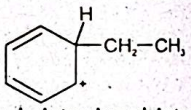
(viii) How would you prepare 3-chloronitrobenzene from benzene?

**Q.3 Extensive Questions.** (4 + 4 = 8)

(a) Discuss Friedel-Crafts reactions of benzene with mechanisms.

(b) Write a note on orientation in electrophilic substitution reactions of benzene.

## ENTRANCE TEST MCQs

1. The reaction of benzene with bromine in the presence of $FeBr_3$ follows the mechanism of _____ reactions: (UHS 2017)
   (A) Electrophilic addition (B) Electrophilic substitution
   (C) Nucleophilic substitution (D) Nucleophilic addition
2. The extra-ordinary stability of benzene molecule is due to: (ECAT 2014)
   (A) Cyclic structure (B) That it gives addition reactions
   (C) Large delocalization of π-electrons (D) That it has three alternate single and double bonds
3. Benzene in the presence of $AlCl_3$ produces acetophenone when reacts with: (UHS 2011)
   (A) Acetyl chloride (B) Ethyl benzene (C) Acetic acid (D) Ethanoic acid
4. The substitution of a '–H' by '–$NO_2$' group in benzene is called: (UHS 2011)
   (A) Nitration (B) Sulphonation (C) Ammonolysis (D) Hydrogenation
5. The introduction of RCO group in benzene is called: (UHS 2012)
   (A) Acylation (B) Alkylation (C) Carbonyl reduction (D) Formylation
6. Which one of the following is powerful electrophile used to attack on the electrons of benzene ring? (UHS 2015)
   (A) $FeCl_3$ (B) $Cl^+$ (C) $FeCl_4^-$ (D) $Cl_2$
7. When a hydrogen atom is removed from benzene, the group left behind is called: (UHS 2010)
   (A) Alkyl group (B) Benzyl group (C) Phenyl group (D) Methyl group
8. The introduction of an alkyl group in benzene takes place in the presence of $AlCl_3$ and: (UHS 2013)
   (A) $R-\overset{O}{\overset{\|}{C}}-OH$ (B) $R-Cl$ (C) $R-\overset{O}{\overset{\|}{C}}-Cl$ (D) $R-\overset{O}{\overset{\|}{C}}-O-$
9. When benzene reacts with acetyl chloride ($CH_3COCl$) in the presence of $AlCl_3$, acetophenone is formed. The electrophile in this reaction is: (UHS 2017)
   (A) $CH_3C^+O$ (B) $AlCl_3$ (C) $C^+H_3$ (D) $CH_3COCl$
10. Intermediate product formed when propanoyl chloride reacts with benzene is: (UHS 2017)
    (A)  (B)  (C)  (D) 
11. Which of the following species are meta-directing groups when second group is introduced into the benzene ring: I = $-NH_2$ II = –CHO III = –COOH IV = $-CH_3$ (UHS 2017)
    (A) III, III and IV (B) II and III (C) I and IV (D) I, II and IV
12. Acetophenone can be formed by which of the following reaction of benzene? (NUMS 2023)
    (A) Alkylation (B) Acylation (C) Halogenation (D) Nitration
13. Alkyl benzene is formed when benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride. Identify the type of reaction: (MDCAT 2023)
    (A) Friedel-Crafts alkylation reaction (B) Halogenation
    (C) Friedel-Craft acylation reaction (D) Sulphonation

**Answers Key**

| 1. B | 2. C | 3. A | 4. A | 5. A | 6. B | 7. C | 8. B | 9. A | 10. C | 11. B | 12. B | 13. A |
|---|---|---|---|---|---|---|---|---|---|---|---|---|



21 CHAPTER

# HALOGENOALKANES

## Student Learning Outcomes (SLOs)

[C-12-D-30 to C-12-D-37]

- Classify haloalkanes based on the type of halogen atom and its position in the carbon chain, and explain how the molecular structure affects their reactivity.
- Explain the organic functional groups involved in a simple haloalkane synthesis and predict the major product(s) based on the reaction conditions.
  This includes:
  a. the free-radical substitution of alkanes by Cl or Br in the presence of ultraviolet light, exemplified by the reactions of ethane.
  b. electrophilic addition of an alkene with a halogen, $X_2$, or hydrogen halide, $HX_{(g)}$ at room temperature.
  c. substitution of alcohol, e.g. by reaction with HX or KBr with $H_2SO_4$ or $H_3PO_4$; or with $PCl_5$ and heat; or with $PCl_5$; or with $SOCl_2$.
- Describe nucleophilic substitution reactions specifically:
  a. the reaction with $NaOH_{(aq)}$ and heat to produce an alcohol
  b. the reaction with KCN in ethanol and heat to produce a nitrile
  c. the reaction with $NH_3$ in ethanol heated under pressure to produce an amine
  d. the reaction with aqueous silver nitrate in ethanol as a method of identifying the halogen present, exemplified by bromoethane
- Describe the elimination reaction with NaOH in ethanol and heat to produce an alkene as exemplified by bromoethane.
- Describe the production of halogenoarenes, i.e., the reaction of benzene with $Cl_2$ and $Br_2$ in the presence of a catalyst.
- Compare the reactivity of halogenoalkanes and halogenoarenes using chloroethane and chlorobenzene as examples.
- Predict the major product(s) based on the reaction conditions and the molecular structure of the halogenoalkane.
- Analyze the mechanism and products of a reaction pathway involving a halogenoalkane and use retrosynthesis to deduce the starting materials. (It will discussed in chapter 25).

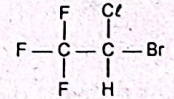
**Q.1 What are the uses of halogenoalkanes in daily life?** S/Q

**Ans.** **Halogenoalkanes** are very useful in daily life, mainly fluorocarbons due to their specialised chemical stability. In the past, chlorofluorocarbons (CFCs) were used as refrigerants and aerosol propellants, though these are being replaced by ozone-friendly alternatives, such as Hydrofluorocarbons (HFCs). In medicine, halogenated compounds serve as powerful anesthetic agents. Furthermore, they are vital intermediates in manufacturing polymers, such as PVC (polyvinyl chloride) for piping and PTFE (Teflon) for non-stick cookware.

**Q.2 What is Halothane? What is its use?** S/Q

**Ans.** **Halothane** is a halogenated hydrocarbon widely used as a powerful inhalation anesthetic. It induces a reversible loss of consciousness during surgeries. Previously, chloroform and other chlorinated anesthetics were used, which are banned now due to their toxicity and safety concerns.



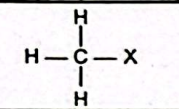
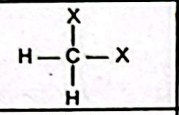
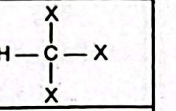


**IUPAC Name:** 2-Bromo-2-chloro-1,1,1-trifloroethane

CamScanner

**Q.3 What are halogenoalkanes?** S/Q

**Ans.** A halogenoalkane is formed when one or more hydrogen atoms of an alkane are replaced by halogen atoms. They may be mono, di, tri or poly halogenoalkanes depending upon the number of halogen atoms (-x) present in the molecule.

| Halogenoalkanes | Monohalogenoalkane | Diahalogenoalkane | Trihalogenoalkane |
|---|---|---|---|
| Structure |  |  |  |
| General Formula | $C_nH_{2n+1}X$ | $C_nH_{2n}X_2$ | $C_nH_{2n-1}X_3$ |
| Examples: | $CH_3Cl$ | $CH_2Cl_2$ | $CHCl_3$ |

**Q.4 What are alkyl halides? How are they classified?** S/Q

**Ans.** **Alkyl Halides:**

*Monohalogenoalkanes are called alkyl halides* (i.e. they contain only one halogen atom).

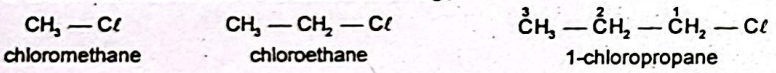
Their general formula is R – X.

Where R may be methyl, ethyl, propyl, etc., and X represents halogen atoms (F, Cl, Br, I).

➢ **Classification of Alkyl Halides:**

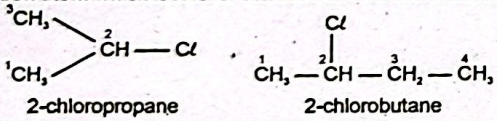
Monohalogenoalkane or alkyl halides are further classified into primary, secondary and tertiary monohalogenoalkanes depending upon the type of carbon atom bearing the halogen atom.

- **Primary Halogenoalkane:** In a primary halogenoalkane, the halogen atom is attached with a carbon which is further attached to one or no carbon atom e.g.,



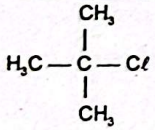
chloromethane chloroethane 1-chloropropane

- **Secondary Halogenoalkanes:** Secondary halogenoalkanes are those in which the halogen atom is attached with a carbon atom which is further attached to two other carbon atoms directly.



2-chloropropane 2-chlorobutane

- **Tertiary Halogenoalkane:** In a tertiary halogenoalkane, the halogen atom is attached to a carbon atom which is further attached to three carbon atoms directly.

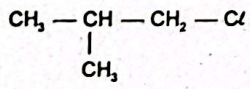
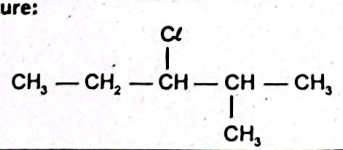


2 – chloro – 2 – methylpropane

**QUICK CHECK 21.1**

**a) Write down the IUPAC name of the compound, $(CH_3)_2CH-CH_2-Cl$, $CH_3CH_2CH(Cl)CH(CH_3)CH_3$**

**Ans.**

| Structure: | Structure: |
|---|---|
|  |  |
| **IUPAC Name:** 1-Chloro-2-methylpropane | **IUPAC Name:** 3-chloro-2-methylpentane |



**b) Draw the primary, secondary and tertiary structures of the compound having molecular formula $C_5H_{11}Cl$.**

**Ans.** The molecular formula $C_5H_{11}Cl$ has 8 structural isomers.

| No. | Structure | IUPAC Name | Type of Chloride |
|---|---|---|---|
| 1. | $CH_3-CH_2-CH_2-CH_2-CH_2Cl$ | 1-Chloropentane | Primary (1°) |
| 2. | $CH_3-CH(Cl)-CH_2-CH_2-CH_3$ | 2-Chloropentane | Secondary (2°) |
| 3. | $CH_3-CH_2-CH(Cl)-CH_2-CH_3$ | 3-Chloropentane | Secondary (2°) |
| 4. | $ClCH_2-CH(CH_3)-CH_2-CH_3$ | 1-Chloro-2-methylbutane | Primary (1°) |
| 5. | $ClCH_2-CH_2-CH(CH_3)-CH_3$ | 1-Chloro-3-methylbutane | Primary (1°) |
| 6. | $CH_3-C(Cl)(CH_3)-CH_2-CH_3$ | 2-Chloro-2-methylbutane | Tertiary (3°) |
| 7. | $CH_3-CH(Cl)-CH(CH_3)-CH_3$ | 2-Chloro-3-methylbutane | Secondary (2°) |
| 8. | $(CH_3)_3C-CH_2Cl$ | 1-Chloro-2,2-dimethylpropane | Primary (1°) |

Classification: Primary chlorides (1°): 4, Secondary chlorides (2°): 3, Tertiary chlorides (3°): 1

## PREPARATION OF HALOGENOALKANES

**Q.5 Describe how substitution of alcohol with following reagents help to synthesize halogenoalkanes:** Exercise Q.No. 4

**i) KBr with $H_2SO_4$ ii) $SOCl_2$/Pyridine iii) $PCl_3$ iv) $PCl_5$**

**Ans.**

(i) Halogenoalkanes can be prepared by the halogenation of alkanes in the presence of light.

$$\underset{\text{ethane}}{CH_3-CH_3} + Cl_2 \xrightarrow{\text{light}} \underset{\text{chloroethane}}{CH_3-CH_2-Cl} + HCl$$

(ii) They can also be prepared by the electrophilic addition of hydrogen halides to alkenes.

$$\underset{\text{ethene}}{H_2C=CH_2} + HBr \longrightarrow \underset{\text{bromoethane}}{CH_3-CH_2-Br}$$

(iii) Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the presence of $ZnCl_2$ which acts as a catalyst.

$$\underset{\text{ethanol}}{CH_3-CH_2-OH} + HCl \xrightarrow{ZnCl_2} \underset{\text{chloroethane}}{CH_3-CH_2-Cl} + H_2O$$

(iv) Alcohols also react with thionyl chloride in the presence of pyridine (base to neutralize HCl) to give alkyl chlorides. This method is especially useful since the by-products (HCl and $SO_2$) are gases which escape from the mixture leaving behind the pure product (with no rearrangement). This is one of the best methods to prepare halogenoalkanes.

$$\underset{\text{ethanol}}{CH_3-CH_2-OH} + SOCl_2 \xrightarrow{\text{pyridine}} \underset{\text{chloroethane}}{CH_3-CH_2-Cl} + SO_2 + HCl$$

(v) Phosphorus trihalides or phosphorus pentahalides react with alcohols to replace OH group by a halo group.

$$\underset{\text{ethanol}}{3CH_3-CH_2-OH} + PBr_3 \longrightarrow \underset{\text{bromoethane}}{3CH_3-CH_2-Br} + H_3PO_3$$

$$\underset{\text{ethanol}}{3CH_3-CH_2-OH} + PCl_5 \longrightarrow \underset{\text{chloroethane}}{CH_3-CH_2-Cl} + POCl_3 + HCl$$

(vi) Alcohols can be converted to halogenoalkanes by reacting with potassium bromide and an acid like sulphuric acid ($H_2SO_4$) or phosphoric acid ($H_3PO_4$). This method is commonly used to prepare bromoalkanes and iodoalkanes.

➢ **Mechanism:**

**Step I.** The acid first reacts with potassium bromide to give hydrogen bromide.

$$KBr + H_2SO_4 \longrightarrow KHSO_4 + 2HBr$$

**Step II.** HBr then further reacts with alcohols to give bromoalkanes.

$$CH_3CH_2OH + HBr \longrightarrow CH_3CH_2Br + H_2O$$

CamScanner

**Overall Reaction:**

$$\underset{\text{ethanol}}{CH_3-CH_2-OH} + KBr + H_2SO_4 \xrightarrow{\Delta} \underset{\text{bromoethane}}{CH_3-CH_2-Br} + H_2O + KHSO_4$$

Phosphoric acid is preferably used to prepare iodoalkanes because it is a weak oxidizing agent and less likely to oxidize iodide ions to iodine.

**Interesting Information**

Bromoethane ($CH_3Br$) is naturally emitted primarily by **marine algae and phytoplankton such as trichodesmium**. These organisms convert seawater bromide into volatile organobromides. Once in the atmosphere, bromoethane contributes to the global bromine cycle and plays a role in stratospheric ozone depletion.



## QUICK CHECK 21.2

**a) Give two methods to convert methanol into chloromethane.**

**Ans.** Methanol can be converted into chloromethane by the following methods:

**Method 1: Reaction with hydrogen chloride (HCl)**

$$CH_3-OH + HCl \xrightarrow{ZnCl_2} CH_3-Cl + H_2O$$

This reaction is usually carried out in the presence of anhydrous zinc chloride ($ZnCl_2$), which acts as a catalyst.

**Method 2: Reaction with thionyl chloride ($SOCl_2$)**

$$CH_3-OH + SOCl_2 \longrightarrow CH_3-Cl + SO_2 + HCl$$

**Use:** This method is preferred because the by-products ($SO_2$ and HCl) are gases and escape from the reaction mixture, leaving the alkyl halide in a pure form.

**b) Give reactions of propanol with $SOCl_2$ and $PBr_3$.**

**Ans.** Assuming propanol refers to **1-propanol**, the reactions are:

**Reaction with thionyl chloride ($SOCl_2$):**

$$CH_3-CH_2-CH_2-OH + SOCl_2 \longrightarrow CH_3-CH_2-CH_2-Cl + SO_2 + HCl$$

**Reaction with phosphorus tribromide ($PBr_3$):**

$$3CH_3-CH_2-CH_2-OH + PBr_3 \longrightarrow 3CH_3-CH_2-CH_2-Br + H_3PO_3$$

**c) Can we prepare fluoromethane using methane and fluorine gas? Give reason.**

**Ans.** No, fluoromethane cannot be prepared conveniently by the direct reaction of methane with fluorine gas because this reaction is extremely fast and highly exothermic and explosive. Instead of producing only fluoromethane ($CH_3F$), it gives a mixture of products such as $CH_3F$, $CH_2F_2$, $CHF_3$, and $CF_4$.

Due to the violent nature of the reaction and the formation of multiple products, this method is not suitable for the preparation of pure fluoromethane.

## REACTIVITY OF HALOGENOALKANES

**Q.6 Discuss the factor on which reactivity of halogenoalkanes depends.** L/Q

**Ans.** **Reactivity of Halogenoalkanes:**

A halogenoalkane molecule (R – X) consists of two parts, an alkyl group with a partial positive charge on the carbon atom attached to halogen atom and the halide atom with a partial negative charge.

➢ **Main Factor:**

Experiments have shown that the strength of carbon halogen bond is the main factor which decides the reactivity of haloalkanes. The weaker bond will be more easily broken and make the molecule more reactive. Table shows the bond energies of C – X bonds in alkyl halides.

Table: Bond energies of different C – X bonds

| Bond | Bond Energy (kJ/mol) |
|---|---|
| C – F | 467 |
| C – Cl | 346 |
| C – Br | 290 |
| C – I | 238 |



➢ **Conclusion:**

The strength of the bonds shows that iodo compounds (with the weakest bonds) would be the most reactive halogenoalkanes, while fluoro compounds will be the least reactive i.e., the order of reactivity of halogenoalkanes should be:

$$R-I > R-Br > R-Cl > R-F.$$

In fact, the C – F bond is so strong that fluoroalkanes do not react under ordinary conditions. Some other factors which may affect the reactivity of halogenoalkanes are, bond polarity, steric hindrance, inductive effect, etc.

## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Monohalogenoalkanes are commonly known as:**
   (A) Arenes (B) Alkyl halides (C) Alcohols (D) Ethers
2. **The general formula of a monohalogenoalkane is:**
   (A) R–OH (B) R–X (C) R–COOH (D) R–$NH_2$
3. **In a primary halogenoalkane, the carbon bearing the halogen atom is attached to:**
   (A) Three carbon atoms (B) Two carbon atoms (C) One or no carbon atom (D) Four carbon atoms
4. **Which of the following is a secondary halogenoalkane?**
   (A) Chloromethane (B) Chloroethane (C) 2-Chloropropane (D) 2-Chloro-2-methylpropane
5. **2-Chloro-2-methylpropane is a:**
   (A) Primary halogenoalkane (B) Secondary halogenoalkane
   (C) Tertiary halogenoalkane (D) Polyhalogenoalkane
6. **A compound formed by replacing one or more hydrogen atoms of an alkane with halogen atoms is called a:**
   (A) Haloarene (B) Halogenoalkane (C) Alcohol (D) Ester
7. **Halogenoalkanes can be prepared from alkanes by:**
   (A) Halogenation in the presence of light (B) Halogenation in the absence of light
   (C) Hydrolysis (D) Hydrogenation
8. **Addition of HBr to ethene produces:**
   (A) Chloroethane (B) Bromoethane (C) Ethanol (D) Ethyne
9. **Ethanol reacts with HCl in the presence of $ZnCl_2$ to form:**
   (A) Ethene (B) Chloroethane (C) Ethanal (D) Ethanoic acid
10. **Which reagent converts alcohols into alkyl chlorides with gaseous by-products only?**
    (A) $PBr_3$ (B) $SOCl_2$ (C) HBr (D) KBr
11. **Pyridine is used with thionyl chloride mainly as:**
    (A) Oxidizing agent (B) Catalyst (C) Reducing agent (D) Solvent
12. **$PBr_3$ converts alcohols into:**
    (A) Alkyl fluorides (B) Alkyl chlorides (C) Alkyl bromides (D) Alkyl iodides
13. **Phosphoric acid is preferred over sulphuric acid for preparing iodoalkanes because it is:**
    (A) A stronger oxidizing agent (B) A weaker oxidizing agent
    (C) A stronger acid (D) More volatile
14. **The reactivity order of halogenoalkanes is:**
    (A) R–F > R–Cl > R–Br > R–I (B) R–Cl > R–Br > R–I > R–F
    (C) R–I > R–Br > R–Cl > R–F (D) R–Br > R–I > R–Cl > R–F
15. **The most reactive halogenoalkanes are:**
    (A) Fluoroalkanes (B) Chloroalkanes (C) Bromoalkanes (D) Iodoalkanes
16. **The least reactive halogenoalkanes are:**
    (A) Fluoroalkanes (B) Chloroalkanes (C) Bromoalkanes (D) Iodoalkanes
17. **The main factor determining the reactivity of halogenoalkanes is the strength of the:**
    (A) C–H bond (B) C–C bond (C) C–X bond (D) H–X bond
18. **Which carbon–halogen bond has the highest bond energy?**
    (A) C–I (B) C–Br (C) C–Cl (D) C–F
19. **The carbon atom attached to the halogen in a halogenoalkane behaves as:**
    (A) A nucleophilic center (B) An electrophilic center (C) A free radical (D) A neutral center
20. **Besides bond strength, another factor affecting the reactivity of halogenoalkanes is:**
    (A) Hydrogen bonding only (B) Steric hindrance (C) Aromaticity (D) Resonance only

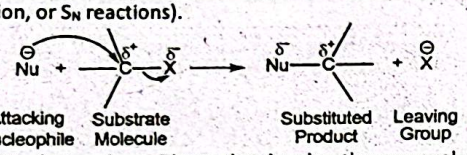
CamScanner

# REACTIONS OF HALOGENOALKANES

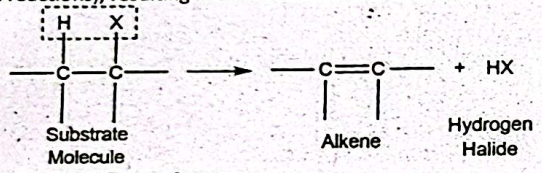
**Q.7 What are the two types of reactions given by halogenoalkanes?** L/O

**Ans.** The C – X bond in halogenoalkanes is polar due to the difference of electronegativity between C and the halogen atom. The carbon of C – X acts as an electrophilic centre, which can be attacked by a nucleophile. Alternatively, the hydrogen on the carbon adjacent to the C – X bond atom may be attacked by a base. These two possibilities result in two types of reaction of halogenoalkanes.

**a) $S_N$ Reactions:** Those reactions in which the halogen is replaced by some other atom or a group (nucleophilic substitution, or $S_N$ reactions).




**b) Elimination (β-Elimination) Reactions:** Those that involve the removal of HX from halogenoalkanes (elimination, or E reactions), resulting in the formation of alkenes.




## Nucleophilic Substitution Reactions

Alkyl halides may undergo nucleophilic substitution reactions in two different ways:

**a.** Nucleophilic Substitution Bimolecular ($S_N2$).

**b.** Nucleophilic Substitution Unimolecular ($S_N1$).

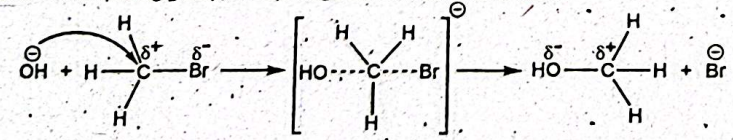
Nucleophilic substitution reactions on alkyl halides involve two main processes, the departure of leaving group (breaking of C – X bond) and the attack of nucleophile (the formation of C – Nu bond). If the two processes occur simultaneously in single step the mechanism is called $S_N2$. But if the two changes occur in two separate steps, i.e., the bond breaks in first step followed by the formation of a new bond in second step, then the mechanism is called $S_N1$.

**Q.8 Primary halogenoalkane follow $S_N2$ mechanism. Explain.** Exercise D/Q.7

**Ans.**

### i) Nucleophilic Substitution Bimolecular ($S_N2$)

- This is a single step mechanism.
- As soon as the nucleophile starts attacking the electrophilic carbon of the substrate, the bond with which the leaving group is attached, starts breaking. In other words, the extent of bond formation is equal to the extent of bond breaking.
- An important feature of this mechanism is the **direction of the attack of the attacking nucleophile.** It attacks from the side which is opposite to the leaving group. The attack of the nucleophile and the departure of the leaving group, everything occurs at the same time.




- Since in this mechanism, the reaction takes place in only one step, which is also a rate determining step and two molecules are participating in this step, it is a **bimolecular reaction.**



- Kinetic studies of the reactions involving $S_N2$ mechanism have shown that the rates of such reactions depend upon both the concentrations of alkyl halide and the attacking nucleophile.
- Mathematically, the rate can be expressed as:

$$\text{Rate} = k\,[\text{Alkyl halide}]^1\,[\text{Nucleophile}]^1 \quad \text{order} = 1 + 1 = 2$$

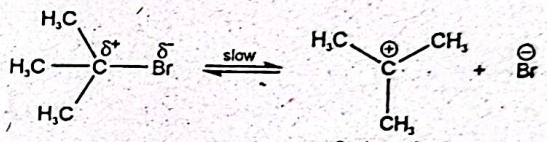
A typical $S_N2$ reaction is a second order reaction.

- Among the monohalogenoalkanes, **primary monohalogenoalkanes** generally follow $S_N2$ mechanism whenever they are attacked by nucleophiles. This is due to steric reasons, as in primary monohalogenoalkanes the substrate carbon is attached with hydrogen atoms or only one carbon atom, the nucleophile can approach and attack the electrophilic carbon easily.
- Tertiary monohalogenoalkanes always follow $S_N1$ mechanism whenever they are attacked by a nucleophile.

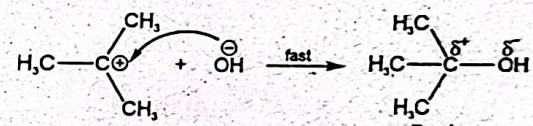
### ii) Nucleophilic Substitution Unimolecular ($S_N1$)

- This type of mechanism involves two steps.
- The first step is the reversible ionization of the alkyl halide in the presence of aqueous acetone or aqueous ethyl alcohol. This step provides a **carbocation as an intermediate.** In the second step, this carbocation is attacked by the nucleophile to give the product.

**First Step of $S_N1$:**



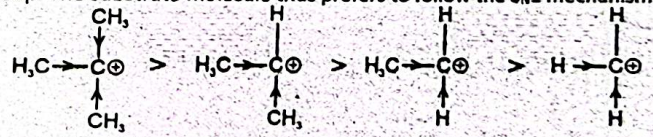

**Second Step of $S_N1$:**




- Since the first step involves the breaking of a covalent bond so it is a slow step as compared to the second step, which involves the energetically favourable combination of ions. The first step is, therefore, called the **rate-determining step.** The mechanism is called unimolecular because only one molecule takes part in the rate-determining step.
- Reactions involving $S_N1$ mechanism show first order kinetics and the rates of such reactions depend only upon the concentration of the alkyl halide. The rate equation of such reactions can be written as follows:

**Rate = k [Alkyl halide]**

- The major reason is the formation of the stable tertiary carbocation. Moreover three bulky groups attached with the electrophilic carbon prevent the attacking nucleophile to attack from the backside of leaving group. The substrate molecule thus prefers to follow the $S_N1$ mechanism.




**Decreasing stability order of carbocations due to decrease in positive inductive effect (+I).**

- The mechanism shows that a carbocation is formed in the rate-determining step, so, the more stable the carbocation, the more easily it is formed. Tertiary carbocations are more stable than secondary carbocations which are in turn, more stable than the primary carbocations.

**Note:** A **secondary halogenoalkane** can undergo both $S_N2$ and $S_N1$ reaction mechanism, depending upon the nature of solvent (polar or non-polar) and the strength of the nucleophile and leaving group.

CamScanner

| Factor | $S_N1$ | $S_N2$ |
|---|---|---|
| Nucleophile | Weak Lewis base | Strong Lewis base. |
| Solvent | Polar protic e.g., water, alcohols. | Polar aprotic e.g., DMSO (Dimethyl sulphoxide) |
| Leaving Group | A good leaving group helps s° R – X lose the halogen first to form carbocation faster. | A good leaving group makes it easier for a nucleophile to push the group out from the back side in one smooth step. |

**Q.9 How do you differentiate between $S_N1$ and $S_N2$ mechanism?** LIQ

**Ans.**

| $S_N1$ Reaction | $S_N2$ Reaction |
|---|---|
| 1. "The nucleophilic substitution reaction mechanism in which breaking of C – X bond and the formation of C – Nu bond occur one after the other in two different steps is called $S_N1$ reaction." $(CH_3)_3C-Cl + KOH_{(aq)} \longrightarrow (CH_3)_3C-OH + KCl$ | 1. "The nucleophilic substitution reaction mechanism in which breaking of C – X bond and the formation of C – Nu bond occur simultaneously in one step is called $S_N2$ reaction." $C_2H_5Br + KOH_{(aq)} \longrightarrow C_2H_5OH + KBr$ |
| 2. It completes in two steps. **First Step** $CH_3-C(CH_3)_2-Cl \underset{\text{Polar Solvent}}{\overset{\text{Slow}}{\rightleftharpoons}} (CH_3)_3C^+ + Cl^-$ (Carbocation) **Second Step** $(CH_3)_3C^+ + OH^- \xrightarrow{\text{Fast}} CH_3-C(CH_3)_2-OH$ Carbocation → Product | 2. It completes in single step. $OH^- + H-C-Br \longrightarrow HO-C-H + Br^-$ (Transition state → Inverted molecule; Leaving group) |
| 3. The attacking nucleophile can attack from either side. | 3. The attacking nucleophile attacks from opposite side of the leaving group. |
| 4. There is 50% inversion of configuration and 50% retention of configuration. | 4. There is 100% inversion of configuration from alkyl halide into the product molecule. |
| 5. Since one molecule takes part in rate determining step, so its molecularity is one (unimolecular). | 5. Since two molecules i.e. substrate and attacking nucleophile take part in rate determining step, so its molecularity is two (bimolecular). |
| 6. Kinetic study of reaction shows 1st order reaction. **Rate = k [Alkyl halide]** | 6. Kinetic study of reaction shows 2nd order reaction. **Rate = k [substrate]$^1$ [attacking nucleophile]$^1$** |
| 7. Tertiary alkyl halides when attacked by a nucleophile always follow $S_N1$ mechanism. | 7. Usually primary alkyl halides follow $S_N2$ mechanism depending upon their structure and the nature of the solvent. |

## ➲ β-Elimination Reactions

**Q.10 What are β-Elimination reactions? Discuss their types.** LIQ

**Ans. β-Elimination Reaction:**

**β-elimination is a reaction in which a hydrogen atom attached to the β-carbon of the alkyl halide and the halogen atom on the adjacent carbon atom are removed from a halogenoalkane.**

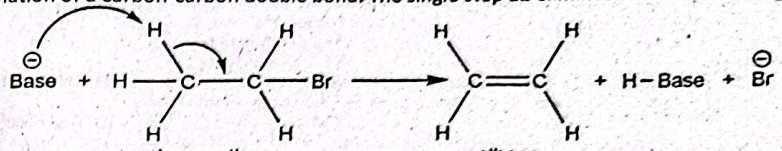
This reaction occurs when a base attacks the β-hydrogen atom of the halogenoalkane. The removal of the halogen takes place either simultaneously or after the removal of the hydrogen atom. Thus, an alkene molecule is obtained instead of a substitution product.

β-Elimination reactions take place simultaneously with substitution reactions and often compete with them. Like nucleophilic substitution, the elimination reactions can follow two types of mechanism; E2 or E1.



### Elimination Bimolecular (E2)

In E2 mechanism, the base attacks the β hydrogen atom and the leaving group leaves at the same time with the formation of a carbon-carbon double bond. The single step E2 elimination mechanism is given below.




bromoethane ethene

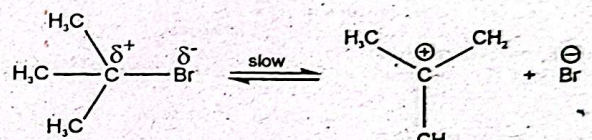
E2 reaction is bimolecular and the rate of this reaction depends upon the concentrations of the alkyl halide and the bases Like $S_N2$ reactions, the molecularity of E2 reactions is also two and these reactions show second order kinetics.

Rate = k [Alkyl halide]$^1$ [Base]$^1$ Order = 1 + 1 = 2

### Elimination Unimolecular (E1)

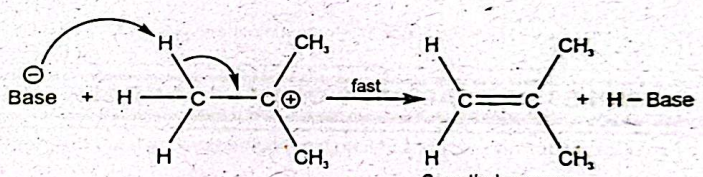
In E1 mechanism, like $S_N1$ mechanism, the first step is the slow ionization of the substrate to give a carbocation. In the second step, the base attacks the β-hydrogen atom to give an alkene as a product.

**Step-1:**




2-bromo-2-methylpropane 3° carbocation

**Step-2:**




2-methylpropene

E1 mechanism is a unimolecular mechanism and the rate of the reaction depends only upon the concentration of the alkyl halide molecule. Primary halogenoalkanes generally follow E2 mechanism whereas tertiary halogenoalkanes follow E1 mechanism. However, secondary halogenoalkanes can show both E2 and E1 reactions according to the choice of the solvent.

**Note:** For difference between E1 and E2, See Ex. Q.3. (d)

## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **The carbon atom bonded to the halogen in a halogenoalkane acts as a(n):**
   (A) Nucleophile (B) Electrophilic centre (C) Free radical (D) Base
2. **Replacement of a halogen atom by another atom or group is called:**
   (A) Elimination reaction (B) Addition reaction
   (C) Nucleophilic substitution reaction (D) Oxidation reaction
3. **Removal of HX from a halogenoalkane produces:**
   (A) Alcohol (B) Alkane (C) Alkene (D) Ether
4. **In the $S_N2$ mechanism, bond breaking and bond formation occur:**
   (A) In separate steps (B) Simultaneously
   (C) Only after carbocation formation (D) After proton removal
5. **In an $S_N2$ reaction, the nucleophile attacks:**
   (A) From the same side as the leaving group (B) From either side
   (C) From the opposite side of the leaving group (D) Only from above the plane

CamScanner

6. $S_N2$ reactions proceed through:
(A) A carbocation intermediate (B) A free radical intermediate
(C) A transition state (D) A carbanion intermediate
7. The rate of an $S_N2$ reaction depends upon concentration of:
(A) Alkyl halide only (B) Nucleophile only
(C) Both alkyl halide & nucleophile (D) Temperature only
8. $S_N2$ reactions show:
(A) Zero-order kinetics (B) First-order kinetics (C) Second-order kinetics (D) Third-order kinetics
9. Which class of halogenoalkanes generally undergoes $S_N2$ reactions most readily?
(A) Primary (B) Secondary (C) Tertiary (D) Aryl halides
10. The $S_N1$ mechanism proceeds through the formation of a:
(A) Carbanion (B) Carbocation (C) Free radical (D) Transition state only
11. In the $S_N1$ mechanism, the rate-determining step is:
(A) Attack of the nucleophile (B) Formation of the carbocation
(C) Removal of a proton (D) Formation of the product
12. $S_N1$ reactions follow:
(A) Zero-order kinetics (B) First-order kinetics (C) Second-order kinetics (D) Third-order kinetics
13. Tertiary halogenoalkanes generally undergo:
(A) $S_N2$ mechanism (B) $S_N1$ mechanism (C) Free radical substitution (D) Electrophilic substitution
14. Secondary halogenoalkanes may undergo _____ depending on the solvent:
(A) $S_N1$ Only (B) $S_N2$ Only (C) Both $S_N1$ and $S_N2$ (D) Neither $S_N1$ nor $S_N2$
15. β-Elimination reactions result in the formation of:
(A) Alcohols (B) Aldehydes (C) Alkenes (D) Carboxylic acids
16. In the E2 mechanism, the base removes:
(A) α-Hydrogen (B) β-Hydrogen (C) Halogen atom only (D) Carbon atom
17. E2 reactions occur in:
(A) One step (B) Two steps (C) Three steps (D) Four steps
18. The rate of an E2 reaction depends upon:
(A) Alkyl halide only (B) Base only (C) Both alkyl halide and base (D) Product concentration
19. Tertiary halogenoalkanes usually undergo which elimination mechanism?
(A) E1 (B) E2 (C) $S_N2$ (D) Radical elimination
20. Primary halogenoalkanes generally favor which elimination mechanism?
(A) E1 (B) E2 (C) $S_N1$ (D) Electrophilic substitution

## EXAMPLES OF REACTIONS OF HALOGENOALKANES

**Q.11 Describe nucleophilic substitution reactions of halogenoalkane starting from bromoethane with following reagents:** Exercise D/Q.5
**i) Aqueous NaOH ii) Ethanolic KCN iii) Ethanolic $NH_3$**

**Ans.**

**i. Reaction With Sodium Hydroxide**

A halogenoalkane reacts with aqueous sodium hydroxide to give both substitution and elimination products depending upon the reaction conditions. In the aqueous solutions, the major reaction is substitution, while in ethanol, elimination is predominant.

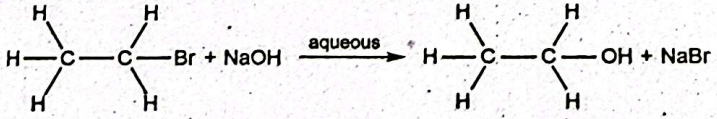
Hydroxide ion is both a good nucleophile and a good base.

(a) When $OH^-$ attacks as a nucleophile, it replaces the halogen atom of the halogenoalkane to form a substitution product, alcohol.

(b) When $OH^-$ attacks a base, it removes both the β-hydrogen atom and the halogen atom to give an elimination product, an alkene. The reaction takes place at higher temperature under reflux conditions to avoid the loss of volatile products.

Bromoethane reacts with aqueous sodium hydroxide to give ethanol as well as ethene.

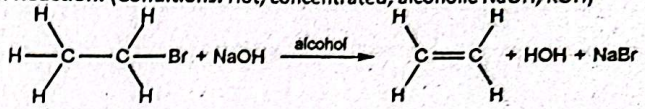
- **Substitution Reaction: (Conditions:** Cold, dilute, aqueous NaOH)




bromoethane ethanol



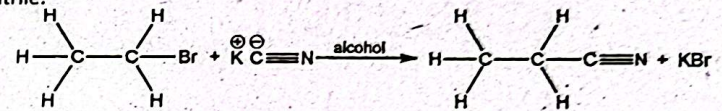
- **Elimination Reaction: (Conditions:** Hot, concentrated, alcoholic NaOH, KOH)




bromoethane ethene

**ii. Reaction with KCN**

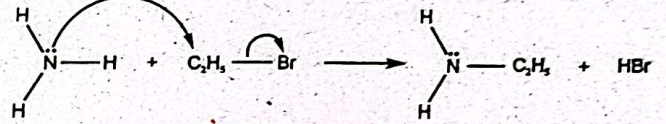
Since cyanide ion ($CN^-$) is a strong nucleophile but a weak base so it reacts with halogenoalkanes to give substitution product, a nitrile. The reaction is typically carried out by heating the halogenoalkane with an ethanolic solution of potassium cyanide under reflux. Bromoethane reacts with potassium cyanide to give propane nitrile.




bromoethane propanenitrile

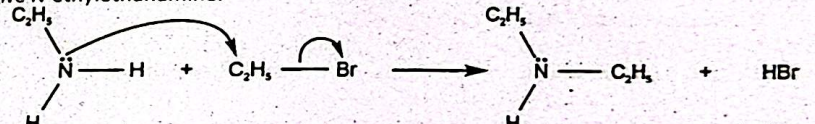
**iii. Reactions with Ammonia:**

a) Ammonia is a good nucleophile and it reacts with halogenoalkanes a favourably. Different types of amines can be produced if the amounts of halogenoalkane and ammonia are carefully controlled.



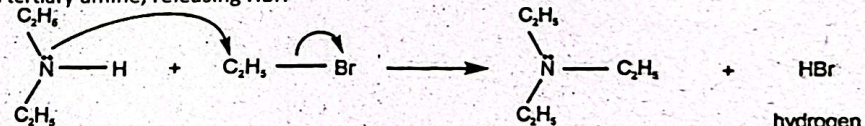

ammonia bromoethane ethylamine hydrogen bromide

b) Since ethanamine is also a nucleophile, it can compete with ammonia to react with halogenoalkane to give N-ethylethanamine.



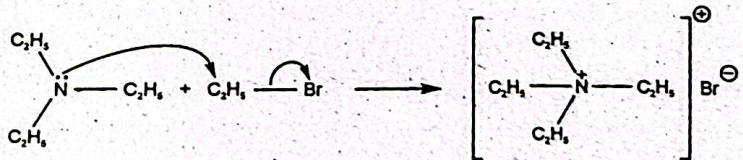

ethanamine bromoethane N-ethylethanamine hydrogen bromide

c) N-ethylethanamine will act as a nucleophile and will attack on another bromoethane molecule to form a tertiary amine, releasing HBr.




N-ethylethanamine bromoethane N,N-diethylethanamine hydrogen bromide

d) If a large excess of bromoethane is used, the reaction may proceed to give the quaternary ammonium salt as the final product.




N,N-diethylethanamine bromoethane N,N,N-triethylethanaminebromide

CamScanner

**Q.12 Discuss the reactions of halogenoalkanes with aqueous silver nitrate.** U/O

Ans.

**iv. Reactions of Halogenoalkanes with Aqueous Silver Nitrate**

This reaction is carried out in a mixture of water and ethanol, the alcohol in this mixture helps to dissolve the halogenoalkane. Water reacts with halogenoalkane as a nucleophile replacing the halide ion.

$$CH_3 - CH_2 - X + H - OH \longrightarrow CH_3 - CH_2 - OH + H^+ + X^-$$

haloethane ethanol

The released halide ion then reacts with silver nitrate to give a precipitate with a characteristic colour corresponding to the halide ion present. Thus, the reaction helps to detect the halide ion present in halogenoalkanes.

$Ag^+ + Cl^- \longrightarrow AgCl$ (White ppt.)

$Ag^+ + Br^- \longrightarrow AgBr$ (Cream Yellow ppt.)

$Ag^+ + I^- \longrightarrow AgI$ (Bright Yellow ppt.)

➢ **Comparison of reactivity of Halides:**

Comparing the rates of formation of silver halides in this reaction gives us a clue about the different reactivities of halides. The quicker the precipitate appears, the more reactive is the halogenoalkane. An iodoalkane produces a precipitate very quicker than bromoalkane. A chloroalkane, however, reacts very slowly and fluoroalkanes do not give a precipitate.

## ☑ QUICK CHECK 21.3

**a) Why halogenoalkanes are considered as very reactive class of organic compounds?**

Ans. Halogenoalkanes are considered highly reactive organic compounds because the carbon-halogen bond is polar in nature due to the difference in electronegativity between carbon and the halogen atom.

The halogen atom attracts the shared pair of electrons towards itself and acquires a partial negative charge (δ−), while the carbon atom acquires a partial positive charge (δ+).

$$C^{\delta+} - X^{\delta-}$$

As a result, the carbon atom becomes susceptible to attack by nucleophiles, making halogenoalkanes readily undergo substitution and elimination reactions.

**b) Complete the following equation: $C_2H_5Br + CH_3COONa \longrightarrow$**

Ans. $C_2H_5Br + CH_3COONa \longrightarrow CH_3COOC_2H_5 + NaBr$

The product formed is ethyl ethanoate (ethyl acetate).

**c) How will you convert ethane into ethanol and ethene?**

Ans. **Conversion of ethane into ethanol:**

First, ethane is converted into chloroethane by chlorination.

$$H_3C - CH_3 + Cl_2 \xrightarrow{hv} C_2H_5Cl + HCl$$

Chloroethane is then hydrolysed with aqueous potassium hydroxide to produce ethanol.

$$C_2H_5Cl + KOH_{(aq)} \longrightarrow C_2H_5OH + KCl$$

**Conversion of ethane into ethene:**

Ethane is converted into ethene as follows:

$$H_3C - CH_3 + Cl_2 \longrightarrow CH_3 - CH_2 - Cl + HCl$$

$$CH_3 - CH_2 - Cl + KOH_{(alcoholic)} \longrightarrow H_2C = CH_2 + KCl + H_2O$$

**d) Give the reaction of bromopropane with KCN. Is this a substitution reaction or an elimination reaction? Name the main product of this reaction.**

Ans. Bromopropane reacts with potassium cyanide in alcoholic medium to form a nitrile.

$$CH_3 - CH_2 - CH_2 - Br + KCN \longrightarrow CH_3 - CH_2 - CH_2 - CN + KBr$$

This reaction is a **nucleophilic substitution reaction** because the cyanide ion ($CN^-$) replaces the bromine atom.

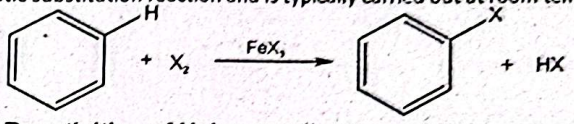
The main product formed is **butanenitrile (butyronitrile)**.



# HALOGENOARENES

**Q.13 What are halogenoarenes?** S/Q

Ans. Halogenoarenes e.g., chlorobenzene and bromobenzene are prepared by reacting benzene with either chlorine or bromine in the presence a of catalyst, anhydrous $FeCl_3$ or $FeBr_3$. The reaction is called electrophilic aromatic substitution reaction and is typically carried out at room temperature.




## Comparison of Reactivities of Halogenoalkanes and Halogenoarenes

**Q.14 Compare the reactivity of halogenoalkanes and halogenoarenes using chloroethane and chlorobenzene as examples.** Exercise D/Q.6

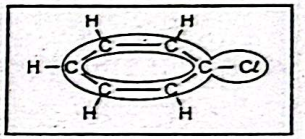
Ans. **Halogenoalkanes are More Reactive:**

i. Halogenoalkanes are aliphatic organic compounds in which halogen atom is attached with an alkyl group. Owing to the difference in the electronegativity values of carbon and halogen a partial positive charge is developed on the carbon atom attached to the halogen making it an electrophile centre. This electrophilic carbon atom invites nucleophiles to attack on it giving a vast body of reactions called nucleophilic substitution ($S_N$) reactions.

ii. The attack by bases on the hydrogen atom attached with the carbon atom adjacent to it gives another important class of reactions called elimination reactions.

➢ **Halogenoalkanes are Less Reactive:**

In halogenoarenes, the electron pair on the chlorine atom is delocalised due to the involvement of the chlorine lone pair with the aromatic ring as shown below. The carbon-halogen (C — X) bond is stronger due to the partial double-bond character, resulting from this delocalisation. The strength of C — Cl bond, thus increases making it difficult to break. As a result, the halogenoarenes, are less reactive and synthetically less useful.



Other factors that make helogenoarenes less reactive are the $sp^2$ hybridization of the ring carbon and the repulsion of the incoming nucleophile by the π-electron cloud.

## ☑ QUICK CHECK 21.4

**a) What is the role of iron halide in the preparation of halogenoarene?**

Ans. Iron halide such as **$FeCl_3$** or **$FeBr_3$** acts as Lewis catalyst in the halogenation of benzene.

It generates a strong electrophile by polarizing the halogen molecule.

$$Cl_2 + FeCl_3 \longrightarrow Cl^+ + FeCl_4^-$$

The chlorine electrophile or chloronium ion ($Cl^+$) then attacks the benzene ring, resulting in the formation of chlorobenzene.

**b) Chlorobenzene does not react with NaOH under normal conditions, but chloroethane does; explain why?**

Ans. In chlorobenzene, the lone pair of electrons on chlorine overlaps with the π-electron cloud of the benzene ring. As a result, the C – Cl bond acquires partial double bond character due to resonance. Thus, the C – Cl bond becomes shorter and stronger and it is difficult to break the bond.

Thus, Nucleophilic substitution does not occur easily under ordinary conditions.

In chloroethane, the C – Cl bond is a normal single bond and can be broken relatively easily so it readily reacts with aqueous NaOH to form ethanol, whereas chlorobenzene does not react under normal conditions.

**c) Can chlorobenzene undergo elimination? Explain why or why not?**

Ans. No, chlorobenzene does not undergo elimination reactions because elimination reactions require the removal of β-hydrogen atom which is not accessible.

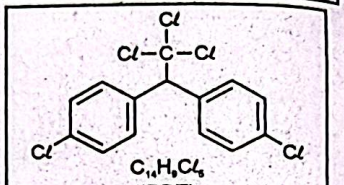
CamScanner

**In Chlorobenzene:**

- The carbon atom attached to chlorine is part of the benzene ring and is already involved in a stable conjugated π-electron system.
- The C – Cl bond possesses partial double bond character due to resonance and is difficult to break.
- Formation of an additional double bond would disturb the aromatic stability of benzene.

**Interesting Information**

Some halogen compounds like DDT (Dichlorodiphenyl trichloroethane) have been used as pesticides, but their persistence in the environment as organic pollutant or non-biodegrable pollutant has led to restrictions or banning of their use in developed countries. Because DDT is a cheap and effective mosquito control agent, some developing countries have experienced a sharp increase in malaria deaths following its removal from stores. It is therefore, advised to restrict its use for environmental protection. DDT use is heavily restricted or banned globally.



$C_{14}H_9Cl_5$
(DDT)

## BLOCK # 03 MULTIPLE CHOICE QUESTIONS (MCQs)

1. When a halogenoalkane reacts with aqueous NaOH as a nucleophile, the major product is:
(A) Alkene (B) Alcohol (C) Aldehyde (D) Ether
2. Under elimination conditions, reaction of a halogenoalkane with NaOH produces:
(A) Alcohol (B) Alkene (C) Carboxylic acid (D) Ester
3. Hydroxide ion ($OH^-$) behaves as:
(A) Only a nucleophile (B) Only a base
(C) Both a nucleophile and a base (D) Neither a base nor a nucleophile
4. Potassium cyanide (KCN) reacts with halogenoalkanes to produce:
(A) Alcohols (B) Nitriles (C) Amines (D) Alkenes
5. Cyanide ion ($CN^-$) acts primarily as a:
(A) Strong base only (B) Strong nucleophile (C) Lewis acid (D) Electrophile
6. Bromoethane reacts with KCN to form:
(A) Ethanenitrile (B) Propanenitrile (C) Butanenitrile (D) Ethanoic acid
7. Reaction of halogenoalkanes with ammonia initially forms:
(A) Alcohol (B) Primary amine (C) Secondary alcohol (D) Alkene
8. Excess halogenoalkane reacting with ammonia ultimately produces:
(A) Ammonium ion (B) Secondary ammonium ion
(C) Tertiary ammonium ion (D) Quaternary ammonium salt
9. Aqueous silver nitrate is mainly used to:
(A) Detect alkyl radical in halogenoalkanes (B) Detect halide ions in halogenoalkanes
(C) Detect silver ions in halogenoalkanes (D) Oxidize halogenoalkanes
10. Which silver halide forms a white precipitate?
(A) AgBr (B) AgI (C) AgCl (D) AgF
11. Which silver halide gives a cream-colored precipitate?
(A) AgCl (B) AgBr (C) AgI (D) AgF
12. Which silver halide produces a bright yellow precipitate?
(A) AgCl (B) AgBr (C) AgI (D) $Ag_2O$
13. Which halogenoalkane gives the fastest precipitate with aqueous silver nitrate?
(A) Fluoroalkane (B) Chloroalkane (C) Bromoalkane (D) Iodoalkane
14. Halogenoarenes are commonly prepared by reacting benzene with halogens in the presence of:
(A) $ZnCl_2$ (B) $FeCl_3$ or $FeBr_3$ (C) NaOH (D) $KMnO_4$
15. Preparation of chlorobenzene from benzene is an example of:
(A) Nucleophilic aromatic substitution (B) Electrophilic aromatic substitution
(C) Elimination (D) Addition polymerization
16. Halogenoarenes are less reactive than halogenoalkanes because:
(A) Their C–X bond is weaker (B) They contain fewer carbon atoms
(C) Their C–X bond has partial triple-bond character (D) Their C–X bond has partial double-bond character
17. Delocalization of the halogen lone pair in halogenoarenes results in:
(A) Weaker C–X bond (B) Stronger C–X bond (C) Ionic bonding (D) Formation of radicals
18. Chlorobenzene does not readily react with NaOH under normal conditions because:
(A) The C–Cl bond is strengthened by resonance (C) It contains no chlorine
(B) The C–Cl bond is weakened by resonance (D) NaOH is a weak nucleophile



19. Which pesticide of the following has been restricted because of its persistence in the environment?
(A) Malathion (B) Glyphosate (C) DDT (D) Carbaryl
20. Compared with halogenoalkanes, halogenoarenes are generally:
(A) More reactive toward nucleophilic substitution (B) Equally reactive
(C) Less reactive toward nucleophilic substitution (D) Stronger acids

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

**BLOCK # 01**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. C | 4. C | 5. C | 6. B | 7. A | 8. B | 9. B | 10. B | 11. B | 12. C | 13. B | 14. C | 15. D |
| 16. A | 17. C | 18. D | 19. B | 20. B | | | | | | | | | | |

**BLOCK # 02**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. C | 4. B | 5. C | 6. C | 7. C | 8. C | 9. A | 10. B | 11. B | 12. B | 13. B | 14. C | 15. C |
| 16. B | 17. A | 18. C | 19. A | 20. B | | | | | | | | | | |

**BLOCK # 03**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. C | 4. B | 5. B | 6. B | 7. B | 8. D | 9. B | 10. C | 11. B | 12. C | 13. D | 14. B | 15. B |
| 16. D | 17. B | 18. A | 19. C | 20. C | | | | | | | | | | |

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I) Which of the following compound is a primary halogenoalkane?
a) 1-bromo-2,2-dimethyl propane b) 2-bromo-3-methyl butane
c) 2-bromopropane d) 2-bromo-2-methyl propane

II) The reactivity order of halogenoalkanes for a particular alkyl group is:
a) Fluoride > Chloride > Bromide > Iodide b) Chloride > Bromide > Fluoride > iodide
c) Iodide > Bromide > Chloride > Fluoride d) Bromide > Iodide > Chloride > Fluoride

III) $S_N2$ reactions can be best carried out with:
a) Primary halogenoalkanes b) Secondary halogenoalkanes
c) Tertiary halogenoalkanes d) Halogenoarenes

IV) Elimination bimolecular reactions involve:
a) First order kinetics b) Second order kinetics c) Third order kinetics d) Zero order kinetics

V) For which mechanisms, the first step involved is the same:
a) E1 and E2 b) E2 and $S_N2$ c) $S_N1$ and E2 d) E1 and $S_N1$

VI) Halogenoalkanes are considered to be very reactive compounds towards nucleophiles, because:
a) They have an electrophilic carbon
b) They have an electrophilic carbon and a good leaving group
c) They have an electrophilic carbon and a bad leaving group
d) They have a nucleophilic carbon and a good leaving group

VII) 1-chloropropane will follow which mechanism when it reacts with aqueous KOH resulting in the formation of an alcohol.
a) $S_N1$ b) $S_N2$ c) Mixed $S_N1$ and $S_N2$ d) E1

VIII) Which one of the following is not a nucleophile?
a) $H_2O$ b) $H_2S$ c) $BF_3$ d) $NH_3$

IX) When aqueous solution of alkyl halides are reacted with $AgNO_3$, the most rapid ppt. formation occurs with:
a) fluoroalkane b) chloroalkane c) bromoalkane d) iodoalkane

X) The rate of E1 reaction depends upon:
a) The concentration of the substrate only. b) The concentration of the base only.
c) The concentrations of substrate as well as base. d) Neither the concentration of substrate nor the base.

CamScanner

## Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | a | 1-bromo-2,2-dimethylpropane | The carbon atom attached to bromine is bonded to only one other carbon atom; therefore, it is a primary halogenoalkane. |
| II. | c | Iodide > Bromide > Chloride > Fluoride | Reactivity increases as the carbon-halogen bond becomes weaker. Since the C–I bond is the weakest, iodoalkanes are the most reactive. |
| III. | a | Primary halogenoalkanes | Primary halogenoalkanes have minimum steric hindrance, allowing easy backside attack by the nucleophile in reactions. |
| IV. | b | Second order kinetics | The rate of an E2 reaction depends on the concentration of both the substrate and the base. |
| V. | d | E1 and Sub | Both E1 and Sub mechanisms start with the slow formation of a carbocation intermediate. |
| VI. | b | They have an electrophilic carbon and a good leaving group | The carbon atom bonded to the halogen becomes partially positive and can be attacked by nucleophiles, while the halide ion leaves easily. |
| VII. | b | $S_N2$ | 1-chloropropane is a primary haloalkane, so $OH^-$ attacks the carbon in a one-step backside substitution. |
| VIII. | c | $BF_3$ | $BF_3$ is electron deficient and acts as an electron pair acceptor (Lewis acid) but not as a nucleophile. |
| IX. | d | Iodoalkane | Iodide is the best leaving group among halides; therefore, iodoalkanes react fastest with $AgNO_3$ solution and give precipitate most rapidly. |
| X. | a | The concentration of the substrate | E1 reactions are unimolecular reactions. Their rate depends only on the concentration of the substrate and is independent of the concentration of the base. Rate = k[Substrate] |

## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) How does chloropropane react with alcoholic KOH?**

**Ans.** With alcoholic KOH and heat, 1-chloropropane undergoes β-elimination (dehydrohalogenation) to form propene:

$$CH_3CH_2CH_2Cl + KOH_{(alc)} \longrightarrow CH_3CH = CH_2 + KCl + H_2O.$$

**b) Why fluoroalkanes rarely undergo nucleophilic substitution reactions?**

**Ans.** Fluoroalkanes rarely undergo nucleophilic substitution because the C – F bond is very strong due to good overlap of C and F orbitals, thus difficult to break. Therefore, fluoride ion is a poor leaving group.

**c) Why primary halogenoalkanes undergo substitution reactions by $S_N2$ mechanism?**

**Ans.** Primary halogenoalkanes have less steric hindrance around the carbon attached to the halogen. This allows the nucleophile to attack easily from the opposite side, so they mainly follow the SN2 mechanism.

**d) Does 1-bromo-2,2-dimethylpropane undergo elimination reaction or not? Justify.**

**Ans.** No, 1-bromo-2,2-dimethylpropane does not undergo elimination reaction because there is no β-hydrogen atom present on the adjacent carbon. Since elimination requires the removal of a β-hydrogen, the reaction cannot occur.

**e) Why tertiary halogenoalkanes undergo elimination reaction by E1 mechanism?**

**Ans.** Tertiary halogenoalkanes easily form stable tertiary carbocations. Since E1 reactions proceed through carbocation formation, tertiary halogenoalkanes readily undergo elimination by the E1 mechanism.



**f) Hydroxide ion is a good base as well as a good nucleophile. Justify.**

**Ans.** Hydroxide ion contains a negative charge and lone pair of electrons. It can accept a proton, so it acts as a base, and it can donate an electron pair to an electron-deficient carbon atom, so it also acts as a nucleophile.

**g) What is the role of iron chloride ($FeCl_3$) during the chlorination of benzene?**

**Ans.** Iron chloride acts as a catalyst during chlorination. It helps in the formation of the electrophile ($Cl^+$), which attacks the benzene ring and forms chlorobenzene.

**h) Which among haloalkanes or haloarenes, is more reactive towards nucleophiles?**

**Ans.** Haloalkanes are more reactive towards nucleophiles than haloarenes because the carbon-halogen bond in haloarenes has partial double bond character due to resonance and is difficult to break.

**i) Write the equation for the reaction of 1-chloropropane with $AgNO_3$.**

**Ans.** $CH_3 — CH_2 — CH_2 — Cl + AgNO_3 \longrightarrow CH_3 — CH_2 — CH_2 — ONO_2 + AgCl\downarrow$

A white precipitate of silver chloride is formed during the reaction.

## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) Explain the mechanisms which the chloroalkane will adopt while giving nucleophilic substitution reactions.**

**Ans.** The mechanism adopted by a chloroalkane depends mainly upon the structure of the alkyl group attached to chlorine.

- **Primary chloroalkanes** generally follow the **$S_N2$ mechanism** because there is less steric hindrance and the nucleophile can easily attack the carbon atom from the back side.
- **Tertiary chloroalkanes** usually follow the **$S_N1$ mechanism** because they form stable tertiary carbocations.
- **Secondary chloroalkanes** may undergo either **$S_N1$ or $S_N2$ mechanism** depending upon the reaction conditions and the nature of the nucleophile.

Therefore, the mechanism adopted by a chloroalkane depends upon the stability of the carbocation and the amount of steric hindrance around the carbon atom.

**b) Why nucleophilic substitution and elimination reactions of haloalkanes proceed together under similar conditions?**

**Ans.** Nucleophilic substitution and elimination reactions often occur under similar conditions because both reactions involve the breaking of the carbon-halogen bond.

The hydroxide ion and alkoxide ions can behave both as nucleophiles and as bases.

- When the reagent acts as a **nucleophile**, substitution occurs.
- When the reagent acts as a **base**, elimination occurs.

The type of reaction depends upon factors such as temperature, the nature of the substrate and the strength of the base.

Therefore, both reactions often compete with each other and may proceed simultaneously.

**c) It is difficult for chlorobenzene to undergo nucleophilic substitution reactions but it is easier for it to undergo electrophilic substitution reactions. Give reasons.**

**Ans.** Chlorobenzene does not easily undergo nucleophilic substitution reactions because the carbon-chlorine bond has partial double bond character due to resonance.

**As a result:**

- The C–Cl bond becomes shorter and stronger.
- The bond is difficult to break.
- Formation of carbocation or backside attack by nucleophile becomes difficult.

On the other hand, benzene contains a cloud of π-electrons which attracts electrophiles.

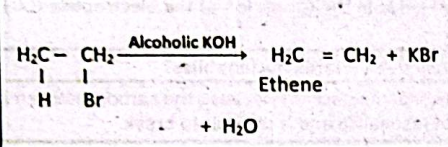
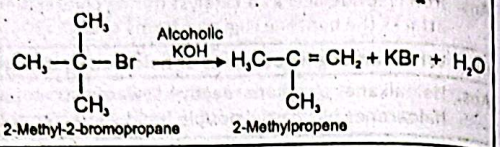
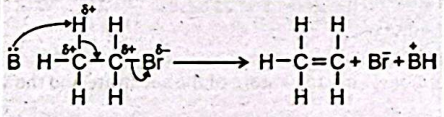
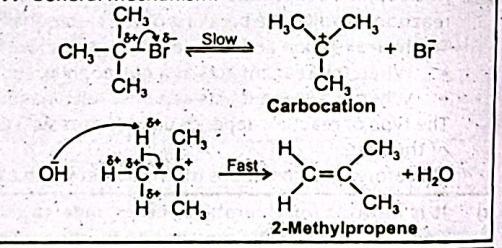
During electrophilic substitution, the aromatic character of benzene is restored after the reaction, making such reactions favorable.

Therefore, chlorobenzene resists nucleophilic substitution but readily undergoes electrophilic substitution reactions.

CamScanner

**d) Differentiate between E2 and E1 reactions. Draw a table for your response.**

**Ans.**

| E2 REACTION | E1 REACTION |
|---|---|
| One step elimination reaction in which both the atoms or groups leave simultaneously is called E2 reaction.   | Two steps elimination reaction in which the leaving group leaves first followed by the removal of hydrogen is called E1 reaction.   |
| 1. It is bimolecular reaction because two molecules are taking part in the rate determining step. | 1. It is unimolecular reaction. |
| 2. It is a single step reaction which is slow and rate determining step. In the same step, base attacks on the acidic hydrogen and halogen atom is removed simultaneously resulting in alkene formation. | 2. It's a two step reaction. The first step is slow, reversible and carbocation is formed. In the second step the base (sometimes solvent) removes acidic hydrogen and alkene is formed. |
| 3. Rate = k [alkyl halide] [base] | 3. Rate = k [alkyl halide] |
| 4. Chemical kinetics shows that it is 2nd order reaction. | 4. Chemical kinetics shows that it is 1st order reaction. |
| 5. Usually primary alkyl halides follow E2– mechanism. Order of ease of E2 reaction in alkyl halides are Primary alkyl halide > Secondary alkyl halide > Tertiary alkyl halide. | 5. Usually tertiary alkyl halides show E1 mechanism. Order of ease of E1 reaction in alkyl halides are T° alkyl halide > S° alkyl halide > P° alkyl halide. |
| 6. It competes $S_N2$ reaction. | 6. It competes $S_N1$ reaction. |
| 7. General mechanism.   | 7. General mechanism.   |

**e) Why does $CH_3 - CH_2 - I$ give a precipitate with aqueous silver nitrate earlier than $CH_3 - CH_2 - Cl$?**

**Ans.** Ethyl iodide gives a precipitate earlier because the carbon-iodine bond is weaker than the carbon-chlorine bond. As a result, iodide ion leaves more easily than chloride ion.
The iodide ion quickly reacts with silver nitrate to form yellow silver iodide precipitate, whereas chloride ion reacts more slowly to form white silver chloride precipitate.
Therefore, $CH_3CH_2I$ gives a precipitate earlier than $CH_3CH_2Cl$ with aqueous silver nitrate solution.



## DESCRIPTIVE QUESTIONS DQs

**Q.4 Describe how substitution of alcohol with following reagents help to synthesize halogenoalkanes**
**I) KBr with $H_2SO_4$ II) $SOCl_2$ / Pyridine III) $PCl_3$ IV) $PCl_5$**

**Ans.** See Question No. 5

**Q.5 Describe nucleophilic substitution reactions of halogenoalkane starting from bromoethane with following reagents: I) Aqueous NaOH II) Ethanolic KCN III) Ethanolic $NH_3$**

**Ans.** See Question No. 11

**Q.6 Compare the reactivity of halogenoalkanes and halogenoarenes using chloroethane and chlorobenzene as examples.**

**Ans.** See Question No. 14

**Q.7 Describe the $S_N1$ and $S_N2$ mechanisms of nucleophilic substitution in halogenoalkanes.**

**Ans.** See Question No. 8

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 Classify haloalkanes on the basis of carbon atom attached to halogen.**

**Ans.** Haloalkanes are classified as primary, secondary and tertiary haloalkanes depending upon the carbon atom to which the halogen is attached. If the halogen is attached to a primary carbon atom, it is called a primary haloalkane and similarly for secondary and tertiary carbons.
**Examples:**
- **Primary:** $CH_3CH_2Cl$
- **Secondary:** $CH_3CHCl$
- **Tertiary:** $(CH_3)_3CCl$

**Q.2 Explain the preparation of haloalkanes by free radical substitution.**

**Ans.** Haloalkanes are prepared by reacting alkanes with chlorine or bromine in the presence of ultraviolet light. The reaction proceeds through a free radical mechanism involving initiation, propagation and termination steps.
**Equation:**

$$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$$

- Methane produces chloromethane by free radical substitution.

**Q.3 Explain the preparation of haloalkanes from alkenes.**

**Ans.** Alkenes react with halogens or hydrogen halides at room temperature through electrophilic addition reactions to produce haloalkanes. The double bond breaks and new sigma bonds are formed.
**Equation:**

$$CH_2 = CH_2 + HBr \longrightarrow CH_3CH_2Br$$

Ethene reacts with hydrogen bromide to form bromoethane.

**Q.4 Explain the preparation of haloalkanes from alcohols.**

**Ans.** Alcohols are converted into haloalkanes by replacing the hydroxyl group with a halogen atom using reagents such as HX, $PCl_5$, $PCl_3$ or $SOCl_2$. These reactions are commonly used in organic synthesis.
**Equation:** $R - OH + HX \longrightarrow R - X + H_2O$

**Q.5 Describe the reaction of haloalkanes with aqueous NaOH.**

**Ans.** Haloalkanes react with aqueous sodium hydroxide on heating to produce alcohols through nucleophilic substitution reactions. Hydroxide ions replace the halogen atom in the molecule.
**Equation:**

$$CH_3CH_2Br + NaOH_{(aq)} \xrightarrow{heat} CH_3CH_2OH + NaBr$$

Bromoethane gives ethanol as the product.

CamScanner

**Q.6 Describe the reaction of haloalkanes with KCN.**

**Ans.** Haloalkanes react with potassium cyanide in ethanol under reflux conditions to produce nitriles. This reaction increases the carbon chain length by one carbon atom.

**Equation:**

$$CH_3CH_2Br + KCN \xrightarrow{\text{ethanol, heat}} CH_3CH_2CN + KBr$$

Bromoethane produces propanenitrile.

**Q.7 Describe the reaction of haloalkanes with ammonia.**

**Ans.** Haloalkanes react with ammonia in ethanol under pressure and heat to form primary amines. The reaction occurs through nucleophilic substitution.

**Equation:**

$$CH_3CH_2Br + 2NH_3 \xrightarrow{\text{ethanol, pressure}} CH_3CH_2NH_2 + NH_4Br$$

Bromoethane forms ethylamine.

**Q.8 Explain the test for halogens using silver nitrate.**

**Ans.** In the aqueous silver nitrate test carried out in water/ethanol, water first hydrolyses the halogenoalkane and releases the halide ion. The halide then forms a characteristic silver halide precipitate: AgCl white, AgBr cream-yellow, and AgI bright yellow. Faster precipitate formation indicates a more reactive halogenoalkane.

$$C_2H_5X + H_2O \longrightarrow C_2H_5OH + H^+ + X^-$$

$$Ag^+ + X^- \longrightarrow AgX_{(s)}$$

**Q.9 Describe the elimination reaction of haloalkanes.**

**Ans.** Haloalkanes react with alcoholic sodium hydroxide on heating to eliminate hydrogen halide and form alkenes. This reaction is called dehydrohalogenation.

**Equation:**

$$CH_3CH_2Br + NaOH_{(alc)} \xrightarrow{\text{ethanol, heat}} CH_2 = CH_2 + NaBr + H_2O$$

**Q.10 Why is chlorobenzene less reactive than chloroethane?**

**Ans.** In chlorobenzene, the lone pair of electrons on chlorine participates in resonance with the benzene ring, giving the C – Cl bond partial double bond character. This makes the bond shorter and stronger than in chloroethane. Therefore, chlorobenzene is much less reactive towards nucleophilic substitution reactions

**Q.11 Explain the preparation of haloarenes from benzene.**

**Ans.** Haloarenes are prepared by the reaction of benzene with chlorine or bromine in the presence of a Lewis acid catalyst such as $FeCl_3$ or $FeBr_3$. The reaction proceeds through an electrophilic substitution mechanism.

**Equation:**

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + HCl$$

Thus, benzene is converted into chlorobenzene.

**Q.12 Compare the reactivity of haloalkanes and haloarenes.**

**Ans.** Haloalkanes are generally more reactive towards nucleophilic substitution reactions than haloarenes. In **haloarenes,** the lone pair of electrons on the halogen atom participates in resonance with the aromatic ring, giving the C – X bond partial double bond character.
Therefore, the carbon-halogen bond in haloarenes is stronger and more difficult to break.

**Q.13 Why are C – X bonds polar in haloalkanes?**

**Ans.** Halogen atoms are more electronegative than carbon atoms and attract the bonding electrons towards themselves. As a result, the carbon atom acquires a partial positive charge while the halogen atom acquires a partial negative charge.

$$C^{\delta+} — X^{\delta-}$$



This polarity makes haloalkanes susceptible to nucleophilic attack.

**Q.14 What is nucleophilic substitution?**

**Ans.** Nucleophilic substitution is a reaction in which a nucleophile replaces a halogen atom or another leaving group in an organic compound. The reaction occurs because the carbon attached to the halogen atom is electron deficient.

**General Equation:**

$$R — X + Nu^- \longrightarrow R — Nu + X^-$$

**Q.15 Why does iodide act as a better leaving group than chloride?**

**Ans.** The C–I bond is longer and weaker than the C – Cl bond because iodine has a larger atomic size. Therefore, the bond breaks more easily and iodide ions leave more readily.
The order of leaving group ability is:

$$I^- > Br^- > Cl^-$$

**Q.16 Explain why fluoroalkanes are less reactive than iodoalkanes.**

**Ans.** Fluorine forms a very strong C – F bond because of its small atomic size and effective orbital overlap with carbon. In contrast, the C – I bond is weaker and breaks more easily.
Therefore, fluoroalkanes are less reactive towards nucleophilic substitution than iodoalkanes.

**Q.17 Explain the effect of molecular structure on reactivity of haloalkanes.**

**Ans.** The reactivity of haloalkanes depends upon the strength of the carbon-halogen bond and the steric hindrance around the carbon atom. Weaker C – X bonds and lower steric hindrance generally increase the rate of reaction.
Thus, iodoalkanes are usually more reactive than chloroalkanes.

**Q.18 What is dehydrohalogenation?**

**Ans.** Dehydrohalogenation is the removal of a hydrogen atom and a halogen atom from adjacent carbon atoms of a haloalkane to produce an alkene. This reaction is an example of elimination.

**Equation:**

$$CH_3CH_2Br + NaOH_{(alc)} \xrightarrow{\text{ethanol, heat}} CH_2 = CH_2 + NaBr + H_2O$$

**Q.19 Differentiate between aqueous and alcoholic sodium hydroxide reactions.**

**Ans.** Aqueous sodium hydroxide favors nucleophilic substitution reactions and produces alcohols, whereas alcoholic sodium hydroxide favors elimination reactions and produces alkenes.

**Substitution:**

$$CH_3CH_2Br + NaOH_{(aq)} \longrightarrow CH_3CH_2OH + NaBr$$

**Elimination:**

$$CH_3CH_2Br + NaOH_{(alc)} \longrightarrow CH_2 = CH_2 + NaBr + H_2O$$

**Q.20 Why does the KCN reaction increase carbon chain length?**

**Ans.** The cyanide ion contains an additional carbon atom which becomes part of the product during nucleophilic substitution. Therefore, the resulting nitrile contains one more carbon atom than the original haloalkane.

**For example:**

$$C_2H_5Br \longrightarrow C_2H_5CN$$

The number of carbon atoms increases from 2 to 3.

**Q.21 Explain the importance of haloalkanes in organic synthesis.**

**Ans.** Haloalkanes are useful synthetic intermediates because nucleophilic substitution and elimination allow conversion into alcohols, nitriles, amines, and alkenes. This versatility is why they are important in reaction pathways and retrosynthetic planning.

CamScanner

**Q.22 Predict the major product when bromoethane reacts with aqueous NaOH.**

**Ans.** Aqueous sodium hydroxide acts as a nucleophile and replaces the bromine atom through nucleophilic substitution to form ethanol.

**Equation:**

$$CH_3CH_2Br + NaOH_{(aq)} \longrightarrow CH_3CH_2OH + NaBr$$

The major product is ethanol.

**Q.23 Predict the major product when bromoethane reacts with alcoholic NaOH.**

**Ans.** Alcoholic sodium hydroxide favors elimination of hydrogen bromide from bromoethane and produces ethene.

**Equation:**

$$CH_3CH_2Br + NaOH_{(alc)} \longrightarrow CH_2 = CH_2 + NaBr + H_2O$$

The major product is ethene.

**Q.24 Predict the product formed when bromoethane reacts with KCN.**

**Ans.** The cyanide ion replaces bromine through nucleophilic substitution to form propanenitrile.

**Equation:**

$$CH_3CH_2Br + KCN \longrightarrow CH_3CH_2CN + KBr$$

The product contains one additional carbon atom.

**Q.25 Predict the product formed when bromoethane reacts with ammonia.**

**Ans.** Ammonia acts as a nucleophile and replaces bromine to produce ethylamine. The reaction is carried out under pressure and heat in ethanol.

**Equation:**

$$CH_3CH_2Br + 2NH_3 \longrightarrow CH_3CH_2NH_2 + NH_4Br$$

Ethylamine is formed as the major product.

**Q.26 Explain retrosynthesis involving haloalkanes.**

**Ans.** Retrosynthesis is a problem-solving approach in which the target molecule is broken down into simpler starting materials. Haloalkanes often act as key intermediates because they can be converted into many functional groups.

***For example:***

$$CH_3CH_2Br \longrightarrow CH_3CH_2OH$$

**Q.27 Why are haloalkanes useful in organic synthesis?**

**Ans.** Haloalkanes undergo a wide variety of substitution and elimination reactions, allowing them to be converted into alcohols, amines, nitriles and alkenes. This makes them versatile intermediates in organic chemistry. They are widely used in pharmaceuticals and industrial synthesis.

**Q.28 Summarize the important reactions of bromoethane.**

**Ans.** Bromoethane undergoes several important reactions depending on the reagent used:

| Reagent | Product |
|---|---|
| NaOH(aq) | Ethanol |
| KCN/ethanol | Propanenitrile |
| $NH_3$/ethanol | Ethylamine |
| NaOH(alc) | Ethene |

Therefore, bromoethane serves as an important starting material for the preparation of many organic compounds.



## SELF-ASSESSMENT

**Total Mark: 30**

**Q.1 Encircle the correct option.** **(1 × 6 = 6)**

(i) **2-Chloro-2-methylpropane is a:**
(A) Primary halogenoalkane (B) Secondary halogenoalkane
(C) Tertiary halogenoalkane (D) Polyhalogenoalkane

(ii) **The most reactive halogenoalkanes are:**
(A) Fluoroalkanes (B) Chloroalkanes (C) Bromoalkanes (D) Iodoalkanes

(iii) **In the E2 mechanism, the base removes:**
(A) α-Hydrogen (B) β-Hydrogen (C) Halogen atom only (D) Carbon atom

(iv) **For which mechanisms, the first step involved is the same:**
(A) E1 and E2 (B) E2 and $S_N2$ (C) $S_N1$ and E2 (D) E1 and $S_N1$

(v) **1-chloropropane will follow which mechanism when it reacts with aqueous KOH resulting in the formation of an alcohol.**
(A) $S_N1$ (B) $S_N2$ (C) Mixed $S_N1$ and $S_N2$ (D) E1

(vi) **The rate of E1 reaction depends upon:**
(A) The concentration of the substrate only. (B) The concentration of the base only.
(C) The concentrations of substrate as well as base. (D) Neither the concentration of substrate nor the base.

**Q.2 Write short answers of the following questions.** **(2 × 8 = 16)**

(i) How does chloropropane react with alcoholic KOH?
(ii) Why tertiary halogenoalkanes undergo elimination reaction by E1 mechanism?
(iii) Which among haloalkanes or haloarenes, is more reactive towards nucleophiles?
(iv) How will you convert ethane into ethanol and ethene?
(v) Give the reaction of bromopropane with KCN. Is this a substitution reaction or an elimination reaction? Name the main product of this reaction.
(vi) Draw the primary, secondary and tertiary structures of the compound having molecular formula $C_5H_{11}Cl$.
(vii) Give two methods to convert methanol into chloromethane.
(viii) Differentiate between E2 and E1 reactions. Give two differences.

**Q.3 Extensive Questions.** **(4 + 4 = 8)**

(a) Describe the $S_N2$ mechanisms of nucleophilic substitution in halogenoalkanes.
(b) Describe how substitution of alcohol with following reagents help to synthesize halogenoalkanes
i) KBr with $H_2SO_4$ ii) $SOCl_2$ / Pyridine iii) $PCl_3$ iv) $PCl_5$

CamScanner

## ENTRANCE TEST MCQs

1. What is the order of increasing reactivity of alkyl halides? (UHS 2018)
(A) iodoalkane < bromoalkane < chloroalkane < flouroalkane
(B) flouroalkane > chloroalkane > bromoalkane > iodoalkane
(C) iodoalkane < bromoalkane > chloroalkane > flouroalkane
(D) flouroalkane < chloroalkane < bromoalkane < iodoalkane

2. When purely alcoholic solution of sodium/potassium hydroxide and halogenoalkanes are reacted, an alkene is formed. What is the mechanism of reaction? (UHS 2011)
(A) Elimination (B) Debromination (C) Dehydration (D) Reduction of benzene

3. In substitution reactions, dihaloalkane or secondary halogenoalkane give / show: (UHS 2012)
(A) $S_N1$ Mechanism (B) Both E1 and E2 (C) $S_N2$ Mechanism (D) Both $S_N1$ and $S_N2$

4. Consider the reaction given below: (UHS 2016)

$$CH_3CH_2Br \xrightarrow[\text{alcohol}]{KOH} H_2C = CH_2 + HBr$$

Mechanism followed by the reaction is:
(A) E2 (B) E1 (C) $S_N1$ (D) $S_N2$

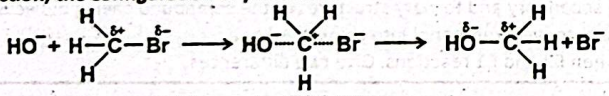
5. Which one of the following is NOT a nucleophile: (UHS 2016)
(A) $NH_2^-$ (B) $H_2O$ (C) $BF_3$ (D) $CH_3^-$

6. Consider the reaction given below: (UHS 2013)

$$H_3C-CH_2-CH_2Br \xrightarrow{I} H_3C-CH_2-CH_2OH \quad \xrightarrow{II} H_3C-CH=CH_2$$

Which statement is true?
(A) Reagent for 1 is KOH in alcohol (B) Reagent for II is KOH in aqueous medium
(C) Reaction 1 is Debromination (D) Reaction II is elimination

7. In the below reaction, the configuration of product is: (UHS 2015)



(A) 100% of the same configuration of the reactant (B) 50% inverted
(C) 50% retained (D) 100% opposite from configuration of reactant

8. The reaction $CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$ is best described by? (ECAT 2013)
(A) Electrophilic substitution (B) Nucleophilic substitution
(C) Nucleophilic substitution Unimolecular (D) Addition reaction

9. In elimination reaction, alcoholic KOH is used, $OH^-$ in this case will act as: (UHS 2017)
(A) Electrophile (B) Base (C) Leaving group (D) Acid

10. During the $S_N1$ reaction, the fast reaction involves: (UHS 2017)
(A) Breakage of covalent bond (B) Formation of carbocation
(C) Transition state (D) Attack of nucleophile

11. The IUPAC name of the given compound is $H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Cl$ (UHS 2016)
(A) 1-Chloro-2-methylpropane (B) 1-Chloro-2-methylbutane
(C) Isobutyl chloride (D) 2-Methyl-3-chloropropane

**Answers Key**

| 1. D | 2. A | 3. D | 4. A | 5. C | 6. D | 7. D | 8. B | 9. B | 10. D | 11. A |
|---|---|---|---|---|---|---|---|---|---|---|



22 CHAPTER

# HYDROXY COMPOUNDS

### Student Learning Outcomes (SLOs)

[C-12-D-41 to C-12-D-58]

- State the reactions (reagents and conditions) by which alcohols can be produced:
  a. electrophilic addition of steam to an alkene, $H_2O_{(g)}$ and $H_3PO_4$ catalyst.
  b. reaction of alkenes with cold dilute alkaline potassium manganate (VII) to form a diol.
  c. substitution of a halogenoalkane using $NaOH_{(aq)}$ and heat.
  d. reduction of an aldehyde or ketone using $NaBH_4$ or $LiAlH_4$.
  e. reduction of carboxylic acid using $LiAlH_4$.
  f. hydrolysis of an ester using dilute acid or dilute alkali and heat, describe the reaction with oxygen (combustion) of organic hydroxy compounds.
- Describe substitution to halogenoalkanes, e.g. by reaction with HX or KBr with $H_2SO_4$ or $H_3PO_4$; or with $SOCl_2$.
- Describe the reaction of hydroxy organic compounds with $Na_{(s)}$.
- Describe the oxidation with acidified $K_2Cr_2O_7$ or acidified $KMnO_4$ to: carbonyl compounds by distillation, carboxylic acids by refluxing (primary alcohols give aldehydes which can be further oxidized to carboxylic acids, secondary alcohols give ketones, tertiary alcohols cannot be oxidized).
- Describe the dehydration of alcohols to alkenes by using a heated catalyst, e.g., $Al_2O_3$ or a concentrated acid.
- Describe the formation of esters by reaction with carboxylic acids and concentrated $H_2SO_4$ or $H_3PO_4$ as catalyst as exemplified by ethanol.
- Classify alcohols as primary, secondary and tertiary alcohols, to include examples with more than one alcohol group.
- State characteristic distinguishing reactions, e.g., mild oxidation with acidified $K_2Cr_2O_7$, color change from orange to green.
- Deduce the presence of a $CH_3CH(OH)$ - group in an alcohol, $CH_3CH(OH) - R$, from its reaction alkane $I_{2(aq)}$ to form a yellow precipitate of tri-iodomethane and an ion, $RCO_2^-$.
- Explain the acidity of alcohols compared with water.
- Describe the reaction with acyl chlorides to form esters using ethyl ethanoate.
- Recall the reactions (reagents and conditions) by which phenol can be produced: reaction of phenylamine with $HNO_2$ or $NaNO_2$ and dilute acid below 10°C to produce the diazonium salt; further warming of the diazonium salt with $H_2O$ to give phenol.
- Recall the chemistry of phenol, as exemplified by the following reactions: with bases, for example $NaOH_{(aq)}$ to produce sodium phenoxide with $Na_{(s)}$ to produce sodium phenoxide and $H_{2(g)}$ in $NaOH_{(aq)}$ with diazonium salts, to give azo compounds nitration of the aromatic ring with dilute $HNO_{3(aq)}$ at room temperature to give a mixture of 2-nitrophenol and 4-nitrophenol bromination of the aromatic ring with $Br_{2(aq)}$ to form 2,4,6-tribromophenol.
- Explain, the acidity of phenol.
- Describe the relative acidities of water, phenol and ethanol.
- Explain, why the reagents and conditions for the nitration and bromination of phenol are different from those for benzene.
- Recall that the hydroxyl group of phenol directs to the 2-, 4- and 6-positions.
- Apply knowledge of the reactions of phenol to those of other phenolic compounds, e.g., naphthol.

CamScanner

**Q.1 What are alcohols and phenols?** S/Q

**Ans.** Alcohols and phenols are hydroxy organic compounds with at least one hydroxyl group attached to an aliphatic carbon.

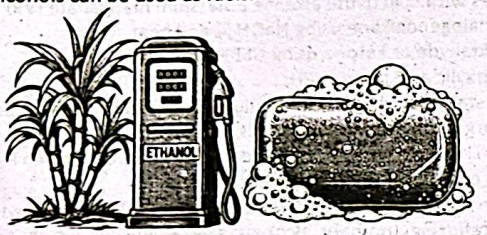
**Examples:** $CH_3-OH$ (methyl alcohol), $CH_3-CH_2-OH$ (ethyl alcohol)

Alcohols and phenols are hydroxy organic compounds with at least one hydroxyl group attached to an aryl carbon. e.g.,



Phenol

The study of alcohols and phenols holds a significant place due to their widespread occurrence and diverse applications. Almost everyone is aware of ethanol, also known as ethyl alcohol or grain alcohol. It is commonly known that alcohols can be used as fuels.




**Left: Alcohol is produced from bio-based materials and is used as a biofuel.**
**Right: Phenol is an ingredient in disinfectants, such as soaps, hospitals disinfectant liquids, etc.**

**Q.2 Who discovered the existence of bacteria and how his discovery changed surgery.** S/Q

**Ans.** After Louis Pasteur's research revealed the existence of bacteria, scientists started cleaning surgical instruments and wounds with phenol solutions in 1867 (Joseph Lister). A patient's chances of surviving surgery significantly increased due to the phenol solution's potent antiseptic properties. Since phenol burns healthy tissues, it was too potent for this use, and alternatives were eventually discovered.

## ALCOHOLS

**Q.3 What are alcohols? Write their general formula and how are they classified.** L/Q

**Ans. Alcohols:**

***Hydroxy derivates of alkanes are called alcohols or an organic compound in which one or more hydroxyl (–OH) groups are directly attached to an aliphatic carbon atom are called alcohols.***

Hydroxyl group (–OH) is the functional group of all alcohols.

➢ **General Formula:**

Alcohols are represented by the general formula ROH, where R is an alkyl or aryl group. The family also includes familiar substances, such as cholesterol and the carbohydrates. Methanol ($CH_3OH$) and ethanol ($CH_3CH_2OH$) are the first two members of the homologous series of monohydric alcohols.

➢ **Classification:**

Depending on the number of hydroxyl groups attached, alcohols can be classified into monohydric and polyhydric alcohols.

➢ **Examples:**

| Monohydric Alcohols | | Polyhydric Alcohols | |
|---|---|---|---|
| $CH_3CH_2OH$ | $CH_3CH_2CH_2OH$ | $CH_2-OH$ \| $CH_2-OH$ | $CH_2-OH$ \| $CH_2-OH$ \| $CH_2-OH$ |
| ethanol | propan-1-ol | 1,2-ethandiol (glycol) | 1,2,3-propantriol (glycerol) |



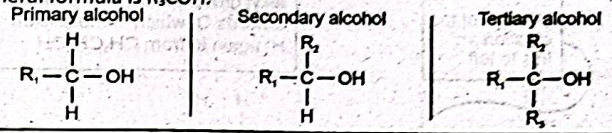
➢ **Classify Monohydric Alcohols:**

Depending on the number of carbon atoms which are directly attached to the carbon that is bonded with the –OH group, alcohols can be classified into three types.

i. **Primary Alcohol:** A primary (1°) alcohol is one in which the OH group is attached to a primary carbon atom. Its general formula is $R_1CH_2OH$.

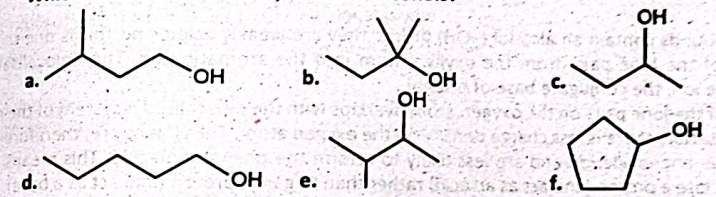
ii. **Secondary Alcohol:** A secondary (2°) alcohol is one in which the OH group is attached to a secondary carbon atom. Its general formula is $R_2CHOH$.

iii. **Tertiary Alcohol:** A tertiary (3°) alcohol is one in which the OH group is attached to a tertiary carbon atom. Its general formula is $R_3COH$.




### ☑ QUICK CHECK 22.1

i. **Which ones of these are 1°, 2° and 3° alcohols?**




**Ans.** Alcohols are classified as primary (1°), secondary (2°) or tertiary (3°) depending upon the number of carbon atoms attached to the carbon bearing the hydroxyl group (–OH).

- **Primary alcohol (1°):** The carbon carrying the –OH group is attached to only one other carbon atom.
- **Secondary alcohol (2°):** The carbon carrying the –OH group is attached to two other carbon atoms.
- **Tertiary alcohol (3°):** The carbon carrying the –OH group is attached to three other carbon atoms.

**Classification of the Given Alcohols:**

| Structure | Type of Alcohol |
|---|---|
| a | Primary alcohol (1°) |
| b | Tertiary alcohol (3°) |
| c | Secondary alcohol (2°) |
| d | Primary alcohol (1°) |
| e | Secondary alcohol (2°) |
| f | Secondary alcohol (2°) |

**Final Answer:**

**Primary (1°) alcohols:** a, d **Secondary (2°) alcohols:** c, e, f **Tertiary (3°) alcohols:** b

## ACIDITY OF ALCOHOLS AND PHENOLS

**Q.4 Explain why ethanol is less acidic than water, but water is less acidic than phenol.** L/Q
**OR Explain the acidity of phenol.** Exercise D/Q.4

**Ans.** Alcohols have a low degree of dissociation. This means that when dissolved in water, alcohol molecules do not dissociate (split up) to a great extent. The position of the equilibrium lies to the left, meaning that there are far more alcohol molecules than $RO^-_{(aq)}$ and $H^+_{(aq)}$ ions.

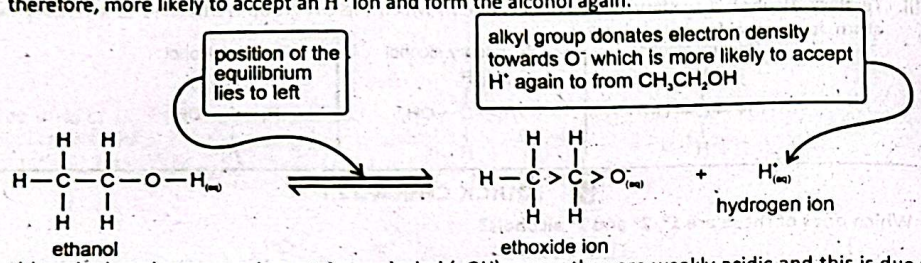
$$ROH_{(aq)} \rightleftharpoons RO^-_{(aq)} + H^+_{(aq)}$$

When water dissociates, the position of the equilibrium still lies to the left, but there are more $H^+$ ions compared to the dissociation of alcohols. As alcohols have a lower $[H^+_{(aq)}]$ in solution compared to water, alcohols are weaker acids than water.

CamScanner

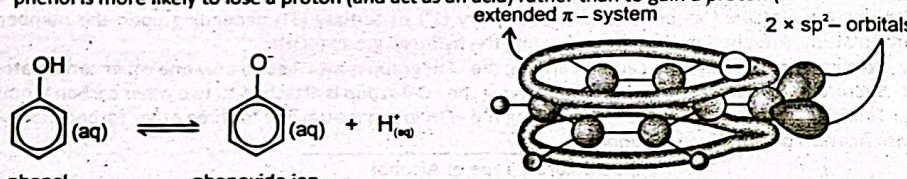
$$H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + H^+_{(aq)}$$

The reason for alcohols being less acidic than water is the presence of alkyl groups. Alkyl groups are electron donating groups. Electron-donating species push electrons into a covalent bond and are said to have a positive inductive effect. The alkyl groups destabilize the alkoxide ion, which is formed by removing one proton ($H^+$) from the alcohol molecule. The oxygen atom in the alkoxide ion is bonded to an electron-donating alkyl group. This means that there is more electron density on the O atom. The alkoxide ion is, therefore, more likely to accept an $H^+$ ion and form the alcohol again.




Although phenol compounds contain an alcohol (–OH) group, they are weakly acidic and this is due to the delocalisation of one of the lone pairs from the oxygen atom into the aromatic ring. The delocalisation stabilises the phenoxide ion, the conjugate base of phenol.

This is possible as one of the lone pairs on the oxygen atom overlaps with the delocalised π system of the ring. Because of this delocalisation, there is less charge density on the oxygen atom. The $H^+$ ions are, therefore, not strongly attracted to the phenoxide ion and are less likely to reform the phenol molecule. This means that phenol is more likely to lose a proton (and act as an acid) rather than to gain a proton (and act as a base).







The negative charge on the oxygen is delocalised and spread on the aromatic ring making it a stable ion

The relative acidities are as follows: **phenol > water > ethanol**

### QUICK CHECK 22.2

**a) Compare the relative acidic strength of methanol and ethanol.**

**Ans.** Methanol (pKa ≈ 15.5 in water) is slightly more acidic than ethanol (pKa ≈ 15.9 in water). Acidic of phenol depends on the stability of alkoxide ion.

The ethyl group shows a stronger electron-releasing (+I) effect than in methyl group. As a result, more electron density is pushed towards O-atom. The ethoxide ion becomes less stable than the methoxide ion. Therefore, the acidic strength decreases in the order:

$$CH_3OH > C_2H_5OH$$

Hence, methanol is more acidic than ethanol.

**b) Showing the electron delocalisation explain why the phenoxide ion ($PhO^-$) is more stable than the ethoxide ion ($C_2H_5O^-$).**

**Ans.** In the phenoxide ion, the negative charge on oxygen is delocalized over the entire benzene ring through resonance. The delocalization increases the stability of the phenoxide ion.

In the ethoxide ion, the negative charge remains localized only on the single oxygen atom and further destabilized +I effect of ethyl group.

Therefore, the phenoxide ion is more stable than the ethoxide ion.

Because of the greater stability of the phenoxide ion, phenol is more acidic than ethanol.



**c) Alkali metals react with stronger acids to produce the hydrogen gas. A piece of sodium is added to two beakers; one containing ethanol and the other phenol.**

**I) Predict in which beaker the hydrogen gas will be evolved earlier and more rapidly.**

**Ans.** Hydrogen gas will be evolved earlier and more rapidly in the beaker containing phenol.

This is because phenol is more acidic than ethanol and reacts more readily with sodium metal.

$$2C_6H_5OH + 2Na \longrightarrow 2C_6H_5ONa + H_2$$

Therefore, the reaction with phenol is faster.

**II) If the phenolphthalein indicator is already present before adding sodium to the above solutions. What will be the visual change and which beaker will show a faster change?**

**Ans.** The phenol beaker will show the pink colour earlier because phenol is more acidic than ethanol and reacts with sodium more readily, producing sodium phenoxide and $H_2$ faster.

Phenolphthalein (works best at pH range of 8.2-10) is colourless in acidic/neutral solution and changes to pink colour in alkaline solution (above 8.2) formation of the ionic phenoxide/alkoxide makes the medium alkaline.

Therefore, the visible change is colourless to pink, and it appears first in the phenol beaker.

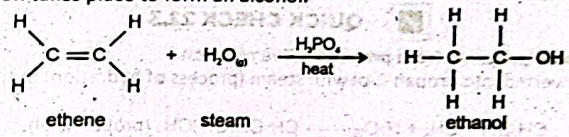
## SYNTHESIS OF ALCOHOLS

**Q.5 Write different methods to prepare alcohols.** LIQ

**Ans.** Alcohols can be prepared from alkenes, halogenoalkanes, carbonyl compounds, carboxylic acids, and esters.

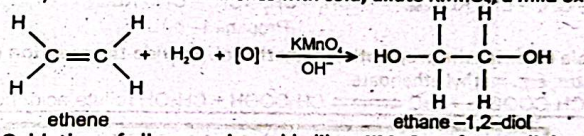
**(i) Hydration of Alkenes:**

When hot steam is reacted with an alkene, using concentrated phosphoric acid ($H_3PO_4$) as a catalyst, electrophilic addition takes place to form an alcohol.




**(ii) Oxidation of Alkenes:**

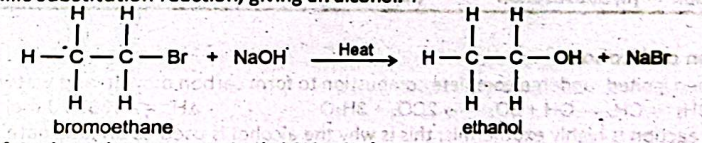
Alcohols are obtained by the oxidation of alkenes with **cold, dilute $KMnO_4$**, a mild oxidising agent.




**Oxidation of alkenes using cold, dilute $KMnO_4$ to from a diol**

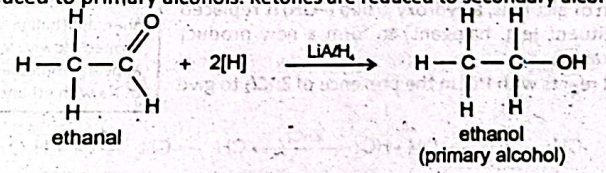
**(iii) Nucleophilic Substitution of Halogenoalkanes:**

The halogen atom in halogenoalkanes can be substituted by –OH group when heated with aqueous NaOH in a nucleophilic substitution reaction, giving an alcohol.

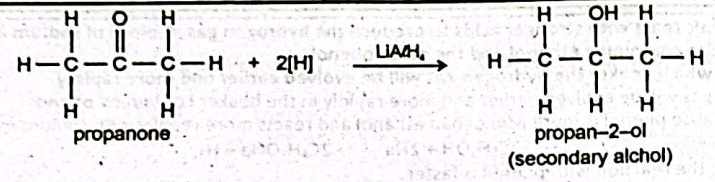



**(iv) Reduction of Carbonyl Compounds: (Aldehydes)**

Aldehydes and ketones can be reduced by reducing agents such as $NaBH_4$ or $LiAlH_4$ to obtain alcohols. Aldehydes are reduced to primary alcohols. Ketones are reduced to secondary alcohols.

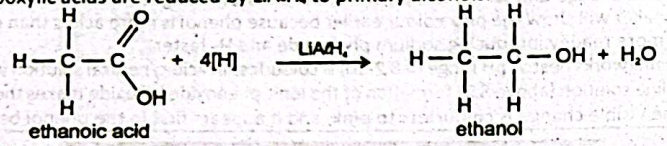



CamScanner



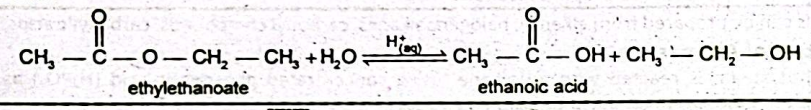

**(v) Reduction of Carboxylic Acids:**

Similarly, carboxylic acids are reduced by $LiAlH_4$ to primary alcohols.




**(vi) Hydrolysis of Esters:**

When an ester is heated with dilute acid or alkali, hydrolysis takes place and a carboxylic acid and alcohol are formed.




## QUICK CHECK 22.3

**a) How will you prepare propanol from propene? Give reaction.**

**Ans.** i) Propene is converted into propan-2-ol with steam (process of hydration) in the presence of $H_3PO_4$ or $H_2SO_4$ as catalyst.

$$CH_3CH = CH_2 + H_2O_{(g)} \longrightarrow CH_3CH(OH)CH_3 \text{ (propan-2-ol).}$$

ii) $H_3C - HC = CH_2 + HBr \xrightarrow{\text{Benzoyl Peroxide}} CH_3 - CH_2 - CH_2 - Br$ (Peroxide effect)

$$CH_3 - CH_2 - CH_2 - Br + KOH_{(aq)} \longrightarrow CH_3 - CH_2 - CH_2 - OH + KBr$$

(Propan–1–ol)

**b) Suggest a suitable ester for the preparation of methanol. Provide the reaction equation.**

**Ans.** Use a methyl ester, e.g. methyl ethanoate:

$$CH_3COOCH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3OH \text{ (dilute acid, heat)}$$

# REACTIONS OF ALCOHOLS

**Q.6 Write down following questions of alcohols.** L/O

**(i) Combustion (ii) Substitution (iii) Reaction with Sodium Metals.**

**Ans.**

**i) Combustion of Alcohols:**

Alcohols when ignited, undergo complete combustion to form carbon dioxide and water.

$$CH_3 - CH_2 - OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O \qquad \Delta H_c^\circ = -1367 \text{ kJ mol}^{-1}$$

The above reaction is highly exothermic; this is why the alcohol is used as an alternate substitute to petrol in some countries.

**ii) Substitution Reaction:**

In the substitution of alcohols, a hydroxy group (–OH) is replaced by another substituent (e.g. halogens) to form a new product (e.g., halogenoalkanes).

**Example:** Ethanol reacts with HCl in the presence of $ZnCl_2$ to give chloroethane.

$$CH_3 - CH_2 - OH + HCl \xrightarrow{ZnCl_2} CH_3 - CH_2 - Cl + H_2O$$

When sodium metal is added to a solution of phenolphthalein and ethanol, pink colour is formed slowly. With water, the pink colour appears immediately. It shows that reaction of Na with ethanol is slower than with water.



**iii) Reaction with Sodium Metal:**

When an alcohol reacts with a reactive metal such as sodium (Na), the oxygen-hydrogen bond in the hydroxyl group breaks. Though the reaction is less vigorous than sodium reacting with water, hydrogen gas is given off and a base (alkoxide) is formed. This reaction can be used as a test for hydroxy (–OH) group. Bubbles of hydrogen gas are released if a hydroxy group is present. If the excess ethanol is evaporated off after the reaction, a white crystalline solid of sodium alkoxide is left. The longer the hydrocarbon chain in the alcohol, the less vigorous the reaction becomes.

$$2CH_3 - CH_2 - OH + 2Na \longrightarrow 2CH_3 - CH_2 - ONa + H_{2(g)}$$



**Q.7 Describe the oxidation reactions of alcohols.** Exercise D/Q.6

**Ans.**

**iv. Oxidation of Alcohols:**

Primary alcohols can be oxidised to form aldehydes and the secondary alcohols can be oxidised to form only ketones using oxidizing agents. Tertiary alcohols do not undergo oxidation. The oxidising agents for alcohols include acidified $K_2Cr_2O_7$ and acidified $KMnO_4$. Acidified potassium dichromate (VI), $K_2Cr_2O_7$, is an orange oxidising agent. When alcohols are oxidised the orange dichromate ions ($Cr_2O_7^{2-}$) are reduced to green $Cr^{3+}$ ions.

**Keep in Mind**

For potassium dichromate(VI) to act as an oxidising agent, it must first be reduced. This reduction requires hydrogen ($H^+$) ions which are provided by the acidic medium.

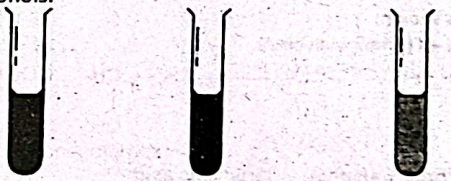
$$CH_3 - CH_2 - OH \xrightarrow{[O]} CH_3 - CHO + H_2O$$

ethanol → ethanal

$$CH_3 - CH(OH) - CH_3 \xrightarrow[\text{Heat}]{[O]} CH_3 - CO - CH_3 + H_2O$$

propan–2–ol → propanone

Therefore, only the oxidation of primary and secondary alcohols will change the colour of acidified $K_2Cr_2O_7$ solution as the orange $Cr_2O_7^{2-}$ ions are reduced to green $Cr^{3+}$ ions, which is used to check the presence of primary or secondary alcohols.




Only propan-1-ol and propan-2-ol, which are primary and secondary alcohols respectively, can get oxidised, turning the orange solution green; no colour change is observed with 2-methyl-propan-2-ol, which is a tertiary alcohol.

**Interesting Information**

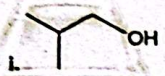
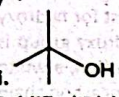
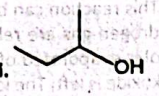
Driving after consuming alcohol is very dangerous. A breathalyser is a device that is used by the traffic officers to check if a driver is drunk or not. This device uses the oxidation of ethanol, which requires electrons. The amount of current used is proportional to the amount of alcohol consumed.



CamScanner

## QUICK CHECK 22.4

**a) Three alcohols A, B and C are structural isomers of $C_4H_{10}O$. Each alcohol is refluxed with acidified dichromate(VI), $H^+/Cr_2O_7^{2-}$.**

i.  ii.  iii. 

**Ans. Result of Refluxing with Acidified Dichromate:**

i. **P°-alcohol:** 2-Methy propanoic acid $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

ii. None.

iii. **S°-alcohol:** $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

**i) Write the systematic name for alcohol C.**

**Ans.** Alcohol C (iii) is a secondary alcohol having **IUPAC name:** Butan-2-ol

**ii) Write the equation for the complete combustion of alcohol A.**

**Ans.** Alcohol A (i) is **2-methylpropan-1-ol** having molecular formula $C_4H_{10}O$.

The balanced equation for its complete combustion is:

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH \longrightarrow 4CO_2 + 5H_2O$$

**b) Acidified potassium manganate (VII), $KMnO_4$, is a purple oxidising agent. What colour change would you observe when alcohols are oxidised with manganate ions ($MnO^{4-}$).**

**Ans.** During the oxidation of alcohols, the purple colour of acidified potassium manganite (VII) disappears because manganate ions are reduced to manganese ions ($Mn^{2+}$).

**Colour change observed:** Purple ⟶ Colourless

**c) Draw the structures for the organic products of the oxidation of the above. If there is no reaction, write 'NONE'.**

**Ans. For the three alcohols shown:**

**1. 2-methylpropan-1-ol (primary alcohol)**

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH \xrightarrow{\text{acidified } K_2Cr_2O_7/H^+,[O]} CH_3-\underset{\underset{CH_3}{|}}{CH}-COOH$$

2-methylpropanoic acid

**Primary alcohol → Carboxylic acid**

**2. 2-methylpropan-2-ol (tertiary alcohol)**

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow{\text{acidified } K_2Cr_2O_7/H^+,[O]} \underset{\text{(No oxidation under normal conditions)}}{\text{NONE}}$$

Because there is no hydrogen on C containing OH.

**3. Butan-2-ol (secondary alcohol)**

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 \xrightarrow{\text{acidified } K_2Cr_2O_7/H^+,[O]} CH_3-CO-CH_2-CH_3$$

butan-2-one

Secondary alcohol an oxidized to ketone only but no further oxidation.



**v. Dehydration of Alcohols:**

Alcohols can also undergo dehydration to form alkenes. Dehydration is the type of the elimination reaction in which a water molecule is removed.

$$\underset{\text{Ethanol}}{H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH} \xrightarrow[\text{Heat}]{Al_2O_3} \underset{\text{Ethene}}{\overset{H}{\underset{H}{>}}C=C\overset{H}{\underset{H}{<}}} + H_2O$$

Dehydrating agents may be aluminium oxide, conc. sulphuric acid, conc phosphoric acid, etc.

## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **The functional group present in alcohols is:**
(A) –COOH (B) –CHO (C) –OH (D) $-NH_2$

2. **The general formula of alcohols is:**
(A) ROH (B) RCOOH (C) RX (D) $RNH_2$

3. **Methanol belongs to which class of alcohols?**
(A) Secondary (B) Tertiary (C) Monohydric (D) Polyhydric

4. **An alcohol containing two hydroxyl groups is called:**
(A) Monohydric alcohol (B) Dihydric alcohol (C) Trihydric alcohol (D) Aromatic alcohol

5. **Glycerol is classified as a:**
(A) Monohydric alcohol (B) Dihydric alcohol (C) Trihydric alcohol (D) Phenol

6. **In a primary alcohol, the carbon bearing the –OH group is attached to:**
(A) Three carbon atoms (B) Two carbon atoms (C) One or no carbon atom (D) Four carbon atoms

7. **A secondary alcohol has the –OH group attached to a carbon bonded directly with:**
(A) One carbon atom (B) Two carbon atoms (C) Three carbon atoms (D) Four carbon atoms

8. **Tertiary alcohols contain the –OH group on a carbon attached to:**
(A) One carbon atom (B) Two carbon atoms (C) Three carbon atoms (D) No carbon atom

9. **Alcohols are:**
(A) Strong acids (B) Weak acids (C) Strong bases (D) Neutral salts

10. **Alcohols are weaker acids than water because alkyl groups:**
(A) Withdraw electrons (B) Donate electrons (C) Remove oxygen (D) Increase resonance

11. **Alkyl groups show:**
(A) Negative inductive effect (B) Positive inductive effect
(C) Mesomeric effect only (D) Electromeric effect only

12. **The correct order of acidity is:**
(A) Ethanol > Water > Phenol (B) Water > Phenol > Ethanol
(C) Phenol > Water > Ethanol (D) Water > Ethanol > Phenol

13. **Phenol is more acidic than ethanol because:**
(A) It contains more hydrogen atoms (B) Phenoxide ion is resonance stabilized
(C) It as fewer carbon atoms (D) It is more volatile

14. **Alcohols are prepared from alkenes by:**
(A) Hydrogenation (B) Hydration with steam (C) Chlorination (D) Polymerization

15. **Hydration of ethene gives:**
(A) Methanol (B) Ethanol (C) Ethanal (D) Ethanoic acid

16. **Cold dilute $KMnO_4$ converts alkenes into:**
(A) Alcohols (B) Diols (C) Ketones (D) Carboxylic acids

17. **Halogenoalkanes react with aqueous NaOH to produce:**
(A) Alkenes (B) Alcohols (C) Ethers (D) Esters

18. **Aldehydes are reduced to:**
(A) Secondary alcohols (B) Primary alcohols (C) Tertiary alcohols (D) Ketones

19. **Ketones are reduced to:**
(A) Primary alcohols (B) Secondary alcohols (C) Tertiary alcohols (D) Carboxylic acids

20. **Carboxylic acids are reduced by:**
(A) NaOH (B) HCl (C) $LiAlH_4$ (D) $Br_2$

21. **Hydrolysis of an ester produces:**
(A) Alcohol and carboxylic acid (B) Alkene and water
(C) Ketone and alcohol (D) Aldehyde and acid

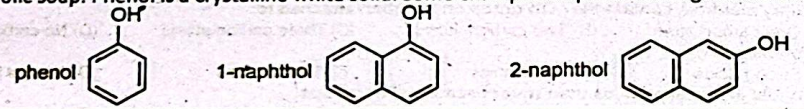
CamScanner

22. Complete combustion of alcohol produces:
(A) CO and $H_2$ (B) $CO_2$ and $H_2O$ (C) C and $H_2O$ (D) $CH_4$ and $CO_2$
23. Alcohols are considered good fuels because combustion is:
(A) Endothermic (B) Highly exothermic (C) Reversible (D) Slow
24. During substitution reactions, the –OH group is replaced by:
(A) Hydrogen (B) Halogen (C) Oxygen (D) Nitrogen
25. Alcohol reacts with sodium metal to produce:
(A) Alkene (B) Alkoxide and hydrogen gas (C) Ketone (D) Ether
26. Reaction of sodium with ethanol is:
(A) More vigorous than with water (B) Less vigorous than with water
(C) Identical to water (D) Impossible
27. Primary alcohols on oxidation produce:
(A) Ketones (B) Aldehydes (C) Alkenes (D) Esters
28. Secondary alcohols on oxidation produce:
(A) Aldehydes (B) Ketones (C) Carboxylic acids (D) Alkanes
29. Tertiary alcohols:
(A) Readily oxidize to ketones (B) Readily oxidize to aldehydes
(C) Do not undergo oxidation under ordinary conditions (D) Form carboxylic acids
30. Dehydration of alcohols produces:
(A) Alkanes (B) Alkenes (C) Aldehydes (D) Esters

## PHENOLS

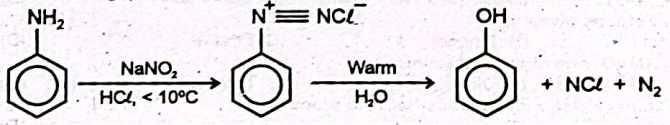
**Q.8 What are phenols give some examples?** S/Q

**Ans.** ***Compounds in which a hydroxyl group is bonded to the benzene ring (an arene) are called phenols.***
The chemical formula of the simplest phenol is $C_6H_5OH$. Phenol is also known as carbolic acid and was used as carbolic soap. Phenol is a crystalline white solid. Some examples of phenols are given below:




**Q.9 Describe how phenylamine can be converted into phenol, including reagents and conditions.** S/Q
**OR How phenyol can be prepared from aniline?** S/Q

**Ans. Preparation of Phenols (Conversion of Phenol to Phenyl Amine):**
Phenols can be produced by the reaction of phenylamine with nitrous acid ($HNO_2$). The nitrous acid used here is produced in situ. The reaction occurs in three steps.
**Step 1:** The $HNO_2$ is so unstable that it needs to be prepared in a test-tube by reacting sodium nitrite ($NaNO_2$) and dilute hydrochloric acid ($HC\ell$) while keeping the temperature below 10°C using ice.
**Step 2:** Phenylamine is then reacted with the $HNO_2$ to form an unstable diazonium salt.
**Step 3:** On further warming, phenol is produced as the diazonium salt is decomposed (hydrolysed).




## REACTIONS OF PHENOL

**Q.10 Discuss the reactions of –OH group in Phenol.** L/Q

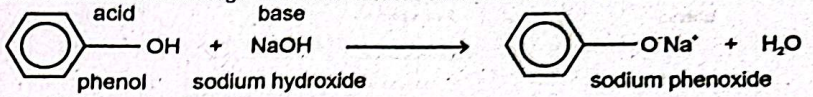
**Ans.** Phenols can undergo many types of reactions as both the electron-rich benzene ring and the polar OH group can participate in chemical reactions. Some of the reactions of phenol are given below.

### ➲ Reactions of the –OH Group in Phenols

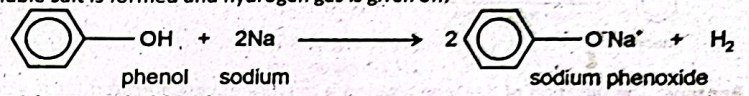
The –OH group in phenols has a slightly acidic character. It can therefore act as an acid and take part in acid-base reactions.



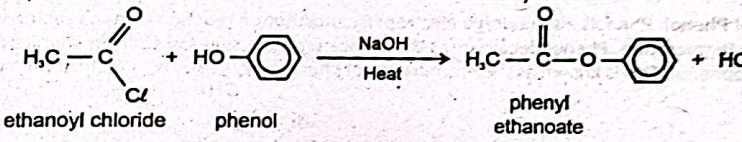
**I. Reaction with Bases:**
Phenols are only slightly soluble in water due to the large non-polar benzene ring. However, they do dissolve in alkaline solutions and undergo acid-base reactions with bases to form a soluble salt and water.

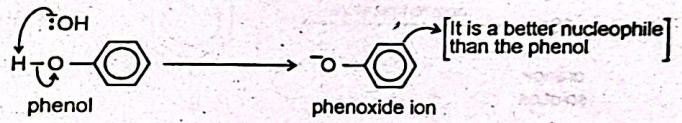



**II. Reaction with Reactive Metals:**
Molten phenols react vigorously with reactive metals such as sodium (Na). This is also an acidbase reaction. Now, a soluble salt is formed and hydrogen gas is given off.




**III. Reaction with an Acyl Chloride:**
When phenol is heated with an acyl chloride in the presence of a base, an ester is produced. The base is needed to deprotonate the phenol and form a phenoxide ion. The phenoxide ion is a better nucleophile than the original phenol molecule and will be able to attack the carbonyl carbon.




**IV. Reaction with Diazonium Ions:**
**(Note:** This reaction of phenol will be discussed in Chapter 24 (Organic Nitrogen Compounds)).

### ➲ Reactions of the Aromatic Ring in Phenols

**Q.11 How aromatic ring in phenols participates in reactions of phenols.** S/Q

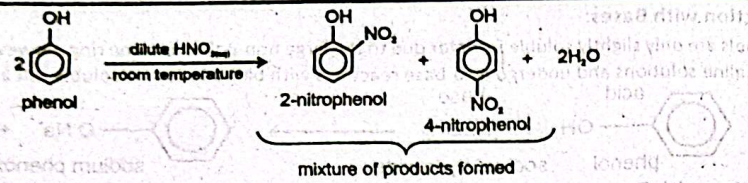
**Ans.** Phenols consist of a hydroxyl (–OH) group attached to a benzene ring. The oxygen atom in this hydroxyl group donates electron density into the ring. One of the lone pairs of the oxygen atom overlaps with the $\pi$ system of the benzene ring and becomes delocalised, causing an increased electron density in the aromatic ring. Due to the increased electron density, the benzene ring is more likely to undergo electrophilic attack and becomes activated. The incoming electrophiles are directed by the hydroxyl group of phenol to the 2, 4, and 6 positions.

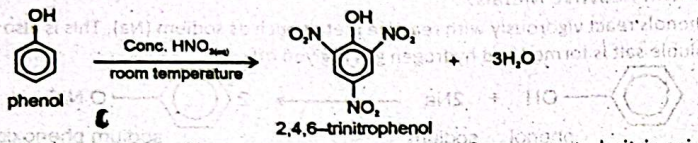
**Q.12 Explain why the reagents and conditions for the nitration and bromination of phenol are different from those for benzene.** Exercise D/Q.7

**Ans.**

**I. Nitration:**
**Nitration of Phenol:** Phenols can undergo electrophilic substitution reactions when reacted with dilute nitric acid ($HNO_3$) at room temperature to give a mixture of 2-nitrophenol and 4-nitrophenol. When concentrated $HNO_3$ is used, the product will be 2,4,6-trinitrophenol instead. A hydrogen atom in the benzene ring is substituted by a nitro ($-NO_2$) group. This is known as the nitration of phenol.

CamScanner

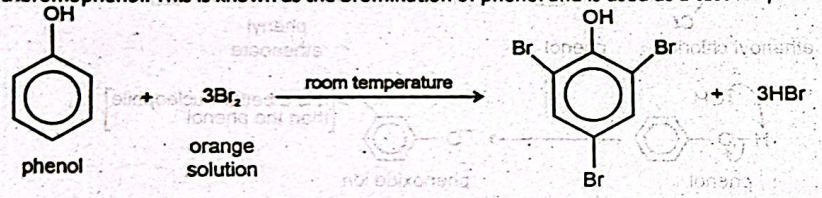



**Nitration of Benzene:** The nitration of benzene requires a mixture of concentrated nitric acid ($HNO_3$) and sulfuric acid ($H_2SO_4$) refluxed with benzene between 25°C and 60°C. Since phenol is more reactive, nitration can occur under milder conditions by reacting it with dilute nitric acid at room temperature. If concentrated nitric acid is used, 2,4,6-trinitrophenol is formed.

**ii. Bromination:**

**Bromination of Phenol:** Phenols also undergo electrophilic substitution reactions when reacted with bromine water at room temperature. Phenol decolourises the orange bromine solution to form a white precipitate of 2,4,6- tribromophenol. This is known as the bromination of phenol and is used as a test for phenol.




2,4,6 – tribromophenol (white precipitate)

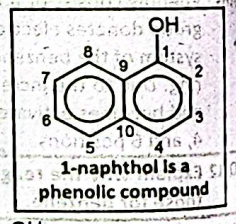
**Bromination of Benzene:** Benzene will undergo bromination only when reacted with pure bromine (not a solution) and in the presence of anhydrous aluminium bromide ($AlBr_3$) catalyst at room temperature. Phenol on the other hand readily reacts with bromine water in the absence of a catalyst.

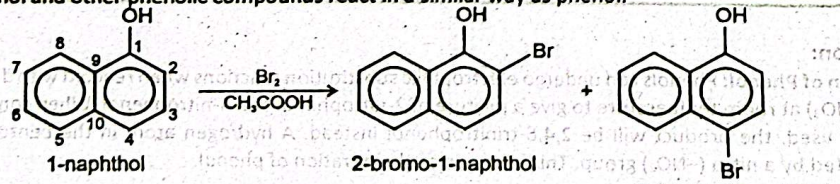
**Q.13 Discuss the structure and reactivity of 1-Naphtol.** U/Q

**Ans. 1-Naphthol:**

There exist many phenolic compounds other than phenol ($C_6H_5OH$). An example of a phenolic compound is 1-naphthol.

1-naphthol contains a hydroxy group attached to position of 1 of naphthalene. Just like with phenol, the -OH group in 1-naphthol is also electron-donating and activates the naphthalene ring for electrophilic substitution reactions. The electrophiles are directed to the 2 and/or 4 positions. Substitution at the 9 and 10 positions is not possible as there is no hydrogen atom on these carbons. 1-naphthol and other phenolic compounds react in a similar way as phenol.



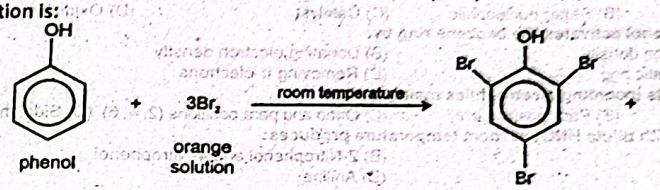



## QUICK CHECK 22.5

a) **The reaction of phenol with bromine water is used for the identification of phenol. What will be the visual change during the reaction, also give the systematic name of the compound formed.**

Ans. When bromine water is added to phenol, the reddish-brown (orange-brown) colour of bromine water disappears and a white precipitate is formed. The white precipitate is **2,4,6-tribromophenol.**

The reaction is:




2,4,6 – tribromophenol (white precipitate)

Thus, the disappearance of bromine water colour and formation of a white precipitate confirms the presence of phenol.

b) **Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why?**

Ans. Phenol is more easily nitrated than benzene.

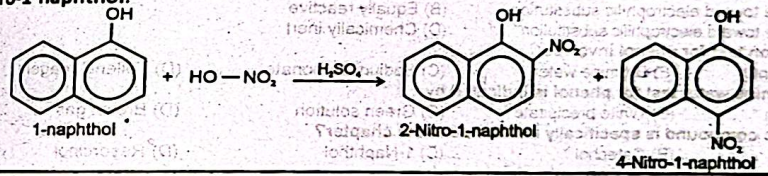
This is because the hydroxyl group (–OH) present in phenol donates electrons to the benzene ring through resonance (mesomeric effect) and increases the electron density of the ring.

As a result, the benzene ring in phenol becomes more reactive towards electrophiles and undergoes nitration more readily than benzene.

Therefore, phenol is nitrated more easily than benzene.

c) **Write the reaction equation for nitration of 1-naphthol.**

Ans. When 1-naphthol is treated with dilute nitric acid, nitration occurs mainly at the 2-position to form **2-nitro-1-naphthol.**




## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **A phenol is a compound in which the –OH group is attached directly to a:**
   (A) Alkane (B) Alkene (C) Arene (benzene ring) (D) Alkyne
2. **The molecular formula of phenol is:**
   (A) $C_6H_6$ (B) $C_6H_5OH$ (C) $C_6H_5Cl$ (D) $C_7H_8$
3. **Phenol is also known as:**
   (A) Wood alcohol (B) Grain alcohol (C) Carbolic acid (D) Glycol
4. **Phenol was formerly used mainly as a:**
   (A) Fertilizer (B) Antiseptic (C) Fuel (D) Plasticizer
5. **Phenol reacts with sodium hydroxide to form:**
   (A) Sodium phenoxide and water (B) Sodium chloride
   (C) Sodium carbonate (D) Phenyl chloride
6. **Phenol dissolves in alkaline solution because it:**
   (A) Undergoes esterification (B) Forms sodium phenoxide
   (C) Forms benzene (D) Forms alcohol
7. **Reaction of phenol with sodium metal produces:**
   (A) Oxygen gas (B) Carbon dioxide (C) Hydrogen gas (D) Chlorine gas
8. **The salt formed when phenol reacts with sodium metal is:**
   (A) Sodium acetate (B) Sodium phenoxide (C) Sodium benzoate (D) Sodium ethoxide

CamScanner

9. Phenol can be prepared from phenylamine using:
(A) Nitrous acid (B) Sulphuric acid (C) Hydrochloric acid only (D) Bromine water
10. Nitrous acid used in the preparation of phenol is produced from:
(A) NaCℓ and HCℓ (B) $NaNO_2$ and dilute HCℓ (C) NaOH and $HNO_3$ (D) $NH_4Cℓ$ and NaOH
11. Phenol reacts with acyl chloride in the presence of NaOH to produce:
(A) Alcohol (B) Ester (phenyl ethanoate) (C) Aldehyde (D) Ketone
12. During acylation, the phenoxide ion acts as a:
(A) Strong acid (B) Better nucleophile (C) Catalyst (D) Oxidizing agent
13. The –OH group in phenol activates the benzene ring by:
(A) Withdrawing electron density (B) Donating electron density
(C) Breaking the aromatic ring (D) Removing π-electrons
14. The –OH group directs incoming electrophiles mainly to the:
(A) Meta positions (B) Para position only (C) Ortho and para positions (2, 4, 6) (D) Side chain
15. Nitration of phenol with dilute $HNO_3$ at room temperature produces:
(A) Nitrobenzene only (B) 2-Nitrophenol and 4-Nitrophenol
(C) Benzoic acid (D) Aniline
16. Nitration of phenol with concentrated $HNO_3$ forms:
(A) Nitrobenzene (B) 2-Nitrophenol (C) 4-Nitrophenol (D) 2,4,6-Trinitrophenol
17. Phenol undergoes nitration under milder conditions than benzene because phenol is:
(A) Less reactive (B) More reactive (C) Non-aromatic (D) Saturated
18. Bromination of phenol is carried out using:
(A) Bromine water (B) Pure bromine with $FeBr_3$ (C) Chlorine water (D) HBr
19. During bromination, phenol decolourises:
(A) Purple $KMnO_4$ (B) Orange bromine water (C) Blue litmus (D) Acidified dichromate
20. Bromination of phenol gives a white precipitate of:
(A) Bromobenzene (B) 2,4,6-Tribromophenol (C) 1-Bromophenol (D) Bromoethane
21. Benzene requires _____ for bromination.
(A) Bromine water only (B) Anhydrous $AlBr_3$ catalyst (C) NaOH (D) UV light
22. Phenol undergoes bromination:
(A) Only at high temperature (B) Without any catalyst
(C) Only under pressure (D) Only in sunlight
23. Compared with benzene, phenol is:
(A) Less reactive toward electrophilic substitution (B) Equally reactive
(C) More reactive toward electrophilic substitution (D) Chemically inert
24. The identification test for phenol involves:
(A) Acidified $KMnO_4$ (B) Bromine water (C) Sodium carbonate (D) Tollens' reagent
25. A positive bromine water test for phenol is indicated by:
(A) Blue solution (B) White precipitate (C) Green solution (D) Brown gas
26. Which phenolic compound is specifically mentioned in the chapter?
(A) Cresol (B) Catechol (C) 1-Naphthol (D) Resorcinol
27. In 1-naphthol, the –OH group activates the ring toward:
(A) Nucleophilic substitution (B) Electrophilic substitution
(C) Free radical substitution (D) Elimination
28. In 1-naphthol, electrophilic substitution mainly occurs at:
(A) Positions 2 and 4 (B) Positions 3 and 5 (C) Positions 9 and 10 (D) Position 1 only
29. The higher acidity of phenol compared with ethanol is due to:
(A) Greater molecular mass (B) Resonance stabilization of the phenoxide ion
(C) Hydrogen bonding only (D) Presence of more hydrogen atoms
30. Which statement is correct?
(A) Phenol is less acidic than ethanol. (B) Phenol does not react with NaOH.
(C) Phenol undergoes electrophilic substitution more readily than benzene.
(D) Bromination of phenol requires an $AlBr_3$ catalyst.

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

**BLOCK # 01**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. C | 2. A | 3. C | 4. B | 5. C | 6. C | 7. B | 8. C | 9. B | 10. B | 11. B | 12. C | 13. B | 14. B | 15. B |
| 16. B | 17. B | 18. B | 19. B | 20. C | 21. A | 22. B | 23. B | 24. B | 25. B | 26. B | 27. B | 28. B | 29. C | 30. B |

**BLOCK # 02**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. C | 2. B | 3. C | 4. B | 5. A | 6. B | 7. C | 8. B | 9. A | 10. B | 11. B | 12. B | 13. B | 14. C | 15. B |
| 16. D | 17. B | 18. A | 19. B | 20. B | 21. B | 22. B | 23. C | 24. B | 25. B | 26. C | 27. B | 28. A | 29. B | 30. C |



# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. Which compound can be oxidised to form $(CH_3)_2CHCOCH_3$?
a) 2-methylpropan-1-ol b) 2,2-dimethylpropanol c) 2-methylbutan-2-ol d) 3-methylbutan-2-ol

II. Which alcohol forms a mixture of alkenes when dehydrated?
a) propan-1-ol b) propan-2-ol c) pentan-1-ol d) pentan-2-ol

III. Which alcohol can be oxidised by acidified potassium dichromate (VI) but cannot be dehydrated by heating with concentrated sulphuric acid?
a) 2,3-dimethylbutan-2-ol b) 2,2-dimethylpropan-1-ol
c) 2-methylpropan-2-ol d) pentan-3-ol

IV. Which one of the following mechanisms is not involved in the reaction sequence below?
$CH_3CH_3 \longrightarrow CH_3CH_2Cℓ \longrightarrow CH_3CH_2OH \longrightarrow CH_2 = CH_2 \longrightarrow CH_3CH_2Br$
a) electrophilic addition b) electrophilic substitution
c) nucleophilic substitution d) free-radical substitution

V. Which one of the following does not represent an oxidation?
a) ethanal → ethanol b) propan-1-ol → propanal
c) propan-2-ol → propanone d) ethanol → ethanoic acid

VI. Dehydration of alcohol is an example of:
a) substitution Reaction b) addition reaction c) elimination Reaction d) redox reaction

VII. Bromine reacts with phenol and decolourise orange colour and turns it to which of the colored precipitate?
a) white precipitate b) pink precipitate c) blue precipitate d) black precipitate

VIII. When phenol is treated with excess bromine water it gives:
a) o- and p-bromophenol b) 2,4-dibromophenol c) 2,4,6-tribromophenol d) m-bromophenol

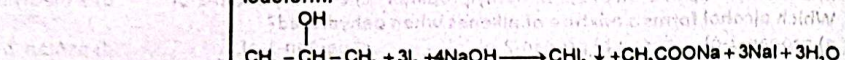
IX. What are the correct reagents for the conversion below?
$CH_3CH_2CHOHCH_3 \longrightarrow CH_3CH_2CHBrCH_3$
a) $Br_2$ and $H_2SO_4$ b) $Br_2$ and NaOH c) HBr/$ZnBr_2$ d) NaBr and NaOH

X. The reagent for the chemical test used in distinguishing propan-1-ol and propan-2-ol.
a) $Br_2$ and NaOH b) $I_2$ and NaOH c) Acidified $K_2Cr_2O_7$ d) $NaOH_{(aq)}$

### Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | d | 3-methylbutan-2-ol | The given product is a ketone, so it must be obtained by oxidation of a secondary alcohol. 3-Methylbutan-2-ol is a secondary alcohol and gives the required ketone on oxidation. |
| II. | d | pentan-2-ol | Dehydration of pentan-2-ol can produce two different alkenes, pent-1-ene and pent-2-ene, therefore a mixture of alkenes is obtained. |
| III. | b | 2,2-dimethylpropan-1-ol | This primary alcohol can be oxidised but cannot undergo dehydration because the β-carbon does not contain any hydrogen atom required for elimination. |
| IV. | b | Electrophilic substitution | The sequence involves free-radical substitution, nucleophilic substitution, elimination and electrophilic addition, but electrophilic substitution does not occur. |
| V. | a | ethanal → ethanol | Conversion of ethanal into ethanol is reduction because hydrogen is added to ethanal. |
| VI. | c | Elimination reaction | During dehydration, water is removed from the alcohol molecule resulting in formation of an alkene. |
| VII. | a | White precipitate | Phenol reacts with bromine water to form white precipitates of 2,4,6-tribromophenol. |

CamScanner

| | | | |
|---|---|---|---|
| VIII. | c | 2,4,6-tribromophenol | Excess bromine water causes substitution at ortho and para positions producing 2,4,6-tribromophenol. |
| IX. | c | $HBr/ZnBr_2$ | HBr converts the –OH group of the secondary alcohol into Br; $ZnBr_2$ helps activate the C – O bond. |
| X. | b | $I_2$ and NaOH | Propan-2-ol is a secondary alcohol which is a yellow precipitate of iodoform.  Propan-1-ol does not give this precipitate. |

## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) Four alcohols are given below:**

**i. butan-2-ol ii. 2-methylpentan-3-ol iii. 2-methylpropan-2-ol vi. propan-1-ol**

**i) Which alcohol is an example of a tertiary alcohol?**

**ii) Which alcohol is an example of an alcohol that can be oxidized to carboxylic acid?**

**iii) Which alcohols are examples of an alcohol that can be oxidised to a ketone?**

**iv) Which alcohol cannot change color of acidified potassium dichromate?**

**Ans. (i) The tertiary alcohol is: 2-methylpropan-2-ol (iii)**

This is because the carbon carrying the hydroxyl group is attached to three other carbon atoms.

**Ans. (ii)** Primary alcohols are oxidized to carboxylic acids.

From the given list:

**Propan-1-ol (vi)** can be oxidized to propanoic acid.

$$CH_3-CH_2-CH_2-OH \longrightarrow CH_3-CH_2-COOH$$

**ii)** Secondary alcohols are oxidized to ketones.

One suitable example from the list is:

**Butan-2-ol (i)** which is oxidized to **butan-2-one.**

$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3 \xrightarrow{[O]} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2-CH_3$$

**(Note:** Some other examples i.e., 2-methylpentan-3-ol and propan-2-ol can also be oxidized to ketones.)

**Ans. (iv)** Tertiary alcohols do not undergo oxidation with acidified potassium dichromate and therefore do not change its colour.

**2-methylpropan-2-ol (ii)**

Here the orange colour of acidified potassium dichromate remains unchanged.

**b) 4-methylaniline reacts with $HNO_{2(aq)}$ at 4°C to form compound P. Compound P reacts with NaOH. The product of this reaction is compound Q.**

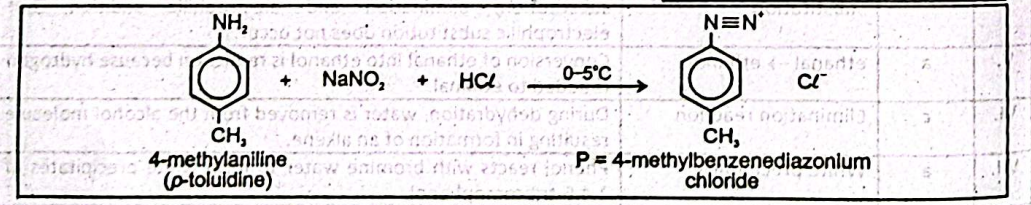
**i) Draw the structure of compound P and Q.**

**ii) Circle the azo group on your structure.**

**iii) Give the IUPAC name of Q.**

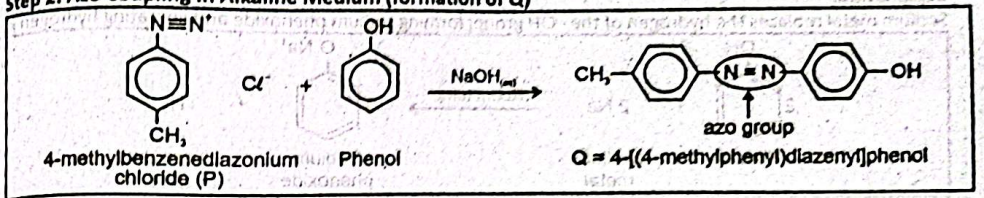
**Ans. Step 1: Diazotization (formation of P)**

**Note:** This has been explained in ch. 24.






**Step 2: Azo Coupling in Alkaline Medium (formation of Q)**




**(i)** P = 4-methylbenzenediazonium chloride.

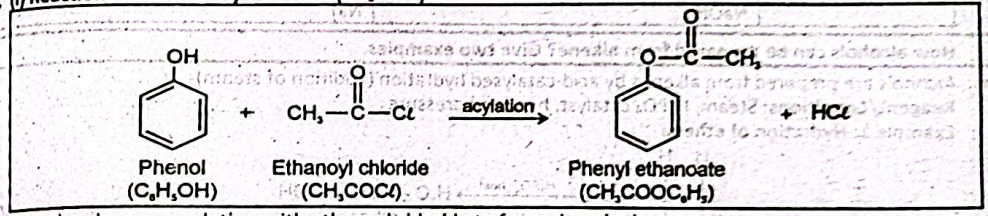
**(ii)** The azo group is: — N = N —

This linkage joins the two aromatic rings in the azo compound.

**(iii)** IUPAC name of Q = 4-[(4-methylphenyl)diazenyl]phenol.

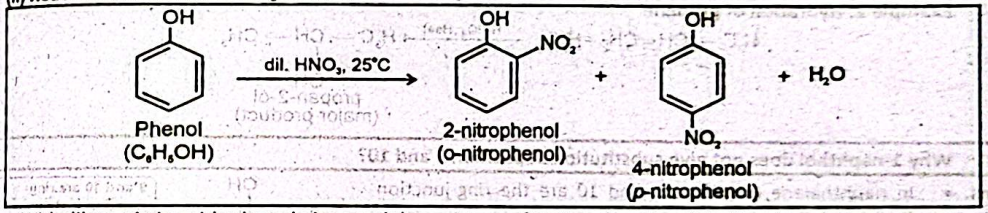
**c) How phenol reacts with: i) $CH_3COCl$ ii) dil.$HNO_3$/25°C**

**Ans. (i) Reaction with ethanoyl chloride ($CH_3COCl$)**




Phenol undergoes acylation with ethanoyl chloride to form phenyl ethanoate.

**(ii) Reaction with dilute $HNO_3$ at 25°C**




With dilute nitric acid, phenol gives mainly a mixture of 2-nitrophenol and 4-nitrophenol.

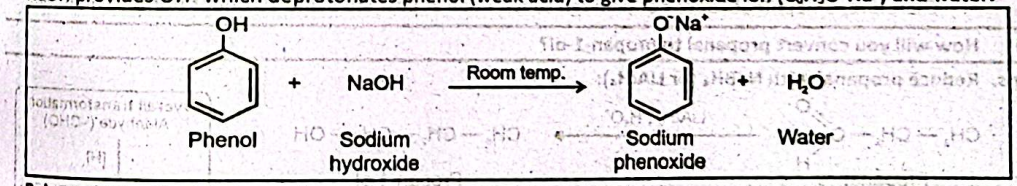
**d) What is difference between the reactions of phenol with: i) NaOH ii) Na metal**

**Ans. i) NaOH**

Phenol behaves as a weak acid reacts with NaOH to form sodium phenoxide and water.

**Explanation:**

NaOH provides $OH^-$ which deprotonates phenol (weak acid) to give phenoxide ion ($C_6H_5O^-Na^+$) and water.




**Balanced Equation:**

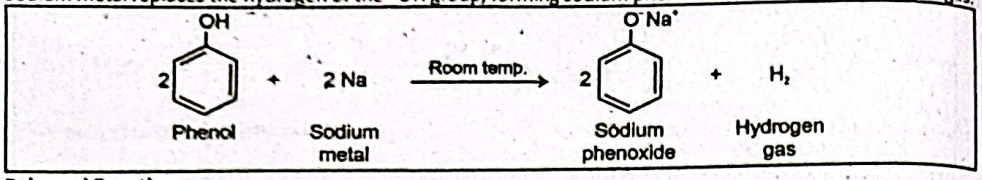
$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$$

**ii) Na Metal**

Phenol reacts with sodium metal to form sodium phenoxide and hydrogen gas.

CamScanner

**Explanation:**
Sodium metal replaces the hydrogen of the –OH group, forming sodium phenoxide and liberating hydrogen gas.



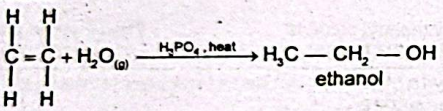

**Balanced Equation:**

$$2C_6H_5OH + 2Na \longrightarrow 2C_6H_5ONa + H_2$$

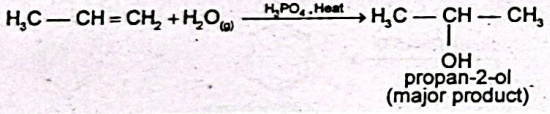
| Key Difference | Reaction with NaOH | Reaction with Na Metal |
|---|---|---|
| Nature of reaction | Acid-base reaction (deprotonation) | Redox reaction (metal displacement) |
| Products | Sodium phenoxide + Water | Sodium phenoxide + Hydrogen gas |
| Equation type | 1 : 1 (one mole phenol with one mole NaOH). | 2 : 2 (two moles phenol with two moles Na). |

**e) How alcohols can be prepared from alkene? Give two examples.**

**Ans.** Alcohols are prepared from alkenes by acid-catalysed hydration (addition of steam)
**Reagent/Conditions:** Steam, $H_3PO_4$ catalyst, heat and pressure.
**Example 1: Hydration of ethene**

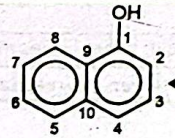



**Example 2: Hydration of propene**




**f) Why 1-naphthol does not give substitution at position 9 and 10?**

**Ans.**
- In naphthalene, positions 9 and 10 are the ring-junction (fusion) carbon atoms.
- These carbons do not have any hydrogen atoms attached.
- Electrophilic aromatic substitution replaces a ring hydrogen with an electrophile.
- Substitution at 9 or 10 would require breaking the fused ring system and destroy aromaticity.
- Therefore, 1-naphthaol does not undergo substitution at position 9 and 10 under normal conditions.

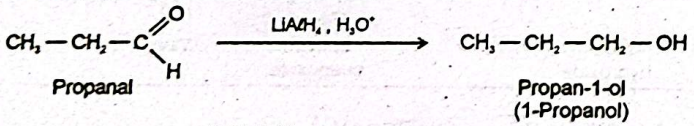


1–naphthol

**9 and 10 are ring-junction carbons**
- No hydrogen atoms present.
- Electrophilic substitution cannot occur here without breaking the fused ring system.

**g) How will you convert propanal to propan-1-ol?**

**Ans.** **Reduce propanal with $NaBH_4$ (or $LiAlH_4$):**




**Overall transformation:**
Aldehyde (–CHO)
↓ [H]
Primary alcohol ($-CH_2OH$)

$$CH_3CH_2CHO + 2[H] \xrightarrow{NaBH_4/H_3O^+} CH_3CH_2CH_2OH$$

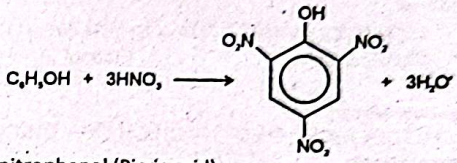
*The aldehyde carbonyl group is reduced to a primary alcohol.*



## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) Why nitration of phenol is easier than benzene. Which product is formed when phenol is nitrated with conc. $HNO_3$ at room temperature?**

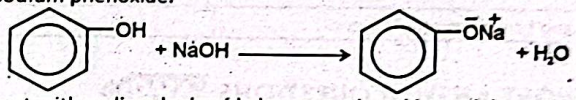
**Ans.** Nitration of phenol is easier than benzene because the hydroxyl group (–OH) donates electrons to the benzene ring through resonance and increases the electron density of the ring.
As a result, the benzene ring in phenol becomes more reactive towards electrophiles and undergoes nitration more readily than benzene. When phenol is treated with concentrated nitric acid at room temperature, **2,4,6-trinitrophenol (picric acid)** is formed.
**Reaction:**




**Product formed:** 2,4,6-Trinitrophenol (Picric acid)

**b) Sodium hydroxide reacts with phenol but not with ethanol. Give reason.**

**Ans.** Phenol reacts with sodium hydroxide because phenol is acidic in nature and can donate a proton to sodium hydroxide to form sodium phenoxide.




Ethanol does not react with sodium hydroxide because ethanol is much less acidic than phenol and cannot donate a proton to NaOH. Therefore, sodium hydroxide reacts with phenol but not with ethanol.

**c) How propanol can be converted into propanal?**

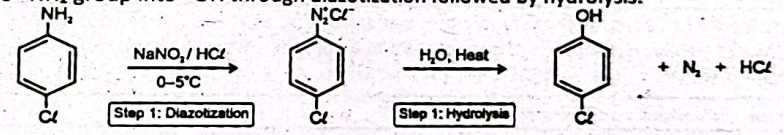
**Ans.** Propan-1-ol is converted into propanal by controlled oxidation using acidified potassium dichromate ($K_2Cr_2O_7/H_2SO_4$)

$$CH_3 — CH_2 — CH_2 — OH + [O] \longrightarrow CH_3 — CH_2 — \overset{O}{\overset{\|}{C}} — H + H_2O$$

The reaction is carried out by gentle heating and immediate distillation of propanal to prevent further oxidation to propanoic acid.

**d) Convert 4-chloroaniline into 4-chlorophenol.**

**Ans.** Convert the $–NH_2$ group into –OH through diazotization followed by hydrolysis:




4-Chloroaniline (*p*-Chloroaniline) | 4-Chlorobenzene-diazonium chloride (*p*-Chlorobenzenediazonium Chloride) | 4-Chlorophenol (*p*-Chlorophenol)

## DESCRIPTIVE QUESTIONS DQs

**Q.4 Explain the acidity of phenol.**

**Ans.** See Questions No. 4

**Q.5 Describe any four methods for the preparation of ethanol.**

**Ans.** Four methods for preparing ethanol are:

CamScanner

**1. Hydration of Ethene:**

$$\underset{\text{Ethene}}{CH_2 = CH_2} + H_2O_{(g)} \xrightarrow{H_3PO_4, \text{heat}} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

**2. Hydrolysis of a haloalkane:**

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + NaOH_{(aq)} \xrightarrow{\text{heat}} \underset{\text{Ethanol}}{CH_3CH_2OH} + NaBr$$

**3. Reduction of Ethanal:**

$$\underset{\text{Ethanal}}{CH_3CHO} + 2[H] \xrightarrow{NaBH_4/LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

**4. Reduction of ethanoic aicd:**

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} + H_2O$$

**Other Routes:**

**Hydrolysis of ethyl ethanoate (ester):**

$$CH_3COOCH_2CH_3 + H_2O \longrightarrow CH_3CH_2OH + CH_3COOH$$

**Biological method (Fermentation):**

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$

**Q.6 Describe the oxidation reactions of alcohols.**

**Ans.** See Question No. 7

**Q.7 Explain nitration and bromination of phenol.**

**Ans.** See Question No. 12

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 Describe the preparation of alcohol by hydration of alkenes.**

**Ans.** Alcohols are prepared by passing steam over an alkene in the presence of phosphoric acid catalyst under high temperature and pressure. The reaction occurs through electrophilic addition.

**Equation:** $CH_2 = CH_2 + H_2O \longrightarrow H_3PO_4CH_3CH_2OH$

Thus, ethene is converted into ethanol.

**Q.2 Explain the preparation of alcohol from haloalkanes.**

**Ans.** Haloalkanes react with aqueous sodium hydroxide on heating to produce alcohols through nucleophilic substitution reactions. The hydroxide ion replaces the halogen atom.

**Equation:** $CH_3CH_2Br + NaOH_{(aq)} \longrightarrow CH_3CH_2OH + NaBr$

**Q.3 Describe the reduction of aldehydes to alcohols.**

**Ans.** Aldehydes are reduced to primary alcohols using reducing agents such as sodium borohydride or lithium aluminium hydride. Hydrogen is effectively added across the carbonyl group.

**Equation:** $CH_3CHO + 2[H] \xrightarrow{NaBH_4} CH_3CH_2OH$

**Q.4 Describe the reduction of ketones to alcohols.**

**Ans.** Ketones are reduced to secondary alcohols using sodium borohydride or lithium aluminium hydride. The carbonyl group is converted into a hydroxyl group.

**Equation:** $CH_3COCH_3 + 2[H] \xrightarrow{LiAlH_4} LiAlH4\ CH_3CHOHCH_3$

Propanone is converted into propan-2-ol.

**Q.5 Explain the oxidation of primary alcohols.**

**Ans.** Primary alcohols are oxidized by acidified potassium dichromate or potassium permanganate. Under distillation conditions they form aldehydes, while under reflux they undergo further oxidation to carboxylic acids.

**Equations:** $CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$



**Q.6 Explain the oxidation of secondary alcohols.**

**Ans.** Secondary alcohols are oxidized by acidified potassium dichromate to form ketones. Further oxidation generally does not occur under ordinary conditions.

**Equation:** $CH_3CHOHCH_3 + [O] \longrightarrow CH_3COCH_3 + H_2O$

**Q.7 Why do tertiary alcohols resist oxidation?**

**Ans.** Tertiary alcohols do not contain a hydrogen atom attached to the carbon bearing the hydroxyl group. Therefore, oxidation cannot occur without breaking carbon-carbon bonds.

As a result, tertiary alcohols are resistant to oxidation under normal conditions.

**Q.8 Describe the dehydration of ethanol.**

**Ans.** Ethanol undergoes dehydration in the presence of concentrated sulfuric acid or heated aluminium oxide catalyst to produce ethene. Water is eliminated from adjacent carbon atoms.

**Equation:** $CH_3CH_2OH \xrightarrow{\text{conc.}H_2SO_4} CH_2 = CH_2 + H_2O$

**Q.9 Explain esterification.**

**Ans.** Esterification is the reaction between an alcohol and a carboxylic acid in the presence of concentrated sulfuric acid catalyst to form an ester and water.

**Equation:** $CH_3COOH + CH_3CH_2OH \xrightarrow{\text{conc.}H_2SO_4} CH_3COOCH_2CH_3 + H_2O$

**Q.10 Describe the reaction of alcohols with sodium metal.**

**Ans.** Alcohols react with sodium metal to form sodium alkoxides and hydrogen gas. The reaction demonstrates the weak acidic nature of alcohols.

**Equation:** $2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2$

**Q.11 Explain the iodoform test for alcohols.**

**Ans.** Alcohols containing the $CH_3CH(OH)$– group give a positive iodoform test when heated with iodine and sodium hydroxide solution. A yellow precipitate of iodoform (CHI3)(CHI_3)(CHI3) is formed, indicating the presence of this functional group.

**Equation:** $CH_3CH(OH)R + 4I_2 + 6NaOH \longrightarrow CHI_3 + RCOONa' + 5NaI + 5H_2O$

**Observation:** A yellow precipitate of iodoform with antiseptic smell is produced.

**Q.12 Which alcohols give a positive Iodoform test?**

**Ans.** Alcohols containing the $CH_3CH(OH)$- group give a positive iodoform test. Ethanol also gives this test because it is first oxidized to ethanal, which contains the required structural feature.

**Examples:** • Ethanol ($CH_3CH_2OH$) • Propan-2-ol ($CH_3CHOHCH_3$)

**Q.13 Compare primary, secondary and tertiary alcohols.**

**Ans.** Alcohols are classified according to the number of alkyl groups attached to the carbon atom carrying the hydroxyl group.

| Type | Structure | Example |
|---|---|---|
| Primary | $RCH_2OH$ | Ethanol |
| Secondary | $R_2CHOH$ | Propan-2-ol |
| Tertiary | $R_3COH$ | 2-Methylpropan-2-ol |

**Q.14 Explain the acidity of alcohols.**

**Ans.** Alcohols are weak acids because they can lose the hydrogen atom attached to oxygen to form alkoxide ions. However, they are much less acidic than water and phenol because alkoxide ions are not stabilized effectively.

**Equation:** $2C_2H_5OH + 2Na \longrightarrow 2C_2H_5ONa + H_2$

**Q.15 Explain the preparation of phenol from diazonium salts.**

**Ans.** Phenol is prepared by first converting phenylamine into benzene diazonium chloride using sodium nitrite and dilute hydrochloric acid below 5°C. The diazonium salt is then warmed with water to produce phenol.

**Equations:** $C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5N_2^+ Cl^- + NaCl + 2H_2O$

CamScanner

**Q.16 Describe the reaction of phenol with sodium hydroxide.**

**Ans.** Phenol reacts with sodium hydroxide because it is sufficiently acidic to donate a proton. Sodium phenoxide and water are formed.

Equation: $C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$

This reaction distinguishes phenol from alcohols, which do not react with NaOH.

**Q.17 Describe the reaction of phenol with sodium metal.**

**Ans.** Phenol reacts with sodium metal to form sodium phenoxide and hydrogen gas. The reaction demonstrates the acidic nature of phenol.

Equation: $2C_6H_5OH + 2Na \longrightarrow 2C_6H_5ONa + H_2$

Effervescence is observed due to the evolution of hydrogen gas.

**Q.18 Explain nitration of phenol.**

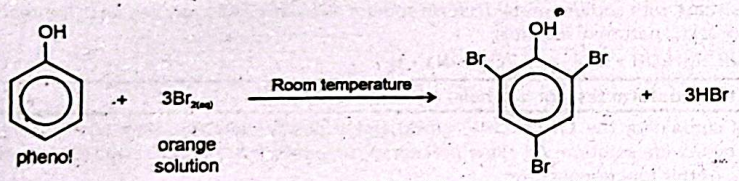
**Ans.** Phenol reacts readily with dilute nitric acid at room temperature to form a mixture of 2-nitrophenol and 4-nitrophenol. The hydroxyl group activates the benzene ring and directs substitution to ortho and para positions.

Equation: $C_6H_5OH + HNO_3 \longrightarrow$ 2-nitrophenol + 4-nitrophenol + $H_2O$

**Q.19 Explain bromination of phenol.**

**Ans.** Phenol reacts with bromine water at room temperature without requiring a catalyst. A white precipitate of 2,4,6-tribromophenol is formed.

Equation:




phenol

2,4,6 – tribromophenol (white precipitate)

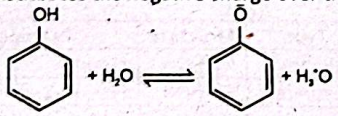
**Q.20 Why does phenol react more readily than benzene?**

**Ans.** The hydroxyl group donates electrons to the benzene ring through resonance, increasing electron density especially at the ortho and para positions. Therefore, phenol is more reactive towards electrophilic substitution than benzene.

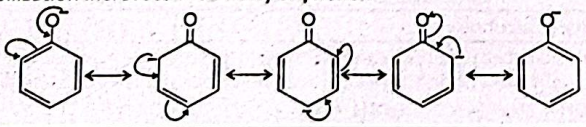
As a result, phenol undergoes nitration and bromination under milder conditions.

**Q.21 Explain the acidity of phenol.**

**Ans.** Phenol is weakly acidic because it can lose a proton to form the phenoxide ion. The phenoxide ion is stabilized by resonance, which distributes the negative charge over the benzene ring.




This resonance stabilization increases the acidity of phenol.



**Q.22 Why is phenol more acidic than ethanol?**

**Ans.** Phenol is more acidic than ethanol because the phenoxide ion formed after loss of a proton is stabilized by resonance. In contrast, the ethoxide ion formed from ethanol has no resonance stabilization.

Therefore, phenol releases protons more readily than ethanol.



**Q.23 Compare the acidity of phenol, water and ethanol.**

**Ans.** The order of acidity is:

Phenol > Water > Ethanol

Phenol is the strongest because of resonance stabilization of phenoxide ion, while ethanol is the weakest because the ethoxide ion is unstable and electron-releasing alkyl groups further reduce acidity.

**Q.24 Why does phenol react with NaOH but ethanol does not?**

**Ans.** Phenol is sufficiently acidic to react with sodium hydroxide and form sodium phenoxide. Ethanol is a much weaker acid and cannot donate protons to hydroxide ions effectively.

Therefore, ethanol does not react with aqueous sodium hydroxide.

**Q.25 Why does phenol not require a catalyst for bromination?**

**Ans.** The hydroxyl group strongly activates the benzene ring by donating electrons through resonance. This increases the electron density of the ring and allows bromination to occur readily without any catalyst. Benzene, however, requires $FeBr_3$ as a catalyst.

**Q.26 Why does the hydroxyl group direct substitution to ortho and para positions?**

**Ans.** The hydroxyl group donates electrons to the benzene ring through resonance, increasing electron density mainly at the ortho and para positions. These positions therefore become more reactive towards electrophilic attack.

Hence, phenol is an ortho-para directing compound.

**Q.27 State the distinguishing test for phenol.**

**Ans.** Phenol can be identified by its reaction with bromine water. It rapidly decolourizes bromine water and produces a white precipitate of 2, 4, 6-tribromophenol.

Equation: $C_6H_5OH + 3Br_2 \longrightarrow C_6H_2Br_3OH + 3HBr$

**Q.28 Explain the formation of sodium phenoxide.**

**Ans.** Sodium phenoxide is formed when phenol reacts with sodium hydroxide or sodium metal. In both reactions, phenol loses a proton from the hydroxyl group.

Equation: $C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$

**Q.29 How do reactions of phenol differ from those of benzene?**

**Ans.** Phenol is more reactive than benzene because the hydroxyl group activates the aromatic ring through resonance. Therefore, phenol undergoes nitration and bromination under mild conditions without requiring catalysts. Benzene, on the other hand, requires catalysts and harsher conditions.

**Q.30 State the importance of phenolic compounds.**

**Ans.** Phenolic compounds are widely used in the manufacture of antiseptics, disinfectants, dyes, plastics and pharmaceuticals. Naphthols and related phenolic compounds are important raw materials in the dye industry. Thus, phenolic compounds have significant industrial and medical applications.

CamScanner

## SELF-ASSESSMENT

Total Mark: 30

**Q.1 Encircle the correct option.** (1 × 6 = 6)

(i) **Glycerol is classified as a:**
(A) Monohydric alcohol (B) Dihydric alcohol (C) Trihydric alcohol (D) Phenol

(ii) **Phenol is more acidic than ethanol because:**
(A) It contains more hydrogen atoms (B) Phenoxide ion is resonance stabilized
(C) It as fewer carbon atoms (D) It is more volatile

(iii) **Aldehydes are reduced to:**
(A) Secondary alcohols (B) Primary alcohols (C) Tertiary alcohols (D) Ketones

(iv) **Phenol dissolves in alkaline solution because it:**
(A) Undergoes esterification (B) Forms sodium phenoxide
(C) Forms benzene (D) Forms alcohol

(v) **Bromine reacts with phenol and decolourise orange color and turns it to which of the colored precipitate?**
(A) white precipitate (B) pink precipitate (C) blue precipitate (D) black precipitate

(vi) **Give a chemical test used in distinguishing propan-1-ol and propan-2-ol.**
(A) $Br_2$ and NaOH (B) $I_2$ and NaOH (C) Acidified $K_2Cr_2O_7$ (D) $NaOH_{(aq)}$

**Q.2 Write short answers of the following questions.** (2 × 8 = 16)

(i) How will you prepare propanol from propene? Give reaction.
(ii) The reaction of phenol with bromine water is used for the identification of phenol. What will be the visual change during the reaction, also give the systematic name of the compound formed.
(iii) How phenol reacts with: i) $CH_3COCl$ ii) dil.$HNO_3$/25°C
(iv) What is difference between the reactions of phenol with: i) NaOH ii) Na metal
(v) How alcohols can be prepared from alkene? Give two examples.
(vi) Why 1-naphthol does not give substitution at position 9 and 10?
(vii) How will you convert propanal to propan-1-ol?
(viii) Define a tertiary alcohol give its general formula.

**Q.3 Extensive Questions.** (4 + 4 = 8)

(a) Explain the acidity of phenol.
(b) Describe any four methods for the preparation of ethanol.

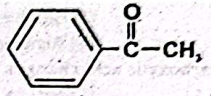


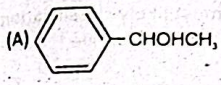
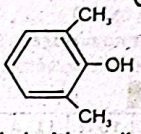
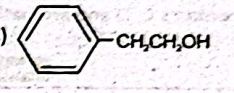
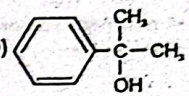
## ENTRANCE TEST MCQs

1. **Which of the following is a tertiary alcohol?** (UHS 2018)
(A) 1-propanol (B) 2-methyl-1-propanol (C) 2-methyl-2-propanol (D) 2-propanol

2. **Alcohols in which carbon atom bonded to OH group is further attached with three alkyl groups is:** (UHS 2018)
(A) Primary alcohol (B) Secondary alcohol (C) Tertiary alcohol (D) Aromatic alcohol

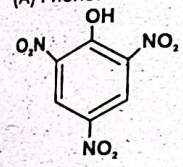
3. **What is the structure of alcohol which on oxidation with acidified $Na_2Cr_2O_7$ gives:** (UHS 2013)



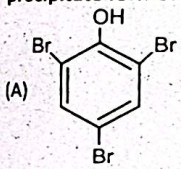
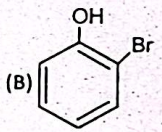
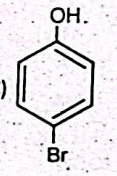
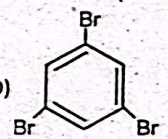
(A)  (B)  (C)  (D) 

4. **A student mixed ethyl alcohol with small amount of sodium dichromate and added it to the hot solution of dilute sulphuric acid. A vigorous reaction took place. He distilled the product formed immediately. What was the product?** (UHS 2014)
(A) Acetone (B) Dimethyl ether (C) Acetic acid (D) Acetaldehyde

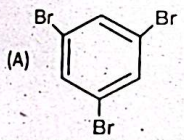
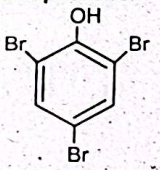
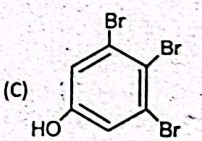
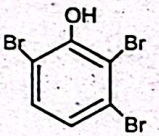
5. **Which one of the following was used as one of the earliest antiseptic and disinfectant?** (UHS 2015)
(A) Phenol (B) Ethanol (C) Ether (D) Methanol

6.  **is named as:** (UHS 2013,2016)
(A) Picric acid (B) Nitro phenol (C) Benzoic acid (D) Malonic acid

7. **Aqueous phenol decolorizes bromine water to form a white precipitate. What is the structure of the white precipitate formed?** (UHS 2013, 2016)

(A)  (B)  (C)  (D) 

8. **The formula of 2, 4, 6-tribromophenol is:** (UHS 2017)

(A)  (B)  (C)  (D) 

9. **The phenoxide ion is more stable than ethoxide ion as:** (UHS 2017)
(A) lone pair on oxygen atoms overlaps with the delocalized π-bonding system in benzene
(B) Oxygen atom is directly bonded with benzene ring in phenoxide ion
(C) The negative charge is localized in oxygen atom of phenoxide ion
(D) The negative charge is delocalized on oxygen atom of ethoxide ion

CamScanner

10. If phenol is treated with 2 moles of conc. $HNO_3$ in the presence of conc. $H_2SO_4$, what will be the product? (UHS 2023)
(A) o-nitrophenol (B) o-nitro and p-ntirophenol
(C) p-nitrophenol (D) Picric acid

11. Which application most likely requires plasticised rather than rigid PVC?
(A) A flexible blood bag (B) A rigid window frame
(C) A drainage pipe (D) A hard floor tile

12. Which application best exploits nylon elasticity?
(A) Glass windows (B) Soluble fertilizers
(C) Stockings and activewear (D) Rigid sewer pipes

13. Using a dioyl chloride instead of a dicarboxylic acid changes the nylon by-product from:
(A) $H_2O$ to $HCl$ (B) $HCl$ to $H_2$ (C) $NH_3$ to $H_2O$ (D) $CO_2$ to $O_2$

14. A polymer backbone contains C, O and aromatic rings but no nitrogen. The most likely classification is:
(A) Poly(alkene) (B) Natural rubber (C) Aromatic polyester (D) Polyamide

**Answers Key**

| 1.C | 2.C | 3.A | 4.C | 5.A | 6.A | 7.A | 8.B | 9.A | 10.D | 11. A | 12. C | 13.A | 14.C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|



23 CHAPTER

# CARBONYL COMPOUNDS AND CARBOXYLIC ACIDS

## Student Learning Outcomes (SLOs)

[C-12-D-59 to C-12-D-78]

**Part 1: Aldehydes and Ketones (Carbonyl Compounds)**

- State the reactions (reagents and conditions) by which aldehydes and ketones can be produced: a. the oxidation of primary alcohols using acidified $K_2Cr_2O_7$ or acidified $KMnO_4$ and distillation to produce aldehydes; b. the oxidation of secondary alcohols using acidified $K_2Cr_2O_7$ or acidified $KMnO_4$ and distillation to produce ketones.
- Describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH reagent) to detect the presence of carbonyl compounds.
- Deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (Fehling's and Tollens' reagents; ease of oxidation).
- Deduce the presence of a $CH_3CO$ - group in an aldehyde or ketone, $CH_3COR$, from its reaction with alkaline $I_{2(aq)}$ to form a yellow precipitate of tri-iodomethane and an ion, $RCO_2^-$.
- Describe: a. the reduction of aldehydes and ketones, using $NaBH_4$ or $LiAlH_4$ to produce alcohols; b. the reaction of aldehydes and ketones with HCN, KCN as catalyst, and heat to produce hydroxy nitriles exemplified by ethanal and propanone.
- Describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones.

**Part 2: Carboxylic Acids**

- Recall the reactions by which carboxylic acids can be produced: a. oxidation of primary alcohols and aldehydes with acidified $K_2Cr_2O_7$ or acidified $KMnO_4$ and refluxing; b. hydrolysis of nitriles with dilute acid or dilute alkali followed by acidification; c. hydrolysis of esters with dilute acid or dilute alkali and heat followed by acidification.
- State the reaction which benzoic acid can be produced: reaction of alkylbenzene with hot alkaline $KMnO_4$ and then dilute acid, exemplified by methylbenzene.
- Describe the reaction of carboxylic acids with $PCl_3$ and heat, $PCl_3$ and heat, $PCl_5$, or $SOCl_2$ to form acylchlorides.
- Recognize that some carboxylic acids can be further oxidized: a) the oxidation of methanoic acid, HCOOH, with Fehling's reagent or Tollens' reagent or acidified $KMnO_4$ or acidified $K_2Cr_2O_7$ to carbon dioxide and water b) the oxidation of ethanedioic acid $\begin{matrix}COOH\\|\\COOH\end{matrix}$, with warm acidified $KMnO_4$ to carbon dioxide.
- Describe: a. the redox reaction with reactive metals to produce a salt and $H_{2(g)}$; b. the neutralization reaction with alkalis to produce a salt and $H_2O_{(l)}$; c. the acid-base reaction with bicarbonates to produce a salt and $H_2O_{(l)}$ and $CO_{2(g)}$; d. esterification with alcohols with concentrated $H_2SO_4$ as catalyst; e. reduction by $LiAlH_4$ to form a primary alcohol.
- Explain the relative acidities of carboxylic acids, phenols and alcohols.
- Explain the relative acidities of chlorine substituted carboxylic acids.

**Part 3: Esters (Revisited and Expanded)**

- Recall the reactions (reagents and conditions) by which esters can be produced: the condensation reaction between an alcohol and a carboxylic acid with concentrated $H_2SO_4$ as catalyst.
- Describe the hydrolysis of esters by dilute acid and by dilute alkali and heat.

CamScanner

**Part 4: Acyl Chlorides (Acid Halides)**

- Recall the reactions (reagents and conditions) by which acyl chlorides can be produced: reaction of carboxylic acids with $PCl_3$ and heat, $PCl_5$, or $SOCl_2$.
- Explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and halogenoarenes (aryl chlorides).
- Describe the following reactions of acyl chlorides: a. hydrolysis on addition of water at room temperature to give the carboxylic acid and HCl; b. reaction with an alcohol at room temperature to produce an ester and HCl; c. reaction with phenol at room temperature to produce and ester and HCl; d. reaction with ammonia at room temperatures to produce and amide and HCl; e. reaction with a primary or secondary amine at room temperature to produce an amide and HCl.
- Describe the addition-elimination mechanism of acyl chlorides in reactions.
- Recall the reaction by which esters can be produced: reaction of alcohols with acyl chlorides using the formation of ethyl ethanoate and phenyl benzoate as examples.

# CARBONYL COMPOUNDS

**Q.1 What are aldehydes and Ketones? Give their general structures and occurrence.** UQ

**Ans. Aldehydes:**

- In aldehydes, the carbonyl group is bonded to at least one hydrogen atom, and so it occurs at the end of a chain.
- An aldehyde can be represented by the general formula:

$R-\overset{\overset{O}{\|}}{C}-H$, where R may be H or an alkyl or aryl group.

**Examples**

| | | | |
|---|---|---|---|
| $H-\overset{\overset{O}{\|}}{C}-H$ | $CH_3-\overset{\overset{O}{\|}}{C}-H$ | $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$ | $CH_3-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-H$ |
| **Methanal** | **Ethanal** | **Propanal** | **Butanal** |

➢ **Ketones:**

- In ketones, the carbonyl group is bonded to two carbon atoms, and so it occurs within a chain. A ketone may be represented by the general formula **(RCOR)**.

**Examples**

| | |
|---|---|
| $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ | $CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$ |
| **Dimethyl ketone (Acetone)** | **Ethyl methyl ketone** |

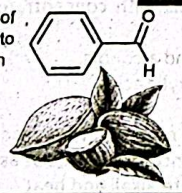
The homologous series of both aldehydes and ketones have the general formula, $C_nH_{2n}O$.

➢ ***Occurrence:***

These compounds are abundant in nature and their large quantities are synthesised every year. Aldehydes are present in many spices, fruits, and natural fragrances. Ketones are used in pharmaceuticals, chemicals, and paint industries. The most common ketone is acetone, which is used in nail polish removers.

**Interesting Information**

The smell and taste of bitter almond is due to benzaldehyde, which is produced by the oxidation process.



Acetone (Propanone) $H_3C-\overset{\overset{O}{\|}}{C}-CH_3$

Acetone (propanone) are used in nail polish removers





## Preparation of Aldehydes

**Q.2 Give one method each for the preparation of aldehydes and ketones.** UQ

**Ans. Preparation of Aldehyde:**

Aldehydes are prepared by the oxidation of primary alcohols with acidified $K_2Cr_2O_7$ or acidified $KMnO_4$.

$$CH_3-CH_2-OH + [O] \xrightarrow[\text{Heat}]{K_2Cr_2O_7 + H_2SO_{4(aq)}} CH_3-\overset{\overset{O}{\|}}{C}-H + H_2O$$

In the example of the preparation of ethanal, the acidified $K_2Cr_2O_7$ is added dropwise to the warm ethanol. The aldehyde produced is distilled off as soon as it is formed. This prevents the further oxidation of ethanal to ethanoic acid. The temperature is kept above the boiling point of ethanal but below to that of ethanol, since ethanol has higher boiling point than that of ethanal. Pure ethanal is obtained by redistillation.

Methanal, HCHO, is a gas at room temperature. It is often encountered as a 40% aqueous solution called 'formalin', which has a pungent, unpleasant smell and is used for preserving biological specimens. Other short-chain aldehydes and ketones are liquids.

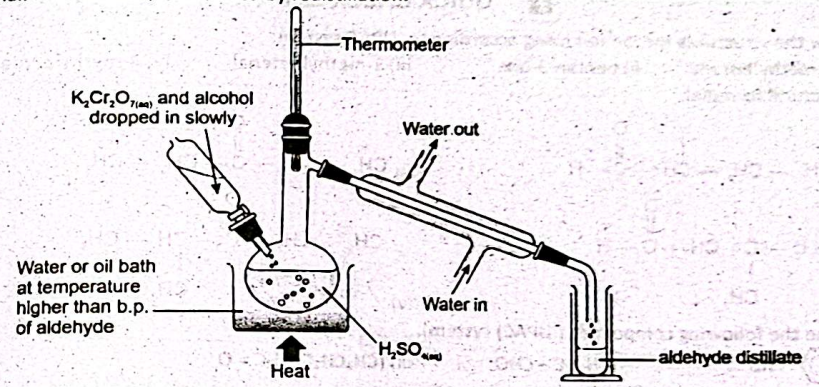



**Figure: Apparatus for distilling off the ethanal as it is formed by the oxidation of ethanol.**

## Preparation of Ketones

Ketones are also prepared by the same procedure from secondary alcohols but since ketones are not converted into carboxylic acids under these conditions, therefore, a ketone is not distilled off immediately.

$$\underset{\text{propan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_3} + [O] \xrightarrow[\text{Heat}]{K_2Cr_2O_7 + H_2SO_{4(aq)}} \underset{\text{propanone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + H_2O$$

# REACTIONS OF CARBONYL COMPOUNDS

The carbonyl group $>C=O$ governs the chemistry of aldehydes and ketones. There are two basic reactions of carbonyl compounds.

A. Nucleophilic addition reactions B. Alpha (α) carbon specific reactions

## Structure and Reactivity of Carbonyl Group

**Q.3 Discuss the structure and reactivity of carbonyl group.** S/Q

**Ans.** In carbonyl group $>C=O$, both carbon and oxygen are $sp^2$ hybridized. Carbon is bonded to an oxygen atom through a double bond and to other two groups through single bonds.

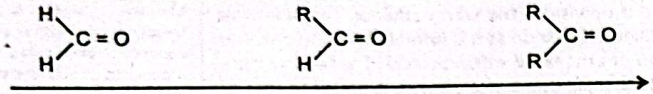
Carbonyl group is polar in nature because oxygen, being more electronegative, gets partial negative charge ($\delta^-$) and carbon gets partial positive charge ($\delta^+$). Two structural features of the carbonyl group determine the chemistry and properties of aldehydes and ketones.

CamScanner

1. The carbonyl carbon is electrophilic in nature due to its $\delta^+$ charge, and can be attacked by nucleophiles.
2. The double bond can undergo addition reactions because $\pi$ bond is easily broken down. Moreover, planar shape of the group makes the carbonyl carbon uncrowded thus giving further support to addition reactions.

Aldehydes are more reactive than ketones for two reasons. First; in a ketone, the electron releasing (inductive) effect of two alkyl groups reduces the positive charge on the carbonyl carbon making it less easily attacked by nucleophiles. Secondly, the two alkyl groups of a ketone tend to get in the way of attacking nucleophiles. This is also called steric hindrance.

Increasing reactivity towards nucleophiles



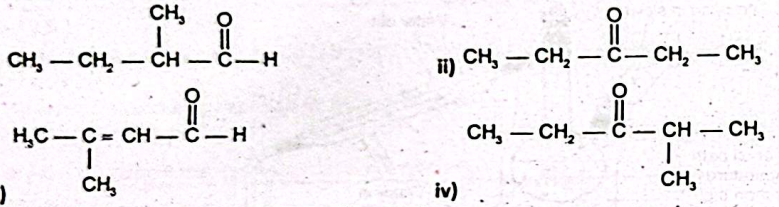
Increasing steric hindrance

## QUICK CHECK 23.1

**a) Draw the structures for the following according to IUPAC system.**

**i) 2-,methylbutanal ii) pentan-3-one iii) 3-methylbutenal iv) 4-methylpentan-3-one**

**Ans. Structural formulae:**



**b) Name the following compounds (IUPAC) system).**

**i) –CHO ii) $(CH_3)_2C-CHO$ iii) $(CH_3CH_2CH_2)_2C=O$**

**Ans. i) IUPAC Name:** Benzaldehyde

**ii) IUPAC Name:** 2-Methylpropanal

**iii) IUPAC Name:** Heptan-4-one

**c) Rank the following compounds in order of increasing reactivity towards nucleophilic attack.**

**i) $(CH_3)_3CCOCH_3$ ii) $(CH_3)_3CCOC(CH_3)_3$ iii) $(CH_3)_2CO$**

**Ans.**
- Nucleophilic reactivity decreases as steric hindrance around the carbonyl carbon increases.
- Bulkier alkyl groups block the attacking nucleophile and reduce the partial positive charge on the carbonyl carbon through inductive electron donation (+I effect).
- Compound ii has two highly bulky tert-butyl groups.
- Compound i has one tert-butyl group and one small methyl group.
- Compound iii has two small methyl groups, making it the least hindered and most reactive.

Therefore, the increasing order of reactivity is:

$(CH_3)_3CCOC(CH_3)_3 < (CH_3)_3CCOCH_3 < (CH_3)_2CO$ (OR) ii < i < iii

## ➲ Nucleophilic Addition Reactions

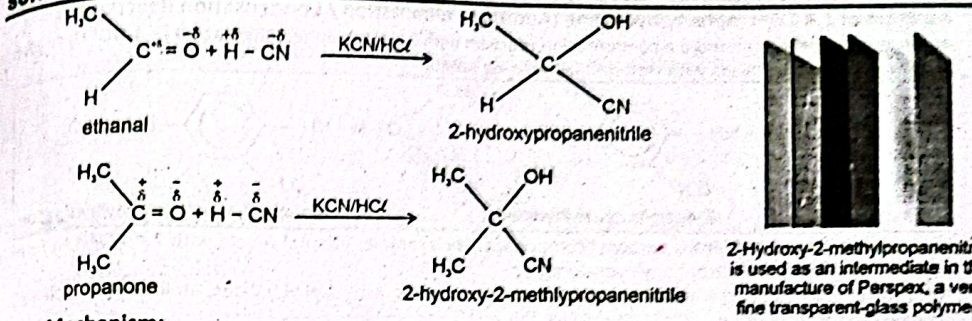
**Q.4 Give the mechanisms of the reactions of carbonyl compounds with: a) HCN. b) $NaBH_4$** Exercise D/Q.7

**Ans.**

### 1. Addition of Hydrogen Cyanide (HCN):

Aldehydes and ketones react with hydrogen cyanide to form hydroxynitriles (cyanohydrins). HCN itself is not used directly as it is an extremely poisonous gas. Instead, it is produced by adding slowly a mineral acid (HCl) to a mixture of aqueous solution of sodium cyanide or potassium cyanide and the carbonyl compound.



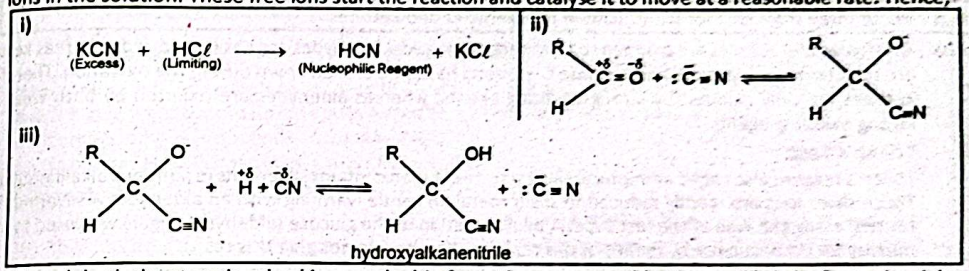





2-Hydroxy-2-methylpropanenitrile is used as an intermediate in the manufacture of Perspex, a very fine transparent-glass polymer.

**Mechanism:**

HCN is neither a nucleophile (absence of a lone pair on the carbon atom) nor a strong acid to be ionized to a reasonable extent. Therefore it does not produce enough nucleophile ($CN^-$) to start a reaction and complete the reaction in a shorter time. This is done by adding a slight excess of KCN, so that there are some free $CN^-$ ions in the solution. These free ions start the reaction and catalyse it to move at a reasonable rate. Hence,

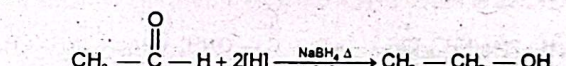


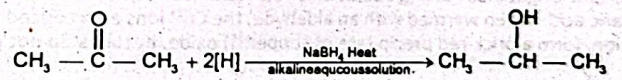

Although both the steps involved in cyanohydrin formation are reversible, the equilibria lie far to the right. Most of carbonyl compounds giving high yields of cyanohydrins at the equilibrium. Nitriles are hydrolysed by dilute acid or aqueous alkali to form carboxylic acids or carboxylate ions; this will be discussed later.

### 2. Addition of hydride ion ($H^-$) Using $NaBH_4$:

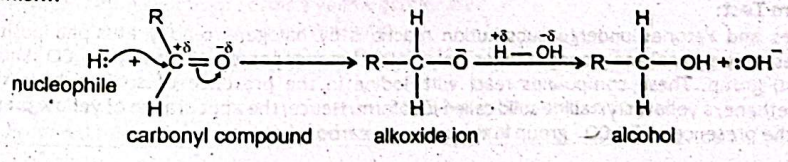
Since aldehydes and ketones are synthesised by oxidation of alcohols, alcohols can be produced by the reduction of aldehydes and ketones. With a reducing agent such as $NaBH_4$ or $LiAlH_4$, aldehydes give primary alcohols and ketones gives secondary alcohols.

Notice that reducing H in brackets [ ] comes from $NaBH_4$ to balance the equation. It does not represent atomic hydrogen.



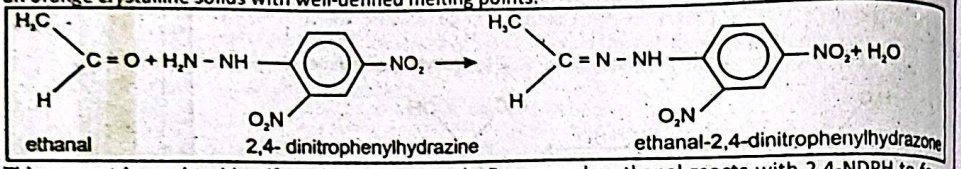




**Mechanism:**



**3. Addition of 2,4-Dinitrophenylhydrazine (Addition - elimination / Condensation Reaction):**

Aldehydes or ketones undergo a condensation reaction with 2,4-dinitrophenylhydrazine (2,4-NDPH) to give an orange crystalline solids with well-defined melting points.




This reagent is used to identify carbonyl compounds. For example, ethanal reacts with 2,4-NDPH to form orange crystals of 2,4-dinitrophenylhydrazone.

**Note:** Other classes of organic compounds like carboxylic acids, esters, acyl halides, amides etc which also contain the carbonyl group $\geq C = O$ do not give this test.

## OXIDATION OF ALDEHYDES AND KETONES

### ➲ Test of Aldehydes and Ketones

**Q.5 Write three main test for identification of aldehydes and ketones.** U.P.

**Ans.** Aldehydes and ketones are oxidized to form carboxylic acids. Aldehydes are easily oxidized, whereas ketones are reluctant towards oxidation because C – C bond has to be broken down during the oxidation. Therefore, ketones are only oxidized by strong oxidizing agents, whereas aldehydes are oxidized by both weak and strong oxidizing agents.

**i) Tollen's Test:**

Tollen's reagent also called ammonical silver nitrate solution contains silver ions in aqueous alkaline solution. These silver ions are readily reduced to silver metal on gentle warming with an aldehyde. A silver mirror is formed along the wall of the test tube. A dilute solution of the glucose (aldehydic sugar) was used to make mirrors for domestic use by means of this reaction. **Ketones do not give this test.**



**Figure: Ethanal gives orange crystalline 2,4-DNPH**



**Figure: Only aldehydes give a positive Tollen's test**

$$AgNO_3 + 3NH_4OH \longrightarrow [Ag(NH_3)_2]OH + NH_4NO_3 + 2H_2O$$

$$R-\overset{O}{\overset{\|}{C}}-H + 2[Ag(NH_3)_2]OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-\bar{O}NH_4^+ + 2Ag + 3NH_3 + H_2O$$

**ii. Fehling's solution Test:**

Fehling's solution is the bright blue Fehling's solution of $Cu^{2+}$ ions in an aqueous alkaline medium; complexed with a salt of tartaric acid. When warmed with an aldehyde, the $Cu^{2+}$ ions are reduced to $Cu^{1+}$ ions, which, in the alkaline solution, form a brick-red precipitate of copper (I) oxide. **Ketones do not give this test.**

$$R-\overset{O}{\overset{\|}{C}}-H + 2Cu(OH)_2 + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{N}a + Cu_2O\downarrow + 3H_2O$$

**iii. Iodoform Test:**

Aldehydes and ketones undergo substitution reactions by halogens readily at alpha position. Among aldehydes, only ethanal and among ketones, only methyl ketones possess the group $CH_3CO$ - known as acetyl (ethanoyl) group. These compounds react with iodine in the presence of sodium hydroxide to form triiodomethane, a yellow crystalline solid called iodoform. Hence, the appearance of **yellow precipitates** will identify the presence of $CH_3CO$ - group in the unknown carbonyl compound.



$$CH_3-\overset{O}{\overset{\|}{C}}-H + 3I_2 + 4NaOH \longrightarrow CHI_3\downarrow + HCO\bar{O}\overset{+}{N}a + 3NaI + 3H_2O$$

Ethanal — Iodoform

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3\downarrow + HCO\bar{O}\overset{+}{N}a + 3NaI + 3H_2O$$

Acetone (2 – one)

Ethanol also gives this test, while methanol does not. The reason for this is the presence of $CH_3-CH_2-O$, which acts as a methyl ketone-like structure ($CH_3-C=O$). Thus it can also form iodoform, and the test is positive for ethanol.

$$CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

Aldehydes and Ketones having $CH_3CO$ group, whereas alcohols having $CH_3-CH(OH)$ group give iodoform test. Yellow coloured iodoform is formed in this reaction.



### ☑ QUICK CHECK 23.2

**a) If compound A has the molecular formula $C_3H_6O$, it reacts with $NaBH_4$ to give compound B, $C_3H_8O$. Both A and B give a yellow precipitate with $I_2$/NaOH. Identify both compounds (A & B).**

**Ans.**
- **Compound A** is propanone (Acetone), $CH_3COCH_3$.
- **Compound B** is Propan-2-ol, $CH_3CH(OH)CH_3$.

**Explanation:**
- $C_3H_6O$ reacts with $NaBH_4$.
- This indicates a carbonyl group.
- It undergoes the iodoform test.
- This proves it is a methyl ketone.
- Thus, A must be propanone.
- Reduction of propanone yields propan-2-ol.
- Propan-2-ol contains the $CH_3CH(OH)$-group.
- This group yields a positive iodoform test.

**b) Why methanol does not give iodoform test while ethanol does?**

**Ans.**
- Ethanol ($CH_3CH_2OH$) contains a $CH_3CH(OH)$-group.
- Iodine and base oxidize it to ethanol ($CH_3CHO$).
- Ethanal contains the required methyl carbonyl group.
- It forms a yellow $CHI_3$ precipitate.
- Methanol ($CH_3OH$) has only one carbon.
- It cannot form a methyl carbonyl group.
- Therefore, it fails the iodoform test.

**c) Describe a test (a different one in each case) that you could use to distinguish between the following pairs of compounds. $CH_3CH_2CHO$**

**i) $CH_3CH_2CHO$ and $CH_3COCH_3$** **ii) $CH_3CH_2COCH_2CH_3$ and $CH_3CH_2CH_2COCH_3$**

**iii) $CH_2=CH-CH_2-OH$ and $CH_3CH_2CHO$**

**Ans.** i) Propanal ($CH_3CH_2CHO$) and Propanone ($CH_3COCH_3$)
- **Test:** Tollen's Test.
- **Propanal reaction:** Forms a bright silver mirror.
- **Propanone reaction:** Shows no reaction.

ii) Pentan-3-one ($CH_3CH_2COCH_2CH_3$) and Pentan-2-one ($CH_3CH_2CH_2COCH_3$)
- **Test:** Iodoform test ($I_2$/NaOH).
- **Pentan-2-one reaction:** Forms a yellow precipitate.
- **Pentan-3-one reaction:** Shows no reaction.

iii) Allyl alcohol ($CH_2=CH-CH_2-OH$) and Propanal ($CH_3CH_2CHO$)
- **Test:** Bromine water test.
- **Allyl alcohol reaction:** Decolorizes the reddish-brown bromine water.
- **Propanal reaction:** Does not decolorize bromine water.

CamScanner

## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. The functional group present in aldehydes and ketones is:
(A) –OH (B) –COOH (C) Carbonyl (C=O) (D) $–NH_2$
2. In aldehydes, the carbonyl carbon is attached to:
(A) Two alkyl groups (B) One hydrogen atom and one alkyl/aryl group
(C) Two hydrogen atoms only (D) One oxygen atom only
3. Ketones differ from aldehydes because the carbonyl carbon is attached to:
(A) One hydrogen atom (B) Two alkyl or aryl groups (C) One hydroxyl group (D) One halogen atom
4. Acetone is the IUPAC name:
(A) Methanal (B) Propanal (C) Propanone (D) Butanone
5. Aldehydes are prepared by oxidation of:
(A) Secondary alcohols (B) Primary alcohols (C) Tertiary alcohols (D) Carboxylic acids
6. Ketones are prepared by oxidation of:
(A) Primary alcohols (B) Secondary alcohols (C) Tertiary alcohols (D) Alkenes
7. During preparation of aldehydes, the product is distilled immediately to:
(A) Increase boiling point (B) Prevent further oxidation (C) Remove catalyst (D) Increase yield of alcohol
8. Formalin is an aqueous solution of:
(A) Ethanal (B) Methanal (C) Propanone (D) Methanol
9. In the carbonyl group, both carbon and oxygen are:
(A) sp hybridized (B) $sp^2$ hybridized (C) $sp^3$ hybridized (D) $dsp^2$ hybridized
10. Oxygen in the carbonyl group carries:
(A) Positive charge (B) Partial negative charge (C) Neutral charge (D) Double positive charge
11. The carbonyl carbon behaves as:
(A) Nucleophile (B) Electrophile (C) Free radical (D) Base
12. The π bond of the carbonyl group:
(A) Is stronger than the σ bond (B) Easily undergoes addition reactions
(C) Never breaks (D) Is ionic
13. Aldehydes are generally more reactive than ketones because:
(A) They contain more oxygen (B) They experience less steric hindrance
(C) They are aromatic (D) They contain fewer carbon atoms
14. The electron-donating effect of alkyl groups in ketones:
(A) Increases positive charge on carbonyl carbon (B) Decreases electrophilicity of carbonyl carbon
(C) Makes ketones acidic (D) Produces radicals
15. Carbonyl compounds mainly undergo:
(A) Electrophilic substitution (B) Nucleophilic addition
(C) Elimination (D) Polymerization
16. Aldehydes and ketones react with HCN to produce:
(A) Alcohols (B) Cyanohydrins (C) Esters (D) Carboxylic acids
17. HCN is generated in the reaction mixture using:
(A) NaOH and HCl (B) KCN and HCl (C) NaCl and $H_2SO_4$ (D) KBr and $HNO_3$
18. $NaBH_4$ reduces aldehydes to:
(A) Ketones (B) Primary alcohols (C) Secondary alcohols (D) Carboxylic acids
19. $NaBH_4$ reduces ketones to:
(A) Primary alcohols (B) Secondary alcohols (C) Aldehydes (D) Esters
20. 2,4-DNPH is mainly used to identify:
(A) Alcohols (B) Carboxylic acids (C) Carbonyl compounds (D) Esters
21. A positive 2,4-DNPH test gives:
(A) Blue solution (B) Green precipitate
(C) Orange crystalline precipitate (D) White precipitate
22. Which compound gives a positive Tollen's test?
(A) Ketone (B) Aldehyde (C) Ester (D) Ether
23. A positive Tollen's test produces:
(A) Brick-red precipitate (B) Silver mirror (C) White precipitate (D) Yellow crystals
24. Fehling's solution contains:
(A) $Ag^+$ ions (B) $Cu^{2+}$ ions (C) $Fe^{3+}$ ions (D) $MnO_4^-$ ions
25. A positive Fehling's test gives:
(A) Silver mirror (B) Brick-red precipitate of $Cu_2O$
(C) White precipitate (D) Yellow precipitate

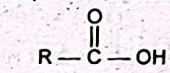


26. Ketones generally do not give:
(A) Iodoform test (B) Tollen's test (C) Reduction reaction (D) Cyanohydrin formation
27. The iodoform test detects the presence of:
(A) –CHO group only (B) $CH_3CO–$ group (C) –COOH group (D) –OH group only
28. The yellow precipitate obtained in the iodoform test is:
(A) AgI (B) $Cu_2O$ (C) $CHI_3$ (Iodoform) (D) $PbI_2$
29. Which alcohol also gives a positive iodoform test?
(A) Methanol (B) Ethanol (C) Propan-1-ol (D) Butan-1-ol
30. Methanol does not give the iodoform test because it lacks the:
(A) –OH group (B) $CH_3CO–$ or equivalent structure
(C) Carbon atom (D) Oxygen atom

## CARBOXYLIC ACIDS

**Q.6 What are carboxylic acids? Give their general formula and examples.** S/Q

Ans. Carboxylic acids are the organic compounds having the carboxyl functional group (–COOH) in their molecules. The general structure of carboxylic acids is as below.

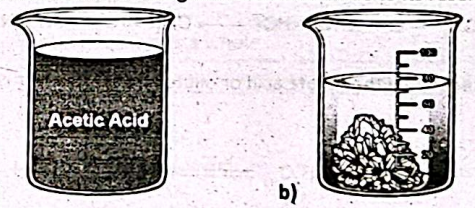


carboxylic aicds

Common examples of carboxylic acids are methanoic acid (formic acid, found in ants) ethanoic acid (acetic acid, found in vinegar), and butanoic acid (butyric acid, in the rancid butter).
Lower carboxylic acids are generally liquids at the room temperature, having high boiling points. This is due to their ability to make the hydrogen bond.

**Q.7 What is glacial acetic acid?** S/Q

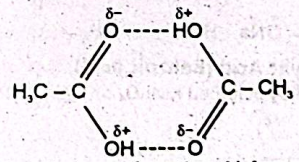
Ans. Ethanoic acid exists as a dimer due to its extensive hydrogen bonding. The melting point of ethanoic acid is 17°C, and its boiling point is 118°C. The melting point of this acid is close to room temperature (25°C), this is why it solidifies in winter.
The solid form of pure ethanoic acid is called glacial acetic acid due to its resemblance with glaciers.




Left: (a) acetic acid at room temperature
Right: (b) Glacial acetic acid at temperature below the room temperature

**Q.8 Why lower carboxylic acids are soluble?** S/Q

Ans. Due to their ability to form the hydrogen bond, lower acids, i.e., methanoic acid and ethanoic acid are soluble in water.



Dimeric form of acetic acid formed due to the hydrogen bonding

CamScanner

**Q.9 What are fatty acids?** S/Q

**Ans.** Long chain aliphatic monocarboxylic acids are called fatty acids.
**Examples:** Stearic acid, palmitic acid, and oleic acid are found in vegetable oils in the form of triglycerides. They are insoluble in water due to their long hydrophobic alkyl chains.

## ➲ Preparation of Carboxylic Acids

**Q.10 Give four methods for the preparation of carboxylic acids.** Exercise D/Q.5

**Ans.** Carboxylic acids can be prepared by the following methods.

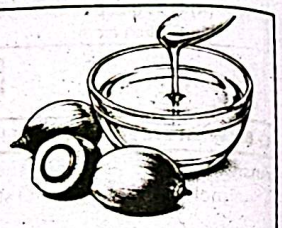
**a) Oxidation of Primary Alcohols and Aldehydes:**
Carboxylic acids are prepared by the oxidation of primary alcohols and aldehydes. The starting material is refluxed with excess of either acidified $KMnO_4$ or acidified $K_2Cr_2O_7$.

$$CH_3-CH_2-OH + 2[O] \xrightarrow[\text{Heat}]{K_2Cr_2O_7/\text{dil } H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-OH + H_2O$$

ethanol → ethanoic aicd

$$CH_3-\overset{O}{\overset{\|}{C}}-H + [O] \xrightarrow[\text{Heat}]{K_2Cr_2O_7/\text{dil } H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-OH + H_2O$$

ethanal → ethanoic aicd



Palmitic acid ($C_{16}H_{32}O_2$) is a long chain carboxylic acid found in palm oil in large quantities

**b) Hydrolysis of Alkane Nitriles:**
Alkane nitriles can be directly hydrolysed to carboxylic acids in acidic medium. In alkaline hydrolyses, they first produce salts of carboxylic acids, which yield carboxylic acids on acidification.

$$CH_3-CN + 2H_2O + HC\ell \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_4C\ell$$

$$CH_3-CN + H_2O + NaOH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{N}a + NH_3\uparrow$$

$$CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{N}a + HC\ell \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + NaC\ell$$

**c) Hydrolysis of Esters:**
When an ester is refluxed with either dilute acid or dilute alkali, the ester is hydrolyzed to carboxylic acid or carboxylate ion.

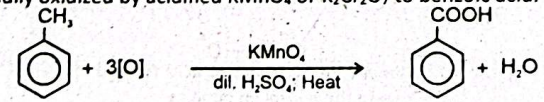
$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + H_2O_{(\ell)} \overset{H_3O^+}{\rightleftharpoons} CH_3-\overset{O}{\overset{\|}{C}}-OH + CH_3-CH_2-OH$$

$$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + NaOH_{(aq)} \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{N}a + CH_3-CH_2-OH$$

↑ Bond breaks

$$CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{N}a + HC\ell \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OH + NaC\ell$$

**d) Preparation of Benzenecarboxylic Acid (Benzoic acid):**
Methyl benzene is readily oxidized by acidified $KMnO_4$ or $K_2Cr_2O_7$ to benzoic acid.




methylbenzene → benzene carboxylic acid



### ☑ QUICK CHECK 23.3

**a) Write the equation for the oxidation of propanol with acidified $K_2Cr_2O_7$?**

**Ans.** Propanol generally refers to **propan-1-ol.** On oxidation with acidified potassium dichromate, it is first converted into propanal and on further oxidation into propanoic acid.

**Step 1: Oxidation to Propanal**

$$CH_3-CH_2-CH_2-OH + [O] \longrightarrow CH_3-CH_2-CHO + H_2O$$

**Step 2: Further Oxidation to Propanoic Acid**

$$CH_3-CH_2-CHO + [O] \longrightarrow CH_3-CH_2-COOH$$

**Overall Reaction:**

$$CH_3-CH_2-CH_2-OH + 2[O] \longrightarrow CH_3-CH_2-COOH + H_2O$$

**b) What products you expect from following? Give the chemical equations.**
**i) Hydrolysis of $CH_3CH_2CN$ ii) Oxidation of ethylbenzene iii) Hydrolysis of ethyl ethanoate**

**Ans. i) Hydrolysis of $CH_3CH_2CN$**
On hydrolysis, nitriles are converted into carboxylic acids.

$$CH_3-CH_2-CN + 2H_2O + H^+ \longrightarrow CH_3-CH_2-COOH + NH_4^+$$

The product formed is **propanoic acid.**

**ii) Oxidation of Ethylbenzene:**
On oxidation with strong oxidising agents such as acidified potassium permanganate, the side chain is converted into a carboxyl group.

$$C_6H_5-CH_2-CH_3 + 3[O] \longrightarrow C_6H_5-COOH + H_2O$$

The product formed is **benzoic acid.**

**iii) Hydrolysis of Ethyl Ethanoate:**
Hydrolysis of ethyl ethanoate produces ethanol and ethanoic acid.

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

The products formed are **ethanoic acid** and **ethanol.**

## REACTIONS OF CARBOXYLIC ACIDS

Reactions of carboxylic acids can be divided into the following types.
A. Reactions involving the acidic hydrogen only.
B. Reactions involving the replacement of the –OH group.
C. Reactions involving the carboxyl group as a whole.

**Q.11 Discuss the reactions involving acidic hydrogen and replacement of –OH group of carboxylic acids.** L/Q

**Ans.**

### A. Reactions Involving Acidic Hydrogen

Carboxylic acids show considerable acidic character because they give $H^+$ ions in water. This is why they can react with the basic species and active metals.

**i) With Active Metals:**

$$2CH_3-\overset{O}{\overset{\|}{C}}-OH + 2Na \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{N}a + H_2$$

**ii) With Alkalis:**

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + NaOH \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{N}a + H_2O$$

**iii) With Metal Carbonates and Bicarbonates:**

$$2CH_3-\overset{O}{\overset{\|}{C}}-OH + Na_2CO_3 \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{N}a + CO_2 + H_2O$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + NaHCO_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}\overset{+}{N}a + CO_2 + H_2O$$

CamScanner

## B. Reactions Involving Replacement of –OH Group

Carboxylic acids can undergo substitution reactions in which the OH group is replaced by some other group like X, OR, $NH_2$ etc.

**a) Reaction with $SOCl_2$:**

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + HCl + SO_2$$

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + HCl + POCl_3$$

**b) Reaction with Alcohols (Esterification):**

Carboxylic acids on heating with alcohols in the presence of concentrated sulphuric acid produce esters.

$$\underset{\text{ethanoic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{ethanol}}{C_2H_5OH} \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{ethyl ethanoate}}{CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5} + H_2O$$

**Q.12 Discuss the reactions involving –COOH group of carboxylic acids.** LIQ

**Ans.**

## C. Reduction involving $-\overset{O}{\overset{\|}{C}}-OH$ group

**Reduction**
i. Gain of $H_2$(or H–)
ii. Loss of O or $O_2$
iii. Loss of $X_2$ (Halogens)
iv. Gain of electrons
v. Decrease in Ox state.

**i) Reduction**

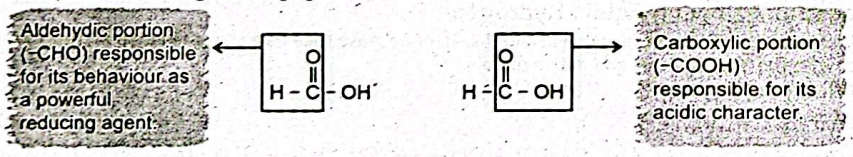
The powerful reducing agent lithium tetrahydridoaluminate (III) reduces carboxylic acids to primary alcohols.

$$\underset{\text{ethanoic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-OH} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{ethanol}}{CH_3-CH_2-OH} + H_2O$$

Other common reducing agents $H_2$/Ni and sodium tetrahydridoborate (III) will not reduce carboxylic acids.

**ii) Oxidation**

Methanoic acid gets oxidized with both weak as well as strong oxidizing agents due to its structure and, hence, acts as a strong reducing agent.




Methanoic acid is the only monocarboxylic acid which gives positive silver mirror test (Tollen's test) and brick red precipitate with Fehling's solution. These reactions are used for the identification of methanoic acid.

$$H-\overset{O}{\overset{\|}{C}}-OH + 2[Ag(NH_3)_2]OH \longrightarrow 2Ag\downarrow + CO_2 + 4NH_3 + 2H_2O$$

$$H-\overset{O}{\overset{\|}{C}}-OH + 2Cu(OH)_2 \longrightarrow Cu_2O\downarrow + CO_2 + 3H_2O$$

(brick red ppt)

**Oxidation**
i) Loss of $H_2$ or (H–)
ii) Addition of O or $O_2$
iii) Addition of $X_2$
iv) Loss of electrons
v) Increase in Ox. State



## RELATIVE ACIDIC STRENGTH OF CARBOXYLIC ACIDS

**Q.13 Discuss the relative acidic strength of carboxylic acids and halo-substituted carboxylic acids.** LIQ

**Ans.** Carboxylic acids are considerably more acidic than phenols and phenols are even more acidic than alcohols. The relative values of acidity constant or ionization constant, $K_a$, are given below (table) for a carboxylic acid, phenol or an alcohol.

The acidic strength i.e., the extent of ionization of an acid depends upon the stability of its conjugate base. For example,

$$\underset{\text{ethanoic acid}}{CH_3-\overset{O}{\overset{\|}{C}}-\overset{\delta-}{O}-\overset{\delta+}{H}} \overset{H_2O}{\rightleftharpoons} \underset{\text{ethanoate ion}}{CH_3-\overset{O}{\overset{\|}{C}}-\bar{O}} + \overset{+}{H} \qquad K_a = 1.8\times10^{-5}, \; pK_a \sim 4.76$$

In the ethanoate ion (the conjugate base), the intensity of the negative charge on oxygen atom is decreased due to delocalization of electrons around the –COOH group. Due to this, the ethanoate ion becomes stabilized thus making it less likely to accept $H^+$ ions to form undissociated acid molecule.

**Table**

| Substance | $K_a$ | $pK_a$ |
|---|---|---|
| RCOOH | $10^{-5}$ | 5 |
| ArOH | $10^{-10}$ | 10 |
| HOH | $10^{-14}$ | 14 |
| R – OH | $10^{-16}$ | 16 |

$pK_a = -\log K_a$
Higher the $K_a$ or lower the $pK_a$, stronger will be the acid and vice versa.

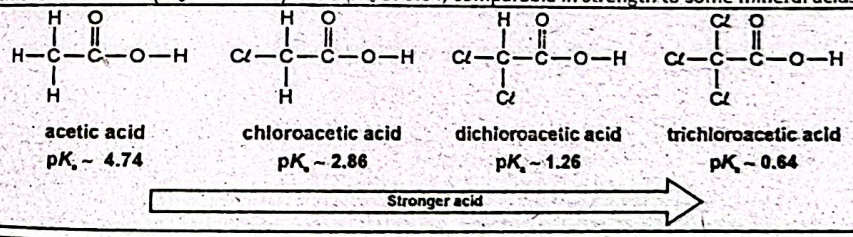
$$CH_3-\overset{O}{\overset{\|}{C}}-\bar{O} \longleftrightarrow CH_3-\overset{\bar{O}}{C}=O$$

The presence of an electron donating group (+ I effect) will tend to destabilize the carboxylate ion by intensifying the negative charge and thus decreases the acidity of the acid. On the other hand, an electron withdrawing group (–I effect) will tend to stabilize the carboxylate ion by dispersing its negative charge and thus increases the acidity of the acid. For example, methanoic acid is 10 times stronger acid than ethanoic acid.

$\boxed{H}-COOH$ (–1 effect) $K_a = 1.8\times10^{-4}$, $pK_a = 3.75$

$\boxed{CH_3}-COOH$ (+1 effect) $K_a = 1.8\times10^{-5}$, $pK_a = 4.75$

For example, chloroacetic acid ($ClCH_2-COOH$) has a $pK_a$ of 2.86, indicating that it is a stronger acid than ethanoic acid ($pK_a$ = 4.76). Dichloroethanoic acid ($Cl_2CH-COOH$) is even stronger, with a $pK_a$ of 1.26. Trichloroacetic acid ($Cl_3C-COOH$) has a $pK_a$ of 0.64, comparable in strength to some mineral acids.




### QUICK CHECK 23.4

a) **Methanoic acid is stronger than ethanoic acid. Give reason.**

**Ans.** Methanoic acid ($H-\overset{O}{\overset{\|}{C}}-OH$) and ethanoic acid ($CH_3-\overset{O}{\overset{\|}{C}}-OH$)

- **Alkyl group effect:** Ethanoic acid contains a methyl group ($CH_3$).

CamScanner

- **Electron donation:** the methyl group releases electrons (+I effect).
- **Charge density:** This increases electron density on the carboxyl group.
- **Bond strengthening:** It strengthens the O – H bond, hindering proton release.
- **Anion destabilization:** It destabilizes the resulting ethanoate conjugate base.
- **Methanoic acid:** It lacks this electron-donating alkyl group.

**b) Place the following acids in order of strength, starting with the strongest acid first.**
**i) $CH_3CH_2COOH$ ii) $CH_3CCl_2COOH$ iii) $CH_3CHClCOOH$**

**Ans.** $CH_3CCl_2COOH > CH_3CHClCOOH > CH_3CH_2COOH$

- **Inductive effect:** Chlorine is highly electronegative (–I effect).
- **Electron withdrawal:** Chlorine pulls electron density away from the carboxylate group.
- **Anion stabilization:** This stabilizes the negative charge after losing H+.
- **Quantity matters:** More chlorine atoms create a stronger acidic effect.
- **Ranking reason:** Compound (ii) has two chlorines, (iii) has one, and (i) has none.

**c) Explain why ethanoic acid is a stronger acid than ethanol.**

**Ans.**
- **Resonance stabilization:** Ethanoate ion delocalizes its negative charge.
- **Oxygen sharing:** The charge is shared equally across two oxygen atoms.
- **High stability:** Resonance makes the ethanoate conjugate base very stable.
- **Localized charge:** Ethoxide ion localizes charge on a single oxygen.
- **Destabilizing effect:** The ethyl group intensifies charge via electron donation (+I effect).
- **Acidity outcome:** Stable conjugate bases make parent molecules much stronger acids.

## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **The functional group present in carboxylic acids is:**
(A) –OH (B) –CHO (C) –COOH (D) –CO–
2. **The general formula of carboxylic acids is:**
(A) RCHO (B) RCOOH (C) ROH (D) RCOOR
3. **Ethanoic acid is commonly known as:**
(A) Formic acid (B) Acetic acid (C) Benzoic acid (D) Oxalic acid
4. **Methanoic acid is naturally found in:**
(A) Vinegar (B) Palm oil (C) Ants (D) Butter
5. **Lower carboxylic acids have relatively high boiling points due to:**
(A) Ionic bonding (B) Hydrogen bonding (C) Metallic bonding (D) Van der Waals forces only
6. **Pure solid ethanoic acid is called:**
(A) Dry acetic acid (B) Glacial acetic acid (C) Frozen acetate (D) Ice acid
7. **Long-chain monocarboxylic acids are known as:**
(A) Amino acids (B) Fatty acids (C) Mineral acids (D) Hydroxy acids
8. **Palmitic acid is mainly found in:**
(A) Vinegar (B) Palm oil (C) Milk (D) Coal tar
9. **Carboxylic acids are prepared by oxidation of:**
(A) Primary alcohols (B) Secondary alcohols only (C) Tertiary alcohols (D) Ketones
10. **The oxidizing agent commonly used is:**
(A) NaOH (B) Acidified $K_2Cr_2O_7$ (C) $Br_2$ water (D) NaCl
11. **Aldehydes are oxidized to form:**
(A) Alcohols (B) Carboxylic acids (C) Ketones (D) Esters
12. **Hydrolysis of alkane nitriles in acidic medium produces:**
(A) Alcohols (B) Carboxylic acids (C) Amines (D) Aldehydes
13. **Alkaline hydrolysis of nitriles first forms:**
(A) Carboxylic acid salts (B) Alcohols (C) Ketones (D) Esters
14. **Hydrolysis of esters produces:**
(A) Alkene and water (B) Carboxylic acid and alcohol
(C) Ketone and alcohol (D) Ether and water
15. **Oxidation of methylbenzene gives:**
(A) Phenol (B) Benzoic acid (C) Benzaldehyde (D) Benzene
16. **Carboxylic acids react with sodium metal to produce:**
(A) Sodium carboxylate and hydrogen (B) Sodium hydroxide
(C) Oxygen gas (D) Carbon dioxide



17. **Carboxylic acids react with NaOH to form:**
(A) Alcohols (B) Sodium carboxylates and water (C) Esters (D) Ketones
18. **Reaction of carboxylic acids with sodium carbonate produces:**
(A) Hydrogen gas only (B) Carbon dioxide, water, and salt
(C) Chlorine gas (D) Oxygen gas
19. **Sodium bicarbonate reacts with carboxylic acids to evolve:**
(A) Hydrogen (B) Oxygen (C) Carbon dioxide (D) Nitrogen
20. **$SOCl_2$ converts carboxylic acids into:**
(A) Alcohols (B) Acyl chlorides (C) Esters (D) Aldehydes
21. **Esterification involves the reaction between a carboxylic acid and:**
(A) Alkene (B) Alcohol (C) Ketone (D) Aldehyde
22. **Concentrated $H_2SO_4$ acts mainly as:**
(A) Oxidizing agent (B) Catalyst (C) Reducing agent (D) Base
23. **$LiAlH_4$ reduces carboxylic acids to:**
(A) Aldehydes (B) Primary alcohols (C) Secondary alcohols (D) Ketones
24. **Which common reducing agent does not reduce carboxylic acids?**
(A) $LiAlH_4$ (B) $NaBH_4$ (C) Both $NaBH_4$ and $H_2/Ni$ (D) None of these
25. **Methanoic acid gives a positive:**
(A) Bromine water test only (B) Tollen's and Fehling's tests (C) Iodoform test only (D) Baeyer's test
26. **The strongest acid among alcohol, phenol, and carboxylic acid is:**
(A) Alcohol (B) Water (C) Phenol (D) Carboxylic acid
27. **The conjugate base of a carboxylic acid is stabilized by:**
(A) Inductive effect only (B) Resonance (delocalization) (C) Hydrogen bonding (D) Hyper conjugation only
28. **Electron-withdrawing groups generally _____ the acidity of carboxylic acids.**
(A) Decrease (B) Increase (C) Eliminate (D) Do not affect
29. **Electron-donating (+I) groups generally _____ the acidity of carboxylic acids.**
(A) Increase (B) Decrease (C) Double (D) Do not affect
30. **Which of the following is the strongest acid?**
(A) Ethanoic acid (B) Chloroacetic acid (C) Dichloroacetic acid (D) Trichloroacetic acid

## ESTERS

**Q.14 What are esters? Give their general formula.** S/Q

**Ans.** Esters are the derivatives of carboxylic acids that are obtained by their reactions with alcohols.

**General Formula and Functional Group:** $R-\overset{\overset{O}{\|}}{C}-O-R'$ Where R' = alkyl group

**Examples**

| Formula | Common Name | IUPAC Name |
|---|---|---|
| $H-\overset{\overset{O}{\|}}{C}-O-CH_3$ | Methyl formate | Methylmethanoate |
| $CH_3-\overset{\overset{O}{\|}}{C}-O-CH_3$ | Methyl acetate | Methylethanoate |
| $CH_3-\overset{\overset{O}{\|}}{C}-O-C_2H_5$ | Ethyl acetate | Ethylethanoate |

Esters, unlike alcohols and carboxylic acids have no ability to form the hydrogen bond.

**Q.15 Why boiling points of esters are lower than corresponding alcohols and carboxylic acids?** S/Q

**Ans.** This is why their boiling points are lower than the corresponding alcohols and carboxylic acids. The boiling point of ethyl ethanoate ($CH_3COOC_2H_5$) is 77°C, which shows its lower relative volatility compared to ethanoic acid and ethanol. As there is lack of hydrogen bonds in esters, so they are less soluble/insoluble in water.

CamScanner

**Q.16 Esters have fruity smell. Give examples.** S/Q

**Ans.** Esters find many uses as solvents and flavouring agents in fruit drinks and sweets. Volatile esters are liquids with sweet fruity smells.

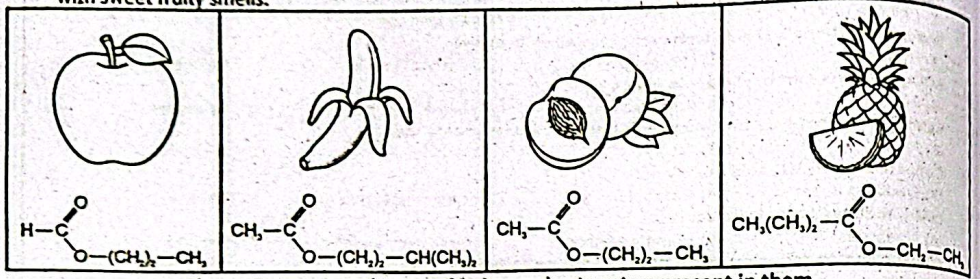



**Figure: Fragrance and tastes of fruits are due to esters present in them**

## ➲ Preparations of Esters

**Q.17 Write methods for the preparations of esters.** L/Q

**Ans. Preparations of Esters:**

Esters can be prepared by the following methods.

**i. By the Reaction of Carboxylic Acids and Alcohol:**

The reaction of carboxylic acids with alcohols in acidic medium results in the formation of an ester. This reaction is known as Fischer's esterification. For example,

$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + CH_3-CH_2-OH \overset{H^+}{\rightleftharpoons} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + H_2O$$

propanoic acid — ethanol — ethyl propanoate

In general

$$R-\overset{O}{\overset{\|}{C}}-\boxed{OH+H}-O-R \overset{H^+}{\rightleftharpoons} R-\overset{O}{\overset{\|}{C}}-OR + H_2O$$

bond cleavage — bond cleavage — Ester

**ii. By the Reaction of Acyl Chlorides and Alcohols:**

Acyl chlorides react vigorously with alcohols to form esters and their reactions go to completion and do not form an equilibrium mixture like the reaction between carboxylic acids and alcohols.

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + CH_3-CH_2-O-H \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + HCl$$

ethanoyl chloride — ethanol — ethylethanoate

**iii. By the Reaction of Acyl Chlorides and Phenol:**

Phenyl esters are formed when acyl chloride is warmed with phenol.

$$H_3C-\overset{O}{\overset{\|}{C}}-Cl + HO-C_6H_5 \xrightarrow[\text{Heat}]{\text{NaOH}} H_3C-\overset{O}{\overset{\|}{C}}-O-C_6H_5 + HCl$$

ethanoyl chloride — phenol — phenyl ethanoate

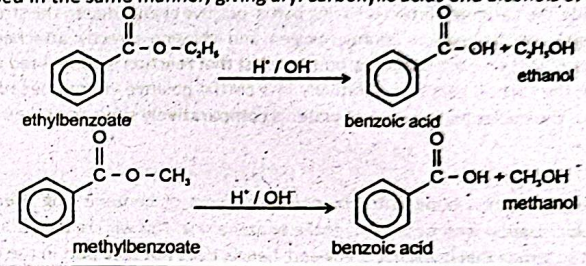


## ➲ Reactions of Esters

**Q.18 What products are formed during hydrolysis of esters?** S/Q

**Ans. Hydrolysis of Esters:**

An ester is hydrolyzed slowly to a carboxylic acid and an alcohol (or a phenol). The reaction is either acid or base-catalyzed. The hydrolysis of aliphatic esters is already discussed earlier in this chapter. Aromatic esters are also hydrolysed in the same manner, giving aryl carboxylic acids and alcohols or phenol.




## ACYL CHLORIDES

**Q.19 What are acyl chlorides? Give their examples.** S/Q

**Ans.** Acyl chlorides have the functional group $-C-Cl$.

**General formula** for saturated aliphatic acyl chlorides: $C_nH_{2n+1}COCl$.

According to the IUPAC system, they are named as **alkanoyl halides.**

**Examples:**

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

ethanoyl chloride — propanoyl chloride

Since acyl chlorides are the most reactive compounds among the functional derivatives of carboxylic acids, they are usually prepared in such a way that they can be used for the preparation of other functional derivatives.

## HYDROLYSIS OF ACYL CHLORIDES, ALKYL CHLORIDES AND ARYL CHLORIDES

**Q.20 Compare the reactivity of acyl chlorides, alkyl chlorides and aryl chlorides.** L/Q

**Ans. Hydrolysis**

The reactivity of acyl chlorides, alkyl chlorides and aryl (arene) chlorides can be compared with the ease of hydrolysis they undergo. Let us consider the following reactions.

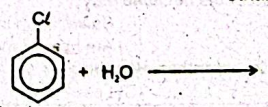
➢ **Acyl Chloride:**

$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + H_2O \xrightarrow{\text{Room temperature}} CH_3-\overset{O}{\overset{\|}{C}}-OH + HCl \quad \text{(rapid)}$$

ethanoyl chloride — ethanoic acid

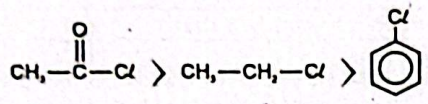
$$CH_3-CH_2-Cl + H_2O \xrightarrow{\text{Heat under reflux}} CH_3-CH_2-OH + HCl \quad \text{(slow)}$$

chloroethane — ethanol




chlorobenzene

## Trend of Hydrolysis



### Alkyl Chlorides:

In ethanoyl chloride, the carbonyl carbon is having partial positive charge due to the strong electron withdrawing effect of two highly electronegative atoms: oxygen and chlorine directly attached to the carbon. Hence nucleophilic attack of $H_2O$ on electrophilic carbon is so fast that reaction is completed within few minutes.
In ethyl chloride, the carbon gets comparatively less partial positive charge because it is attached to only chlorine atom. So, the nucleophilic attack of water is comparatively slow and takes 14 days to be completed even at 100°C.

### Aryl Chlorides:

In chlorobenzene, the carbon bonded to chlorine is the part of benzene ring. Here, lone pair on chlorine participates in delocalization with π elections of the benzene ring. This will create a double bond character in C–Cℓ bond making it so strong that it will not break and, hence, does not take part in the chemical reaction.

### QUICK CHECK 23.5

**a) Why do phenols not react directly with carboxylic acids to form phenyl esters?**

**Ans.** Phenols do not react directly with carboxylic acids to form esters because phenol is less reactive than alcohols in esterification reactions. In phenol, the lone pair of electrons on oxygen is partially involved in resonance with the benzene ring, making the oxygen atom less available for reaction with the carboxylic acid. The reaction is endothermic. Therefore, phenyl esters are usually prepared using acid chlorides or acid anhydrides instead of carboxylic acids.

**b) Phenyl ethanoate is the ester responsible for the fragrance of peach and strawberry. It can be prepared from the ethanoyl chloride and phenol. Write down a chemical reaction for the preparation of this ester.**

**Ans.** Phenyl ethanoate is prepared by reacting phenol with ethanoyl chloride.

$$C_6H_5OH + CH_3COC\ell \longrightarrow CH_3COOC_6H_5 + HC\ell$$

Ethanoyl chloride

**c) Predict the products of the following reactions, write the chemical equations.**
**i) Chlorobenzene and ethanol** **ii) Propanoyl chloride and phenol**

**Ans. i) Chlorobenzene and ethanol**
Chlorobenzene does not react with ethanol under ordinary conditions because C – Cℓ bond in chlorobenzene is very strong because of resonance.

$$C_6H_5C\ell + C_2H_5OH \longrightarrow \text{No reaction}$$

**ii) Propanoyl chloride and phenol**
Propanoyl chloride reacts readily with phenol to form an ester called **phenyl propanoate.**

$$C_6H_5OH + CH_3CH_2COC\ell \longrightarrow CH_3CH_2COOC_6H_5 + HC\ell$$

## BLOCK # 03 MULTIPLE CHOICE QUESTIONS (MCQs)

1. Esters are derivatives of:
(A) Alcohols (B) Carboxylic acids (C) Ketones (D) Aldehydes
2. The general functional group of an ester is:
(A) –COOH (B) –CHO (C) –COOR (D) –OH
3. Esters generally have:
(A) Sharp pungent smell (B) Sweet fruity smell (C) Odourless nature (D) Fishy smell
4. Esters have lower boiling points than alcohols because they:
(A) Are ionic compounds (B) Cannot form intermolecular hydrogen bonds
(C) Have stronger covalent bonds (D) Are heavier molecules
5. Esters are generally _____ soluble in water than alcohols.
(A) More (B) Equally (C) Less (D) Completely



6. Esters are widely used as:
(A) Oxidizing agents (B) Flavouring agents and solvents
(C) Bleaching agents (D) Fertilizers
7. Fischer esterification is the reaction between:
(A) Alcohol and aldehyde (B) Carboxylic acid and alcohol
(C) Ketone and alcohol (D) Carboxylic acid and ketone
8. Concentrated $H_2SO_4$ in esterification acts mainly as:
(A) Oxidizing agent (B) Catalyst (C) Reducing agent (D) Base
9. The product formed from ethanoic acid and ethanol is:
(A) Ethyl methanoate (B) Ethyl ethanoate (C) Methyl ethanoate (D) Ethanal
10. Acyl chlorides react with alcohols to produce:
(A) Aldehydes (B) Esters (C) Ketones (D) Carboxylic acids
11. Reactions of acyl chlorides with alcohols:
(A) Do not occur (B) Go to completion
(C) Require UV light (D) Produce equilibrium mixtures only
12. Phenyl esters are prepared by reacting acyl chlorides with:
(A) Benzene (B) Phenol (C) Ethanol (D) Toluene
13. Hydrolysis of esters produces:
(A) Alcohol (or phenol) and carboxylic acid (B) Ketone and alcohol
(C) Alkane and water (D) Ether and acid
14. The functional group present in acyl chlorides is:
(A) –COOH (B) –COCℓ (C) –CHO (D) –OH
15. According to IUPAC nomenclature, acyl chlorides are called:
(A) Alkyl chlorides (B) Alkanoyl halides (C) Haloalkanes (D) Chloroalkanes
16. Acyl chlorides are the _____ reactive derivatives of carboxylic acids.
(A) Least (B) Moderately (C) Most (D) Non-reactive
17. Ethanoyl chloride reacts rapidly with water at:
(A) 100°C (B) Room temperature (C) 0°C only (D) Under UV light
18. Chloroethane undergoes hydrolysis:
(A) Instantly at room temperature (B) Slowly on heating under reflux
(C) Without heating (D) Not at all
19. Chlorobenzene does not undergo hydrolysis easily because:
(A) It has no chlorine atom
(B) The C–Cl bond has partial double-bond character due to resonance
(C) It is an alkane
(D) Water is a weak nucleophile
20. Which compound shows the highest rate of hydrolysis?
(A) Chlorobenzene (B) Chloroethane (C) Ethanoyl chloride (D) Phenyl chloride

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

**BLOCK # 01**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. C | 2. B | 3. B | 4. C | 5. B | 6. B | 7. B | 8. B | 9. B | 10. B | 11. B | 12. B | 13. B | 14. B | 15. B |
| 16. B | 17. B | 18. B | 19. B | 20. C | 21. C | 22. B | 23. B | 24. B | 25. B | 26. B | 27. B | 28. C | 29. B | 30. B |

**BLOCK # 02**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. C | 2. B | 3. B | 4. C | 5. B | 6. B | 7. B | 8. B | 9. A | 10. B | 11. B | 12. B | 13. A | 14. B | 15. B |
| 16. A | 17. B | 18. B | 19. C | 20. B | 21. B | 22. B | 23. B | 24. C | 25. B | 26. D | 27. B | 28. B | 29. B | 30. D |

**BLOCK # 03**

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. B | 4. B | 5. C | 6. B | 7. B | 8. B | 9. B | 10. B | 11. B | 12. B | 13. A | 14. B | 15. B |
| 16. C | 17. B | 18. B | 19. B | 20. C | | | | | | | | | | |

CamScanner

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. Ketones are prepared by the oxidation of:
a) Primary alcohol b) Secondary alcohol c) Tertiary alcohol d) Phenol

II. Which of the following will not give the Iodoform test?
a) Acetaldehyde b) pentan-2-one c) pentan-3-one d) Acetone

III. When a carboxyl acid reacts with an alcohol, the product is an:
a) Ether b) Ester c) Anhydride d) Amide

IV. Carboxylic acids react with carbonates to produce gas.
a) $H_2$ b) CO c) $CO_2$ d) $CH_4$

V. Which type of alcohols produces aldehydes?
a) Primary b) Secondary c) Tertiary (d) both a and b

VI. The hybridisation of the oxygen of carbonyl group is:
a) sp b) $sp^2$ c) $sp^3$ d) $dsp^2$

VII. Which is the main product of the reaction between acetic acid and $PCl_5$.
a) $CH_3 - Cl$ b) $CH_3COCl$ c) HCl d) $POCl_3$

VIII. Acidic character of chlorine substituted carboxylic acid is higher because chlorine is:
a) Electropositive b) Electron with drawing due to –I
c) Electron donating due to +I d) having three loan pairs

IX. When formic acid is oxidized, which of the following is formed?
a) water b) carbon dioxide
c) carbon dioxide and water d) carbon monoxide

X. The mechanism by which acyl chlorides react with alcohols is.
a) Addition b) Elimination c) Addition-elimination d) Substitution

### Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | b | Secondary alcohol | Ketones are produced by the oxidation of secondary alcohols. |
| II. | c | Pentan-3-one | The iodoform test is given by compounds containing the $CH_3CO-$ group. Pentan-3-one does not contain this group. |
| III. | b | Ester | A carboxylic acid reacts with an alcohol in the presence of concentrated sulphuric acid to produce an ester and water. |
| IV. | c | $CO_2$ | Carboxylic acids react with carbonates to produce carbon dioxide gas, water and a salt. |
| V. | a | Primary | Primary alcohols are oxidized to aldehydes under controlled oxidation conditions. |
| VI. | b | $sp^2$ | The oxygen atom in the carbonyl group is $sp^2$ hybridized because the carbonyl group is planar in structure. |
| VII. | b | $CH_3COCl$ | Ethanoic acid reacts with $PCl_5$ to form ethanoyl chloride. $CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$ |
| VIII. | b | Electron withdrawing due to –I effect | Chlorine withdraws electrons through the inductive effect and stabilizes the carboxylate ion, increasing acidity. |
| IX. | c | Carbon dioxide and water | Methanoic acid is completely oxidized to carbon dioxide and water. $HCOOH + [O] \longrightarrow CO_2 + H_2O$ |
| X. | c | Addition-elimination | Acyl chlorides react with alcohols by nucleophilic addition followed by elimination of chloride ion. |



## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) How is ethanol converted to acetic acid?**

Ans. Ethanol is converted into acetic acid by oxidation using acidified potassium dichromate ($K_2Cr_2O_7/H_2SO_4$) or acidified potassium permanganate ($KMnO_4$).

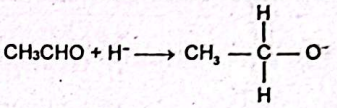
$$CH_3CH_2OH + 2[O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH + H_2O$$

The reaction is carried out under reflux to ensure complete oxidation.

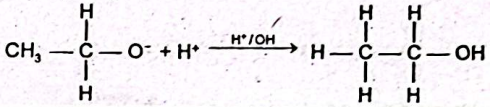
**b) Give the mechanism for the reductions of ethanal with $NaBH_4$.**

Ans. The reduction takes place by nucleophilic addition.

**Step 1:** Hydride ion ($H^-$) from $NaBH_4$ attacks the carbonyl carbon of ethanal.

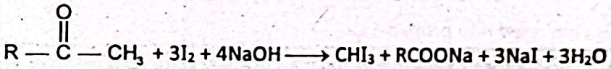


**Step 2:** Protonation of alkoxide ion gives ethanol.



**c) What is iodoform reaction?**

Ans. The iodoform reaction is a test used for compounds containing the $CH_3CO^-$ group or the $CH_3CHOH^-$ group. When such compounds are heated with iodine and sodium hydroxide, a yellow precipitate of iodoform ($CHI_3$) is formed.



**d) Methanoic acid can be oxidized but other carboxylic acids cannot. Why?**

Ans. Methanoic acid contains a hydrogen atom directly attached to the carboxyl carbon, which allows it to be further oxidized to carbon dioxide and water.

$$HCOOH + [O] \longrightarrow CO_2 + H_2O$$

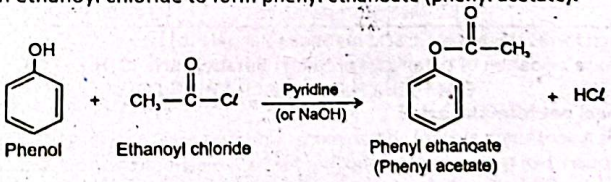
Other carboxylic acids contain alkyl groups instead of hydrogen and therefore resist further oxidation under ordinary conditions.

**e) Explain the influence of chlorine substitution on the acidic strength of carboxylic acids.**

Ans. Chlorine atoms increase the acidity of carboxylic acids because they withdraw electrons through the negative inductive (–I) effect.
This stabilizes the carboxylate ion formed after loss of a proton and increases the acidic strength.
The greater the number of chlorine atoms, the stronger the acid.
**For example:** $CH_3COOH < CH_2ClCOOH < CHCl_2COOH < CCl_3COOH$

**f) Give the reaction of ethanoyl chloride with phenol.**

Ans. Phenol reacts with ethanoyl chloride to form phenyl ethanoate (phenyl acetate):




Phenol | Ethanoyl chloride | Phenyl ethanoate (Phenyl acetate)

CamScanner

**g) Give reaction of methanal with the Tollen's reagent.**

**Ans.** Methanal reduces Tollens' reagent to metallic silver while itself being oxidized to methanoic acid.

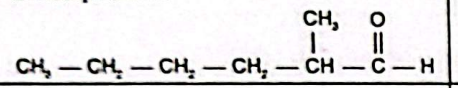
$$HCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow HCOOH + 2Ag + 4NH_3 + 2H_2O$$

A silver mirror is formed on the inner wall of the test tube.

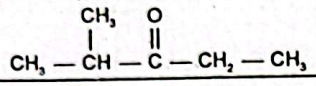
**h) Write down structural formulae of the following compounds.**
**i) 2-methylhexanal ii) 2-methyl-3-pentanone iii) 3-hydroxypentanl**
**iv) 4-nitro-2-pentanone v) 2-chlorobutanol**

**Ans.**

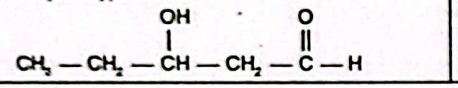
**i) 2-Methylhexanal**



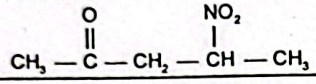
**ii) 2-Methyl-3-pentanone**



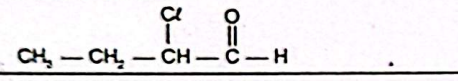
**iii) 3-Hydroxypentanal**



**iv) 4-Nitro-2-pentanone**



**v) 2-Chlorobutanal**



## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) Write down the equation for the reaction of $CH_3CH_2CHO$ with $LiAlH_4$ (dry ether).**

**Ans.** Propanal is reduced by lithium aluminium hydride in dry ether to form propan-1-ol.

$$CH_3CH_2CHO + 2[H] \xrightarrow[LiAlH_4]{\text{dry ether}} CH_3CH_2CH_2OH$$

Thus, propanal is converted into propan-1-ol.

**b) An alcohol, $C_4H_{10}O$ undergoes oxidation to form a butanoic acid, $C_4H_8O_2$. Give a chemical equation along with conditions.**

**Ans.** As Oxidation of alcohol produces a carboxylic acid ($C_4H_8O_2$), the alcohol must be a primary alcohol.
One suitable example is butan-1-ol.

$$CH_3 - CH_2 - CH_2 - CH_2 - OH + 2[O] \xrightarrow[K_2Cr_2O_7/H_2SO_4]{\text{reflux}} CH_3 - CH_2 - CH_2 - COOH + H_2O$$

**Conditions:**
- Acidified potassium dichromate ($K_2Cr_2O_7/H_2SO_4$)
- Heating under reflux.

**c) Write the structures of all the isomeric alcohols with formula $C_4H_{10}O$. Give their systematic names. Which one of them forms butanoic acid? Explain why the others do not.**

**Ans.** There are four alcohol isomers with molecular formula $C_4H_{10}O$.

| Structural Formula | IUPAC Name | Type of Alcohol |
|---|---|---|
| $CH_3CH_2CH_2CH_2OH$ | Butan-1-ol | Primary |
| $CH_3CH(OH)CH_2CH_3$ | Butan-2-ol | Secondary |
| $(CH_3)_2CHCH_2OH$ | 2-Methylpropan-1-ol | Primary |
| $(CH_3)_3COH$ | 2-Methylpropan-2-ol | Tertiary |

The alcohol which forms the butanoic acid mentioned in part (b) is:
**Butan-1-ol** because oxidation of butan-1-ol produces **butanoic acid ($C_4H_8O_2$).**

$$CH_3CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH_2COOH$$

**Why do the others not form this acid?**
- **Butan-2-ol** is a secondary alcohol and on oxidation forms a ketone (butan-2-one).
- **2-Methylpropan-1-ol** is a primary alcohol but forms **2-methylpropanoic acid**, not butanoic acid.
- **2-Methylpropan-2-ol** is a tertiary alcohol and does not undergo oxidation under normal conditions.



**d) Propanoic acid can be reduced to propan-1-ol by reduction with $LiAlH_4$. Give a balanced chemical equation. Can we use $NaBH_4$ for this reaction? If not, give reason.**

**Ans.** Propanoic acid is reduced by lithium aluminium hydride to form propan-1-ol.

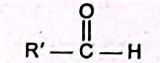
$$CH_3CH_2COOH + 4[H] \xrightarrow[LiAlH_4]{\text{dry ether}} CH_3CH_2CH_2OH + H_2O$$

Thus, propanoic acid is converted into propan-1-ol.
No, $NaBH_4$ cannot be used for this reaction.
This is because sodium borohydride is a weaker reducing agent and can reduce aldehydes and ketones only. It cannot reduce carboxylic acids. Lithium aluminium hydride is a much stronger reducing agent and can reduce carboxylic acids to primary alcohols.

## DESCRIPTIVE QUESTIONS DQs

**Q.4 What are aldehydes and ketones? Give the preparation of each.**

**Ans. Aldehydes:**
Aldehydes are organic compounds containing the aldehyde functional group (–CHO) in which the carbonyl carbon is attached to at least one hydrogen atom. The general formula of an aldehyde is:



(R′ = H or alkyl group.)

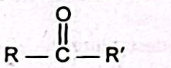
**Examples:**
- Methanal ($HCHO$)
- Ethanal ($CH_3CHO$)
- Propanal ($CH_3CH_2CHO$)

**Preparation of Aldehydes:**
Aldehydes are prepared by the controlled oxidation of primary alcohols using acidified potassium dichromate ($K_2Cr_2O_7/H_2SO_4$). For example, ethanal is prepared from ethanol as follows:

$$CH_3CH_2OH + [O] \xrightarrow[K_2Cr_2O_7/H_2SO_4]{} CH_3CHO + H_2O$$

The aldehyde formed is distilled off immediately to prevent further oxidation to carboxylic acid.

**Ketones:**
Ketones are organic compounds containing the carbonyl functional group (>C=O) in which the carbonyl carbon is attached to two carbon atoms. The general formula of a ketone is:



(Where R = R′ = alkyl group)

**Examples:**
- Propanone ($CH_3COCH_3$)
- Butan-2-one ($CH_3COCH_2CH_3$)

**Preparation of Ketones:**
Ketones are prepared by the oxidation of secondary alcohols using acidified potassium dichromate ($K_2Cr_2O_7/H_2SO_4$). For example, propanone is prepared from propan-2-ol as follows:

$$CH_3CHOHCH_3 + [O] \xrightarrow[K_2Cr_2O_7/H_2SO_4]{} CH_3COCH_3 + H_2O$$

The reaction is usually carried out under reflux.

**Q.5 Give four methods for the preparation of carboxylic acids.**

**Ans.** See Question No. Q.10

**Q.6 How does ethanoic acid reacts with:**
**i) NaOH ii) ethanol iii) $SOCl_2$ iv) $PCl_5$**

**Ans. Ethanoic acid reacts with:**

**i) Sodium hydroxide (NaOH)**

Ethanoic acid reacts with sodium hydroxide in a neutralization reaction to form **sodium ethanoate** and water.

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

This reaction shows the acidic nature of ethanoic acid.

CamScanner

**ii) Ethanol**

Ethanoic acid reacts with ethanol in the presence of concentrated sulphuric acid to form an ester called **ethyl ethanoate** and water.

$$CH_3COOH + C_2H_5OH \xrightarrow{\text{conc } H_2SO_4} CH_3COOC_2H_5 + H_2O$$

This reaction is called **esterification.**

**iii) Thionyl chloride ($SOCl_2$)**

Ethanoic acid reacts with thionyl chloride to form **ethanoyl chloride.**

$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$$

The products formed are ethanoyl chloride, sulphur dioxide and hydrogen chloride.

**iv) Phosphorus pentachloride ($PCl_5$)**

Ethanoic acid reacts with phosphorus pentachloride to form **ethanoyl chloride.**

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

The products formed are ethanoyl chloride, phosphorus oxychloride and hydrogen chloride.

**Q.7 Give the mechanisms of the reactions of carbonyl compounds with: a) HCN b) $NaBH_4$**

**Ans.** See Question NO. Q.4

**Q.8 Explain the relative acidic strength of unsubstituted carboxylic acids and substituted carboxylic acids.**

**Ans.** The acidic strength of carboxylic acids depends mainly on the stability of the conjugate base (carboxylate ion).

> **Greater stability of $RCOO^-$**
> - Greater tendency to ionize.
> - Stronger acid.

**Step 1: Ionization of carboxylic Acids:**

$$RCOOH \rightleftharpoons \underset{\text{(Carboxylate ion)}}{RCOO^-} + H^+$$

**Step 2: Unsubstituted (alkyl) carboxylic acids (baseline acidity):**

- Acidity of unsubstituted carboxylic acids is due to the –COOH group itself.
- Alkyl groups (–R) attached to the –COOH group show +I effect (electron-releasing effect).
  - They pull electron density towards the $-COO^-$ group.
  - This increase electron density on the carboxylate ion.
  - Hence, the carboxylate ion becomes less stable (destabilized).

Therefore, alkyl substituents DECREASE the acidity of carboxylic acids.

**Step 3: Substituted carboxylic acids with electron-withdrawing groups (–I effect)**

- Electron-withdrawing groups (such as halogens, $-NO_2$, –CN, $-SO_3H$, etc.) show –I effect.
  - They pull electron density away from the $-COO^-$ group.
  - This decrease electron density on the carboxylate ion.
  - Hence, the carboxylate ion becomes more stable (destabilized).

Therefore, electron-witchdrawing substituents INCREASE the acidity.

The –I effect becomes stronger when:

1. The substituent is more electron-withdrawing ($-NO_2 > -CN > -Cl > -Br > -F$).
2. More than one electron-withdrawing group is present.
3. The substituent is nearer to the –COOH group.

**Step 4: Substituted carboxylic acids with electron-donating groups (+I effect)**

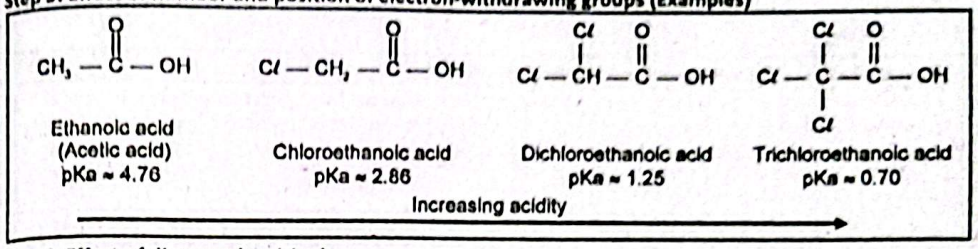
Electron-donating groups (such as $-CH_3$, $-C_2H_5$, $-OCH_3$, $-NH_2$, etc.) show +I effect.

- They push electron density towards the $-COO^-$ group.
- This increase electron density on the carboxylate ion.
- Hence, the carboxylate ion becomes less stable.

Therefore, electron-donating substituents DECREASE the acidity.



**Step 5: Effect of number and position of electron-withdrawing groups (Examples)**




**Step 6: Effect of distance (position)**

The –I effect decreases rapidly with distance from the –COOH group.

| | $ClCH_2COOH$ | > | $ClCH_2CH_2COOH$ | > | $ClCH_2CH_2CH_2COOH$ |
|---|---|---|---|---|---|
| | 2-chloroethanoic acid (α-chloro) | | 3-chloropropanoic acid (β-chloro) | | 4-chlorobutanoic acid (γ-chloro) |
| **Acidity:** | α | > | β | > | γ |

**Q.9 Explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and halogenoarenes.**

**Ans.** The ease of hydrolysis depends upon the strength of the carbon-chlorine bond and the ability of chlorine to leave as a chloride ion. The order of hydrolysis is:

Acyl chlorides > Alkyl chlorides > Halogenoarenes

**1. Acyl chlorides**

Acyl chlorides hydrolyse very rapidly even with cold water.

$$RCOCl + H_2O \longrightarrow RCOOH + HCl$$

This is because the carbonyl group withdraws electrons from the carbon attached to chlorine, making it highly electron deficient and easily attacked by water molecules.

Therefore, acyl chlorides are the most reactive towards hydrolysis.

**2. Alkyl chlorides**

Alkyl chlorides hydrolyse less readily and usually require aqueous alkali and heating.

$$RCl + NaOH \longrightarrow ROH + NaCl$$

The carbon atom attached to chlorine is less positive than in acyl chlorides, so hydrolysis occurs more slowly.

**3. Halogenoarenes**

Halogenoarenes are the least reactive towards hydrolysis.

For example, chlorobenzene does not react with aqueous sodium hydroxide under ordinary conditions.

This is because the lone pair of electrons on chlorine overlaps with the π-electrons of the benzene ring and gives the C – Cl bond partial double bond character.

**As a result:**

The C – Cl bond becomes shorter and stronger.

It is difficult to break the bond.

Hydrolysis does not occur easily.

Therefore, harsh conditions such as high temperature and pressure are required for hydrolysis of halogenoarenes.

Hence, the relative ease of hydrolysis is:

Acyl chlorides > Alkyl chlorides > Halogenoarenes

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 How are aldehydes prepared from primary alcohols?**

**Ans.** Aldehydes are prepared by controlled oxidation of primary alcohols using acidified potassium dichromate or potassium permanganate followed by distillation. Distillation removes the aldehyde immediately after its formation and prevents further oxidation to carboxylic acid.

CamScanner

**Reaction:** $CH_3CH_2OH + [O] \xrightarrow[\text{Distillation}]{K_2Cr_2O_7/H^+} CH_3CHO + H_2O$

Thus, ethanol is converted into ethanal.

**Q.2 How are ketones prepared from secondary alcohols?**

**Ans.** Ketones are prepared by oxidation of secondary alcohols using acidified potassium dichromate under reflux conditions. Unlike aldehydes, ketones generally resist further oxidation under ordinary conditions.

**Reaction:** $CH_3CHOHCH_3 + 2[O] \xrightarrow[\text{Reflux}]{K_2Cr_2O_7/H^+} CH_3COCH_3 + H_2O$

Propan-2-ol is oxidized to propanone.

**Q.3 What is the use of 2,4-DNPH reagent?**

**Ans.** 2,4-Dinitrophenylhydrazine reagent is used to detect the presence of aldehydes and ketones containing the carbonyl group. Carbonyl compounds react with this reagent to form hydrazone derivatives.

**Reaction:** $RCHO + 2,4\text{-}DNPH \longrightarrow \text{Hydrazone} + H_2O$

**Observation:** A yellow or orange precipitate confirms the presence of a carbonyl compound.

**Q.4 How can aldehydes be distinguished from ketones using Tollens' reagent?**

**Ans.** Aldehydes reduce Tollens' reagent whereas ketones do not react with it. During the reaction, silver ions are reduced to metallic silver which deposits on the inner wall of the test tube.

**Reaction:** $RCHO + 2[Ag(NH_3)_2]^+ \longrightarrow RCOO^- + 2Ag$

**Observation:** Formation of a silver mirror confirms the presence of an aldehyde.

**Q.5 How can aldehydes be distinguished from ketones using Fehling's solution?**

**Ans.** Aldehydes reduce Fehling's solution on heating whereas ketones do not give this reaction. Copper(II) ions are reduced to copper(I) oxide during the reaction.

**Reaction:** $RCHO + 2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$

**Observation:** A brick-red precipitate of $Cu_2O$ is produced.

**Q.6 Explain the iodoform test.**

**Ans.** The iodoform test is used to detect the presence of the $CH_3CO-$ group in aldehydes and ketones or the $CH_3CH(OH)-$ group in alcohols. Compounds containing these groups react with iodine in alkaline medium.

**Reaction:** $CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$

**Observation:** A yellow precipitate of iodoform ($CHI_3$) is formed.

**Q.7 How are aldehydes reduced to alcohols?**

**Ans.** Aldehydes are reduced using sodium borohydride or lithium aluminium hydride to form primary alcohols. The carbonyl group is converted into a hydroxyl group during reduction.

**Reaction:** $RCHO + 2[H] \xrightarrow{NaBH_4} RCH_2OHRCHO + 2[H]$

**Q.8 How are ketones reduced to alcohols?**

**Ans.** Ketones are reduced by $NaBH_4$ or $LiAlH_4$ to produce secondary alcohols. The reduction involves conversion of the carbonyl group into an alcohol group.

**Reaction:** $RCOR' + 2[H] \xrightarrow{NaBH_4} RCHOHR'RCOR' + 2[H].$

**Q.9 Describe the reaction of HCN with aldehydes and ketones.**

**Ans.** Hydrogen cyanide undergoes nucleophilic addition with aldehydes and ketones to produce hydroxynitriles. The reaction is usually carried out in the presence of KCN catalyst.

**Reaction:** $CH_3CHO + HCN \xrightarrow{KCN} CH_3CH(OH)CNC$

Ethanal produces 2-hydroxypropanenitrile.

**Q.10 How can carboxylic acids be prepared from primary alcohols?**

**Ans.** Primary alcohols are oxidized using acidified potassium dichromate under reflux conditions to produce carboxylic acids. Reflux ensures complete oxidation of the aldehyde intermediate.



**Reaction:** $CH_3CH_2OH + 2[O] \xrightarrow[\text{Reflux}]{K_2Cr_2O_7/H^+} CH_3COOH + H_2O$

Ethanol is converted into ethanoic acid.

**Q.11 How can carboxylic acids be prepared from nitriles?**

**Ans.** Carboxylic acids are prepared by hydrolysis of nitriles using dilute acids or alkalis followed by acidification. During hydrolysis, the nitrile group (–CN) is converted into a carboxyl group (–COOH).

**Reaction:** $CH_3CN + 2H_2O + HCl \xrightarrow{Heat} CH_3COOH + NH_4Cl$

Thus, ethanenitrile is converted into ethanoic acid.

**Q.12 How can carboxylic acids be prepared from esters?**

**Ans.** Carboxylic acids can be prepared by hydrolysis of esters using dilute acids or dilute alkalis followed by acidification. The ester bond breaks to form an alcohol and a carboxylic acid.

**Reaction:** $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+, Heat} CH_3COOH + C_2H_5OH$

Ethyl ethanoate produces ethanoic acid and ethanol.

**Q.13 How is benzoic acid prepared from methylbenzene?**

**Ans.** Benzoic acid is prepared by oxidation of methylbenzene using hot alkaline potassium permanganate followed by acidification. The entire side chain is oxidized to a carboxyl group.

**Reaction:** $C_6H_5CH_3 \xrightarrow{\text{Heat } KMnO_4/H^+} C_6H_5COOH$

Thus, methylbenzene is converted into benzoic acid.

**Q.14 How are acyl chlorides prepared from carboxylic acids?**

**Ans.** Acyl chlorides are prepared by reacting carboxylic acids with thionyl chloride, phosphorus pentachloride or phosphorus trichloride. In these reactions, the hydroxyl group of the acid is replaced by chlorine.

**Reaction:** $CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$

Ethanoic acid produces ethanoyl chloride.

**Q.15 Describe the reaction of methanoic acid with oxidizing agents.**

**Ans.** Methanoic acid behaves like an aldehyde and can be oxidized by acidified potassium dichromate, potassium permanganate, Tollens' reagent or Fehling's solution. It is ultimately converted into carbon dioxide and water.

**Reaction:** $HCOOH + [O] \longrightarrow CO_2 + H_2O$

This property distinguishes methanoic acid from other carboxylic acids.

**Q.16 Describe the oxidation of ethanedioic acid.**

**Ans.** Ethanedioic acid is readily oxidized by warm acidified potassium permanganate to produce carbon dioxide and water. The purple colour of potassium permanganate disappears during the reaction.

**Reaction:** $HOOCCOOH + [O] \xrightarrow{KMnO_4/H^+} 2CO_2 + H_2O$

This reaction is commonly used in redox titrations.

**Q.17 Describe the reaction of carboxylic acids with reactive metals.**

**Ans.** Carboxylic acids react with active metals such as sodium and magnesium to produce salts and hydrogen gas. This reaction demonstrates the acidic nature of carboxylic acids.

**Reaction:** $2CH_3COOH + 2Na \longrightarrow 2CH_3COONa + H_2$

**Observation:** Effervescence due to hydrogen gas is observed.

**Q.18 Describe the reaction of carboxylic acids with alkalis.**

**Ans.** Carboxylic acids react with alkalis in neutralization reactions to produce salts and water. The reaction is similar to that of mineral acids.

**Reaction:** $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

Ethanoic acid forms sodium ethanoate.

CamScanner

**Q.19 Describe the reaction of carboxylic acids with bicarbonates.**

**Ans.** Carboxylic acids react with bicarbonates to produce salts, water and carbon dioxide gas. The evolution of carbon dioxide causes brisk effervescence.

**Reaction:** $CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + H_2O + CO_2$

**Observation:** Brisk effervescence due to $CO_2$ is observed.

**Q.20 How are esters prepared by esterification?**

**Ans.** Esters are prepared by heating an alcohol with a carboxylic acid in the presence of concentrated sulfuric acid catalyst. The reaction is reversible and is called esterification.

**Reaction:** $CH_3COOH + C_2H_5OH \xrightarrow{\text{conc. } H_2SO_4} CH_3COOC_2H_5 + H_2O$

Ethanoic acid reacts with ethanol to form ethyl ethanoate.

**Q.21 What is the role of concentrated sulfuric acid in esterification?**

**Ans.** Concentrated sulfuric acid acts as both a catalyst and a dehydrating agent during esterification. It increases the reaction rate and removes water formed during the reaction, thereby increasing ester yield.

**Q.22 Describe acid hydrolysis of esters.**

**Ans.** Esters undergo hydrolysis when heated with dilute acids to produce an alcohol and a carboxylic acid. Acid hydrolysis is a reversible reaction.

**Reaction:** $CH_3COOC_2H_5 + H_2O \xrightarrow{dil\ H^+, Heat} CH_3COOH + C_2H_5OH$

Ethyl ethanoate forms ethanol and ethanoic acid.

**Q.23 Describe alkaline hydrolysis of esters.**

**Ans.** Esters react with aqueous alkalis on heating to produce a carboxylate salt and an alcohol. Unlike acid hydrolysis, this reaction is irreversible.

**Reaction:** $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

This reaction is commonly called saponification.

**Q.24 Describe the hydrolysis of acyl chlorides.**

**Ans.** Acyl chlorides react vigorously with water at room temperature to produce carboxylic acids and hydrogen chloride gas. The reaction is highly exothermic.

**Reaction:** $CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$

Ethanoyl chloride forms ethanoic acid.

**Q.25 Describe the reaction of acyl chlorides with alcohols.**

**Ans.** Acyl chlorides react readily with alcohols at room temperature to form esters and hydrogen chloride gas. The reaction proceeds rapidly without the need for a catalyst.

**Reaction:** $CH_3COCl + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + HCl$

Ethanoyl chloride produces ethyl ethanoate.

**Q.26 Describe the reaction of acyl chlorides with phenol.**

**Ans.** Acyl chlorides react with phenol to produce aromatic esters and hydrogen chloride gas. This reaction is commonly used for the preparation of phenyl esters.

**Reaction:** $C_6H_5COCl + C_6H_5OH \longrightarrow C_6H_5COOC_6H_5 + HCl$

Benzoyl chloride reacts with phenol to produce phenyl benzoate.

**Q.27 Describe the reaction of acyl chlorides with ammonia.**

**Ans.** Acyl chlorides react with ammonia at room temperature to produce primary amides and hydrogen chloride gas. The reaction occurs readily due to the high reactivity of acyl chlorides.

**Reaction:** $CH_3COCl + 2NH_3 \longrightarrow CH_3CONH_2 + NH_4Cl$

Ethanoyl chloride forms ethanamide.



**Q.28 Describe the reaction of acyl chlorides with amines.**

**Ans.** Acyl chlorides react with primary or secondary amines to produce substituted amides. Hydrogen chloride is also formed as a by-product.

**Reaction:** $CH_3COCl + CH_3NH_2 \longrightarrow CH_3CONHCH_3 + HCl$

This reaction is widely used in organic synthesis.

**Q.29 Explain the relative acidity of carboxylic acids, phenols and alcohols.**

**Ans.** The acidity order is: Carboxylic Acids > Phenols > Alcohols

Carboxylate ions are highly stabilized by resonance, phenoxide ions are moderately stabilized, while alkoxide ions are not resonance stabilized. Therefore, carboxylic acids are the strongest among them.

**Q.30 Explain the acidity of chloro-substituted carboxylic acids.**

**Ans.** Chloro-substituted carboxylic acids are stronger acids than unsubstituted carboxylic acids because chlorine withdraws electrons through the inductive effect. This stabilizes the carboxylate ion and facilitates the release of $H^+$ ions. **For example:** $ClCH_2COOH > CH_3COOH$

Therefore, chloroethanoic acid is stronger than ethanoic acid.

## SELF-ASSESSMENT

**Total Mark: 30**

**Q.1 Encircle the correct option.** **(1 × 6 = 6)**

(i) **A positive Fehling's test gives:**
(A) Silver mirror (B) Brick-red precipitate of $Cu_2O$
(C) White precipitate (D) Yellow precipitate

(ii) **Methanol does not give the iodoform test because it lacks the:**
(A) –OH group (B) $CH_3CO–$ or equivalent structure
(C) Carbon atom (D) Oxygen atom

(iii) **The oxidizing agent commonly used is:**
(A) NaOH (B) Acidified $K_2Cr_2O_7$ (C) $Br_2$ water (D) $NaCl$

(iv) **Hydrolysis of esters produces:**
(A) Alkene and water (B) Carboxylic acid and alcohol
(C) Ketone and alcohol (D) Ether and water

(v) **The hybridizalion of the oxygen of carbonyl group is:**
(A) sp (B) $sp^2$ (C) $sp^3$ (D) $dsp^2$

(vi) **The mechanism by which acyl chlorides react with alcohols is.**
(A) Addition (B) Elimination (C) Addition-elimination (D) Substitution

**Q.2 Write short answers of the following questions.** **(2 × 8 = 16)**

(i) Draw the structures for the following according to IUPAC system.
i) 2-,methylbutanal ii) pentan-3-one

(ii) Write the equation for the oxidation of propanol with acidified $K_2Cr_2O_7$?

(iii) Methanoic acid is stronger than ethanoic acid. Give reason.

(iv) Explain why ethanoic acid is a stronger acid than ethanol.

(v) Why do phenols not react directly with carboxylic acids to form phenyl esters?

(vi) Predict the products of the following reactions, write the chemical equations.
i) Chlorobenzene and ethanol ii) Propanoyl chloride and phenol

(vii) Methanoic acid can be oxidized but other carboxylic acids cannot. Why?

(viii) Give the reaction of ethanoyl chloride with phenol.

**Q.3 Extensive Questions.** **(4 + 4 = 8)**

(a) How does ethanoic acid reacts with: i) NaOH ii) ethanol iii) $SOCl_2$ iv) $PCl_5$

(b) Give four methods for the preparation of carboxylic acids (Equations Only).

CamScanner

## ENTRANCE TEST MCQs

1. Complete reduction of carboxylic acids to alkanes is carried out with? (ECAT 2013)
(A) HI/P (B) $LiAlH_4$ (C) $NaBH_4$ (D) $H_2$

2. Which of the following compounds, in the form of aqueous solution, on reaction with sodium carbonate will produce carbon dioxide gas? (UHS 2010)
(A) $H_3C-COO-C_2H_5$ (B) $H_5C_2-CO-OH$ (C) $H_5C_2-COO-CH_3$ (D) $H_5C_2-COO-C_2H_5$

3. $CH_3COOH + PCl_5 \longrightarrow$ ? The products of the above reaction are: (UHS 2011)
(A) $CH_3COCl + POCl_3 + HCl$ (B) $CH_3Cl + POCl_3 + HCl$
(C) $CH_3COCl + POCl_2 + HCl$ (D) $CH_3COCl + POCl_3 + H_2$

4. Carboxylic acids are rather hard to reduce, which powerful reducing agent can be used to convert them to the corresponding primary alcohol: (UHS 2015)
(A) $H_2SO_4 / HgSO_4$ (B) $V_2O_5$ (C) $LiAlH_4$ (D) $K_2Cr_2O_7/H_2SO_4$

5. $CH_3COOH + CH_3CH_2OH \longrightarrow CH_3COOC_2H_5 + H_2O$: Which one of the following will act as a catalyst in above reaction? (UHS 2016) (UHS 2018)
(A) $HNO_3$ (B) Acidified potassium dichromate
(C) $H_2SO_4$ (D) $SOCl_2$

6. Which one of the following reaction of carboxylic acid is reversible? (UHS 2016)
(A) Esterification (B) Reaction with $PCl_5$ (C) Salt formation (D) Reaction with $SOCl_2$

7. Which product is obtained by the reaction of carboxylic acid with alcohol? (UHS 2018)
(A) Alkane (B) Ether (C) Aldehyde (D) Ester

8. Complete oxidation of an alcohol gives which of the following: (UHS 2023)
(A) Aldehyde (B) Carboxylic acid (C) Alkane (D) Ketone

9. Compounds having $-C \equiv N$ group are called: (UHS 2017)
(A) Cyano compounds (B) Nitro compounds
(C) Carbon nitrogen molecules (D) Nitriles

10. Formaldehyde reacts with HCN (NaCN + HCl) to give a compound: (UHS 2017)
(A) $H_3C-C(OH)=C(CN)-H$ (B) $H-C(OH)=C(CN)-H$ (C) $H_3C-C(OH)=C(CN)-H_3C$ (D) $H_3C-\overset{O}{\overset{\|}{C}}-CN$

11. Hydrolysis of cyano group by an aqueous acid results into: (UHS 2010)
(A) Carboxylic acid (B) Cyanohydrin (C) Acid Amide (D) Formaldehyde

12. Which one of the following test is given by both aldehyde and ketone? (UHS 2016)
(A) Silver mirror test (B) 2, s 4 DNPH test
(C) Fehling's solution test (D) Benedict's solution test

13. Iodoform test will not be positive with: (UHS 2012)
(A) $H_3C-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ (B) $H_3C-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$
(C) $C_2H_5OH$ (D) $H_3C-\overset{O}{\overset{\|}{C}}-H$

14. Which one of the following is an appropriate indication of positive iodoform test? (UHS 2016)
(A) Formation of $H_2O$ (B) Release of $H_2$ gas (C) Brick red precipitate (D) Yellow crystal

15. Which group gives a yellow precipitate of triodo methane when warmed with alkaline aqueous Iodine? (UHS 2013)
(A) An amide group, $H_3C-\overset{O}{\overset{\|}{C}}-NH_2$ (B) Ethyl ketone group, $H_5C_2-\overset{O}{\overset{\|}{C}}-R$
(C) A primary alcohol group as in propanol $H_3C-CH_2-CH_2-OH$
(D) Methyl ketone group, $H_3C-\overset{O}{\overset{\|}{C}}-R$



16. The structural formula of the product of reaction of acetone with 2, 4-dinitrophenyl hydrazine is: (UHS 2015)
(A) $H_3C-C(=N-NH-C_6H_3(NO_2)-H)-CH_3$ (B) $H_3C-C(=N-NH-C_6H_3(NO_2)-NO_2)-CH_3$
(C) $H_3C-C(=N-NH-C_6H_3(NO_2)-H)-CH_3$ (D) $H_3C-C(=N-NH-C_6H_3(NO_2)-NO_2)-CH_3$

17. Which of the following compound will give Iodoform test on treatment with aqueous $NaOH/I_2$: (UHS 2017)
(A) 3-pentanone (B) propanone (C) Propanal (D) butanal

18. Which one of the following reagents is used to distinguish between aldehydes and ketones? (UHS 2018)
(A) 2, 4-DNPH (B) Tollen's reagent (C) Alkaline iodine (D) Bromine

19. Which one of the following is also called silver mirror test? (UHS 2015)
(A) Fehling's solution test (B) Iodoform test
(C) Tollen's regent (D) Benedict's solution tests

20. The appearance of a silver mirror in Tollen's test indicates the presence of which of the following? (UHS 2023)
(A) A Ketone (B) An acid (C) An aldehyde (D) An alcohol

21. Ethyl butyrate is the ester with the flavour of: (UHS 2014)
(A) Pear (B) Banana (C) Pineapple (D) Apple

### Answers Key

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.A | 2.B | 3.A | 4.C | 5.C | 6.A | 7.D | 8.C | 9. D | 10. C | 11. A | 12. B |
| 13. A | 14. D | 15. D | 16. D | 17. B | 18. B | 19. C | 20. B | 21.C | | | |

CamScanner

FIND US ON
Facebook
LIKE OUR PAGE TODAY
@SCHOLARPUBLICATIONS.PK

SCHOLAR PUBLICATIONS



24 CHAPTER

# ORGANIC NITROGEN COMPOUNDS

## Student Learning Outcomes (SLOs)

[C-12-D-79 to C-12-D-97]

**Part 1: Amines - Fundamentals and Classification**

- Define primary and secondary amines, and explain their basic properties and reactivity.
- Identify the differences between primary and secondary amines in terms of their structure and chemical properties.
- Define the basicity of aqueous solutions of amines.

**Part 2: Synthesis of Amines and Related Nitriles**

- Describe the reactions by which nitriles can be produced: reaction of a halogenoalkane with KCN in ethanol and heat.
- Recall the reactions by which hydroxy nitriles can be produced: the reaction of aldehydes and ketones with HCN, KCN as catalyst, and heat.
- Describe the hydrolysis of nitriles with dilute acid or dilute alkali followed by acidification.
- Describe the preparation methods of primary and secondary amines, including nucleophilic substitution reactions and reduction of nitro compounds.
- Recall the reactions (reagents and conditions) by which primary and secondary amines are produced: a) reaction of halogenoalkanes with $NH_3$ in ethanol heated under pressure; b) reaction of halogenoalkanes with primary amines in ethanol, heated in a sealed tube / under pressure. c) The reduction of amides with $LiAlH_4$; d) The reduction of nitriles with $LiAlH_4$ or $H_2$/Ni.

**Part 3: Phenylamine and Azo Compounds (Aromatic Amines)**

- Explain the relative basicity of aqueous ammonia, ethylamine and phenylamine.
- Explain the properties and reactivity of phenylamine and azo compounds, including their use as dyes and pigments.
- Define the reaction of phenylamine with $Br_{2(aq)}$ at room temperature.
- Define the reaction of phenylamine with $HNO_2$ or $NaNO_2$ and dilute acid below 10°C to produce the diazonium salt; further warming of the diazonium salt with $H_2O$ to give phenol.
- Identify the properties of azo compounds (some examples include: a) Describe the coupling of benzene-diazonium chloride with phenol in $NaOH_{(aq)}$ to form an azo compound; b) Identify the azo group; c) State that azo compounds are often used as dyes; d) Recognize that other azo dyes can be formed via a similar route).

**Part4: Amides and Amino Acids**

- Identify the reactions (reagents and conditions) by which amides are produced (some examples include: a) The reaction between ammonia and an acyl chloride at room temperature; b) The reaction between a primary amine and an acyl chloride at room temperature).
- Describe the reactions of amides (some examples include: a) Hydrolysis with aqueous alkali or aqueous acid; b) The reduction of the CO group in amides with $LiAlH_4$ to form an amine).
- Explain why amides are much weaker bases than amines.
- Describe the acid/base properties of amino acids and the formation of zwitter ions.
- Describe the formation of amide (peptide) bonds between amino acids to give di- and tripeptides.
- Predict the results of electrophoresis on mixtures of amino acids and dipeptides at varying pHs.

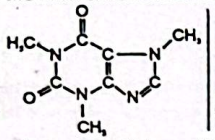
CamScanner

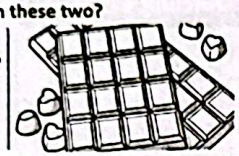
Organic nitrogen compounds are essential to life and the modern world. They form the basis of life in the form of amino acids and nucleotides, making the most vital compounds for life, i.e. proteins. Amines and nitro compounds have the core significance in the dye industry and medicines. Nylon, Kevlar®, and polyurethane are the nitrogen containing polymers, which are found in every home and office. Apart from these, nitrogen compounds are also part of our food, fertilisers, explosives, etc.

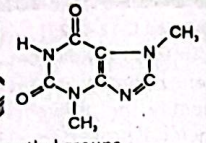
**Interesting Information**

**Caffeine in coffee and theobromine in chocolate both are organic nitrogen compounds. These are active compounds that make our mood happy. The name theobromine originated from its source tree *theobroma cocoo*. What is the difference between these two?**









**Ans.** The primary difference between caffeine and theobromine is number of methyl groups.

- **Caffeine:** 1,3,7-trimethyl × anthine has three methyl groups.
- **Theobromine:** 3,7-dimethyl × anthine has two methyl groups.

## AMINES

Amines are considered as organic derivatives of ammonia, where alkyl or aryl groups may replace one, two or three hydrogen atoms of ammonia.

**Q.1 How are amines classified?** S/Q

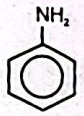
**Ans. Classification:**

The number of hydrogen atoms replaced by alky or aryl groups provides a foundation for the classification of amines as:

i. Primary amines ii. Secondary amines iii. Tertiary amines

- **Primary Amines:** In the primary amines one alky or aryl group is attached to $-NH_2$ group. In IUPAC nomenclature system, amines are referred to as **alkanamines**.

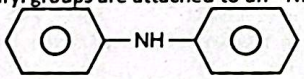
$CH_3 - NH_2$ methanamine; $CH_3 - CH_2 - NH_2$ ethaneamine; $CH_3 - CH_2 - CH_2 - NH_2$ propan-1-amine



phenyl amine (aniline)

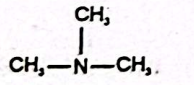
- **Secondary Amines:** In secondary amines, two alky or aryl groups are attached to an $-NH-$ group e.g.,

$CH_3 - NH_2 - CH_3$ N-methylmethanamine; $CH_3 - NH_2 - CH_2 - CH_3$ N-methylethanamine

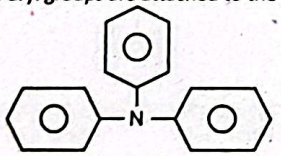


diphenyl amine

- **Tertiary Amines:** In tertiary amines, three alkyl or aryl groups are attached to the same nitrogen atom e.g.,

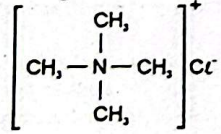


N-N-dimethylmethanamine



triphenylamine

**Note:** Tetra-substituted nitrogen derivatives are also known, and are termed as quaternary ammonium salts e.g.,



tetramethylammonium chloride

It is important to note that the branching takes place at the nitrogen atom, rather than at the carbon atom attached to it, that determines whether an amine is primary, secondary or tertiary. This is not the same as in the case of the alcohols or monohaloalkanes (alkyl halides).



### QUICK CHECK 24.1

a) **Give IUPAC names of the following compounds.**

i) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - CH_2 - CH_2 - NH_2$

**Ans.** 4-methylpentan-1-amine

ii) $CH_3 - CH_2 - \underset{\displaystyle NH_2}{\underset{|}{CH}} - CH_3$

**Ans.** Butan-2-Amine

iii) $CH_3 - CH_2 - CH_2 - CH_2 - NH - CH_2 - CH_3$

**Ans.** N-Ethylbutan-1-amine.

b) **Draw a structure corresponding to each amine.**

i) **2,4 dimethylhexan-3-amine**

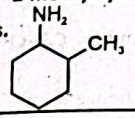
**Ans.** $CH_3 - CH(CH_3) - CH(NH_2) - CH(CH_3) - CH_2 - CH_3$

ii) **N-methylpentan-1-amine**

**Ans.** $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - NH - CH_3$

iii) **2-methylcyclohexan-1-amine**

**Ans.**



iv) **N,N-dimethylethanamine**

**Ans.** $CH_3 - CH_2 - N(CH_3)_2$

## PREPARATION OF AMINES

**Q.2 Give two preparation methods of each of the following.** Exercise D/Q.5

**i) Primary amines ii) Secondary amines**

**Ans.**

### A) Aliphatic Primary Amines

i) **From Halogeno alkanes and Aminonia:** Primary amines can be prepared by the nucleophilic substitution reactions of halogenoalkanes with ammonia. Excess of ethanolic ammonia under pressure is used to avoid the formation of secondary amines or a mixture of products.

In the preparation of amines, if $NH_3$ is in excess, the major product will be primary amine and if halogenoalkane is in excess, tertiary amine is the major product.

$$\underset{\text{bromoethane}}{CH_3 - CH_2 - Br} + \underset{\text{(excess)}}{NH_3} \xrightarrow[\text{Highly pressure}]{\text{ethanol}} \underset{\text{(ethanamine)}}{CH_3 - CH_2 - NH_2} + HBr$$

ii) **By reduction of Alkane Nitriles:** Primary amines are prepared by the reduction of alkanenitriles. For example, propanenitrile is reduced with $H_2/Ni$ or $LiAlH_4$ ro prepare propane-1-amine

$$\underset{\text{propanenitrile}}{CH_3 - CH_2 - C \equiv N} + 4[H] \xrightarrow{LiAlH_4} \underset{\text{propan-1-amine}}{CH_3 - CH_2 - CH_2 - NH_2}$$

iii) **By reduction of Alkanoamide in the presence of $LiAlH_4$:** Alkanamides are reduced by $LiAlH_4$ to form primary amines in good yield since no byproduct is formed in this reaction.

$$\underset{\text{ethanamide}}{CH_3 - \overset{\displaystyle O}{\overset{\|}{C}} - NH_2} + 4[H] \xrightarrow[H_2O/H^+]{LiAlH_4} \underset{\text{ethanamine}}{CH_3 - CH_2 - NH_2} + H_2O$$

This reaction yields the amine with one carbon less than the starting amide.

### B) Aliphatic Secondary Amines

i) Secondary amines can be prepared by the alkylation of primary amines. When a halogenolkane reacts with a primary amine in the presence of ethanol under pressure secondary amine is formed.

$$\underset{\text{bromoethane}}{CH_3 - CH_2 - Br} + CH_3 - NH_2 \xrightarrow{\text{ethanol}} \underset{\text{N-methylethanamine}}{CH_3 - CH_2 - NH - CH_3} + HBr$$

ii) **By the reduction of N-substituted amides:** Secondary amines are also prepared by the reduction of N-substituted amides.

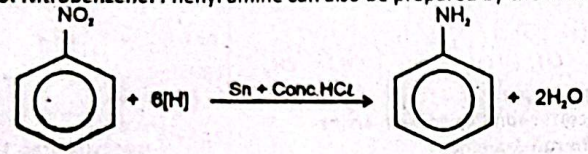
CamScanner

$CH_3-\overset{O}{\overset{\|}{C}}-NH-CH_3 + 4[H] \xrightarrow[H_2O/H^+]{LiAlH_4} CH_3-CH_2-NH-CH_3 + H_2O$

N-methylethanamide → N-methylethanamine

### C) Phenyl Amine (Aromatic Amine)

**By the Reduction of Nitrobenzene:** Phenyl amine can also be prepared by the reduction of nitrobenzene.



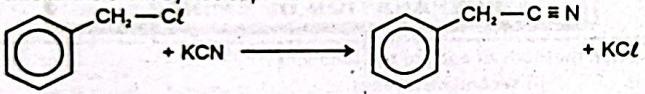

nitrobenzene → phenyl amine (aniline)

## QUICK CHECK 24.2

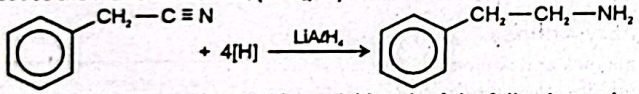
**a) The "feel good factor" in chocolate has been identified as 2-phenylethanamine, $C_6H_5CH_2CH_2NH_2$. Suggest a synthesis of this compound from chloromethylbenzene, $C_6H_5CH_2Cl$.**

**Ans.** It is observed that 2-Phenylethanamine, has one more carbon than chloromethyl benzene.

**Step I:** we can extend the chain by nucleophilic substitution with KCN:




**Step II:** Then reduce the nitrile with $LiAlH_4$ (or $H_2$/Ni):




**b) Provide the reactions of a nitrile and an amide to yield each of the following amines.**

**I)** $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-NH_2$

**Ans. 1. From a Nitrile:**

$CH_3-\underset{\underset{CH_3}{|}}{CH}-C\equiv N \xrightarrow[LiAlH_4]{4[H]} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-NH_2$

2-methylpropanenitrile (isobutyronitrile) → 2-methylpropan-1-amine (isobutylamine)

**2. From an Amide:**

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[LiAlH_4]{4[H]} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-NH_2 + H_2O$

2-methylpropanamide (isobutyramide) → 2-methylpropan-1-amine (isobutylamine)

**II)** $CH_3-CH_2-CH_2-CH_2-NH_2$

**Ans.** To prepare butan-1-amine, $CH_3CH_2CH_2CH_2NH_2$:

**1. From a Nitrile:**

$CH_3-CH_2-CH_2-C\equiv N \xrightarrow[LiAlH_4]{4[H]} CH_3-CH_2-CH_2-CH_2-NH_2$

Butanenitrile (Butyronitrile) → Butan-1-amine (n-Butylamine)



**2. From an Amide:**

$CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[LiAlH_4]{4[H]} CH_3-CH_2-CH_2-CH_2-NH_2 + H_2O$

Butanamide (Butyramide) → Butan-1-amine (n-Butylamine)

## REACTIONS OF AMINES

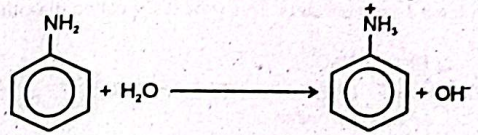
### Basicity of Amines

**Q.3 Describe the relative basicity of aqueous ammonia, ethyl amine and phenyl amine.** Exercise D/Q.4

**Ans.** Amines that are soluble in water form weakly alkaline solutions, just as ammonia does, due to partial reaction with solvent forming $OH^-$ ions.

$\ddot{N}H_3 + H_2O \rightleftharpoons \overset{+}{N}H_4 + OH^-$ ($pK_b \sim 4.75$)

$CH_3-CH_2-\ddot{N}H_2 + H_2O \rightleftharpoons CH_3-CH_2-\overset{+}{N}H_3 + OH^-$ ($pK_b \sim 3.29$)




($pK_b \sim 9.38$)

phenylamine → phenyl ammonium ion

The basicity of amines depends on the availability of the "lone pair" of electrons on the nitrogen atom. Reactions of different amines and ammonia with water show their $pK_b$ values. The Larger the $K_b$ (or smaller the $pK_b$), the stronger is the base.

It is clear that electron-donating alkyl groups attached to the nitrogen atom increase the basicity of amines, whereas the electron-withdrawing groups decrease it.

Basicity is an indicator of the stronger nucleophilic character of a compound, mostly.

- **Ethanamine** is a stronger base than ammonia and methanamine (primary amine). Alkyl amines are stronger bases than ammonia as well.
- **Ammonia** is a stronger base than aromatic amines like **phenyl-amine.**

  **Reason:** In phenylamine, the lone pair of electrons on the nitrogen atom is delocalised over the benzene ring (as shown in Figure). The lone pair on nitrogen is in a p orbital which is parallel to the p orbitals of carbons in benzene. This can overlap with the delocalized π electrons of benzene ring. Therefore, the electron pair is not readily available, making phenylamine less basic.

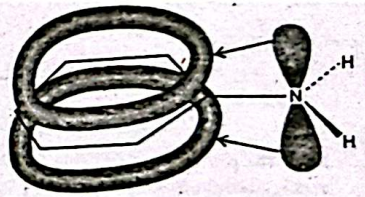



**Figure: Delocalisation of the nitrogen lone pair in phenylamine**

In basicity order:

Ethylamine > Ammonia > Phenyl amine

**Table: The basicity of some amines**

| Sr.No. | Amine | Formula | $K_b$ | $pK_b$ |
|---|---|---|---|---|
| 1. | Ammonia | $NH_3$ | $1.8 \times 10^{-5}$ | 4.75 |
| 2. | Ethanamine | $CH_3-CH_2-NH_2$ | $5.1 \times 10^{-4}$ | 3.29 |
| 3. | Phenylamine (Aniline) |  | $4.2 \times 10^{-10}$ | 9.38 |

CamScanner

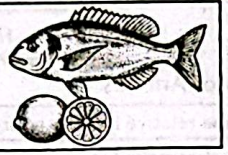
Ammonia and ethanamine react with an acid to form salts because of their basic nature. In this reaction, the N-atom donates an electron pair to form a dative bond with a proton, forming a salt.

$$\ddot{N}H_3 + H^{+\delta} - C\ell^{-\delta} \longrightarrow NH_4^+C\ell^-$$

$$CH_3 - CH_2 - \ddot{N}H_2 + H^{+\delta} - C\ell^{-\delta} \longrightarrow CH_3 - CH_2 - \overset{+}{N}H_3C\ell^-$$

**Did You Know?**

The foul smell from fish is due to N, N-dimethylmathanamine (trimethylamine). When lemon juice is sprinkled on fish, its acid (citric acid) reacts with the amine making it less smelly. The same happens when the fish is processed with vinegar.



## ➲ Distinction between Primary and Secondary Amines

**Q.4 How will you distinguish between primary and secondary amines by chemical test?** L/Q

**Ans.** Primary, secondary and tertiary aliphatic amines are identified and distinguished by reacting them with nitric (III) acid (nitrous acid).

**i.** **Primary amines** react with nitrous acid ($HNO_2$) to form diazonium salts. This process is called diazotization. Only primary amines give diazonium salts.

$$NaNO_2 + HC\ell \longrightarrow HNO_2 + NaC\ell$$

$$CH_3 - CH_2 - NH_2 + HNO_2 + HC\ell \longrightarrow CH_3 - CH_2 - \overset{+}{N} \equiv NC\ell^- + 2H_2O$$

Ethaneamine — ethane diazonium chloride

$$CH_3CH_2 - \overset{+}{N} \equiv NC\ell^- + H_2O \xrightarrow{heat} CH_3CH_2OH + N_2 + HC\ell$$

**ii.** **Secondary amines** form N-nitrosoamines (yellow, neutral, oily liquid) on reaction with nitrous acid.)

$$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{N}} - HNO_2 \xrightarrow{NaNO_2 + HC\ell} CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{N}} - NO + H_2O$$

N-methylethanamine — N-methyl-N-nitrosoethanamine

**iii.** **Tertiary amines** react with nitrous acid to form soluble salts. There is no azo coupling.

$$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{N}}}} + HNO_2 \longrightarrow \left[ CH_3 - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{N}}}} - H \right]^+ NO_2^-$$

N,N-dimethylethanamine — N,N-dimethylethanammonium nitrite (soluble)

**iv.** **Aliphatic primary amines** give diazonium salts which are unstable. However, Aromatic primary amines give stable diazonium salts.

**In short, in the above reaction:**

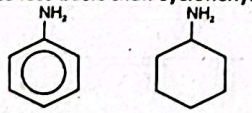
i) Primary amines react with nitrous acid to produce nitrogen gas (seen as bubbles).

ii) Secondary amines react with nitrous acid to produce yellow oily liquid.

iii) Tertiary amines react with nitrous acid to form soluble nitrite salts (simple acid-base salt). There is no visible sign of reaction.

### ☑ QUICK CHECK 24.3

**a) Phenylamine is about a million times less basic than cyclohexylamine. Give reason.**



phenylamine $K_b = 4.2 \times 10^{-10}$ — cyclohexylamine $K_b = 3.3 \times 10^{-4}$



**Ans.** In phenylamine, the nitrogen's lone pair of electrons overlap with π-system of benzene ring thus it delocalizes into the electron pair (conjugated with the π system), which makes it far less available to accept a proton. So it is a weak base in cyclohexylamine the ring is saturated and the lone pair of nitrogen is localized i.e. no ring conjugation and it further pushed towards nitrogen by the electron-donating cyclohexyl group, making it highly available to bind a proton, i.e., cyclohexylamine is a much stronger base.

**b) Which of ethanamine and propan-2-amine is more basic? Explain.**

**Ans.** Propan-2-amine is more basic than ethanamine. A secondary carbon bearing two electron-donating methyl groups (Proppan-2-amine) pushes more electron density (+1 effect) onto the nitrogen than a single ethyl group does in ethanamine, thus increasing the availability of the lone pair the branching close to N also gives a modest steric or inductive boost to base strength in the gas phase.

**c) Show the reaction of propan-2-amine with HCℓ. Name the salt formed.**

**Ans.** $(CH_3)_2CH - NH_2 + HC\ell \longrightarrow (CH_3)_2CH - NH_3^+C\ell^-$. The salt formed is propan-2-ammonium chloride.

**d) Which acid reacts with N, N-dimethylammine in fish when it is treated with vinegar? Write a chemical equation to show this reaction.**

**Ans.** Ethanoic acid (acetic acid, present as 6-10% in vinegar) reacts with the fishy-smelling N, N-dimethylmethanamine (trimethylamine):

$$(CH_3)_3N + CH_3COOH \longrightarrow (CH_3)_3NH^+CH_3COO^-$$

trimethylammonium ethanoate

The non-volatile ammonium ethanoate (salt) formed has little smell, this vinegar removes fishy odours.

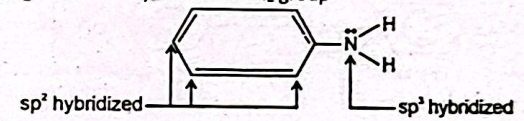
## ➲ Reactions of Phenylamine (Aromatic Amine)

**Q.5 Discuss the two types of reactions of phenyl amines.** L/Q

**OR Discuss in detail the reaction of phenyl amines with: i. Bromine water ii. Nitrous acid**

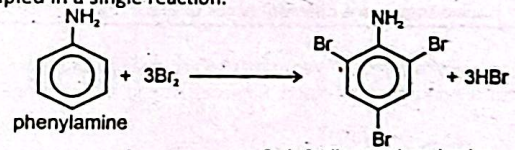
**Ans.** Phenylamine gives two types of reactions:

a) due to benzene ring b) due to $-NH_2$ group




### a) Reaction with Bromine Water:

Amino group ($-NH_2$) is an ortho-para directing group. Therefore, the incoming electrophile attacks at "o" and "p" positions. The presence of the amino group makes benzene ring fairly reactive, especially at these positions. Hence, bromination of phenylamine is faster than benzene, and its two ortho and the para positions, all are occupied in a single reaction.



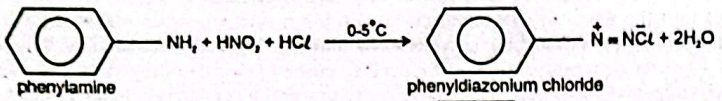

phenylamine — 2, 4, 6-tribromophenylamine (white precipitates)

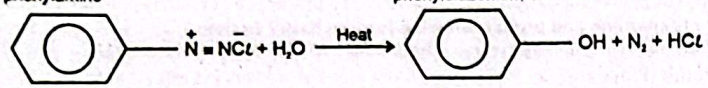
### b) Reaction with Nitrous Acid and Formation of Azo Compounds:

- **Diazotization:** Phenylamine is a primary amine. It reacts with nitrous acid to form phenyldiazonium salt. This reaction is called diazotization. The organic compounds having diazonium ion, $-N^+ \equiv N-$ (diazo group) as a functional group are called diazo compounds. Both aliphatic and aromatic primary amines react with nitrous acid to yield diazonium salts.
- **Precaution:** Nitrous acid is unstable and is prepared in situ by the reaction of sodium nitrite and HCℓ. The reaction mixture is kept between 0-5°C using ice.
- **Reason:** The diazonium salts are unstable and decompose easily, to release nitrogen gas ($N_2$), even at room temperature.

CamScanner

$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$




- **Instability of Alkyl Diazonium Salts:** The alkyl diazonium salts are highly unstable under all conditions and therefore cannot be isolated.
- **Stability of Aryl Diazonium Salts:** The aryl diazonium salts are, however, fairly stable at low temperatures. The extra stability of aromatic diazo compounds compared to aliphatic diazo compounds is due to the delocalization of the positive charge over the aromatic ring.
- Benzene diazonium salts are the important intermediates in the synthesis of many organic compounds.

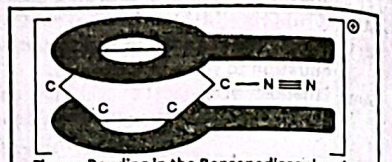


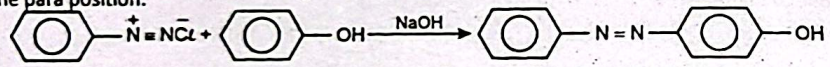
Figure: Bonding in the Benzenediazonium Ion

➢ **Coupling Reactions of Diazonium Compounds:**

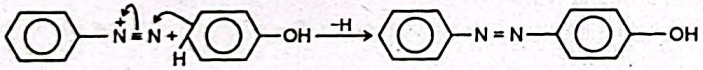
The reactions of aryl diazonium salts with strongly activated aromatic compounds, e.g., phenols and amines, are called **coupling reactions.**

The products of such reactions containing a –N = N– bond are called azo compounds. In the coupling reaction, the positively charged diazonium ion acts as an electrophile. It substitutes into the benzene ring of phenol at the para position.

Coupling with phenol occurs in mild alkaline solution and with aromatic amines in mild acidic conditions.



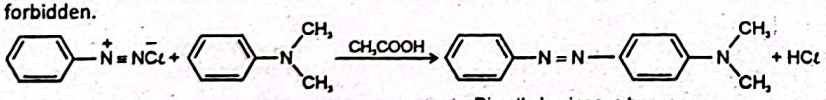

➢ **Mechanism:**




**Q.6 How coupling reaction is used to prepare different types of azo dyes?** LIQ

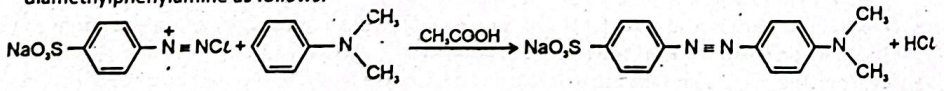
**Ans. Formation of Dyes:**

Coupling reaction can be used to form different types of azo dyes. p-Dimethylaminoazo benzene is called Butter yellow, which was previously used in food. However, due to its carcinogenic nature, its use in food is now forbidden.




**Methyl Orange Indicator:**

Methyl orange is an acid-base indicator and is prepared from diazotized sulfanilic acid and N, N-diamethylphenylamine as follows.






The azo group (Ph – N = N – Ph) in azo dyes is called a **chromophore.** This group is responsible for the intense colour of the dyes ranging from yellow and orange to red, blue and green depending upon what other groups are attached to the benzene rings.



Different food colours often contain azo dyes

## QUICK CHECK 24.4

Azo dyes are the coloured compounds which are prepared by the reaction of diazonium salt of phenylamine and some aryl compound having activated benzene ring.

i) **How will you prepare a dye from phenylamine and 2-methylphenol?**

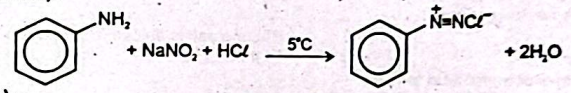
Ans. Diazotise phenylamine below 10°C to give phenyldiazonium chloride, then couple it with 2-methylphenol in mildly alkaline (NaOH) solution; coupling occurs at the position para to the –OH group.

ii) **Give equations stepwise along with reaction conditions.**

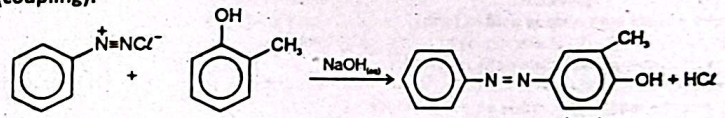
Ans. **Step 1: (Preparation of Nitrous Acid):**

$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$

**Step 2: (diazotization):**




**Step 3: (coupling):**




## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Amines are organic derivatives of:**
   (A) Water (B) Ammonia (C) Methane (D) Benzene
2. **In a primary amine, nitrogen is attached to:**
   (A) One alkyl/aryl group (B) Two alkyl groups (C) Three alkyl groups (D) Four alkyl groups
3. **Secondary amines contain:**
   (A) One alkyl group (B) Two alkyl/aryl groups (C) Three alkyl groups (D) Four alkyl groups
4. **Tertiary amines have:**
   (A) One alkyl group (B) Two alkyl groups (C) Three alkyl/aryl groups (D) Four alkyl groups
5. **Quaternary ammonium compounds are:**
   (A) Neutral molecules (B) Salts (C) Alcohols (D) Ketones
6. **According to IUPAC nomenclature, primary amines are named as:**
   (A) Alkanols (B) Alkanamines (C) Alkanals (D) Alkanoic acids
7. **The classification of amines depends upon:**
   (A) Number of carbon atoms (B) Branching of carbon chain
   (C) Number of alkyl/aryl groups attached to nitrogen (D) Molecular mass
8. **Primary amines are prepared from halogenoalkanes by reaction with:**
   (A) NaOH (B) Ammonia (C) HCl (D) $Br_2$

CamScanner

9. Excess ammonia is used during preparation of primary amines to:
(A) Increase pressure (B) Prevent formation of higher amines
(C) Produce alcohols (D) Increase boiling point

10. Reduction of nitriles gives:
(A) Alcohols (B) Primary amines (C) Ketones (D) Esters

11. A reducing agent used for nitriles is:
(A) $KMnO_4$ (B) $LiAlH_4$ (C) $H_2SO_4$ (D) NaOH

12. Reduction of nitroalkanes produces:
(A) Aldehydes (B) Carboxylic acids (C) Primary amines (D) Esters

13. Reduction of alkanamides yields:
(A) Alcohols (B) Primary amines (C) Ketones (D) Nitriles

14. Hofmann reaction converts an amide into:
(A) Alcohol (B) Amine with one less carbon atom.
(C) Carboxylic acid (D) Ester

15. Secondary amines are prepared by alkylation of:
(A) Alcohols (B) Primary amines (C) Ketones (D) Aldehydes

16. Phenylamine is commonly called:
(A) Benzylamine (B) Aniline (C) Toluidine (D) Nitrobenzene

17. Phenylamine can be prepared by reduction of:
(A) Benzene (B) Nitrobenzene (C) Benzoic acid (D) Phenol

18. Amines dissolved in water produce:
(A) Acidic solution (B) Neutral solution (C) Weakly alkaline solution (D) Strongly acidic solution

19. Basicity of amines depends on the availability of:
(A) π electrons (B) Lone pair on nitrogen (C) Hydrogen atoms (D) Oxygen atom

20. Electron-donating alkyl groups _____ the basicity of amines.
(A) Decrease (B) Increase (C) Eliminate (D) Do not affect

21. Which is the strongest base?
(A) Phenylamine (B) Ammonia (C) Ethanamine (D) Nitrobenzene

22. Phenylamine is less basic because:
(A) It has no nitrogen (B) Lone pair is delocalized into the benzene ring
(C) It contains oxygen (D) It is acidic

23. Amines react with hydrochloric acid to form:
(A) Alcohols (B) Salts (C) Esters (D) Ketones

24. Primary amines react with nitrous acid to form:
(A) Alcohols (B) Diazonium salts (C) Ketones (D) Esters

25. The process of forming diazonium salts is called:
(A) Bromination (B) Esterification (C) Diazotization (D) Hydrogenation

26. Secondary amines react with nitrous acid to produce:
(A) Nitrogen gas (B) Yellow oily liquid (C) Silver mirror (D) White precipitate

27. Tertiary amines react with nitrous acid to form:
(A) Insoluble precipitate (B) Soluble nitrite salts (C) Nitrogen gas (D) Azo dyes

28. Phenylamine undergoes rapid bromination because:
(A) $-NH_2$ activates the benzene ring (B) Bromine is very reactive
(C) It contains chlorine (D) It is acidic

29. Bromination of phenylamine gives:
(A) Monobromophenylamine (B) 2,4,6-Tribromophenylamine
(C) Bromobenzene (D) Phenol

30. A positive bromination test of phenylamine gives:
(A) Blue solution (B) White precipitate (C) Yellow crystals (D) Green solution

31. Nitrous acid is prepared in situ from:
(A) NaOH + HCl (B) $NaNO_2$ + HCl (C) NaCl + $H_2SO_4$ (D) $NH_3$ + HCl

32. Diazotization is carried out below:
(A) 100°C (B) 50°C (C) 10°C (D) 80°C

33. Aromatic diazonium salts are stable:
(A) At high temperature (B) At low temperature (C) In sunlight (D) At boiling point

34. Diazonium salts react with phenols to form:
(A) Ketones (B) Alcohols (C) Azo compounds (D) Esters

35. Coupling reactions involve diazonium salts acting as:
(A) Nucleophiles (B) Electrophiles (C) Bases (D) Oxidizing agents



36. The –N=N– linkage present in azo dyes is called:
(A) Auxochrome (B) Chromophore (C) Carbonyl group (D) Nitro group

37. Butter Yellow is an example of:
(A) Acid-base indicator (B) Azo dye (C) Carboxylic acid (D) Ester

38. Methyl Orange is used as:
(A) Fertilizer (B) Acid-base indicator (C) Solvent (D) Catalyst

39. Coupling of diazonium salts with phenol occurs in:
(A) Strongly acidic medium (B) Mild alkaline medium (C) Neutral medium only (D) Concentrated sulfuric acid

40. Coupling of diazonium salts with aromatic amines occurs in:
(A) Mild acidic medium (B) Strong alkaline medium (C) Neutral water (D) Concentrated NaOH

## ALKANENITRILES

**Q.7 What are alkane nitriles? Give equation for acid and alkanline hydrolysis of $CH_3CN$.** S/Q

**Ans.** The organic compounds containing-CN functional group are called alkanenitriles.

**Examples:** $CH_3 - CN$ ethanenitrile; $CH_3 - CH_2 - CN$ propanenitrile

Alkanenitriles are important compounds in many chemical reactions. Their most important application is their hydrolysis to carboxylic acids (which can occur with both dilute acid and dilute alkali).

### Acid Hydrolysis of Nitriles:

When a nitrile is heated with a dilute acid, such as dilute hydrochloric acid or dilute sulphuric acid, a carboxylic acid is formed.

$$\underset{\text{ethanenitrile}}{CH_3CN_{(aq)}} + 2H_2O_{(\ell)} + HCl_{(aq)} \longrightarrow \underset{\text{ethanoic acid}}{CH_3COOH_{(aq)}} + NH_4Cl_{(aq)}$$

### Alkaline Hydrolysis of Nitriles:

When a nitrile is heated with a dilute sodium hydroxide solution, a salt of carboxylic acid is produced, which on acidification with dilute hydrochloric acid, gives the free carboxylic acid.

$$CH_3CN_{(aq)} + H_2O_{(l)} + NaOH_{(aq)} \longrightarrow CH_3COONa_{(aq)} + NH_{3(g)}$$
$$CH_3COONa_{(aq)} + HCl_{(aq)} \longrightarrow CH_3COOH_{(aq)} + NaCl_{(aq)}$$

## AMIDES

**Q.8 What are amides? Give any two methods of preparation.** UQ

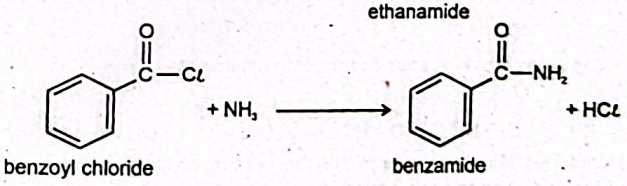
**Ans.** Amides contain the functional group $-\overset{O}{\overset{\|}{C}}-NH_2$. As they are prepared from carboxylic acids so they are sometimes called as "acid amides".

### Preparation of Amides:

Amides can be prepared by the following methods.

**1. By the Reaction of Acyl chlorides with Ammonia:**

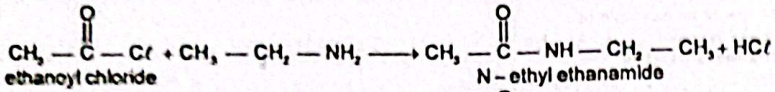
$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + NH_3 \longrightarrow \underset{\text{ethanamide}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2} + HCl$$

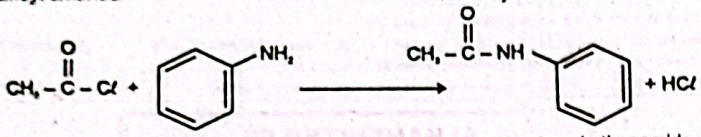



benzoyl chloride benzamide

CamScanner

**2. By the Reaction of Acyl chlorides with Primary Amines:**




**Note:** In the above two methods, all the reactions take place at room temperature, releasing white fumes of hydrogen chloride (HCℓ). The HCℓ produced reacts with another molecule of ammonia or amine to form a salt.

$$R-NH_2 + HC\ell \longrightarrow R-\overset{+}{N}H_3C\ell^-$$

$$NH_3 + HC\ell \longrightarrow \overset{+}{N}H_4C\ell^-$$

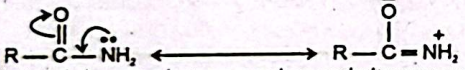
Therefore, an excess of ammonia or amine is used to ensure complete reaction.

> All amides except methanamide, which is a liquid, are solids. They have sharp melting point. They have high boiling points because of strong intermolecular hydrogen bonding. In N-substituted amides, the melting and boiling points decrease as the sites for hydrogen bonding, minimize (diminish) with increasing number of alkyl substituents.

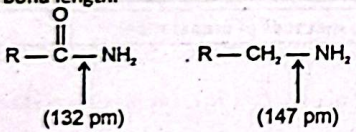
**Q.9 Why amides are less basic than aliphatic amines?** S/Q

**Ans. Basic Properties of Amides:**

Amides are less basic than aliphatic amines. Unlike amines, amides form neutral solutions in water. They exhibit resonance where the lone pair on nitrogen participates in delocalization with oxygen of carbonyl group. This reduces the availability of electrons on nitrogen, thereby decreasing the basicity.



The introduction of double bond character between carbon and nitrogen reduces the C – N bond length to less than the usual C – N single bond length.




**Reactions of Amides:**

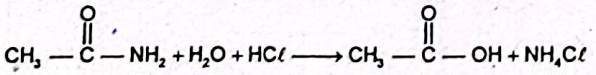
Amides are the **least reactive** of all acid derivatives, because the lone pair of nitrogen is delocalized over the oxygen of carbonyl group, thus decreasing the electrophilic power (+δ charge) of the carbonyl carbon. The reactions of amides are generally slow and require prolonged heating or catalysts (acid or base) for them to take place. Some of them are given as under:

**Q.10 Discuss: I. Hydrolysis of amides II. Reduction of amides** U/Q

**Ans.**

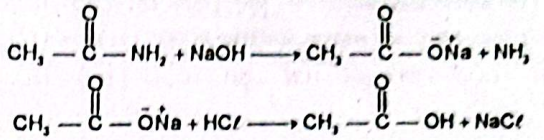
**1. Hydrolysis:**

Unsubstituted amides yield carboxylic acids and the ammonium salts.



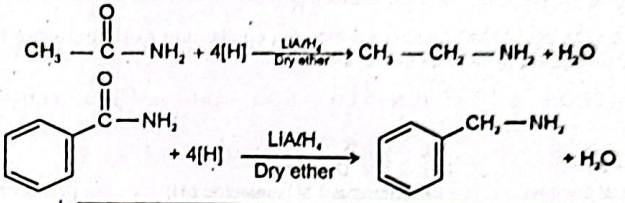
In the base-catalyzed reaction, the products are the salts of carboxylic acids and ammonia. The free carboxylic acid is obtained when this salt is treated with dilute hydrochloric acid.





**2. Reduction of Amides:**

Amides are reduced to primary amines with lithium tetrahydridoaluminate (III) in dry ethoxyethane(ether).



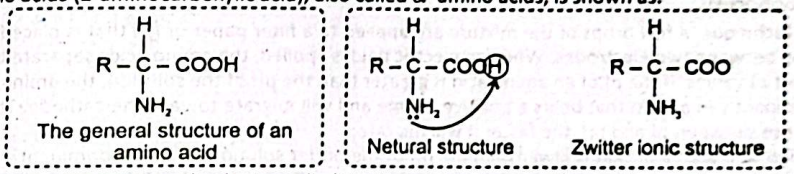

## AMINO ACIDS

**Q.11 What are amino acids and zwitter ion?** S/Q

**Ans.** Amino acids are an important group of compounds that contain:

- the basic amino group ($-NH_2$), and
- the acidic carboxylic acid group (–COOH).

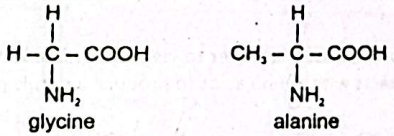
This makes amino acids amphoteric, as they can behave as both an acid and a base. The general structure of amino acids (2-aminocarboxylic acid), also called α -amino acids, is shown as.




An α-amino acid exists as a dipolar ion called Zwitter ion, having a positive and a negative end within the same molecule. In the formation of a Zwitter ion, the proton goes from the carboxyl group to the amino group. The dipolar structure is also called the internal salt. The R group is the side chain that varies between amino acids.

- **Glycine:** The simplest amino acid is glycine (aminoethanoic acid) in which R is a hydrogen atom.
- **Alanine:** Alanine (2-amino propanoic acid) is an amino acid in which the R group is the methyl group, $-CH_3$. Where, R may or may not contain a functional group (FG). If R contains a carboxylic group, the amino acid will be acidic, whereas, if it has an amino group, it will be basic. If there is no FG in R, the amino acid will be neutral in nature.

> Except glycine, all α-amino acids are chiral.




> Out of 20 α-amino acids, 9 are essential (body cannot synthesis) and others are non-essential (body can synthesis) amino acids.

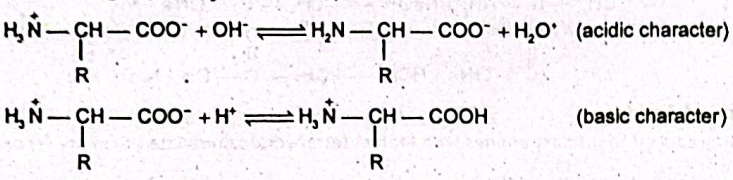
### Acidic and Basic Properties of Amino Acids

**Q.12 Discuss acidic and basic properties of amino acids.** U/Q

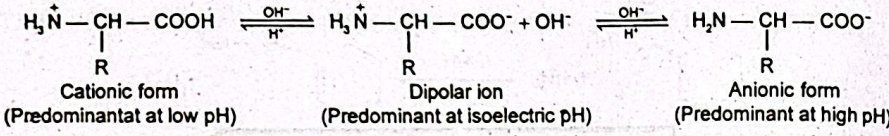
**Ans.** Amino acids are amphoteric in nature, i.e., they show both acidic and basic properties. However, they are less acidic than most carboxylic acids, and are less basic than most amines.

CamScanner

- The acidic part of the amino acid molecule is $-NH_3^+$, group, not $-COO^-$ group, and the basic part is $-COO^-$ group, not $-NH_2$, group. $RNH_3^+$ is a weaker acid than RCOOH, as shown below:




- Depending on the pH of the aqueous solution, an equilibrium exists between the dipolar ion and the cationic and an anionic form of an amino acid.




- **Isoelectric Point:** For each amino acid, there is specific pH at which the concentration of the zwitter ion reaches its maximum value. This pH is called the **isoelectric point (pI)**, and each amino acid has its own unique pI.

## ➲ Separation of Amino Acids via Electrophoresis

**Q.13 Write a note on electrophoresis.** Exercise D/Q.6

**Ans.** Amino acids can be separated from each other by a variety of techniques. One method, called **electrophoresis**, is used to separate amino acids in a mixture based on their charge.

### ➢ Electrophoresis:

In this technique, a few drops of the mixture are applied to a filter paper or gel that is placed in a buffered solution between two electrodes. When an electric field is applied, the amino acids separate based on their different **pI** values. If the **pI** of an amino acid is greater than the pH of the solution, the amino acid will exist predominantly in a form that bears a positive charge and will migrate toward the cathode. The greater the difference between pI and pH, the faster it will migrate.

An amino acid with a pI that is lower than the pH of the buffer solution exists predominantly in a form that bears a negative charge and will migrate toward the anode. The greater the difference between pI and pH, the faster it will migrate (Figure).

If two amino acids have very similar pI values (e.g., glycine and leucine), the amino acid with the larger molecular weight will move more slowly, because the charge has to carry a greater mass.

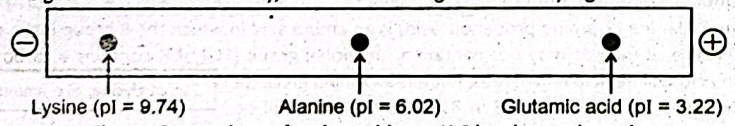
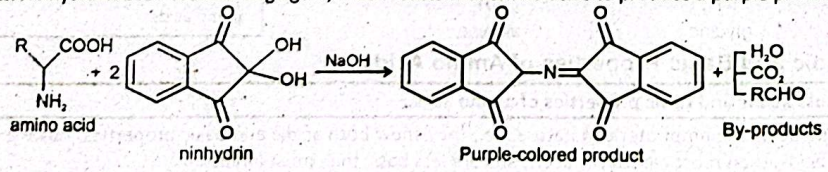



Figure: Separations of amino acids at pH 6 by electrophoresis

### ➢ Detection of Amino Acids by Locating Agent:

Amino acids are colorless, so a detection technique is necessary in order to visualize the location of the various spots. Ninhydrin is used as a locating agent, which reacts with amino acids to produce a purple product.






It is used just as an analytical method for determining the number of amino acids in a mixture. In order to actually separate an entire mixture of amino acids, other laboratory techniques are used, such as column chromatography.

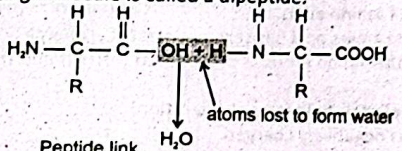
### ➢ Limitation:

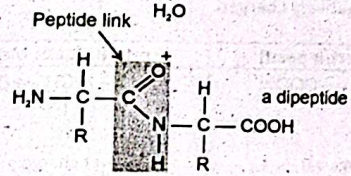
Electrophoresis cannot be used to separate large quantities of amino acids.

## ➲ Peptides

**Q.14 What are dipeptides? Show peptide linkage.** S/Q

**Ans. Dipeptide:** Amino acid molecules can also react with each other. The acidic –COOH group in one amino acid molecule reacts with the basic-NH, group in another molecule. When two amino acids react together, the resulting molecule is called a dipeptide.




- **Isoelectric point:** the pH value at which there is no overall charge on a particular amino acid in its aqueous solution.
- **tripeptide:** a compound formed from the condensation reaction between three amino acids.
- **polypeptide:** a compound formed from the condensation between a large number of amino acids.

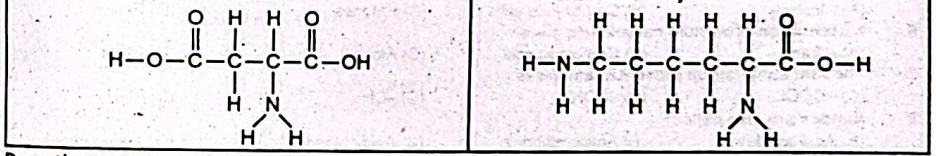
- Note that the shaded area is the amide bond between the two amino acids.
- **Peptide bond or Link:** An amide bond between two amino acid molecules is also called a **peptide bond or peptide link**. This is a condensation reaction, because a small molecule, e.g., water is eliminated when the reactant molecules join together.

### ☑ QUICK CHECK 24.5

The R groups in the amino acids aspartic acid and lysine are $(-CH_2 - COOH)$ and $(-CH_2 - (CH_2)_3NH_2)$ respectively.

I) **Draw the displayed formulae of these amino acid.**

**Ans.** Displayed formulae (general R — CH($NH_2$) — COOH skeleton with the given R group):




ii) **Draw the structures of their Zwitterions.**

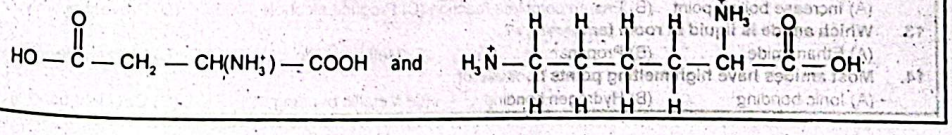
**Ans. Zwitterions:**

**Aspartic acid:** $-{}^-OOC-CH_2-CH(NH_3^+)-COO^-$

**Lysine:** $H_3N^+-(CH_2)_4-CH(NH_3^+)-COO^-$

iii) **Draw the structures of their ions in acidic conditions.**

**Ans. In Acidic Conditions:**



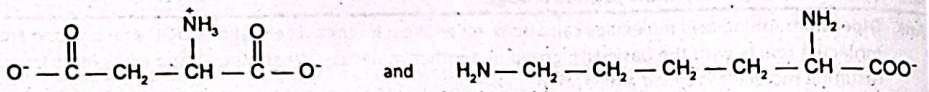
**iv) Draw the structures of their ions in basic conditions.**

**Ans.** In basic conditions (high pH), all $-NH_3^+$ groups lose a proton to form $-NH_2$ and all $-COOH$ groups also lose $H^+$ to form $-COO^-$. Thus, both amino acids carry an overall negative charge (anionic form).

The isoelectric point (pI) is the pH at which a particular amino acid exists predominantly as the neutral, dipolar zwitter ion (net charge zero). Because aspartic acid has an extra acidic side-chain $-COOH$, its pI is low (acidic amino acid); because lysine has an extra basic side-chain $-NH_2$, its π is high (basic amino acid).

**In Basic Conditions:**

**Aspartic acid** **Glycine**



and



**v) Discuss what we mean by the isoelectric point of amino acids.**

**Ans.**
- The isoelectric point (pI) is the pH at which an amino acid has zero net electrical charge.
- **At this pH, it exists mainly as a zwitterion:** the amino group is protonated ($-NH^+_3$) and the carboxyl group is deprotonated ($-COO^-$).
- At pI, the amino acid does not migrate in an electric field (no net migration).
- Below pI it is positively charged; above pI it is negatively charged.

**Example: General amino acid (R – CH(NH₂)COOH)**

| pH < pI (Acidic Medium) | pH = pI (Isoelectric point) | pH > pI (Basic Medium) |
|---|---|---|
| $H_3N^+ - CH(R) - COOH$ | $H_3N^+ - CH(R) - COO^-$ | $H_2N - CH(R) - COO^-$ |
| Net charge = +1 (Cation) | Net charge = 0 (Zwitterion) | Net charge = −1 (Anion) |

## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Organic compounds containing the –CN functional group are called:**
(A) Amines (B) Alkanenitriles (C) Amides (D) Esters
2. **The functional group present in nitriles is:**
(A) –COOH (B) $-NH_2$ (C) –CN (D) –CHO
3. **Acid hydrolysis of nitriles produces:**
(A) Alcohols (B) Carboxylic acids (C) Ketones (D) Ethers
4. **During acid hydrolysis of nitriles, the nitrogen-containing product is:**
(A) $NH_3$ (B) $NH_4Cl$ (C) $NO_2$ (D) $N_2$
5. **Alkaline hydrolysis of nitriles initially forms:**
(A) Alcohols (B) Carboxylate salts (C) Ketones (D) Esters
6. **Acidification of sodium carboxylate gives:**
(A) Alkane (B) Carboxylic acid (C) Alcohol (D) Ether
7. **The functional group present in amides is:**
(A) $-COCl$ (B) $-CONH_2$ (C) –CN (D) $-NH_2$
8. **Amides are also called:**
(A) Acid amides (B) Amino alcohols (C) Acid chlorides (D) Alkyl amines
9. **Amides are prepared by reacting acyl chlorides with:**
(A) Ammonia (B) Primary amines (C) Both A and B (D) Alcohols
10. **Preparation of amides from acyl chlorides occurs at:**
(A) 100°C (B) Room temperature (C) 250°C (D) 0°C
11. **White fumes produced during amide formation are due to:**
(A) $NH_3$ (B) $H_2$ (C) HCl (D) $CO_2$
12. **Excess ammonia is used during amide preparation to:**
(A) Increase boiling point (B) Ensure complete reaction (C) Produce alcohols (D) Prevent hydrolysis
13. **Which amide is liquid at room temperature?**
(A) Ethanamide (B) Propanamide (C) Methanamide (D) Benzamide
14. **Most amides have high melting points because of:**
(A) Ionic bonding (B) Hydrogen bonding (C) Metallic bonding (D) Covalent bonding



15. **Compared with amines, amides are:**
(A) More basic (B) Less basic (C) Strong acids (D) Neutral hydrocarbons
16. **The lower basicity of amides is due to:**
(A) Presence of chlorine (B) Resonance involving the nitrogen lone pair
(C) Large molecular size (D) Absence of hydrogen
17. **Amides are the _____ reactive acid derivatives.**
(A) Most (B) Least (C) Equally (D) Highly unstable
18. **Hydrolysis of unsubstituted amides gives:**
(A) Alcohol and $NH_3$ (B) Carboxylic acid and ammonium salt
(C) Ketone and water (D) Ester and $NH_3$
19. **Reduction of amides with $LiAlH_4$ produces:**
(A) Alcohols (B) Primary amines (C) Carboxylic acids (D) Ketones
20. **Amino acids contain:**
(A) Only –COOH (B) Only $-NH_2$ (C) Both $-NH_2$ and –COOH (D) –OH and –CN
21. **Amino acids are described as amphoteric because they:**
(A) Are hydrocarbons (B) Act as both acids and bases
(C) Are only acidic (D) Are only basic
22. **The general structure of amino acids is:**
(A) R–CHO (B) R–CH($NH_2$)–COOH (C) R–COOH (D) R–OH
23. **The simplest amino acid is:**
(A) Alanine (B) Glycine (C) Valine (D) Leucine
24. **In alanine, the R group is:**
(A) H (B) $CH_3$ (C) $C_2H_5$ (D) COOH
25. **Except glycine, all α-amino acids are:**
(A) Aromatic (B) Chiral (C) Unsaturated (D) Neutral
26. **A dipolar ion of an amino acid is called:**
(A) Carbocation (B) Zwitter ion (C) Free radical (D) Carbanion
27. **In a zwitter ion, the amino group exists as:**
(A) $-NH_2$ (B) $-NH_3^+$ (C) $-NO_2$ (D) $-N_2^+$
28. **The carboxyl group in a zwitter ion exists as:**
(A) –COOH (B) $-COO^-$ (C) –CHO (D) –CN
29. **The pH at which the concentration of zwitter ions is maximum is called:**
(A) $pK_a$ (B) $pK_b$ (C) Isoelectric point (D) Neutral point
30. **At the isoelectric point, an amino acid has:**
(A) Positive charge only (B) Negative charge only (C) No overall charge (D) Double positive charge
31. **Electrophoresis separates amino acids based on differences in their:**
(A) Colour (B) Boiling point (C) Charge (pI) (D) Solubility only
32. **If pI is greater than the solution pH, the amino acid migrates toward the:**
(A) Anode (B) Cathode (C) Salt bridge (D) Positive electrode only
33. **If pI is lower than the solution pH, the amino acid moves toward the:**
(A) Cathode (B) Anode (C) Neutral electrode (D) Filter paper
34. **Amino acids are detected after electrophoresis using:**
(A) Bromine water (B) Ninhydrin (C) Fehling's solution (D) Tollen's reagent
35. **Ninhydrin produces a:**
(A) Yellow precipitate (B) Purple-coloured product (C) Silver mirror (D) Brick-red precipitate
36. **Electrophoresis is mainly used as:**
(A) An industrial process (B) An analytical technique
(C) A purification method for tons of material (D) A combustion method
37. **A peptide bond is formed between:**
(A) Two alcohol molecules (B) Amino and carboxyl groups of amino acids
(C) Two carboxylic acids (D) Two amines
38. **Formation of peptides is a:**
(A) Substitution reaction (B) Addition reaction (C) Condensation reaction (D) Oxidation reaction
39. **A compound formed from two amino acids is called:**
(A) Tripeptide (B) Dipeptide (C) Polypeptide (D) Protein
40. **The linkage joining two amino acids is called the:**
(A) Ether linkage (B) Ester linkage (C) Peptide (amide) bond (D) Glycosidic bond

CamScanner

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

**BLOCK # 01**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. A | 3. B | 4. C | 5. B | 6. B | 7. C | 8. B | 9. B | 10. B | 11. B | 12. C | 13. B | 14. B | 15. B |
| 16. B | 17. B | 18. C | 19. B | 20. B | 21. C | 22. B | 23. B | 24. B | 25. C | 26. B | 27. B | 28. A | 29. B | 30. B |
| 31. B | 32. C | 33. B | 34. C | 35. B | 36. B | 37. B | 38. B | 39. B | 40. A | | | | | |

**BLOCK # 02**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. B | 4. B | 5. B | 6. B | 7. B | 8. A | 9. C | 10. B | 11. C | 12. B | 13. C | 14. B | 15. B |
| 16. B | 17. B | 18. B | 19. B | 20. C | 21. B | 22. B | 23. B | 24. B | 25. B | 26. B | 27. B | 28. B | 29. C | 30. C |
| 31. C | 32. B | 33. B | 34. B | 35. B | 36 B | 37. B | 38. C | 39. B | 40. C | | | | | |

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. **Primary, secondary and tertiary amine are regarded as:**
a) Tautomers b) Metamers
c) Both metamers and tautomers d) Position isomers

II. **General formula for secondary amines is:**
a) $RNH_2$ b) RNHR c) $R_3N$ d) $RCONH_2$

III. **Which one of the following bases is the strongest one?**
a) Ammonia b) Ethyl amine c) Phenyl amine d) Diethyl amine

IV. **Acid hydrolysis of nitriles produces:**
a) Alcohols b) Ketones c) Carboxylic acids d) Esters

V. **Phenylamine reacts with aqueous $Br_2$ to form:**
a) Phenol b) 2,4,6-Tribromophenylamine
c) An azo compound d) None of these

**Benzenediazonium chloride reacts with phenol in NaOH to form:**
a) Phenyl hydrazine b) Nitro compound c) Azo compound d) Alcohol

VII. **What is the structure of an azo compound:**
a) $R_1-N=N-R_2$ b) $R_1-NH-R_2$ c) $R-O-R$ d) $R-C\equiv N$

VIII. **When diazonium salt is heated with water, the gas evolved is:**
a) Nitrogen b) Ammonia c) Nitric oxide d) Nitrogen dioxide

IX. **An aqueous solution of glycine is neutral because of the formation of:**
a) Carbanion b) Carbocation c) Zwitterion d) Free radical

X. **Which amines are produced by the reduction of unsubstituted amides?**
a) Primary b) Secondary c) Tertiary d) None of these

### Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | b | Metamers | p°, s° and t° - amine have same molecular formula but differ in the distribution of alkyl groups around the N- atoms. Thus they are considered as metamers. |
| II. | b | RNHR | General formulas of: $RNH_2$ = p°- amine, $R_3N$ = t° - amine, $RCONH_2$ = amide |
| III. | d | Diethylamine | Ethyl groups are electron-donating (+I effect) and increase the electron density on nitrogen it makes the lone pair more available for protonation. Order of basicity is: Diethylamine > Ethylamine > $NH_3$ > Phenylamine |



| | | | |
|---|---|---|---|
| IV. | c | Carboxylic acids | $CH_3CN_{(aq)} + 2H_2O_{(\ell)} + HCl_{(aq)} \longrightarrow CH_3COOH_{(aq)} + NH_4Cl_{(aq)}$ ethanenitrile → ethanoic acid |
| V. | b | 2,4,6-tribromophenylamine | $-NH_2$ group activates benzene ring. It directs substitution to occur at ortho and para positions giving 2,4,6-tribromophenylamine. |
| VI. | c | Azo compound | Benzenediazonium chloride reacts with phenol in alkaline medium by coupling reaction and forms an azo compound or dye. |
| VII. | a | $R_1-N=N-R_2$ | $-N=N-$ (azo) linkage is the functional group of azo compounds. |
| VIII. | a | Nitrogen | A diazonium salt when heated with water, decomposes and forms phenol and nitrogen gas. |
| IX. | c | Zwitterion | Glycine exists mainly as a zwitterion in aqueous solution. It contains a positive ($-NH_3^+$) and a negative ($-COO^-$) charge in the same molecule. |
| X. | a | Primary | Reduction of unsubstituted amides with $LiAlH_4$ produces primary amine. $R-CONH_2 + 4[H] \rightarrow R-CH_2-NH_2$ |

## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) Give two preparations of phenyl amine**

Ans. **1. Ammonolysis of chlorobenzene:**

$$C_6H_5Cl + 2NH_3 \xrightarrow{Cu_2O,\ 250°C,\ 50\ atm} C_6H_5NH_2 + NH_4Cl$$

**2. Reduction of nitrobenzene:**

$$C_6H_5NO_2 + 6[H] \xrightarrow{Sn/conc.\ HCl} C_6H_5NH_2 + 2H_2O$$

**b) Give two preparations of secondary amines.**

Ans. **1.** Alkylation of a primary amine with a halogenoalkane in ethanol:

$$CH_3-CH_2-Br + CH_3-NH_2 \xrightarrow[Pressure]{Ethanol} CH_3-CH_2NH-CH_3 + HBr$$

N-methylethanamine

**2.** Reduction of an N-substituted amide with $H_2$/Ni or Pt:

$$CH_3-\overset{O}{\overset{\|}{C}}-NH-CH_3 + 2H_2 \xrightarrow{Ni/Pt} CH_3-CH_2-NH-CH_3 + H_2O$$

N – methylethanamide → N – methylethanamine

This process reduces $>C=O$ to $-CH_2-$

**c) What is the chromophore in azo dyes? What is its function in dyes?**

Ans. The chromophore is the **azo group, –N=N–.** It contains delocalized π electrons that absorb light in the visible region. This absorption is responsible for the intense colour of azo dyes; changing the groups attached to the benzene rings around it shifts the colour from yellow/orange to red, blue or green.

**d) Why amides are less basic than ammonia.**

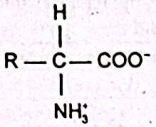
Ans. In amides $R-\overset{O}{\overset{\|}{C}}-NH_2$, the lone pair on nitrogen is delocalized by resonance into the carbonyl group (C=O), spreading electrons density away from nitrogen. This makes the lone pair far less available to accept a proton than the fully localized lone pair on the nitrogen of ammonia, so amides are much weaker bases, almost neutral while $NH_3$ is a moderated base.

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \longleftrightarrow R-\overset{O^-}{\overset{|}{C}}=\overset{+}{N}H_2$$

CamScanner

**e) What is zwitter ion?**

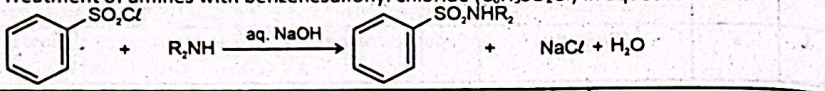
**Ans.** An ion that has positive and negative charges present within the molecule is called zwitter ion. In the formation of zwitter ion, the proton ($H^+$) goes from the carboxyl group to amino group.



**Zwitter Ionic Sturcture**

**f) Differentiate between primary, secondary & tertiary amines by a chemical test.**

**Ans. Hinsberg Test:** Treatment of amines with benzenesulfonyl chloride ($C_6H_5SO_2Cl$) in aqueous NaOH.



| Types of Amine | Reaction with $C_6H_5SO_2Cl$ in aq. NaOH | Solubility in aq. NaOH | On acidification (dil. HCl) |
|---|---|---|---|
| 1. Primary amine $RNH_2$ (e.g., $C_2H_5NH_2$) | $C_6H_5SO_2Cl + RNH_2 + NaOH \longrightarrow C_6H_5SO_2NHR + NaCl + H_2O$ (Sulfonamide) | Sulfonamide has an acidic N – H and forms its sodium salt; hence it dissolves in eq. NaOH | On acidification, the sulfonamide is protonated and becomes insoluble (precipitates). |
| 2. Secondary amine $R_2NH$ (e.g., $(C_2H_5)_2NH$) | $C_6H_5SO_2Cl + R_2NH + NaOH \longrightarrow C_6H_5SO_2NR_2 + NaCl + H_2O$ (N, N-substituted Sulfonamide) | No acidic N – H; does not form a salt, so it remains insoluble in aq. NaOH. | No change; remains insoluble. |
| 3. Tertiary amine $R_3N$ (e.g., $(C_2H_5)_3N$) | No sulfonamide is formed. | Remains insoluble in aq. NaOH. | Dissolves in dilute HCl by forming ammonium salt. $R_3N + HCl \rightarrow [R_3NH]^+Cl^-$ (Soluble) |

**g) Write names and structures of four isomeric amines having the molecular formula $C_3H_9N$.**

**Ans.** (1) $CH_3CH_2CH_2NH_2$ — porpan-1-amine (2) $(CH_3)_2CHNH_2$ — propan-2-amine
(3) $CH_3CH_2NHCH_3$ — N-methylethanamine (4) $(CH_3)_3N$ — N, N-dimethylmethanamine.

**h) How will you synthesize ethanal from ethanenitrile?**

**Ans.** Ethenenitrile (acetonitrile) can be partially reduced by Stephen reduction.

$$\underset{\text{Ethanenitrile (Acetonitrile)}}{CH_3C \equiv N} \xrightarrow{SnCl_2/HCl} \underset{\text{Ethan iminium chloride (Imine hydrochloride)}}{CH_3CH = NH \cdot HCl} \xrightarrow{H_2O} \underset{\text{Ethanal (Acetaldehyde)}}{CH_3CHO}$$

**Explanation:**

1. **Partial reduction (Stephen reduction):**
Ethanenitrile is reduced with staninous chloride in dry HCl to give the iminium chloride (imine hydrochloride).

$$\underset{\text{Ethanenitrile}}{CH_3C \equiv N} \xrightarrow[(dry)]{SnCl_2/HCl} \underset{\text{Ethan iminium chloride}}{CH_3CH = NH \cdot HCl} \quad \text{(Iminium salt)}$$

2. **Hydrolysis of Iminium Salt:**
On treatment with water, the iminium salt is hydrolyzed to give ethanol.

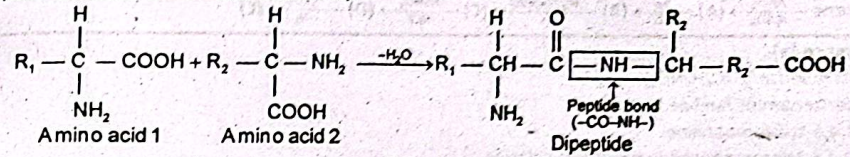
$$\underset{\text{Ethan iminium chloride}}{CH_3C \equiv NH \cdot HCl} \xrightarrow{H_2O} \underset{\text{Ethanal (Acetaldehyde)}}{CH_3CHO} + NH_4Cl$$



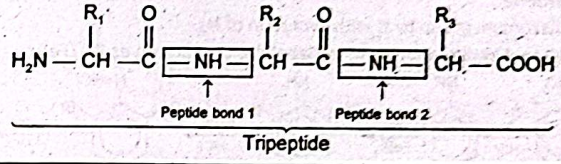
**i) Define peptide bond. How many peptide bonds are there in a tripeptide?**

**Ans.** A peptide bond is the amide linkage –CO – NH– formed when the –COOH group of one amino acid reacts with the $–NH_2$ group of another with loss of $H_2O$. A tripeptide contains two peptide bonds.

**Peptide Bond (Structure and Formation):**



**Structure of a Tripeptide:**



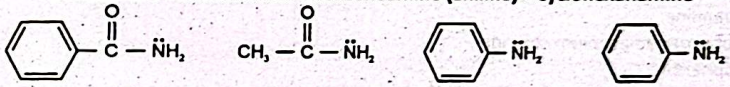
**j) Give all the dipeptides that could possibly be synthesized from glycine (Gly), alanine (Ala).**

**Ans.** All the possible dipeptides that can be formed using glycine (Gly) and alanine (Ala) are as follow:
(i) Gly – Gly (ii) Gly – Ala (iii) Ala – Gly (iv) Ala – Ala

**k) Arrange cyclohexanamine, benzenamine, benzamide and ethanamide in the increasing order of their basic strength. Justify the order as well.**

**Ans. Increasing basic strength:**

**benzamide < ethanamide < benzeneamine (aniline) < cyclohexanamine**

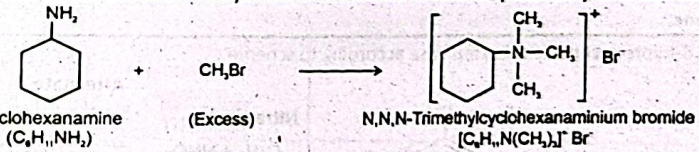


| Benzamide | Ethanamide | Benzenamide (Aniline) | Cyclohexanamine |
|---|---|---|---|
| $pK_b = 14 – 15$ | $pK_b = 14.1 – 14.5$ | $pK_b = 9.38$ | $pK_b = 3.3 – 3.4$ |

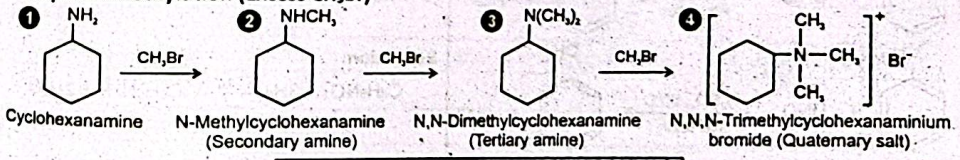
**Reason:** in amides, the N lone pair is strongly delocalized into the C=O group, making them very weak bases; benzamide is further weakened by the benzoyl group. In aniline, the lone pair is delocalized into the benzene ring, so it is less available than in an aliphatic amine. In cyclohexanamine, the lone pair is localized and the alkyl group donates electron density, so it is the strongest base of the four.

**l) Give the chemical equation for the reaction between cyclohexanamine and excess of bromomethane.**

**Ans.** Excess $CH_3Br$ Causes exhaustive methylation of the amine to form a quaternary ammonium salt.



**Stepwise Methylation (Excess $CH_3Br$)**



$$C_6H_{11}NH_2 + 3CH_3Br \longrightarrow [C_5H_{11}N(CH_3)_3] + Br$$

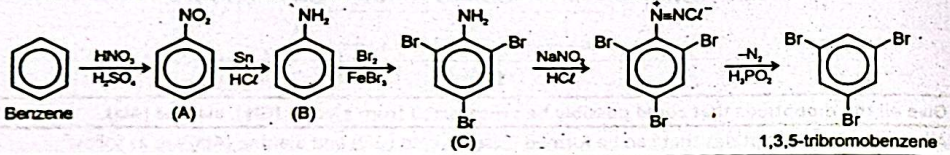
## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**Complete the following reaction sequence by giving the structures of the compounds.**

**a)** benzene $\xrightarrow[H_2SO_4]{HNO_3}$ (A) $\xrightarrow[HCl]{Sn}$ (B) $\xrightarrow{Br_2\ (excess)}$ (C) $\xrightarrow[HCl]{NaNO_2}$ (D) $\xrightarrow[-N_2]{H_3PO_2}$ (E)

**Ans. Sequence (a):**

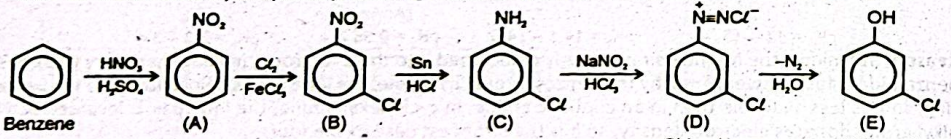
A = nitrobenzene ($C_6H_5NO_2$)
B = benzenamine/aniline ($C_6H_5NH_2$)
C = 2,4,6-tribromoaniline
D = 2,4,6-tribromobenzenediazonium chloride
E = 1,3,5-tribromobenzene.
$H_3PO_2$ replaces the diazonium group by H with evolution of $N_2$.
The given lower reaction diagram appears to mislabel the C → D step as $Br_2/FeBr_3$.




**b)** benzene $\xrightarrow[H_2SO_4]{HNO_3}$ (A) $\xrightarrow[FeCl_3]{Cl_2}$ (B) $\xrightarrow[HCl]{Sn}$ (C) $\xrightarrow[HCl]{NaNO_2}$ (D) $\xrightarrow[-N_2]{H_2O}$ (E)

**Ans. Sequence (b):**

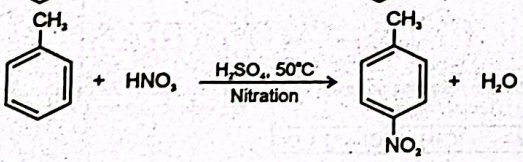
A = nitrobenzene
B = 3-chloronitrobenzene (chlorine enters meta to $-NO_2$)
C = 3-chloroaniline
D = 3-chlorobenzenediazonium chloride
E = 3-chlorophenol.
The diazonium salt is hydrolysed by warming with water, replacing $-N_2^+$ by $-OH$ and releasing $N_2$.




**c) Keeping in view the above (a, b) scheme, devise a reaction sequence to prepare 4-Hydroxybenzoic acid from benzene.**

**Ans.** Benzene to 4-hydroxybenzoic acid step wise according to scheme.

1. 


2. 


**Alternate**

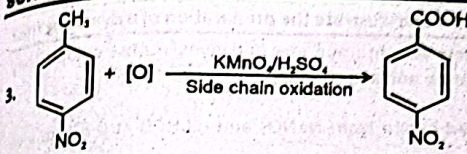
**Nitration:**

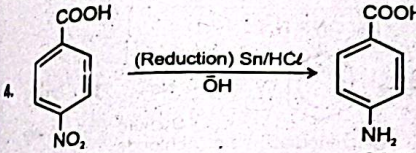
$C_6H_6 + HNO_3 \xrightarrow{conc.\ H_2SO_4} C_6H_5NO_2 + H_2O$

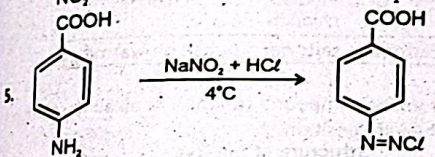
**Reduction:**

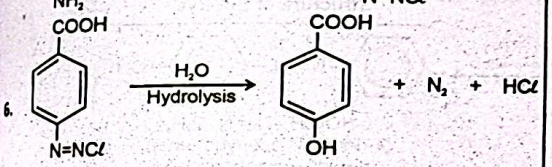
$C_6H_5NO_2 + 3H_2 \xrightarrow{Ni} C_6H_5NH_2 + 2H_2O$



3. 


4. 


5. 


6. 


**Diazotization:**

$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0\text{-}5^\circ C} C_6H_5N_2^+Cl^- + 2H_2O$

**Hydrolysis:**

$C_6H_5N_2^+Cl^- + H_2O \xrightarrow{\Delta} C_6H_5OH + N_2 + HCl$

**Kolbe-Schmitt reaction:**

$C_6H_5OH + KOH \longrightarrow C_6H_5K + H_2O$

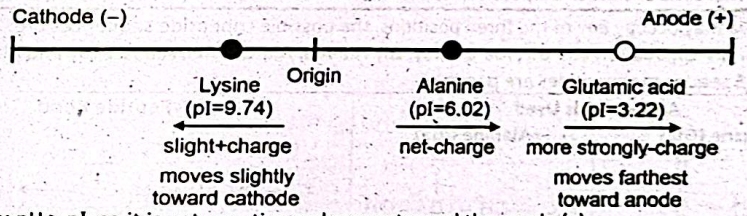
$C_6H_5OK + CO_2 \xrightarrow[4\text{-}7\ atm]{125\text{-}140^\circ C} p\text{-}HOC_6H_4COOK$

**Acidification:**

$p\text{-}HOC_6H_4COOK + HCl \rightarrow p\text{-}HOC_6H_4COOH + NaCl$

**d) Draw the electrophoretic separation of alanine (pI = 6.02), lysine (pI = 9.74) and glutamic acid (pI = 3.22) at pH 9.7.**

**Ans. At pH 9.7:**




- **Alanine:** pH > pI, so it is net negative and moves toward the anode (+).
- **Glutamic acid:** pH >> pI, so it is strongly net negative and moves farther toward the anode (+).
- **Lysine:** pH is slightly below pI, so it has a very small positive charge and moves only slightly toward the cathode (–), remaining near the origin.

## DESCRIPTIVE QUESTIONS DQs

**Q.4 Describe the relative basicity of aqueous ammonia, ethanamine and phenyl amine.**

**Ans.** See Question No. 3

**Q.5 Give two preparation methods of each of the following. i) Primary amines ii) Secondary amines**

**Ans.** See Question No. 2

**Q.6 Write a note on electrophoresis.**

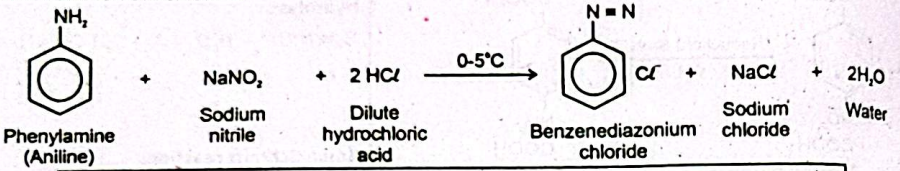
**Ans.** See Question No. 13

CamScanner

**Q.7 Explain the formation of azo compounds from phenylamine and illustrate the preparation of a dye using this?**

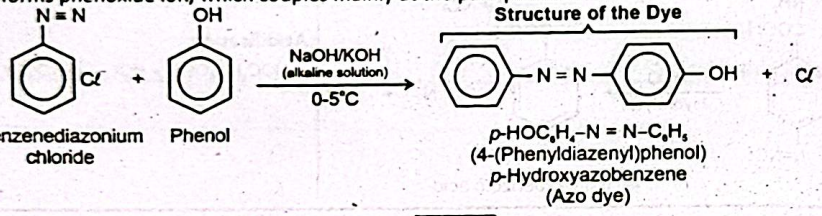
**Ans.** Azo compounds contain the zo group (–N = N–), which acts as a chromophore and gives intense colour. They are prepared from phenylamine in two stages: diazotization and azo coupling.

1. **Diazotization:**
Phenylamine is treated with nitrous acid (generated in situ from $NaNO_2$ and dil.HCl) at 0-5°C to give benzenediazonium chloride.




Low temperature (0-5°C) is essential because diazonium salts decompose on warming.

2. **Azo Coupling:**
The cold diazonium salt is reacted with an activated aromatic compound (phenol) in alkaline solution. Phenol forms phenoxide ion, which couples mainly at the para position.




## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

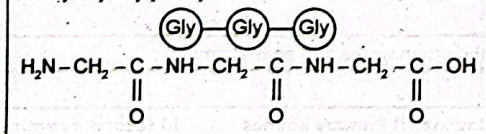
**Q.1 Give all the tripeptides that could possibly be synthesized from glycine (Gly), alanine (Ala).**

**Ans.** If Gly and Ala may occupy any of the three positions, the possible tripeptide sequences are:
Gly-Gly-Gly, Gly-Gly-Ala, Gly-Ala-Gly, Ala-Gly-Gly, Gly-Ala-Ala, Ala-Gly-Ala, Ala-Ala-Gly and Ala-Ala-Ala.
Therefore, 8 sequence tripeptides are possible.

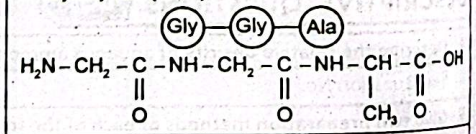
| Amino Acids Used | | Peptide Bond |
|---|---|---|
| Glycine (Gly) | Alanine (Ala) | |
| $H_2N-CH_2-\overset{\overset{O}{\|}}{C}-OH$ | $H_3C-\underset{CH_3}{CH}-\overset{\overset{O}{\|}}{C}-OH$ | $-\overset{\overset{O}{\|}}{C}-OH + H-N- \longrightarrow -\underset{O}{\overset{\|}{C}}-\underset{H}{\overset{\|}{N}}-$ |

**All possible tripeptides (3 residues) From Gly and Ala**

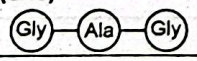
**1. Gly-Gly-Gly (GGG)**



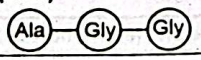

**2. Gly-Gly-Ala (GGA)**




**3. Gly-Ala-Gly (GAG)**

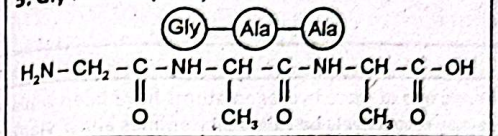



**4. Ala-Gly-Gly (AGG)**

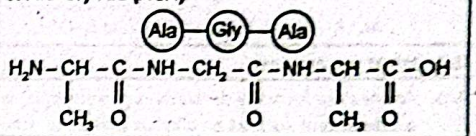




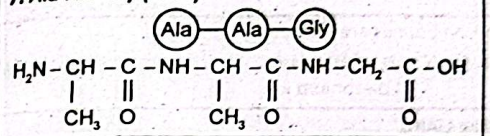

**5. Gly-Ala-Ala (GAA)**



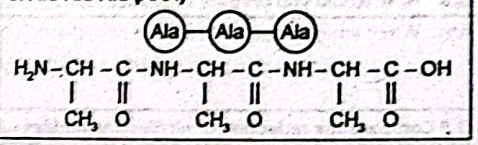

**6. Ala-Gly-Ala (AGA)**




**7. Ala-Ala-Gly (AAG)**



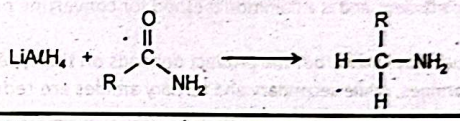

**8. Ala-Ala-Ala (AAA)**




Therefore, 8 sequence tripeptides are possible.

**Q.2 How are Amides are reduced by $LiAlH_4$.**

**Ans. Reduction of Amides:**




**Q.3 What happens when amides undergo reduction?**

**Ans.** An amide on treatment with bromine in the presence of KOH yields primary amines.
The reaction occurs through rearrangement.

$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4KOH \xrightarrow{H_2O} CH_3NH_2 + 2KBr + K_2CO_3 + 2H_2O$$
Acetamide — Methylamine

$$C_6H_5-CH_2-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4KOH \xrightarrow{H_2O} C_6H_5CH_2NH_2 + 2KBr + K_2CO_3 + 2H_2O$$

**Q.4 Why $CH_3-NH_2$ is a stronger base than $NH_3$?**

**Ans.** (i) **Availability of electron pair:** In ammonia, the pair of electrons attracted by s-orbitals of hydrogen atoms where as in $CH_3–NH_2$, $sp^3$-orbital of carbon pushes electrons towards nitrogen. Therefore, the pair of electron on nitrogen is relatively more available in methyl amine than in ammonia.

(ii) **Stability of Cations:** The methyl ammonium ion, $CH_3–\overset{+}{N}H_3$ is stabilized due to electron donating inductive effect of the methyl group. On the other hand, $NH_4^+$ ion is not stabilized by hydrogen atoms.

Both these factors favor methylamine to a stronger base than ammonia.

**Q.5 Why halogen of vinyl chloride is inert?**

**Ans.** The reason for this is that the C – Cl bond in vinyl chloride ($CH_2 = HC–Cl$) is stronger than the C – Cl bond in an alkyl chloride ($CH_3–H_2C–Cl$). This is so because a p orbital on chlorine interacts with the p orbital on the adjacent carbon atom. The new delocalized orbital gives partial double bond character to the C – Cl bond in vinyl chloride. As a result the chlorine atom becomes firmly bound to carbon and cannot be replaced easily. However, the carbon-carbon double bond of vinyl chloride shows the usual addition reactions.

CamScanner

**Q.6 Amines are more basic than analogous alcohols. Why?**

**Ans.** Amines are more basic than analogous alcohols due to following reasons:

i. The lone pair of electrons on nitrogen is more available for proton ($H^+$) than lone pair of oxygen.

ii. The electronegativity of 'N' is less than that of 'O'.

iii. $R - \overset{+}{N}H_3$ is more stable than $R-O^+H_2$.

**Q.7 What are amines?**

**Ans.** *Amines* are formally derivatives of ammonia, wherein one or more hydrogen atoms have been replaced by a substituent such as an alkyl or aryl group (these may respectively be called alkylamines and arylamines.

**Q.8 How would you prepare Diazonium salt?**

**Ans.** When amines react with nitrous acid, diazonium compounds are formed.

$$RNH_2 + HNO_2 \longrightarrow \underset{\text{diazonium ion}}{R - N^+ \equiv N} + OH^- + H_2O$$

**Q.9 Compare the reduction of nitriles and amides using $LiAlH_4$.**

**Ans. Comparison of the Reduction of Nitriles and Amides Using $LiAlH_4$**

**Reduction of Nitriles:**

- Nitriles are reduced by $LiAlH_4$ to primary amines.
- The reaction is highly efficient and is a common method for converting nitriles to amines.

**Reduction of Amides:**

- Amides are also reduced by $LiAlH_4$, but the product depends on the type of amide. Primary amides are reduced to primary amines, while secondary and tertiary amides are reduced to secondary and tertiary amines, respectively.

**Comparison Table:**

| Compound | Product of Reduction with $LiAlH_4$ |
|---|---|
| Nitrile (R–CN) | Primary amine ($R–CH_2NH_2$) |
| Primary Amide ($R–CONH_2$) | Primary amine ($R–CH_2NH_2$) |
| Secondary Amide (R–CONHR') | Secondary amine ($R–CH_2NHR'$) |
| Tertiary Amide (R–CONR'R") | Tertiary amine ($R–CH_2NR'R''$) |



## SELF-ASSESSMENT

**Total Mark: 30**

**Q.1 Encircle the correct option.** **(1 × 6 = 6)**

(i) **Which one of the following bases is a strongest one?**
(A) Ammonia (B) Ethyl amine (C) Phenyl amine (D) Diethyl amine

(ii) **Basicity of amines depends on the availability of:**
(A) π electrons (B) Lone pair on nitrogen (C) Hydrogen atoms (D) Oxygen atom

(iii) **Benzenediazonium chloride reacts with phenol in NaOH to form:**
(A) Phenyl hydrazine (B) Nitro compound (C) Azo compound (D) Alcohol

(iv) **Coupling of diazonium salts with phenol occurs in:**
(A) Strongly acidic medium (B) Mild alkaline medium
(C) Neutral medium only (D) Concentrated sulfuric acid

(v) **Which amines are produced by the reduction of amides?**
(A) Primary (B) Secondary (C) Tertiary (D) None of these

(vi) **The linkage joining two amino acids is called the:**
(A) Ether linkage (B) Ester linkage (C) Peptide (amide) bond (D) Glycosidic bond

**Q.2 Write short answers of the following questions.** **(2 × 8 = 16)**

(i) Give IUPAC names of the following compounds.

i) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - CH_2 - CH_2 - NH_2$ ii) $CH_3 - CH_2 - \underset{\displaystyle NH_2}{\underset{|}{CH}} - CH_3$

(ii) Provide $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2 - NH_2$ from a nitrile and an amide.

(iii) Which of ethanamine and propan-2-amine is more basic? Explain.

(iv) Give two preparations of phenyl amine

(v) Give two preparations of secondary amines.

(vi) What is the chromophore in azo dyes? What is its function in dyes?

(vii) Why amides are less basic than ammonia.

(viii) Write names & structures of four isomeric amines having the molecular formula $C_3H_9N$.

**Q.3 Extensive Questions.** **(4 + 4 = 8)**

(a) Prepare 4-Hydroxybenzoic acid from benzene.

(b) Describe the relative basicity of aqueous ammonia, ethanamine and phenyl amine.

CamScanner

## ENTRANCE TEST MCQs

1. If Kb for ethanamine is $5.1 \times 100^{-4}$, its $pK_b$ is closest to:
   (A) 3.29 (B) 4.75 (C) 9.38 (D) 0.29
2. Which sequence prepares an azo dye from nitrobenzene?
   (A) Add $Br_2$, then KCN
   (B) Reduce directly to azo compound in one step
   (C) Reduce, diazotize cold, then perform azo coupling
   (D) Hydrolyse to acid, then reduce
3. Why is para azo coupling with phenol usually favored over ortho coupling?
   (A) The para carbon is negatively charged before reaction
   (B) Para attack has less steric crowding
   (C) The ortho position contains no hydrogen in phenol
   (D) Meta attack has greater resonance stabilization
4. Which nitrile should be hydrolysed to prepare butanoic acid?
   (A) Propanenitrile (B) Pentanenitrile (C) Ethanenitrile (D) Butanenitrile
5. Resonance in an amide gives the C – N bond:
   (A) Triple-bond character (B) Partial double-bond character
   (C) Pure ionic character (D) No bonding electrons
6. Which end of a peptide has a free carboxyl group?
   (A) The azo terminus (B) The nitrile terminus (C) The C-terminus (D) The N-terminus
7. Select the route that converts bromoethane to propan-1-amine while adding one carbon.
   (A) $Br_2$ water then HCl (B) KCN/ethanol and heat, then $LiAlH_4$
   (C) Excess $NH_3$ directly (D) NaOH then oxidation
8. A compound gives nitrogen bubbles with nitrous acid and forms a salt with HCl. It is most likely:
   (A) A nitrile (B) An azo dye (C) A primary aliphatic amine (D) A tertiary amide
9. Which sequence transforms nitrobenzene into an azo dye with phenol?
   (A) Reduce to cyclohexane, brominate
   (B) React directly with phenol and water
   (C) Reduce, diazotize cold, then couple with phenol/NaOH
   (D) Hydrolyse to benzoic acid, esterify
10. A neutral carbonyl nitrogen compound is reduced by $LiAlH_4$ to an amine. It is:
    (A) An azo dye (B) An amide (C) An aliphatic amine (D) A diazonium salt

**Answers Key**

| 1. A | 2. C | 3. B | 4. D | 5. B | 6. C | 7. B | 8. C | 9. C | 10. B |
|---|---|---|---|---|---|---|---|---|---|



25 CHAPTER

# ORGANIC SYNTHESIS

### Student Learning Outcomes (SLOs)

[C-12-D-109 to C-12-D-115]
- Explain the concept of organic synthesis and functional group interconversions.
- Identify organic functional groups using the reactions in this reaction grid.
- Predict properties and reactions of organic molecules based on functional group presence.
- Devise multi-step synthetic routes for preparing organic molecules.
- Analyze a given synthetic route in terms of type of reaction and reagents used for each step of it, and possible by-products.
- Explain the concept of retro-synthesis and its application in organic synthesis.
- Describe the use of artificial intelligence tools in designing organic molecules which may have the potential to be used as medicine (Halicin can be used as an example).

**Q.1 What are the importance of functional Groups?** S/Q

**Ans. Importance of Functional Groups:**
In organic synthesis we design different possible ways to build a target molecule from simpler easily available components.

**Role of Functional Groups in Synthesis:** Functional groups play a central role in designing a synthesis.
i) Functional group facilitate the chemists to predict and control the reactions which ultimately lead to the desired product.
ii) Identifying a functional group present in a compound can help to predict the properties of the compound.
iii) It helps in the development of new organic products, as well as to ensure the purity and composition of the products such as medicines and food additives.

## SYNTHESIS AND RETROSYNTHESIS

The successful synthesis of a target molecule depends upon the identification of its starting materials, the functional groups involved, and the right reactions. The identification involves breaking an organic molecule into simpler compounds and identifying the useful, cheap starting materials. When the starting materials (chemicals) are identified, the synthesis process is carried out through the most appropriate routes.
There are two processes involved known as: (i) retrosynthesis (ii) synthesis

### ➲ Retrosynthesis

**Q.2 Give a detailed account of importance of retrosynthesis in organic synthesis.** Exercise D/Q.4

**Ans.** It is a process of breaking down the target molecule into simpler fragments. Retrosynthesis starts with the required compound, which is called the target molecule. The target molecule is broken down into simpler fragments by bond breaking at suitable positions. Bond breaking next to a functional group is called disconnection. Each step of disconnection is represented by an open-ended arrow (⇒).
In retrosynthesis, those bonds of the target molecule are disconnected that result in a considerable structural simplification. Following a series of disconnections, we shall eventually arrive at simple, easily available starting materials.

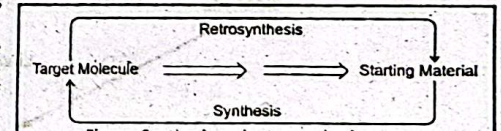


Figure: Synthesis and retrosynthesis routes

### ➲ Synthesis

After the identification of the most suitable chemicals and the synthetic route for the target molecule, synthesis of that compound is planned for the successful preparation.

CamScanner

Synthesis involves the interconversion of functional groups, C–C bond formation, and ring formation strategies.

Simple Terminology Used During Retrosynthesis:

- **Retrosynthetic arrow** is an open-ended arrow and denoted by ⇒.
- **Target Molecule (TM)** is the molecule which is to be prepared by disconnection.
- **Disconnection** is a process which involves the imaginary breaking down of the TM progressively into simpler starting materials.
- **Synthons** are fragments of the target molecule which are generated by a disconnection. They are often an ionic species and represent the building blocks for the synthesis.
- **Synthetic Equivalent (SE)** is a reagent used to carry out the function of a synthon which cannot be used itself because it is usually unstable.
- **Functional Group Interconversion (FGI)** is the conversion of one functional group into another to reach the target molecule.
- **Retrosynthetic Tree** is a diagram showing all possible disconnections and synthons from the target molecule to starting materials.

**Figure** shows all the terminologies in a single scheme.

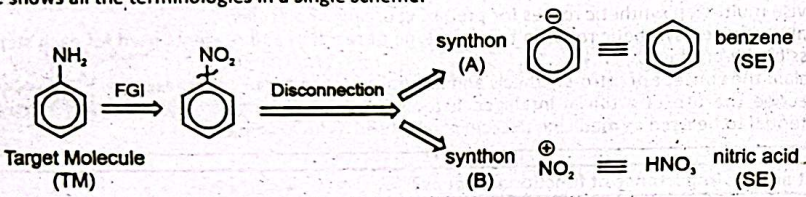



**Figure: Terminologies used in retrosynthesis**

**Q.3 Construct the functional group interconversion flow sheet and highlight the important reagents and conversions involved.** Exercise C/Q 3(a)

**Ans. Functional Group Interconversion**

FGI is a phenomenon to change a functional group into another functional group, required for synthesis of a specific of compound.

➢ **Uses of FGI:**

FGI has a crucial role to play in designing routes which lead to target molecules.

I. Simple starting materials can be converted to more complex target molecules using FGI as building blocks.

II. FGI not only allows to create the carbon skeleton of the target molecule but also select the route to be adopted for this purpose.

The interconversions of functional groups have been studied in detail (in earlier chapters) and a summary of these interconversions is given in Figure.

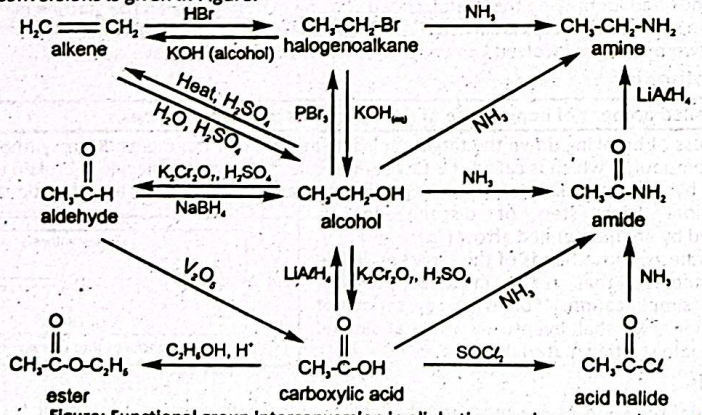



**Figure: Functional group interconversion in aliphatic organic compounds**



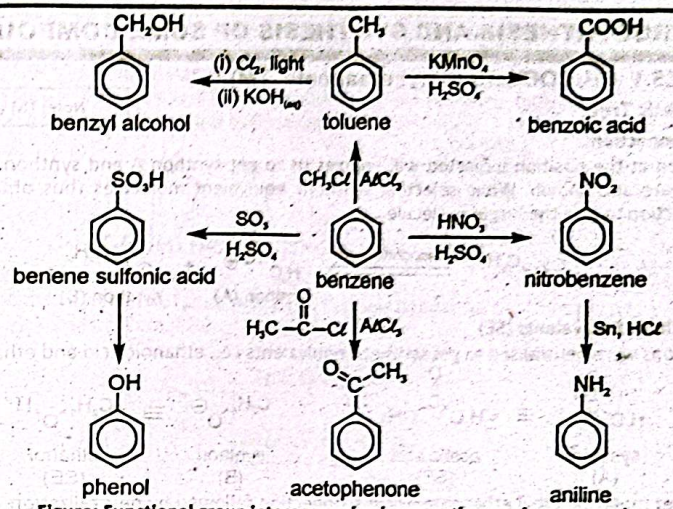



**Figure: Functional group interconversion in aromatic organic compounds**

**QUICK CHECK 25.1**

**a) What are the products of oxidation and reduction of aldehydes?**

**Ans.** Oxidation of an aldehyde gives a carboxylic acid:

1. **Oxidation of An Aldehyde:**

Aldehydes are easily oxidized to carboxylic acids.

$$\underset{\text{Aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + [O] \longrightarrow \underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH}$$

Common oxidizing agents: Acidified $K_2Cr_2O_7$ (or $K_2Cr_2O_7/H_2SO_4$), $KMnO_4$, Tollen's reagent, Fehling's solution, etc.

2. **Reduction of an Aldehyde:**

$$\underset{\text{Aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + 2[H] \longrightarrow \underset{\substack{\text{Primary alcohol}\\(1^{O}\text{ alcohol})}}{R-CH_2-OH}$$

Common reducing agents: $NaBH_4$, $LiAlH_4$, $H_2$/Ni (catalytic hydrogenation), etc.

**b) How will you convert an alcohol into: (i) Bromoalkane (ii) Aldehyde (iii) Ester**

**Ans. (i) Alcohol to Bromoalkane**

$$CH_3-CH_2-OH + HBr \xrightarrow{H_2SO_4} CH_3-CH_2-Br + H_2O$$

**(ii) Alcohol to Aldehyde**

$$CH_3-CH_2-OH + [O] \xrightarrow{H_2SO_4} CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O$$

**(ii) Alcohol to Ester**

$$CH_3COOH + C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + H_2O$$

CamScanner

# RETROSYNTHESIS AND SYNTHESIS OF SOME COMPOUNDS

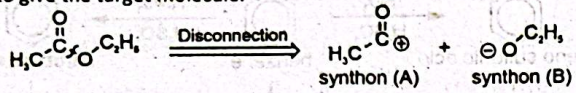
## Example 25.1 $CH_3COOC_2H_5$ (ethyl ethanoate, TM)

Note: TM = Target molecule

**Retrosynthetic Tree:**

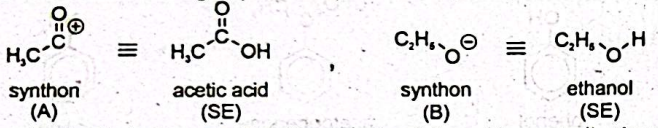
**Step I: Disconnection**

Disconnection at the position indicated will enables us to get synthon A and synthon B whose synthetic equivalents are also shown. While selecting synthetic equivalent molecules thus obtained, they should undergo reaction to give the target molecule.




**Step II: Synthetic Equivalents (SE)**

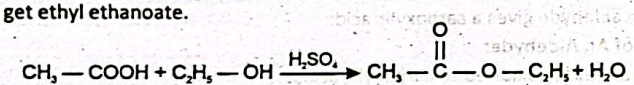
These synthons were neutralised to get synthetic equivalents i.e., ethanoic acid and ethanol.




For our target molecule ethyl ethanoate, the disconnection followed by neutralization yields ethanoic acid and ethanol as simpler staring materials to synthesize the TM (Target Molecule).

**Synthesis of TM (ethyl ethanoate):**

Here we can design the synthesis of our TM by a very familiar esterification reaction between ethanoic acid and ethanol to get ethyl ethanoate.

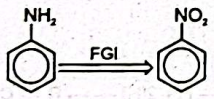



## Example 25.2 $C_6H_5 - NH_2$ (aniline, TM)

**Retrosynthetic Tree:**

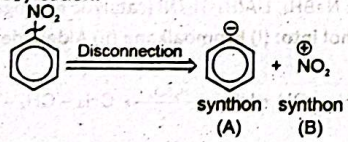
**Step I: Functional group interconversion**

The first step of retrosynthesis here is FGI, where amino group ($-NH_2$) is converted into nitro ($-NO_2$) group. Because it is easy to attach a nitro group on benzene by electrophilic substitution, rather than an amino group by nucleophilic substitution.



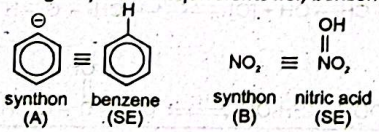

**Step II: Disconnection**

In the second step, the disconnection of nitrobenzene is done at C – N bond, which creates synthons of aryl anion ($C_6H_5^-$) and nitronium ($NO_2^+$) cation.




**Step III: Synthetic Equivalents (SE)**

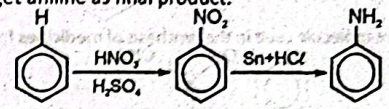
These synthons are neutralised to get synthetic equivalents i.e., benzene and nitric acid molecule.






**Synthesis of TM (aniline)**

Now starting from the simpler starting materials i.e., benzene and nitric acid, the synthesis of (TM) can be designed. First step will be the nitration of benzene to get nitrobenzene, followed by reduction of nitro group to create amino group and get aniline as final product.

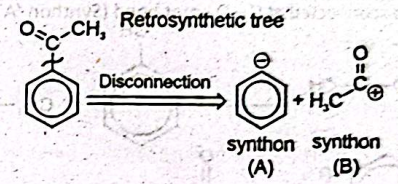



## Example 25.3 $C_6H_5COCH_3$ (acetophenone, TM)

**Step I: Disconnection**

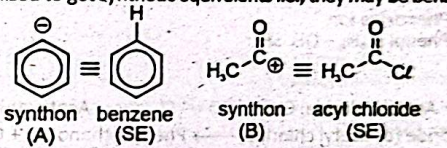
In first step, the disconnection of acetophenone (TM) was done from C – C bond, which created synthons of aryl anion ($C_6H_5^-$) and acylium ($CH_3CO^+$) cation.

**C – C Breakage:**



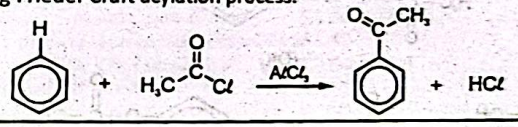

**Step II: Synthetic Equivalents (SE)**

These synthons were neutralized to get synthetic equivalents i.e., they may be benzene and acyl chloride molecule.




**Synthesis of TM (acetophenone)**

Synthesis of acetophenone can be done by reaction between benzene and acyl chloride, in the presence of $AlCl_3$ as catalyst, using Friedel-Craft acylation process.



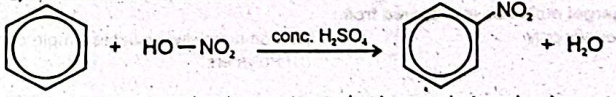

**Interesting Information**

The landmark synthesis of cholesterol was first achieved in early 1950s by two competing groups headed each by Robert Robinson in Oxford and R.B. Woodward at Harvard. These synthetic schemes of cholesterol, had been previously predicted through biological studies.

### QUICK CHECK 25.2

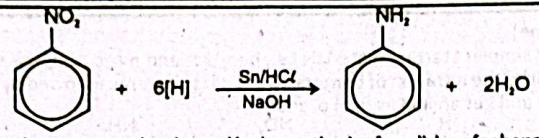
a) **Why is the nitration of benzene is done during the synthesis of aniline?**

Ans. As direct introduction of amino group is not practical, so a method is to introduce a strong electrophile nitro group ($-NO_2$) and form nitro benzene.

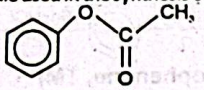



Then reduction of nitrobenzene can be done using Sn/HCl or catalytic reduction.

CamScanner



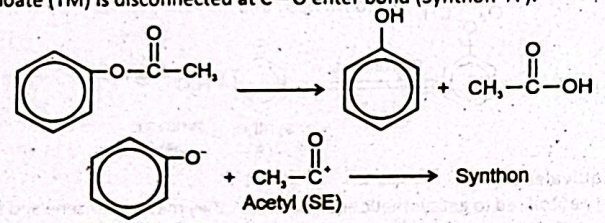

**b) Phenyl ethanoate is an important molecule used in the synthesis of medicines for hepatitis and various infections.**



**i) Draw its retrosynthesis.**
**ii) Write structures of its synthetic equivalents.**
**iii) Design its linear synthesis.**

**Ans. i) Disconnection**

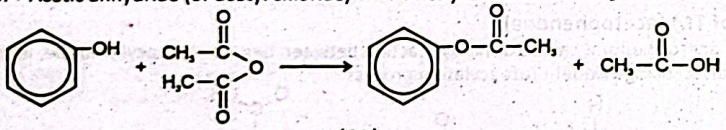
Phenyl Ethanoate (TM) is disconnected at C – O enter bond (Synthon 'A').



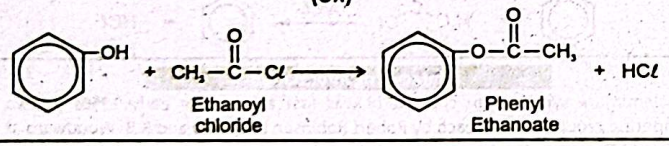

**ii) Synthon (A) $C_6H_5O^-$ = Phenol ($C_6H_5-OH$, SE)**

**Synthon (B) $CH_3-\overset{O}{\overset{\|}{C}}{}^+$ = Acetyl Chloride, $CH_3-CO-C\ell$ or Acetic anhydride $(CH_3CO)_2O$ (SE)**

**iii) Phenol + Acetic anhydride (or acetyl chloride) ⟶ Phenyl ethanoate + $CH_3COOH$:**




**(OR)**




## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Organic synthesis is mainly concerned with:**
   (A) Separation of compounds (B) Preparation of target molecules
   (C) Identification of elements (D) Purification only
2. **A good synthetic route should:**
   (A) Use expensive reagents (B) Involve maximum steps
   (C) Give high overall yield with minimum steps (D) Produce many by-products
3. **In synthesis, the target molecule is prepared from:**
   (A) Complex compounds only (B) Commercially available simple compounds
   (C) Proteins (D) Polymers
4. **Retrosynthesis is:**
   (A) Oxidation of compounds (B) Reverse analysis of synthesis
   (C) Reduction reaction (D) Polymerization



5. **Retrosynthesis involves breaking the target molecule into:**
   (A) More complex compounds (B) Simpler starting materials
   (C) Polymers (D) Catalysts
6. **The approach used in retrosynthesis is called:**
   (A) Electrophilic substitution (B) Disconnection approach
   (C) Hydrolysis (D) Addition reaction
7. **The molecule to be synthesized is called the:**
   (A) Synthon (B) Target Molecule (TM) (C) Catalyst (D) Reagent
8. **The compounds used to begin synthesis are called:**
   (A) By-products (B) Starting Materials (SM) (C) Catalysts (D) Solvents
9. **The retrosynthetic arrow is:**
   (A) → (B) ⇋ (C) ⇒ (D) ←
10. **Disconnection is the:**
    (A) Real breaking of bonds (B) Imaginary breaking of bonds
    (C) Oxidation of bonds (D) Hydrolysis of bonds
11. **Synthons are:**
    (A) Stable reagents (B) Imaginary fragments produced after disconnection
    (C) Catalysts (D) Solvents
12. **Synthetic equivalents are:**
    (A) Imaginary species (B) Real reagents corresponding to synthons
    (C) Products (D) Indicators
13. **Synthetic equivalents are required because synthons are usually:**
    (A) Stable (B) Insoluble (C) Unstable (D) Coloured
14. **Functional Group Interconversion (FGI) means:**
    (A) Breaking carbon chains (B) Converting one functional group into another
    (C) Forming polymers (D) Separating mixtures
15. **FGI is important because it helps:**
    (A) Increase impurities (B) Design synthetic routes
    (C) Reduce molecular weight only (D) Measure boiling point
16. **Carbon–carbon bond formation is important because it:**
    (A) Destroys molecules (B) Builds larger target molecules
    (C) Removes functional groups (D) Produces salts
17. **In retrosynthesis, structural simplification is achieved through:**
    (A) Polymerization (B) Disconnection (C) Combustion (D) Neutralization
18. **The diagram showing all possible disconnections is called:**
    (A) Reaction mechanism (B) Retrosynthetic tree (C) Energy profile (D) Flow chart
19. **Which compound is the target molecule in Example 25.2.1?**
    (A) Ethanol (B) Ethyl acetate (C) Acetic acid (D) Benzene
20. **Ethyl acetate is synthesized from:**
    (A) Methanol and acetic acid (B) Ethanol and acetic acid
    (C) Ethanol and acetone (D) Ethanal and ethanol
21. **The reaction used to prepare ethyl acetate is:**
    (A) Reduction (B) Esterification (C) Hydrogenation (D) Halogenation
22. **Concentrated $H_2SO_4$ acts mainly as:**
    (A) Oxidizing agent (B) Catalyst (C) Reducing agent (D) Base
23. **In the retrosynthesis of aniline, the first step is:**
    (A) Reduction (B) Functional Group Interconversion
    (C) Hydrolysis (D) Bromination
24. **In aniline retrosynthesis, the amino group is converted into:**
    (A) Hydroxyl group (B) Nitro group (C) Carboxyl group (D) Aldehyde group
25. **Benzene is converted into nitrobenzene using:**
    (A) NaOH (B) $HNO_3/H_2SO_4$ (C) $Br_2$ (D) $NH_3$
26. **Nitrobenzene is reduced to aniline using:**
    (A) $KMnO_4$ (B) Sn/HCl (C) NaOH (D) $H_2SO_4$
27. **In acetophenone retrosynthesis, the bond disconnected is:**
    (A) C–O (B) C–C (C) C–H (D) O–H
28. **The acylium ion acts as:**
    (A) Synthon (B) Catalyst (C) Solvent (D) Product

CamScanner

29. The synthetic equivalent of the acylium ion is:
(A) Acyl chloride (B) Alcohol (C) Amine (D) Carboxylic acid
30. Acetophenone is synthesized by reaction of benzene with:
(A) Alcohol (B) Acyl chloride (C) Ketone (D) Alkene
31. The catalyst used in Friedel–Crafts acylation is:
(A) $FeCl_3$ (B) $AlCl_3$ (C) Ni (D) Pt
32. Friedel–Crafts acylation is used to prepare:
(A) Alcohols (B) Aromatic ketones (C) Amines (D) Esters
33. Functional group interconversion helps chemists to:
(A) Predict reaction routes (B) Measure density (C) Increase boiling point (D) Separate mixtures
34. Synthons produced during retrosynthesis are:
(A) Real isolated compounds (B) Theoretical fragments
(C) Catalysts (D) Indicators
35. Which of the following is not a retrosynthetic term?
(A) Synthon (B) Disconnection (C) Retrosynthetic Tree (D) Polymerization
36. The best synthetic route generally uses:
(A) Maximum reagents (B) Minimum steps (C) Maximum by-products (D) High temperatures only
37. Retrosynthesis mainly works in the _____ direction.
(A) Forward (B) Reverse (C) Circular (D) Random
38. Functional group interconversion is abbreviated as:
(A) FGA (B) FGI (C) FGT (D) FGR
39. Synthetic equivalents are selected because they:
(A) Readily undergo reactions to give the target molecule (B) Are always ionic
(C) Never react (D) Are products
40. The ultimate aim of retrosynthesis is to obtain:
(A) Expensive intermediates (B) Simple, readily available starting materials
(C) Highly reactive radicals (D) Complex polymers

## SYNTHESIS OF PHARMACEUTICAL PRODUCTS

One of the most important applications of retrosynthesis is in pharmaceutical product synthesis. There are hundreds of valuable medicinal compounds, which look very complex in their structure, but if they are disconnected properly and efficiently, we can work back to very simple and commonly available starting materials. This is the beauty of organic synthesis, that it makes the highly complex and terrifying structure, look so simple and achievable after a series of efficient retrosynthetic steps. In the following we will discuss synthesis of some common pharmaceutical products.

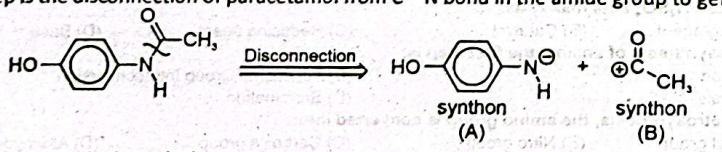
### ➲ Example 25.4 Paracetamol (TM)

**Q.4 Construct the retrosynthetic tree for the paracetamol and then design its synthesis.** Exercise C/Q.3(b)

**Ans. Retrosynthesis of Paracetamol**

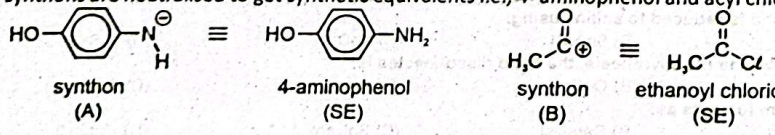
**Step I: Disconnection**

The first step is the disconnection of paracetamol from C – N bond in the amide group to get synthons.




**Step II: Synthetic Equivalents (SE)**

These synthons are neutralised to get synthetic equivalents i.e., 4 -aminophenol and acyl chloride molecule.

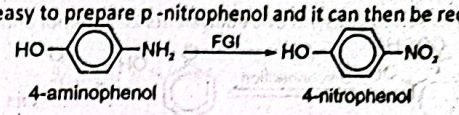





The bond is broken at the position indicated because the synthetic equivalents of the resulting synthons are well known to react through a nucleophilic addition-elimination reaction.

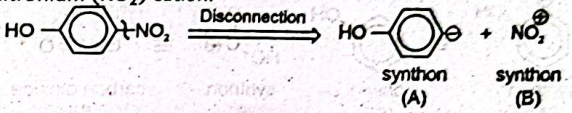
**Step III: Functional Group Interconversion**

FGI is done because it is easy to prepare p -nitrophenol and it can then be reduced to p-aminophenol.



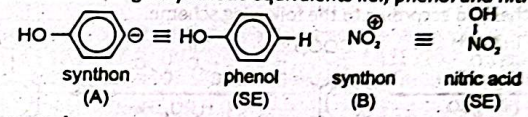

**Step IV: Disconnection**

Then disconnection of 4-nitrophenol is done at from C – N bond, which created synthons of hydroxyphenyl anion ($C_6H_5^-$) and nitronium ($NO_2^+$) cation.



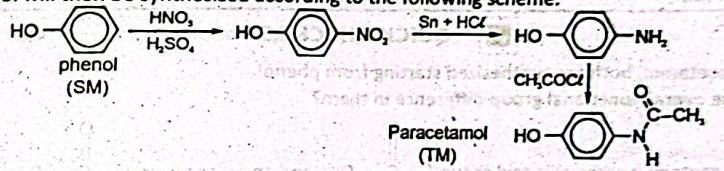

**Step V: Synthetic Equivalents (SE)**

These synthons are neutralised to get synthetic equivalents i.e., phenol and nitric acid.




### Synthesis of Paracetamol

Paracetamol will then be synthesized according to the following scheme.




### ➲ Example 25.5 Aspirin (Acetylsalicylic Acid) TM

**Q.5 Construct the retrosynthetic tree for the aspirin and then design its synthesis.** Exercise D/Q.5

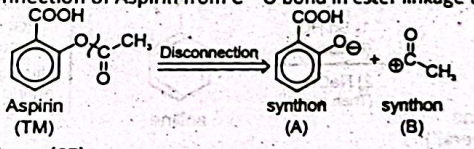
**Ans.** Just like Paracetamol the direct synthesis of Aspirin also requires a series of steps. By retrosynthesis we can truly find how many and which steps are actually needed to prepare Aspirin from phenol (simple starting material).

### Retrosynthesis of Aspirin

**Retrosynthetic Tree**

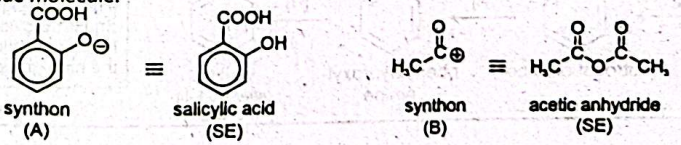
**Step I: Disconnection-I**

The first step is the disconnection of Aspirin from C – O bond in ester linkage to get synthons.




**Step II: Synthetic Equivalents (SE)**

These synthons were neutralized to get synthetic equivalents i.e., 2-hydroxybenzoic acid (salicylic acid) and acetic anhydride molecule.



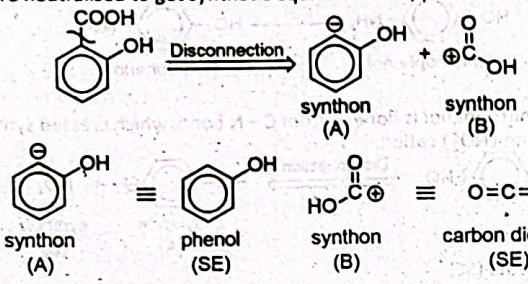

CamScanner

**Step III: Disconnection-II**

Next disconnection is the C – C bond of carboxylic group.

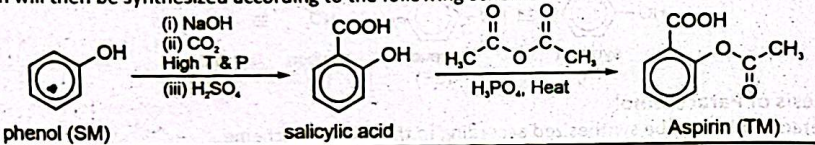
**Step IV: Synthetic Equivalents (SE)**

These synthons were neutralised to get synthetic equivalents i.e., phenol and carbon dioxide molecule.




➤ **Synthesis of Aspirin**

Aspirin will then be synthesized according to the following scheme.




**QUICK CHECK 25.3**

**Aspirin and Paracetamol, both are synthesized starting from phenol.**

**i) What is the overall functional group difference in them?**

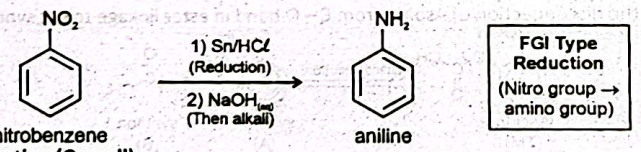
**Ans. Aspirin:** It contains a carboxylic acid group ($-\overset{O}{\overset{\|}{C}}-OH$) and an ester group ($-\overset{O}{\overset{\|}{C}}-O-CH_3$).

**Paracetamol:** It contains a phenolic —OH group and amide group ($-NH-\overset{O}{\overset{\|}{C}}-CH_3$).

Ethanoyl (Acetyl) group is shared by both but aspirin is linked through 'O' (Ester) while paracetamol is linked through 'N' (Amide).

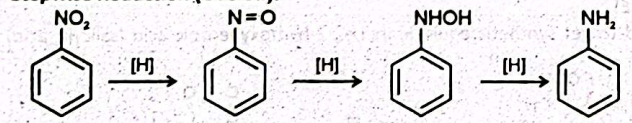
**ii) Which FGI (Functional Group Interconversion) is involved when nitrobenzene is converted into aniline?**

**Ans.**




**FGI Type Reduction** (Nitro group → amino group)

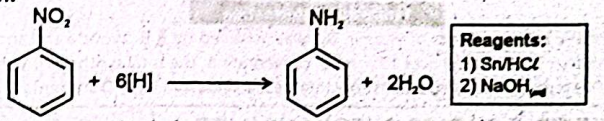
**Stepwise Reduction (Overall):**




**Legend:** [H]=Reducing conditions Sn/HCl provides nascent hydrogen which reduces the nitro group stepwise.

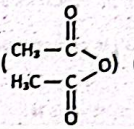


**Overall Reaction:**




**iii) Which synthon is common in their preparation? Write down its structure and also mention its most common synthetic equivalent.**

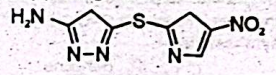
**Ans. Common Synthon:** Acylium ion ($CH_3-\overset{O}{\overset{\|}{C}}{}^+$). It is generated by disconnection of Acetyl group in both paracetamol and aspirin.

Common Synthetic equivalent = Acetic anhydride  (Or) Acetyl chloride ($CH_3-\overset{O}{\overset{\|}{C}}-Cl$)

## USE OF ARTIFICIAL INTELLIGENCE (AI) IN DRUG DESIGNING

**Q.6 Discuss the use of Artificial Intelligence (AI) in drug designing taking the example of halicin.** LOQ

**Ans.** The past few decades have seen the development of very few new antibiotics. Those which have been developed are only slightly different from the existing ones. The methods which are currently used to develop new drugs are very costly, time consuming and are usually limited to a narrow spectrum of chemical activity. We are also facing growing number of cases whereby pathogens become resistant to the prevalent antibiotics.




In order to find out a solution to this problem the researchers at **MIT (Massachusetts Institute of Technology)** designed a machine-learning algorithm to look for chemical features that make molecules effective at killing **E. coli bacteria**. To do so, they applied the model on 2500 molecules and a set of 800 natural products with different structures and a wide range of bioactivities. Once the computer model was applied to these compounds, it picked out one molecule that was predicted to have antibacterial properties with a molecular structure different from the existing antibiotics.

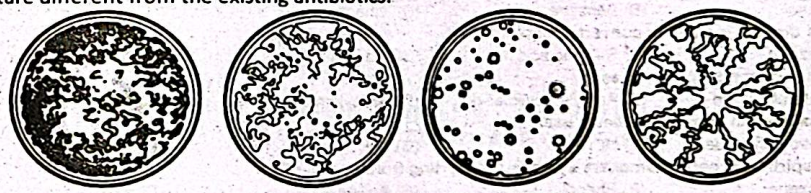


**Figure: Antibacterial activity of Halicin**

Using a different model, the researchers also showed that this molecule would most likely show low toxicity to human cells. Later on, this molecule was named as Halicin and it was tested against a number of bacterial strains isolated from patients. It was found that the new molecule killed many of the world's most problematic disease-causing bacteria which were previously resistant to treatment.

After identifying Halicin, the researchers applied their computer model to screen more than 100 million molecules selected from a database. This screening was completed in only three days, and it selected 23 more such molecules which have different structures from existing antibiotics. Researchers further, found that eight of these molecules showed antibacterial activities and two were particularly powerful. This groundbreaking work points out an altogether different route to discover new organic molecules which may be used as drugs.

CamScanner

**Interesting Information**

The historic total synthesis of vitamin $B_{12}$ was achieved by R.B. Woodward and A. Eschenmoser in 1972 after over 10 years of collaboration. The total synthesis involved over 100 steps and required 91 post-doctoral researchers and 12 PhD students.

## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Retrosynthesis of paracetamol begins with the disconnection of the:**
   (A) C–O bond (B) C–N bond of the amide group (C) O–H bond (D) C–C bond
2. **The synthetic equivalent of one synthon in paracetamol synthesis is:**
   (A) Ethanol (B) 4-Aminophenol (C) Benzaldehyde (D) Phenylamine
3. **The other synthetic equivalent used in paracetamol synthesis is:**
   (A) Acetyl chloride (B) Acetic acid (C) Ethanoic anhydride (D) Ethanol
4. **Functional Group Interconversion (FGI) in paracetamol synthesis converts:**
   (A) –OH to –COOH (B) $-NH_2$ to $-NO_2$ (C) 4-Nitrophenol into 4-aminophenol (D) Benzene into phenol
5. **The starting material for paracetamol synthesis is:**
   (A) Benzene (B) Phenol (C) Aniline (D) Nitrobenzene
6. **Nitration of phenol is carried out using:**
   (A) HCl (B) $HNO_3/H_2SO_4$ (C) $Br_2$ (D) NaOH
7. **The nitro group is reduced to an amino group using:**
   (A) $KMnO_4$ (B) Sn/HCl (C) NaOH (D) $H_2SO_4$
8. **The final step in paracetamol synthesis involves reaction with:**
   (A) Acetyl chloride (B) Sodium hydroxide (C) Bromine water (D) Hydrogen peroxide
9. **Paracetamol contains which functional group introduced in the final step?**
   (A) Ester (B) Amide (C) Aldehyde (D) Carboxylic acid
10. **The bond broken during the first retrosynthetic step of aspirin is:**
    (A) C–N (B) C–O of the ester linkage (C) C=C (D) O–H
11. **One synthetic equivalent for aspirin synthesis is:**
    (A) Salicylic acid (B) Ethanol (C) Benzene (D) Aniline
12. **The second synthetic equivalent for aspirin synthesis is:**
    (A) Acetic acid (B) Acetic anhydride (C) Acetaldehyde (D) Acetone
13. **The second disconnection in aspirin retrosynthesis involves the:**
    (A) C–N bond (B) C–C bond of the carboxyl group (C) O–H bond (D) N–H bond
14. **The simple starting material for aspirin synthesis is:**
    (A) Phenol (B) Benzene (C) Ethanol (D) Methanol
15. **Carbon dioxide is used to convert phenol into:**
    (A) Benzene (B) Salicylic acid (C) Ethanol (D) Acetophenone
16. **Aspirin is chemically known as:**
    (A) Acetaminophen (B) Acetylsalicylic acid (C) Salicylamide (D) Phenyl acetate
17. **The final step in aspirin synthesis uses:**
    (A) Acetic anhydride (B) HCl (C) $NH_3$ (D) Bromine
18. **Both aspirin and paracetamol are synthesized starting from:**
    (A) Benzene (B) Phenol (C) Aniline (D) Toluene
19. **Functional Group Interconversion is specifically involved in the synthesis of:**
    (A) Aspirin only (B) Paracetamol only (C) Both aspirin and paracetamol (D) Neither
20. **Which pharmaceutical synthesis includes reduction of a nitro group?**
    (A) Aspirin (B) Paracetamol (C) Ethyl acetate (D) Acetophenone
21. **Organic retrosynthesis is particularly important in the synthesis of:**
    (A) Fertilizers only (B) Pharmaceutical products (C) Metals (D) Glass
22. **Artificial Intelligence is mainly used in drug designing to:**
    (A) Increase melting point (B) Discover new drug molecules efficiently (C) Purify compounds (D) Measure pH
23. **Researchers at MIT used:**
    (A) Electrolysis (B) Machine-learning algorithms (C) Distillation (D) Chromatography



24. **AI was trained to identify molecules active against:**
    (A) Viruses (B) E. coli bacteria (C) Fungi only (D) Algae
25. **The antibacterial molecule discovered by AI was named:**
    (A) Aspirin (B) Halicin (C) Paracetamol (D) Penicillin
26. **Halicin was predicted to have:**
    (A) High toxicity (B) Low toxicity to human cells (C) No antibacterial activity (D) Strong acidic properties
27. **Halicin showed activity against bacteria that were:**
    (A) Sensitive only (B) Resistant to existing antibiotics (C) Non-pathogenic (D) Anaerobic only
28. **One major advantage of AI in drug discovery is:**
    (A) Longer research time (B) Faster identification of promising compounds (C) Elimination of laboratory testing (D) Increased production cost
29. **AI-based drug designing helps researchers discover compounds with:**
    (A) Similar structures only (B) Different structures from existing antibiotics (C) Higher boiling points (D) Metallic properties
30. **Organic synthesis makes complex molecules appear:**
    (A) Impossible to prepare (B) Simpler through retrosynthetic analysis (C) Unstable (D) Radioactive
31. **Retrosynthesis of pharmaceutical products aims to identify:**
    (A) More expensive reagents (B) Simpler starting materials (C) Final by-products (D) Catalysts only
32. **The synthesis of pharmaceuticals depends greatly on:**
    (A) Functional Group Interconversion (B) Radioactivity (C) Electrolysis (D) Fermentation

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

**BLOCK # 01**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. B | 4. B | 5. B | 6. B | 7. B | 8. B | 9. C | 10. B | 11. B | 12. B | 13. C | 14. B | 15. B |
| 16. B | 17. B | 18. B | 19. B | 20. B | 21. B | 22. B | 23. B | 24. B | 25. B | 26. B | 27. B | 28. A | 29. A | 30. B |
| 31. B | 32. B | 33. A | 34. B | 35. D | 36. B | 37. B | 38. B | 39. A | 40. B | | | | | |

**BLOCK # 02**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. A | 4. C | 5. B | 6. B | 7. B | 8. A | 9. B | 10. B | 11. A | 12. B | 13. B | 14. A | 15. B | 16. B |
| 17. A | 18. B | 19. B | 20. B | 21. B | 22. B | 23. B | 24. B | 25. B | 26. B | 27. B | 28. B | 29. B | 30. B | 31. B | 32. A |

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. **After disconnection the components obtained are called:**
   a) target molecule b) synthons c) synthetic equivalents d) starting material
II. **How will you convert the nitrile functional group (—C≡N) to the amine group?**
   a) by an oxidation reaction b) by a reduction reaction c) by an acid hydrolysis d) by an addition reaction
III. **Which reagent you will choose to convert aldehyde group into alcohol?**
   a) $KMnO_4/H^+$ b) $NaBH_4/H_3O^+$ c) Zn/HCl d) Na/Liquid $NH_3$
IV. **Which reagent is commonly used to oxidize primary alcohol into carboxylic acid?**
   a) $H_2$, Pd/C b) $LiAlH_4$ c) $K_2Cr_2O_7$, $H_2SO_4$ d) $NaBH_4$
V. **When toluene is treated with $KMnO_4/H_2SO_4$, we obtain:**
   a) benzyl chloride b) benzenesulphonic acid c) benzenecarboxylic acid d) acetophenone
VI. **Which functional group is formed when a carboxylic acid reacts with an alcohol in the presence of an acid as a catalyst?**
   a) alkane b) alcohol c) aldehyde d) ester

CamScanner

**VII. What is compound A in the given sequence?**

phenol $\xrightarrow{\text{nitration}}$ nitrophenol $\xrightarrow{\text{reduction}}$ aminophenol $\xrightarrow{\text{acetylation}}$ A

a) Aspirin b) Paracetamol c) Acetophenone d) Halicin

**VIII. In organic synthesis, what is the primary purpose of a 'Functional Group Interconversion' (FGI)?**

a) To break the molecule into smaller fragments
b) To increase total number of carbon atoms in molecule
c) To make the molecule more reactive
d) To change the functional group into another to enable a specific reaction

## Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | b | Synthons | Retrosynthetic disconnection gives idealized fragments called synthons. |
| II. | b | By a reduction reaction | $-C \equiv N$ (nitrile), is reduced to an amine by using $LiAlH_4$ or $H_2$/Ni to form a primary amine. $CH_3-C\equiv N + 4[H] \longrightarrow CH_3CH_2NH_2$ |
| III. | b | $NaBH_4/H_3O^+$ | $NaBH_4$ reduces an aldehyde carbonyl to a primary alcohol. |
| IV. | c | $K_2Cr_2O_7/H_2SO_4$ | Acidified dichromate under reflux oxidizes a primary alcohol fully to a carboxylic acid. |
| V. | c | Benzenecarboxylic acid | Hot acidified $KMnO_4$ oxidizes any benzylic side chain with a benzylic H/–$CH_3$ side chain to –COOH. |
| VI. | d | Ester | A carboxylic acid and alcohol undergo acid-catalysed esterification to form an ester and water. |
| VII. | b | Paracetamol | It is formed by nitration of phenol to p-Nitrophenol ⟶ reduction to p-aminophenol ⟶ acetylation of amino group gives paracetamol. |
| VIII. | d | To change the functional group into another to enable a specific reaction | FGI deliberately converts one functional group into another without changing the basic carbon skeleton. |

## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) Differentiate between synthesis and retrosynthesis.**

Ans.

| Synthesis | Retrosynthesis |
|---|---|
| • Its direction is forward. It moves from simpler starting materials to a complex target molecule. | • It moves from a complex target molecule to simpler structures. |
| • It is shown by standard reaction arrow (⟶). | • Retrosynthetic or disconnection arrow (⇒) means 'is made from'. |
| • Primary goal of 'Synthesis' is to physically execute the reactions in a lab to produce a compound. | • Primary goal of retrosynthesis is to theoretically deconstruct a molecule to plan a viable route. |

**b) How is a carboxylic group is converted to an amide group?**

Ans.

$$CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-ONH_4$$

$$-\overset{O}{\overset{\|}{C}}-ONH_4 \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$$

**Alternate Method**

$$R-COOH \xrightarrow{SOCl_2} R-COCl \xrightarrow{NH_3} R-\overset{O}{\overset{\|}{C}}-NH_2$$

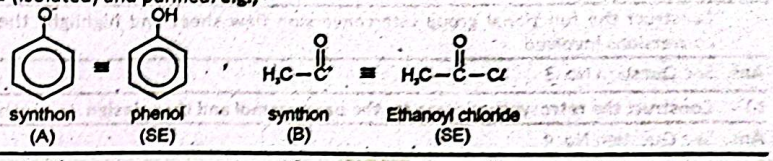
**c) How are synthon and synthetic equivalent are related to each other?**

Ans. Both synthon (the idea) and synthetic equivalent (the reality) are related as follows:

- Synthon is planning (retrosynthesis) and synthetic equivalent is execution (forward synthesis).



- Synthon is highly unstable (usually charged ions) and synthetic equivalent are stable compounds that can be separated (isolated) and purified. e.g.,




**d) Write down the formula of a common reagent used for oxidation of organic compounds.**

Ans. Common reagents (oxidizing agent) used are:

1. Potassium permanganate ($KMnO_4$).
2. Acidified potassium dichromate ($K_2Cr_2O_7$).

**e) Show with equations how an alcohol can be converted into amines, alkenes and halogenoalkanes.**

Ans. **Amine:** $CH_3-CH_2-OH \xrightarrow{SOCl_2} CH_3-CH_2-Cl \xrightarrow{NH_3} CH_3-CH_2-NH_2 + H_2O$

**Alkene:** $CH_3-CH_2-OH \xrightarrow{\text{conc. } H_2SO_4/170^\circ C} H_2C=CH_2 + H_2O$

**Halogenoalkanes:** $CH_3-CH_2-OH \xrightarrow{SOCl_2/\text{Pyridine}} CH_3-CH_2-Cl + SO_2 + HCl$

**f) What is a disconnection in retrosynthesis of a molecule?**

Ans.

- **Disconnection** is a process which involves the imaginary breaking down of the TM progressively into simpler starting materials.
- It is shown by retrosynthetic arrow ⇒.

**g) Mention one useful application of FGI in organic synthesis?**

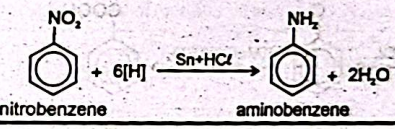
Ans. **Uses of FGI:**

FGI has a crucial role to play in designing routes which lead to target molecules.

i. Simple starting materials can be converted to more complex target molecules using FGI as building blocks.
ii. FGI not only allows to create the carbon skeleton of the target molecule but also select the route to be adopted for this purpose.

**h) Give one method for the reduction of a nitro group ($-NO_2$) to an amino group ($-NH_2$).**

Ans.




**i) How is a carboxylic group is converted to an alcohol?**

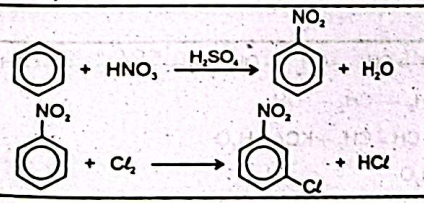
Ans. **Reduction by $LiAlH_4$:**

$$CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{LiAlH_4} CH_3-CH_2-OH$$

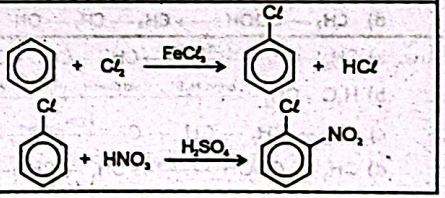
**j) Design synthesis of 3-chloronitrobenzene and 2-chloronitrobenzene starting from benzene in two steps.**

Ans.

**Synthesis of 3-chloronitrobenzene**




**Synthesis of 2-chloronitrobenzene**




CamScanner

## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) Construct the functional group interconversion flow sheet and highlight the important reagents and conversions involved.**

Ans. See Question No. 3

**b) Construct the retrosynthetic tree for the paracetamol and then design its synthesis.**

Ans. See Question No. 4

## DESCRIPTIVE QUESTIONS DQs

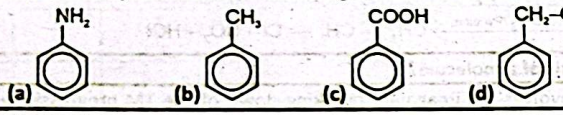
**Q.4 Give a detailed account of importance of retrosynthesis in organic synthesis.**

Ans. See Question No. 2

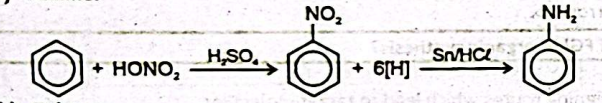
**Q.5 Construct the retrosynthetic tree for the aspirin and then design its synthesis.**

Ans. See Question No. 5

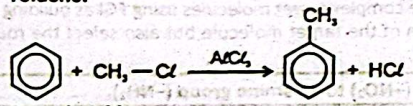
**Q.6 Design the synthesis of the following molecules starting from benzene.**



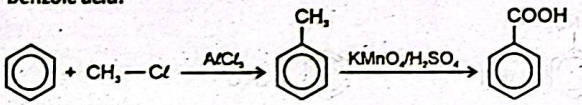

Ans. a) Aniline:



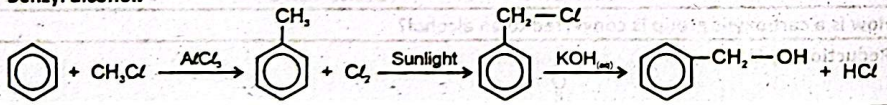

b) Toluene:




c) Benzoic acid:




d) Benzyl alcohol:




**Q.7 How will you carry out the following conversions?**

a) $CH_3—CH_3 \longrightarrow CH_3—COOH$

b) $CH_2=CH_2 \longrightarrow CH_3—CH_2—OH$

c) $CH_3—CH_2—CH_2—Cl \longrightarrow CH_3—CH=CH_2$

d) $CH_3—COOH \longrightarrow CH_3—CH_2—OH$

Ans. a) $CH_3—CH_3 \xrightarrow{Cl_2/Sunlight} CH_3—CH_2—Cl \xrightarrow{KOH_{aq}} CH_3—CH_2—OH + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3—COOH$

b) $H_2C=CH_2 \xrightarrow{conc.\,H_2SO_4,\,Cold\ then\ H_2O(H_2O/H^+)\,Warm} CH_3—CH_2—OH$

c) $CH_3—CH_2—CH_2—Cl \xrightarrow{KOH_{(alcoholic)}} CH_3—CH=CH_2 + KCl + H_2O$

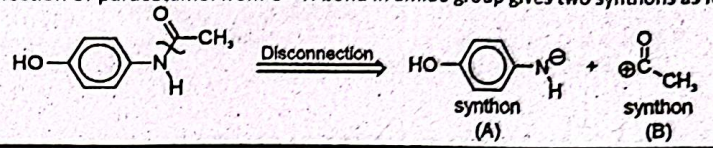
d) $CH_3—COOH \xrightarrow{LiAlH_4} CH_3—CH_2—OH + H_2O$



## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 Write down the two synthons prepared by disconnection of aspirin?**

Ans. The disconnection of paracetamol from C – N bond in amide group gives two synthons as follows:




**Q.2 What is Halicin? How it works?**

Ans. Halicin is an antibiotic discovered using artificial intelligence by researchers at MIT. It disrupts the bacterial membrane and pH gradient. It makes bacteria leak ions. Bacteria find it very hard to develop resistance to it.

**Q.3 Name two functional groups present in aspirin and state their impoartance.**

Ans. **1. Carboxylic Acid, –COOH:** It is responsible for acidic nature and anti-inflammatory activity.
**2. Ester, $–OCOCH_3$:** It makes less irritating to stomach than salicylic acid.

**Q.4 Differentiate between $NaBH_4$ and $LiAlH_4$ in FGI.**

Ans. $NaBH_4$ reduces only aldehydes and ketones.
$LiAlH_4$ is stronger and reduces aldehydes, ketones, esters, acids, amides and nitriles.

**Q.5 Why is aspirin preferred over salicylic acid as a drug?**

Ans. Salicylic acid directly irritates the stomach lining. In Aspirin the –OH group is converted to $–OCOCH_3$ ester by FGI, so it is less acidic and less irritating.

**Q.6 What is retrosynthesis tree and retrosynthetic arrow?**

Ans. **Retrosynthetic Tree** is a diagram showing all possible disconnections and synthons from the target molecule to starting materials.
**Retrosynthetic arrow** is an open-ended arrow and denoted by ⇒.

**Q.7 Define target molecule and synthetic equivalent?**

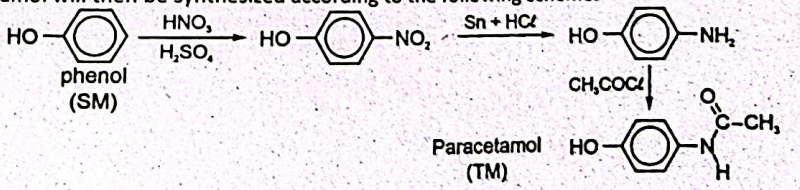
Ans. **Target Molecule (TM)** is the molecule which is to be prepared by disconnection.
**Synthetic Equivalent (SE)** is a reagent used to carry out the function of a synthon which cannot be used itself because it is usually unstable.

**Q.8 Define Organic synthesis.**

Ans. Organic synthesis is the branch of organic chemistry that deals with the planned, step-wise construction of a target molecule from simpler, readily available starting materials using chemical reactions.

**Q.9 How is paracetamol manufactured?**

Ans. **Synthesis of Paracetamol**
Paracetamol will then be synthesized according to the following scheme.




CamScanner

**Q.10 What is the role of functional group interconversion (FGI) in synthesis?**

**Ans. Role of Functional Groups in Synthesis:** Functional groups play a central role in designing a synthesis.

i) Functional group facilitate the chemists to predict and control the reactions which ultimately lead to the desired product.

ii) Identifying a functional group present in a compound can help to predict the properties of the compound.

iii) It helps in the development of new organic products, as well as to ensure the purity and composition of the products such as medicines and food additives.

## SELF-ASSESSMENT

Total Mark: 30

**Q.1 Encircle the correct option.** (1 × 6 = 6)

**(i) FGI is important because it helps:**
(A) Increase impurities (B) Design synthetic routes
(C) Reduce molecular weight only (D) Measure boiling point

**(ii) Retrosynthesis is:**
(A) Oxidation of compounds (B) Reverse analysis of synthesis
(C) Reduction reaction (D) Polymerization

**(iii) Synthons produced during retrosynthesis are:**
(A) Real isolated compounds (B) Theoretical fragments
(C) Catalysts (D) Indicators

**(iv) AI-based drug designing helps researchers discover compounds with:**
(A) Similar structures only (B) Different structures from existing antibiotics
(C) Higher boiling points (D) Metallic properties

**(v) After disconnection the components obtained are called:**
(A) target molecule (B) synthons (C) synthetic equivalents (D) starting material

**(vi) What is compound A in the given sequence?**

phenol $\xrightarrow{\text{nitration}}$ nitrophenol $\xrightarrow{\text{reduction}}$ aminophenol $\xrightarrow{\text{acetylation}}$ A

(A) Aspirin (B) Paracetamol (C) Acetophenone (D) Halicin

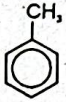
**Q.2 Write short answers of the following questions.** (2 × 8 = 16)

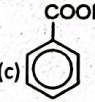
(i) Convert: $CH_3—CH_3 \longrightarrow CH_3—COOH$
(ii) Convert: Phenol into Phenyl ethanoate
(iii) Differentiate between synthesis and retrosynthesis.
(iv) How a carboxylic group is converted to an amide group?
(v) How synthon and synthetic equivalent are related to each other?
(vi) Mention one useful application of FGI in organic synthesis?
(vii) What is the overall functional group difference in aspirin and paracetamol?
(viii) How a carboxylic group is converted to an alcohol?

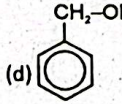
**Q.3 Extensive Questions.** (4 + 4 = 8)

(a) Construct the retrosynthetic tree for the aspirin and then design its synthesis.
(b) Design the synthesis of the following molecules starting from benzene.

(a) 


(b) 


(c) 


(d) 




## ENTRANCE TEST MCQs

1. **Disconnection of an ester at the acyl-oxygen bond commonly suggests which pair of synthetic equivalents?**
(A) An alkane and ammonia (B) Two alkenes
(C) A nitrile and halogen (D) A carboxylic acid or acyl derivative and an alcohol

2. **Disconnection of an aryl ketone between the ring and carbonyl carbon suggests:**
(A) A nitrile and water (B) An arene and an acyl chloride
(C) An alcohol and ammonia (D) An alkene and HBr

3. **A target has two plausible disconnections. Which is generally preferred?**
(A) The one with no forward precedent (B) The route with available reagents and a reliable reaction
(C) The one generating the most fragments (D) The one requiring the rarest catalyst

4. **Retrosynthetic analysis works in the reverse direction of:**
(A) Chromatography (B) Spectroscopy (C) Combustion analysis (D) Forward synthesis

5. **Select the correct sequence to make propan-1-amine from a two-carbon starting material by adding one carbon.**
(A) Ethanal → ethanol → methanamine (B) Ethanoic acid → ethanoyl chloride → methanamine
(C) Bromoethane → propanenitrile → propan-1-amine
(D) Ethanol → ethene → ethanamine

6. **Select the correct sequence for converting ethanol into ethanamine through the progression grid.**
(A) $SOCl_2$, then water only (B) $PBr_3$, then excess ethanolic $NH_3$ under pressure
(C) $NaBH_4$, then $H_2SO_4$ (D) $K_2Cr_2O_7$, then KCN

7. **Which reagent sequence changes benzene into phenol without using diazonium chemistry?**
(A) $SO_3/H_2SO_4$; fused NaOH; HCl (B) $HNO_3/H_2SO_4$; Sn/HCl; $NaNO_2$
(C) $CH_3Cl/AlCl_3$; $KMnO_4$ (D) $Cl_2/FeCl_3$; KCN

8. **Which route has the best atom economy for ethyl ethanoate in principle?**
(A) Ethanoyl chloride plus ethanol (B) A multistep route through bromoethane
(C) Oxidation followed by chlorination (D) Direct esterification of ethanoic acid with ethanol

9. **The practical synthetic equivalents from the first paracetamol disconnection are:**
(A) Phenol and ethanol (B) Aniline and methanoic acid
(C) Benzoic acid and ammonia (D) 4-aminophenol and ethanoyl chloride

10. **Why is the amide C–N bond a strategic first disconnection in paracetamol?**
(A) It requires an unstable amide anion in the lab (B) It maps onto a reliable amine–acyl chloride reaction
(C) It produces two alkanes (D) It avoids all functional groups

11. **The practical synthetic equivalents from the first aspirin disconnection are:**
(A) Phenol and ethanoyl chloride only (B) Aniline and $CO_2$
(C) Salicylic acid and acetic anhydride (D) Benzoic acid and ethanol

12. **Why is retrosynthesis clearer than direct synthesis for aspirin?**
(A) Retrosynthesis changes the molecular formula (B) It reveals familiar steps from simple precursors
(C) Direct synthesis is impossible (D) Aspirin contains no functional groups

13. **Which sequence prepares 3-chloronitrobenzene selectively from benzene?**
(A) Nitration then chlorination with $Cl_2/FeCl_3$ (B) Chlorination then nitration for a meta product
(C) Methylation then oxidation (D) Sulfonation then reduction

14. **Which sequence prepares mainly 2- and 4-chloronitrobenzene from benzene?**
(A) Nitration first, then chlorination (B) Reduction then oxidation
(C) Acylation then hydrolysis (D) Chlorination first, then nitration

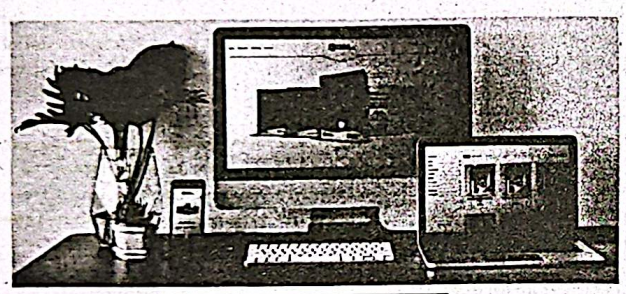
15. **A route to 4-hydroxybenzoic acid from benzene must control:**
(A) Only alkane combustion (B) No ring substitution
(C) COOH introduction and para orientation of OH (D) Only molecular mass

**Answers Key**

| 1. D | 2. B | 3. B | 4. D | 5. C | 6. B | 7. A | 8. D | 9. D | 10. B | 11. C | 12. B | 13. A | 14. D | 15. C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

CamScanner

SCHOLAR PUBLICATIONS'
ONLINE STORE
: www.scholarseries.com



BUY ONLINE
Cash on Delivery (COD) Services
Available Now...!!

SCHOLAR PUBLICATIONS



26 CHAPTER

# POLYMERS

## Student Learning Outcomes (SLOs)

[C-12-D-98 to C-12-D-108]

- Describe the chemical processes of addition and condensation polymerisation and the differences between them. Examples include:
  - Addition polymers such as poly(ethene) and poly(chloroethene), PVC.
  - Polyesters (from reaction of diol and dicarboxylic or dioyl and hydroxy acid.
  - Polyamides (from reactions of a diamine and a dicarboxylic acid or dioyl chloride of an aminocarboxylic acid or between amino acids).
- Describe the condensation reaction of ammonia or an amine with acyl chloride at room temperature to give an amide.
- Explain the chemical processes and properties of PVC and nylon and applications of these polymers in the industry.
- Identify the polymer formed, the monomer present in a section of polymer, and classify them as one of the two polymers.
- Deduce the repeating unit of a polymer obtained from a given monomer or pair of monomers and identify the monomers present in a given section of a polymer molecule.
- Predict the type of polymerisation reaction for a given monomer or pair of monomers.
- Recognize that polyesters and polyamides are biodegradable by acidic and alkaline hydrolysis.
- Recognize that some polymers can be degraded by the action of light.
- Recognize that poly(alkene) is chemically inert and can, therefore, be difficult to biodegrade.
- Explain the challenges associated with the disposal of non-degradable polymers.
- Outline the use of polymers to create artificial organs in biomedical science.

**Q.1 What are polymers? Give the daily life examples.** S/C

**Ans.** ***Polymers are very large molecules made by joining many small molecules called monomers through polymerisation.*** Organic polymers are modern materials of great significance. They have made our lives easier, more efficient, and highly economical due to their superior properties and affordable costs.

**Daily Life Examples:** Polymers can be observed in our daily lives from shopping bags (poly(ethene)) and clothesline (poly(propene)) to plastics used in bulletproof vests (Kevlar®) and aerospace applications as shown in Figure.

The properties of polymers broadly vary depending on the type and number of monomers in the polymer, and the method through which they are manufactured.



(a) (b)

Figure: a) A bulletproof vest made from Kevlar®
b) poly(propene) rope

- **Soft Polymers:**
  Some polymers are very light and soft, which are suitable for applications where soft materials are needed. **Examples:** Poly(ethene) and poly(propene)
- **Hard Polymers:**
  Some polymers are hard and thermally very stable their utilization as hard and durable materials. **Examples:** Kevlar® is a hard material suitable for bulletproof vests.

CamScanner

**Keep in Mind**

**Systematic Names of Polymers**

Synthetic polymers are named systematically by writing the prefix "poly" before the name of the monomer. For example, polythene is systematically named as poly(ethene) and poly(chloroethene) is called poly(chloroethene). For polymers with two or more monomers, common names are usually used because the systematic name is too long. This is why poly(ethane-1, 2-diyl benzene-1,4-dicarboxylate) is commonly called polyethylene terephthalate, i.e. PETE.

## POLYMERISATION

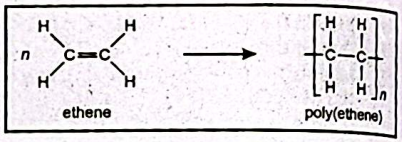
**Q.2 Compare and contrast addition and condensation polymerization, giving details of the specific structural requirements for the monomers in each.** Exercise D/Q.4

**Ans.** Polymerisation is the process of joining monomers to form a polymer. There are two main types of polymerisation:
i) Addition polymerisation ii) Condensation polymerisation.

### ➲ Addition Polymerisation

***In the addition polymerisation, monomers add to each other one by one, forming long chains. All the atoms from the original monomers become part of the polymer.***

Nothing is lost. Monomers must have a carbon-carbon double (C = C) or triple bond (C ≡ C). This bond "opens up" to allow monomers to link together. No small molecules (like water) are produced as side products. This often happens through a "chain reaction" started by a very reactive molecule (an initiator, which forms free radicals).




Poly(ethene), a large number of ethene ($CH_2 = CH_2$) molecules add together by breaking double bonds and linking end-to-end, to form the poly(ethene) chain.

$$n\,CH_2 = CH_2 + \text{initiator} \xrightarrow{\text{heat/pressure}} [-CH_2-CH_2-]_n$$

ethene poly(ethen)

Where, $n$ is very large, e.g., up to 10000

Poly(ethene) is primarily of two types: • low density poly(ethene) (LDPE) • high density poly(ethene) (HDPE)

➢ **Low Density Poly(ethene) Vs. High Density Poly(ethene):**

Low density poly(ethene) is used where a very light and soft material is needed, such as shopping bags, light plastic bottles, etc. HDPE is typically produced from ethene using a coordination catalyst called Zeigler-Natta catalyst at a low pressure and temperature. It finds its uses in plastic containers, thick shopping bags, toys, etc. LDPE and HDPE differ in the nature of their chains with LDPE being more branched. This prevents the chains from packing tightly, giving a less solid and more elastic material. While HDPE has linear chains allowing them to pack closely to give a compact structure with tough and dense material.

**Did You Know?**

Ziegler-Natta catalysts are a Nobel Prize-winning invention that revolutionized plastic production. It was initially discovered by Karl Ziegler in 1953. This catalyst enabled, for the first time, the low-pressure polymerisation of ethene into linear, high-density poly(ethene) (HDPE). This same catalyst family was expanded by Giulio Natta to create stereoregular polymers, such as crystalline polypropylene.

**Q.3 Describe the chemical role of plasticizers in polyvinyl chloride (PVC) and explain how this modification influences the polymer's industrial applications.** Exercise C/Q.3(a)

**Ans.**

### Polyvinyl Chloride (PVC)

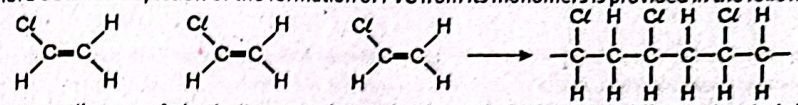
Poly(chloroethene) or PVC is made from a monomer called chloroethene ($CH_2$=$CHCl$) through an addition polymerisation reaction.

$$nCH_2 = CHCl + \text{initiator} \longrightarrow [-CH_2-CHCl-]_n$$

chloroethene poly(chloroethene) or PVC



A more detailed depiction of the formation of PVC from its monomers is provided in the following scheme.



PVC is a versatile type of plastic. Its properties can be changed a lot by adding different chemicals (plasticizers).

- **Plasticizers:** Plasticizers are chemicals added to materials to make them softer, more flexible, and easier to work with. They cause this by reducing the strong forces between polymer chains, allowing them to move more freely.
- **Role of PVC:** Rigid PVC (without plasticizers) is hard and stiff and does not bend easily. It is chemically inert because it does not react with most acids, bases, or oils. It is a good electrical insulator. Due to the chlorine atoms, it is naturally resistant to burning and self-extinguishing. It lasts a long time and resists weathering. Plasticized PVC (with plasticizers) is flexible and soft, so it can be bent and shaped easily. It maintains good chemical and electrical properties, but is less rigid.

➢ **Industrial Applications of PVC:**

Various uses of PVC include:

i. Pipes and fittings for water supply, drainage, and sewage systems due to its corrosion resistance and durability.
ii. Window frames and door profiles, floor vinyl tiles and sheets
iii. Electrical insulation for wires and cables.
iv. Tubing, blood bags, and catheters.
v. Cling films, bottles (e.g., for cooking oil), blister packs.
vi. Raincoats, artificial leather, inflatable products (e.g., swimming pools).




Figure: Various uses of PVC

### ➲ Condensation Polymerisation

**Q.4 Illustrate the formation of two major condensation polymers.** Exercise D/Q.5

**Ans.** ***In condensation polymerisation, monomers join together, but each time a new bond forms, a small molecule is eliminated from the monomers.*** This small molecule is usually water, but can also be $HCl$, $CH_3OH$, or $NH_3$. Monomers must have at least two reactive functional groups (like –OH, –COOH, $–NH_2$) that can react with each other. These groups are present on different ends of the monomer(s). Small molecules are always produced as a side product. This typically happens in a "step-by-step" manner as depicted in Figure.

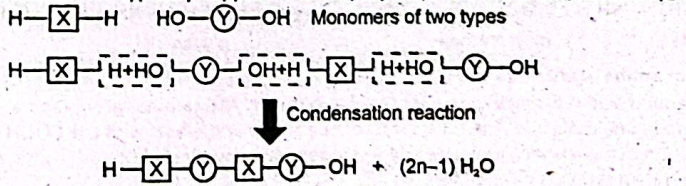



Figure: Illustration of condensation polymerisation

CamScanner

**a) Polyesters:**

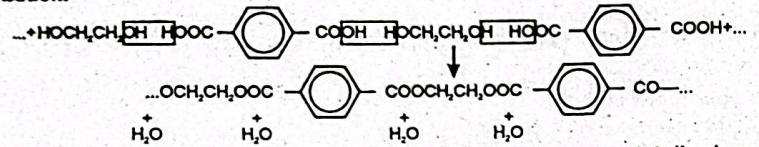
Polyesters have ester linkages [— C(=O) — O —] in their backbone. A diol (molecule with two –OH groups) and a dicarboxylic acid (molecule with two-COOH groups) are combined as monomers are combined to give a polyester. The –OH from the diol reacts with the –COOH from the acid. A molecule of water is removed as shown below.

**Monomers:**

$HOCH_2CH_2OH$ — ethane-1,2-diol

HOOC–C$_6$H$_4$–COOH — benzene-1,4-dicarboxylic acid

**Polymerisation:**



**Preparation of Terylene/PET, a polyester from ethane-1,2-diol and Benzene-1,4-dicarboxylic acid.**

Polyesters have special features, such as high tensile strength, which make them suitable to manufacture fibres. Polyester is used as an alternative to cotton due to its low cost and ability to resist creases. It is also used as a plastic; for example, PET is used in making plastic bottles for beverages and other food packaging. Polyester is also used as cross-linked polymer to obtain hard plastics. Glass fibre-reinforced plastics use glass fibers set in a cross-linked polyester resin.

**b) Polyamides:**

Polyamides have amide linkages [— C(=O) — NH —] in their backbone. They can be prepared from many starting materials.

**i) From a Diamine and a Dicarboxylic Acid:**

A diamine (molecule with two –$NH_2$ groups) and a dicarboxylic acid (molecule with two –COOH groups) are joined together to give polyamide. The –$NH_2$ from the diamine reacts with the –COOH from the acid. A molecule of water is removed.

$$nH_2N-CH_2-NH_2 + nHOOC-CH_2-COOH \longrightarrow [-HN-CH_2-NH-C(=O)-CH_2-C(=O)-]_n + 2nH_2O$$

diamine — dicarboxylic acid — polyamide

**Example:** Nylon 6, 6 is formed by the condensation of hexamethylenediamine and adipic acid.

**ii) From a Diamine and a Dioyl Chloride:**

A diamine and a dioyl chloride (molecule with two –COCℓ groups) as monomers are joined to give polyamide. Dioyl chlorides are more reactive than dicarboxylic acids. The –$NH_2$ from the diamine reacts with the –COCℓ from the dioyl chloride. A molecule of hydrogen chloride (HCℓ) is removed.

The general equation is given below:

$$nH_2N-CH_2-NH_2 + nC\ell OC-CH_2-COC\ell \longrightarrow [-HN-CH_2-NH-C(=O)-CH_2-C(=O)-]_n + 2nHC\ell$$

diamine — dioyl chloride — polyamide

**iii) From amino acids**

An amino acid is a single monomer that has both an –$NH_2$ (amino) group and a –COOH (carboxylic acid) group in one molecule. The –$NH_2$ group of one amino acid reacts with the COOH group of another amino acid removing a water molecule to form a peptide bond. Peptide bond is also a type of amide linkage. General equation is given below:



$$nH_2N-CH_2-COOH \longrightarrow [-HN-CH_2-C(=O)-]_n + nH_2O$$

amino-carboxylic acid — polyamide/polypeptide

Proteins are natural polyamides made from amino acids, which will be discussed in Biochemistry (Chapter 27). Amide linkage is also formed between acyl chloride, a very reactive organic compound and an amine, e.g. ammonia, methanamine ($CH_3-NH_2$), N-methyl-methanamine, $(CH_3)_2NH$ etc. When an acyl chloride reacts with ammonia or an amine, a molecule of hydrogen chloride (HCℓ) gas is removed. This reaction occurs easily at room temperature because acyl chlorides are fairly reactive.

$$R-C(=O)-C\ell + R'-NH_2 \longrightarrow R-C(=O)-NH-R' + HC\ell$$

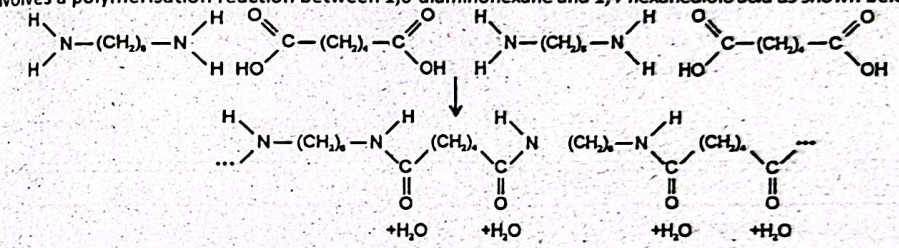
(acyl chloride) (amine) (amide) (hydrogen chloride)

## NYLON

**Q.5 Discuss nylon as a condensation polymer or write a short note on nylon 6, 6.** U/Q

**Ans. Nylon:** Nylon is a type of synthetic polyamide. It is formed by condensation polymerisation, usually from two different monomers (a diamine and a dicarboxylic acid). During the reaction, a small molecule, typically water, is removed. Generally, a diamine ($H_2N-R-NH_2$) and a dicarboxylic acid (HOOC–R–COOH) act as monomers.

**Nylon 6, 6:** Nylon 6, 6 is the most common example of synthetic polyamides. The formation of Nylon 6, 6 involves a polymerisation reaction between 1,6-diaminohexane and 1,4-hexanedioic acid as shown below.

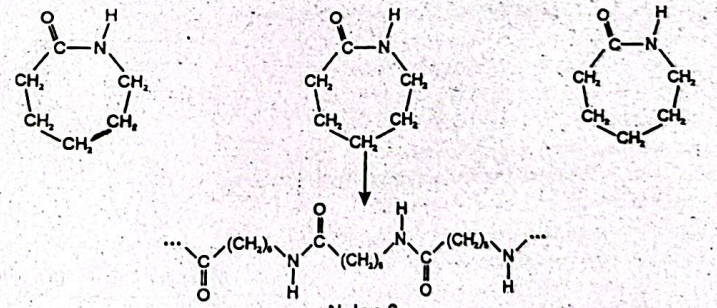


**Preparation of nylon-6,6**

**Nylon-6:** Another type of nylon is nylon-6, which is formed from a single monomer called caprolactam as in the following scheme. It is named nylon-6 because it involves a monomer with six carbon atoms. Caprolactam has a cyclic structure as shown in the following figure. The reaction is not a typical condensation reaction because no small molecule is removed during the reaction. Nylon 6 is classified as a condensation polymer due to the mode of formation of the amide linkage.

The wheels of this skateboard are made from nylon, due to its hard, smooth, and shock-free nature.



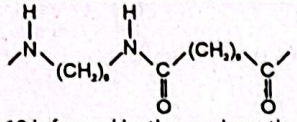


**Nylon 6**

Nylon 6,6 is harder, nylon-6 is tougher (higher impact resistance) with a lower melting point. It is easier to mold as its melting point is lower than nylon 6,6. It is mostly used in rollers, skate board wheels, and power tool handles to avoid shocks.

### QUICK CHECK 26.1

**a) The repeating unit of nylon-6, 10 is shown below. Draw the structures of its monomers from this structure.**



**Ans.** From the repeating unit, nylon-6,10 is formed by the condensation of following two monomers:

**(i) Hexane-1,6-diamine (1,6-diaminohexane):**
$H_2N(CH_2)_6NH_2$ (It is a six-carbon diamine repeating unit).

**(ii) Decanedioic acid (Sebacic acid):**
$HOOC(CH_2)_8COOH$ (It is a ten carbon dicarboxylic repeating unit).

These two monomers combine with the elimination of water molecules to form nylon-6, 10.

**b) Monomers of nylon-6,4 are given below. Draw the structure of the repeating unit of the polymer formed from these monomers.**

$H_2N-(CH_2)_6-NH_2$ $\qquad$ $HOOC-(CH_2)_2-COOH$

**Ans.** Given monomers are:

Hexane-1, 6-diamine ($H_2N-(CH_2)_6-NH_2$) and Butanedioic acid/Succinic acid ($HOOC-(CH_2)_2-COOH$)

During polymerization, the amino group reacts with the carboxyl group to form an amide linkage (–CONH–).

The repeating unit of nylon-6,4 is:

$$[-NH-(CH_2)_6-NH-CO-(CH_2)_2-CO-]_n$$

This polymer contains repeating **amide linkages (–CONH–)** and is therefore classified as a **polyamide.**

**Note Nylon-x, y:** x = c-atoms in diamine, y = c-atoms in diacid.

**Q.6 Write down the properties and industrial applications of nylon.** L/Q

**Ans.**

## Properties of Nylon

- Strong and resistant to breaking and can withstand rubbing and wear and tear.
- Stretchable due to elasticity.
- Slippery surface, reduces friction.
- Generally resistant to oils, many solvents, and alkalis.
- High melting point.

## Industrial Applications of Nylon

- It is used for clothing (stockings, active wear, and swimwear), carpets, and ropes due to its strength and elasticity. Its fabric is used for raincoats, sportswear, and lingerie.
- Nylon is used for the manufacturing of mechanical parts of automotive industry like gears, bearings, bushings, engine covers, and fuel lines due to its strength, low friction, and heat resistance.
- Nylon is also used in making of machine parts such as screws, nuts, bolts, and various industrial components where strength and wear resistance are needed.
- It is also commonly used to make ropes, fishing nets, and lines due to its high tensile strength and resistance to water.

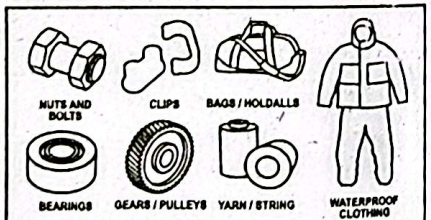



Figure: General uses of different types of nylon

- Consumer goods like zippers, toothbrushes, hairbrushes, and various molded plastic parts are made of nylon.



## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. A polymer is formed by joining many:
(A) Atoms (B) Monomers (C) Molecules of water (D) Ions
2. Polymerisation is the process of:
(A) Breaking polymers (B) Joining monomers to form polymers
(C) Oxidation of polymers (D) Hydrolysis of polymers
3. There are _____ main types of polymerisation.
(A) One (B) Two (C) Three (D) Four
4. Addition polymerisation requires monomers containing:
(A) –OH groups (B) C = C or C ≡ C bonds (C) –COOH groups only (D) $-NH_2$ groups only
5. During addition polymerisation:
(A) Water is eliminated (B) HCℓ is produced
(C) All atoms of the monomer become part of the polymer (D) $NH_3$ is released
6. Addition polymerisation usually proceeds through a:
(A) Neutralization reaction (B) Chain reaction (C) Hydrolysis reaction (D) Esterification reaction
7. The monomer used to prepare poly(ethene) is:
(A) Ethane (B) Ethene (C) Ethanol (D) Ethyne
8. Poly(ethene) is formed by breaking the:
(A) C – C single bond (B) C = C double bond (C) C – H bond (D) O – H bond
9. LDPE stands for:
(A) Low Density Poly(ethene) (B) Linear Density Poly(ethene)
(C) Low Durable Polymer (D) Long Density Plastic
10. HDPE is produced using:
(A) Concentrated $H_2SO_4$ (B) Ziegler-Natta catalyst (C) $KMnO_4$ (D) $LiAlH_4$
11. Compared with HDPE, LDPE has:
(A) More linear chains (B) More branched chains (C) More ester linkages (D) More amide linkages
12. HDPE is:
(A) Softer than LDPE (B) More compact and denser (C) More branched (D) Less durable
13. PVC is prepared from:
(A) Ethene (B) Chloroethene (C) Ethyne (D) Ethanol
14. PVC is the common name for:
(A) Poly(propene) (B) Poly(chloroethene) (C) Poly(ethene) (D) Poly(styrene)
15. Plasticizers are added to PVC to make it:
(A) Harder (B) Softer and flexible (C) More brittle (D) Conductive
16. Rigid PVC is commonly used for:
(A) Blood bags (B) Water pipes (C) Clothing (D) Rubber bands
17. Plasticised PVC is commonly used for:
(A) Pipes only (B) Catheters and blood bags (C) Glass bottles (D) Steel wires
18. Condensation polymerisation differs from addition polymerisation because:
(A) No by-product is formed (B) Small molecules are eliminated
(C) Double bonds are required (D) Only one monomer is used
19. The small molecule most commonly removed during condensation polymerisation is:
(A) $O_2$ (B) $H_2O$ (C) $CO_2$ (D) $C\ell_2$
20. Condensation polymerisation requires monomers having:
(A) One functional group (B) At least two reactive functional groups
(C) Only C=C bonds (D) Only aromatic rings
21. Polyesters contain:
(A) Ether linkages (B) Ester linkages (C) Amide linkages (D) Peptide linkages
22. PET (Terylene) is prepared from:
(A) Ethene and benzene (B) Ethane-1,2-diol and benzene-1,4-dicarboxylic acid
(C) Ethanol and acetic acid (D) Phenol and methanol
23. PET is commonly used for manufacturing:
(A) Steel rods (B) Plastic beverage bottles (C) Rubber tyres (D) Glass windows
24. Polyamides contain:
(A) Ester linkages (B) Amide linkages (C) Ether linkages (D) Alkene groups
25. Nylon is classified as a:
(A) Polyester (B) Polyamide (C) Addition polymer (D) Natural polymer
26. Nylon-6,6 is formed from:
(A) Two different monomers (B) One monomer only (C) Ethene only (D) Propene only

CamScanner

27. Nylon-6 is prepared from:
(A) Caprolactam (B) Ethene (C) Styrene (D) Vinyl chloride
28. Nylon-6 is classified as a condensation polymer because:
(A) It contains ester bonds (B) It forms amide linkages (C) It is biodegradable (D) It contains chlorine
29. Nylon is characterized by:
(A) Low melting point and softness (B) High strength and wear resistance
(C) High electrical conductivity (D) Low durability
30. Nylon has a:
(A) Slippery surface (B) Sticky surface (C) Metallic surface (D) Glassy surface
31. Nylon is resistant to:
(A) Oils and many solvents (B) Strong oxidizing agents only (C) Water only (D) Oxygen only
32. Nylon is widely used in:
(A) Clothing and ropes (B) Cement (C) Glass manufacture (D) Fertilizers
33. Nylon is used in automobile parts because of its:
(A) Low density only (B) Strength and heat resistance
(C) High electrical conductivity (D) Transparency
34. Which property makes nylon suitable for fishing nets?
(A) Solubility (B) High tensile strength (C) Low melting point (D) Brittleness
35. Nylon is commonly used to manufacture:
(A) Toothbrushes (B) Copper wires (C) Wooden furniture (D) Glassware
36. Proteins are natural:
(A) Polyesters (B) Polyamides (C) Polyalkenes (D) Polyethers
37. A peptide bond is a type of:
(A) Ester linkage (B) Amide linkage (C) Ether linkage (D) Glycosidic linkage
38. Acyl chlorides react readily with amines because acyl chlorides are:
(A) Inert (B) Highly reactive (C) Weak acids (D) Non-polar
39. During the reaction of an acyl chloride with an amine, the by-product formed is:
(A) $CO_2$ (B) $H_2$ (C) HCl (D) $NH_3$
40. Which of the following is not an addition polymer?
(A) Poly(ethene) (B) PVC (C) Nylon-6,6 (D) HDPE

## IDENTIFICATION OF THE TYPE OF A POLYMER, REPEAT UNIT AND MONOMERS FROM A POLYMER SECTION

To identify the type of a polymer from its skeletal or structural formula, the key point is to look for the repeating linkage and the monomer units.

On the basis of polymerization process, polymers are classified into following two classes:

i. **Addition polymers**
ii. **Condensation polymers**

**Q.7 Write down the steps to find the type of polymer.** L/Q

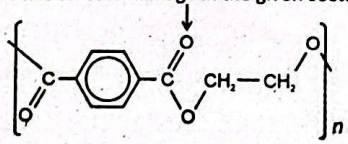
**Ans.** Follow the given steps to identify the type of the polymer by considering the example of poly(ethene)

**1. Identifying the Type of Polymer:**

a. The first thing to check is what atoms make up the main horizontal chain of the polymer, **i.e.,** to identify the backbone. .
b. If the main chain consists only of carbon atoms (–C – C – C – C–), it is an addition polymer. These are formed from alkenes.
c. If the main chain contains oxygen (O) or nitrogen (N) atoms with carbon, it is a condensation polymer (like polyesters or polyamides).

Now, identify the functional linkage. There are again two possibilities:

i. **If a carbonyl group (C = O) is directly attached next to an oxygen (O):** Such polymers are classified as polyesters. For example, PET has an ester linkage in the given section of its structure.





ii. **If there is a carbonyl group (C = O) directly next to a nitrogen (N) with a hydrogen (H) attached, it** presents an amide or peptide linkage. The polymer is, therefore, classified as a polyamide (e.g., Nylon 6,6 or Kevlar).

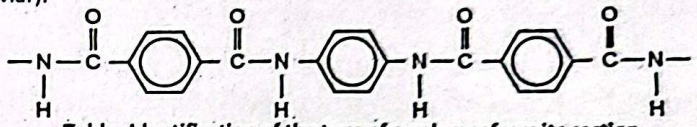


**Table: Identification of the type of a polymer from its section**

| Functional Groups in the Polymer | Type | Example |
|---|---|---|
| Only C-C bonds in the chain | Addition Polymer | Poly(ethene), PVC, PTFE (poly (tetrafluoroethen)) |
| –COO– links | Polyester | Terylene, PLA (poly(lactic acid)) |
| –CONH– links | Polyamide | Nylon-6,6, Kevlar |

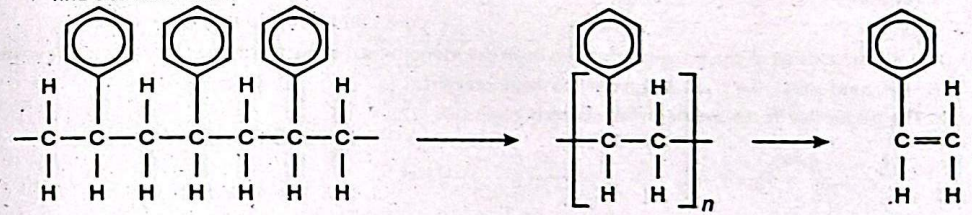
**2. Determining the "Repeat Unit:**

To find the original monomers, one must first identify the smallest section that repeats itself in the section of the polymer.

i. To find the repeating pattern, look for where the sequence starts to duplicate itself. Locate such duplicating sections in the backbone.
ii. Place brackets around one of these recurring sections and add the subscript n. This section within the brackets is the repeat unit of the polymer.

**3. Identifying the Monomer(s):**

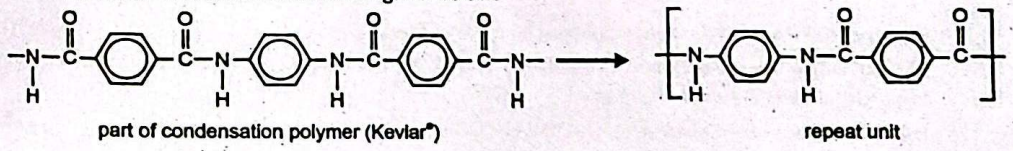
a) **For addition polymers,** change the C – C single bond in the repeat unit back into a C = C double bond to find the monomer.



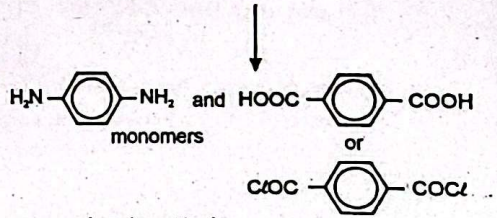
part of addition polymer — repeat unit — monome

**Identification of repeat unit and monomers (addition)**

b) **For Condensation polymers,** add water back in. Break the ester or amide bond. Add -OH to the C = O side and -H to the O or N side as given below.



part of condensation polymer (Kevlar®) — repeat unit



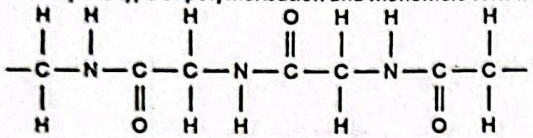
monomers — or

**Identification of repeat unit and monomers (condensation)**

## QUICK CHECK 26.2

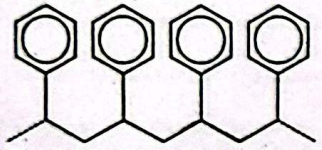
**a) Identify the type of polymerisation and monomers forming the following polymers.**

i)



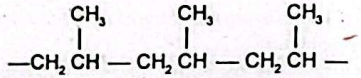
**Ans.** The polymer contains **amide linkages (–CONH–)**, therefore it is formed by **condensation polymerisation.**
**Type of polymerisation:** Condensation polymerisation
**Monomers:** Aminoethanoic acid (Glycine) $H_2NCH_2COOH$
Since each monomer contains both an amino group and a carboxyl group, it undergoes self-condensation to form the polyamide.

ii)



**Ans.** The structure shown is **polystyrene.**
**Type of polymerisation:** Addition polymerization.
**Monomer:** Phenylethene (Styrene)
$C_6H_5CH = CH_2$ or $CH_2 = CHC_6H_5$

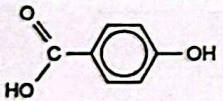
iii)



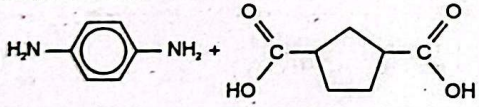
**Ans.** The polymer shown is **polypropene (polypropylene).**
**Type of polymerisation:** Addition polymerization.
**Monomer:** Propene ($CH_2 = CHCH_3$)
The carbon-carbon double bond of propene opens and forms the polymer chain.

**Give the structures of the polymers formed from the monomers. For each polymer identify the following?**
**i. The repeat unit** **ii. The type of linkage present**
**iii. The attractive force between the polymer chains.**

1)



2)



**Ans. 1)** The monomer contains an –OH group and a –COOH group and it undergoes condensation polymerization.
**(i) Repeat unit:** $[-O-C_6H_4-CO-]_n$
**(ii) Type of linkage:** The polymer contains an ester linkage: $-\overset{O}{\overset{\|}{C}}-O-$
**(iii) Attractive forces between the polymer chains:** Permanent dipole-dipole forces and London dispersion forces between the chains.

**2)** The $-NH_2$ groups of the diamine react with the –COOH groups of the dicarboxylic acid, eliminating water.
**(i) Repeat unit:** $-[NH-C_6H_4-NH-CO-C_5H_8-CO]_n-$
**(ii) Type of linkage:** Amide linkage: $-\overset{O}{\overset{\|}{C}}-NH-$
**(iii) Attractive force between the polymer chains:** Hydrogen bonding between N – H and C = O groups of neighbouring polymer chains.



## USING MONOMER(S) TO PREDICT THE TYPE OF POLYMERISATION

**Q.8 How monomer(s) are used to predict the type of polymerization? Give examples.** UQ

**Ans.**

### Addition Polymers

When the given monomer(s) contains C = C bonds, addition polymerisation will take place. The examples include ethene, propene, phenyl ethene (styrene) mostly homopolymers are formed through the addition polymerization. However, sometimes copolymerisation of two different monomers having double bond can also be achieved. Such an example is a copolymer of ethene and propenoic acid ($H_2C = CH - COOH$).

### Condensation Polymers

When there are two functional groups available for the formation of a bond or bridging linkage to create the polymeric chains, the condensation polymerisation takes place. Mostly, a small molecule is removed from the two monomers during the formation of the polymer. The two functional groups may exist in a single molecule (e.g. lactic acid) or two different molecules, as in the case of nylon 6, 6.
The common functional groups that can undergo condensation polymerisation are:

- amino group ($-NH_2$) and carboxylic (–COOH) group (polyamide and $H_2O$)
- amin group ($-NH_2$) and acyl chlorides (–COCl) (polyamide and HCl)
- carboxylic group (–COOH) and alcohols (–OH) (polyester and $H_2O$)
- acyl chlorides (–COCl) and alcohols (–OH) (polyester and HCl).

## CHALLENGE OF NON-DEGRADABLE POLYMERS

**Q.9 What are the challenges of non-degradable polymers?** UQ

**Ans.** Plastic, such as poly(ethene), is the most widely used polymeric material on the globe. ***Conventional polymers are generally non-degradable, which means they cannot be broken down into simpler, non-toxic compounds.*** Due to this reason, they become an environmental nuisance after their disposal. These polymers become part of water bodies, soil, and natural habitats of living organisms. Therefore, scientists are now developing degradable polymers to cope with this issue. The plastic material is either buried underground or even disposed of in the open air in the regions where the municipal waste management systems are inadequate. This is because of the following reasons:

- They stay in the environment for a very long time. This means they accumulate in landfills, oceans, and natural landscapes, leading to persistent pollution.
- They take up huge volumes of space in landfills because they do not decompose. As the amount of plastic grows, finding space for more landfills becomes difficult.
- Animals (especially marine life) can mistake plastic waste for food, leading to choking, internal injuries, or starvation. They can also get tangled in plastic debris.
- Over time, large pieces of non-degradable plastics break down into tiny pieces called microplastics. These microplastics spread everywhere, polluting soil, water, and even the air. They can enter the food chain and potentially harm human health.



Figure: A beach littered with non-degradable poly(alkene) waste

This led to the need for the development of two major classes of polymers biodegradable and photodegradable polymers.

### Biodegradable Polymers

***The plastic that is naturally decomposed by microorganisms into simpler non-toxic compounds when buried for a certain period is called biodegradable plastic.*** Plastics that contain natural polymers, such as starch, are degraded faster, as bacteria in the soil can attack natural polymers easily. Polyesters and polyamides are more biodegradable than poly(alkene)s, because the soil organisms can attack them better through hydrolysis into simpler components.

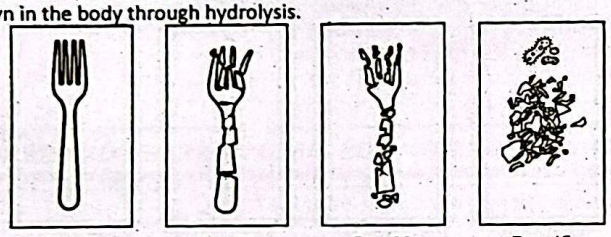
CamScanner

Polyamides produce carboxylic acids and amines, whereas polyesters can be decomposed into carboxylic acids and alcohols. For example, poly(lactic acid) (PLA) can enhance the biodegradability of plastic. Figure shows the degradation of a plastic material containing PLA after a certain period.

### ➲ Photodegradable Plastics

***Some functional groups can absorb more energy from the sunlight in the form of UV light. Polymers with such functionalities can be degraded by light and are termed as photodegradable.*** Some polymers with carbonyl groups in their chains (C = O) have been developed due to their enhanced photosortpion. The absorption of the UV light weakens the bonds within the chain and forces between different chains of the polymers. This makes a polymer more biodegradable, thus accelerating its decomposition into less toxic compounds in the natural environment. However, photodegradable plastics cannot be used for longer time and recycling of such polymers is not efficient. Also, the plastic is buried in landfills where no light is available for photodegradability.

Because polyesters and polyamides can biodegrade under these conditions, it means they don't stay in the environment forever like some other plastics. This helps reduce the adverse effects of the plastic pollution. Scientists and engineers can use this knowledge to design materials that break down when they are no longer needed. For example, some medical implants or dissolvable stitches are made from polyesters that slowly break down in the body through hydrolysis.



Day 0 Day 12 Day 33 Day 45

**Figure: Chemists are devising plastics that can be broken down by microorganisms in soil or by light**

## POLYMERS IN ARTIFICIAL ORGANS

**Q.10 Discuss with examples polymers in artificial organs.** LIO

**Ans.** In biomedical science, polymers are very important for creating artificial organs. These are manmade devices designed to replace or support the function of damaged or diseased body parts. Polymers used in the body need to be biocompatible, mechanically suitable, sterilizable, durable and tunable (can be changed as wished).

They must not harm the body, cause allergies, or be rejected by the immune system.

Their strength, flexibility, or elasticity can be adjusted to match the body part they replace (e.g., flexible for blood vessels, strong for bones). The uses of various polymers in medical science are summarised in Table.

**Table: Polymers in Artificial Organs**

| Application | Polymers Used | Key Properties & Functions |
|---|---|---|
| Artificial Blood Vessels (Grafts) | Poly(tetrafluoroethylene)(PTFE) and Poly(ethylene terephthalate) (PET) | Smooth surfaces to prevent blood clots; used to replace or bypass blocked vessels. |
| Artificial Heart Valves | Specialized Polyurethanes and Silicone | Highly flexible and durable; must be resistant to clotting. |
| Artificial Skin | Collagen (natural) and Polylactic acid (PLA) (synthetic) | Acts as a scaffold for new skin growth; some are designed to dissolve as the wound heals. |
| Artificial Joints (Hip/Knee) | Ultra-high molecular weight polyethylene (UHMWPE) | Provides a smooth, low-friction surface to allow movement and resist wear. |
| Artificial Cornea | Poly(methyl methacrylate) (PMMA) and Hydrogels | Must be perfectly clear (transparent) and biocompatible to restore vision. |



## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **The first step in identifying a polymer is to examine its:**
(A) Colour (B) Backbone (C) Molecular mass (D) Density
2. **A polymer having only carbon atoms in its backbone is classified as:**
(A) Condensation polymer (B) Polyester (C) Addition polymer (D) Polyamide
3. **If oxygen or nitrogen atoms are present in the polymer backbone, it is generally a:**
(A) Homopolymer (B) Addition polymer (C) Condensation polymer (D) Copolymer
4. **A polymer containing the –COO– linkage is classified as a:**
(A) Polyamide (B) Polyester (C) Polyalkene (D) Polyether
5. **The –CONH– linkage indicates a:**
(A) Polyester (B) Polyamide (C) Addition polymer (D) Vinyl polymer
6. **PET is an example of a:**
(A) Polyamide (B) Polyester (C) Addition polymer (D) Natural polymer
7. **Kevlar is classified as a:**
(A) Polyester (B) Polyamide (C) Poly(ethene) (D) PVC
8. **The smallest repeating section of a polymer is called the:**
(A) Monomer (B) Repeat unit (C) Synthon (D) Functional group
9. **To identify the monomer of an addition polymer, the C–C single bond is converted back into a:**
(A) Triple bond (B) Double bond (C) Ionic bond (D) Coordinate bond
10. **To identify monomers of a condensation polymer, one should:**
(A) Remove water (B) Add water back and break the linkage
(C) Remove hydrogen (D) Add chlorine
11. **Addition polymerisation occurs when monomers contain:**
(A) –COOH groups only (B) C=C bonds (C) –OH groups only (D) $–NH_2$ groups only
12. **Ethene and propene undergo:**
(A) Condensation polymerisation (B) Addition polymerization
(C) Hydrolysis (D) Neutralization
13. **Copolymerisation involves:**
(A) One type of monomer (B) Two different monomers (C) Three different monomers (D) Only natural polymers
14. **Condensation polymerisation requires:**
(A) Inert gases (B) Functional groups capable of forming linkages
(C) Only carbon atoms (D) Double bonds only
15. **Amino and carboxyl groups combine to form:**
(A) Polyester (B) Polyamide (C) PVC (D) Poly(propene)
16. **Acyl chloride and alcohol produce:**
(A) Polyamide (B) Polyester (C) Poly(ethene) (D) Nylon-6
17. **Conventional plastics are mainly:**
(A) Easily degradable (B) Non-degradable (C) Water soluble (D) Natural polymers
18. **Non-degradable plastics remain in the environment for:**
(A) A few days (B) A very long time (C) One month (D) One year only
19. **Accumulation of plastic waste mainly affects:**
(A) Only soil (B) Only rivers
(C) Soil, oceans and natural habitats (D) Only air
20. **Tiny plastic particles formed from larger plastics are called:**
(A) Nanoplastics (B) Microplastics (C) Monomers (D) Polymers
21. **Microplastics can enter the:**
(A) Atmosphere only (B) Food chain (C) Earth's core (D) Ozone layer
22. **Biodegradable plastics are decomposed by:**
(A) Heat only (B) Microorganisms (C) UV radiation only (D) Acids only
23. **Biodegradable plastics break down into:**
(A) Toxic gases (B) Simpler non-toxic compounds
(C) Metals (D) Hydrocarbons only
24. **Plastics containing natural polymers such as starch degrade:**
(A) More slowly (B) Faster (C) At the same rate (D) Never
25. **Polyesters are more biodegradable because they undergo:**
(A) Combustion (B) Hydrolysis (C) Oxidation (D) Reduction

CamScanner

26. **Hydrolysis of polyesters produces:**
(A) Alcohols and carboxylic acids (B) Amines only
(C) Alkenes (D) Alkynes

27. **Hydrolysis of polyamides produces:**
(A) Esters (B) Carboxylic acids and amines
(C) Alcohols only (D) Alkanes

28. **PLA stands for:**
(A) Poly(lactic acid) (B) Poly(lactic aldehyde) (C) Poly(lactam) (D) Poly(limonene)

29. **Photodegradable plastics degrade mainly due to:**
(A) Heat (B) UV light (C) Water (D) Oxygen

30. **Carbonyl groups help polymers absorb:**
(A) Infrared radiation only (B) UV light (C) Microwaves (D) Radio waves

31. **Photodegradable plastics are less suitable for long-term use because they:**
(A) Dissolve immediately (B) Degrade upon light exposure
(C) Melt at room temperature (D) Conduct electricity

32. **One limitation of photodegradable plastics is that:**
(A) They cannot be manufactured (B) Recycling is less efficient
(C) They are insoluble (D) They are natural polymers

33. **Artificial organs require polymers that are:**
(A) Toxic (B) Biocompatible (C) Radioactive (D) Magnetic

34. **Polymers used inside the body should:**
(A) Cause allergies (B) Be rejected by the immune system
(C) Be durable and sterilizable (D) Be electrically conductive

35. **Artificial blood vessels commonly use:**
(A) PTFE and PET (B) PVC and Nylon (C) HDPE and LDPE (D) PLA and PMMA

36. **Artificial heart valves commonly use:**
(A) Silicone and specialized polyurethanes (B) Poly(ethene)
(C) PVC (D) Teflon only

37. **Artificial skin commonly uses:**
(A) PLA and collagen (B) Nylon only (C) HDPE (D) PVC

38. **Artificial joints commonly use:**
(A) PMMA (B) UHMWPE (C) PET (D) Nylon-6

39. **Artificial corneas commonly use:**
(A) PVC (B) PMMA and hydrogels (C) Poly(propene) (D) Nylon-6,6

40. **A major goal of developing biodegradable polymers is to:**
(A) Increase plastic pollution (B) Reduce environmental pollution
(C) Increase landfill size (D) Prevent hydrolysis

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

### BLOCK # 01

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. B | 4. B | 5. C | 6. B | 7. B | 8. B | 9. A | 10. B | 11. B | 12. B | 13. B | 14. B | 15. B |
| 16. B | 17. B | 18. B | 19. B | 20. B | 21. B | 22. B | 23. B | 24. B | 25. B | 26. A | 27. A | 28. B | 29. B | 30. A |
| 31. A | 32. A | 33. B | 34. B | 35. A | 36. B | 37. B | 38. B | 39. C | 40. C | | | | | |

### BLOCK # 02

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. C | 4. B | 5. B | 6. B | 7. B | 8. B | 9. B | 10. B | 11. B | 12. B | 13. B | 14. B | 15. B |
| 16. B | 17. B | 18. B | 19. C | 20. B | 21. B | 22. B | 23. B | 24. B | 25. B | 26. A | 27. B | 28. A | 29. B | 30. B |
| 31. B | 32. B | 33. B | 34. C | 35. A | 36. A | 37. A | 38. B | 39. B | 40. B | | | | | |



# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. **Which pair of monomers reacts to form a polyester?**
a) Diamine and dicarboxylic acid b) Diol and dicarboxylic acid
c) Ethene and chloroethene d) Amino-carboxylic acid

II. **What small molecule is eliminated when a diamine reacts with a dioyl chloride?**
a) Water ($H_2O$) b) Hydrogen chloride ($HCl$) c) Ammonia ($NH_3$) d) Ethene ($C_2H_4$)

III. **How do plasticizers affect PVC?**
a) Make it harder. b) Make it brittle
c) Reduce inter-chain forces, make it flexible d) Increase melting point and conductivity

IV. **What are the two monomers for Nylon 6,6?**
a) Vinyl chloride & Adipic acid b) Hexamethylenediamine & Adipic acid
c) Ethane-1,2-diol & Adipic acid d) Only Hexamethylenediamine

V. **A polymer section is shown here: $[-CH_2-CH(CH_3)-CH_2-CH(CH_3)-]$. What is the monomer, and what type of polymer is it?**
a) Propene; Addition b) Propene; Condensation c) Ethene; Addition d) Ethene; Condensation

VI. **Polyesters and polyamides are considered biodegradable because they:**
a) are natural polymers. b) break down in sunlight.
c) have small monomers. d) have hydrolysable ester/amide links.

VII. **What are the products of alkaline hydrolysis (saponification) of a polyester?**
a) Carboxylic acid and alcohol b) Carboxylate salt and alcohol
c) Carboxylic acid and amine d) Carboxylate salt and amine

VIII. **What are the products of acidic hydrolysis of a polyamide?**
a) Carboxylate salt and amine b) Carboxylic acid and alcohol
c) Carboxylic acid and protonated amine d) Carboxylate salt and protonated amine

IX. **What is the primary cause of photodegradation in polymers?**
a) Acidic hydrolysis b) Microorganisms c) Absorption of UV light d) Alkaline hydrolysis

X. **Poly(alkenes) are considered "chemically inert" because they:**
a) Have weak, easily broken bonds. b) Have strong C–C and C–H bonds.
c) React quickly with acids. d) Dissolve in water.

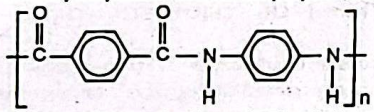
## Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | b | Diol and dicarboxylic acid | Polyesters form by condensation between a diol and a dicarboxylic acid, creating ester links. |
| II. | b | Hydrogen chloride ($HCl$) | $nH_2N-CH_2-NH_2 + nHOOC-CH_2-COOH \longrightarrow$ (diamine, dicarboxylic acid) $[-HN-CH_2-NH-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-]_n + 2nH_2O$ (polyamide). A diamine reacts with a dioyl chloride to form amide links and eliminate $HCl$. |
| III. | c | Reduce inter-chain forces, make it flexible | Plasticizer molecules separate PVC chains and weaken inter-chain attractions, increasing flexibility. |
| IV. | b | Hexamethylenediamine & Adipic acid | Nylon 6, 6 is formed from hexamethylenediamine (6 C) and adipic acid (6 C). |

CamScanner

| | | | |
|---|---|---|---|
| V. | a | Propene; Addition | The repeating unit corresponds to addition polymerization of propene, $CH_2 = CHCH_3$. |
| VI. | d | have hydrolysable ester/amide links | Ester and amide bonds can be hydrolysed or by enzymes to their monomers. |
| VII. | b | Carboxylate salt and alcohol | $\text{Polyester} + NaOH \longrightarrow R-\overset{O}{\overset{\|\|}{C}}-OO^-Na^+ + R-OH$ |
| VIII. | c | Carboxylic acid and protonated amine | $\text{Polyamide} + H^+/H_2O \longrightarrow R-COOH + R-NH^+_3$ |
| IX. | c | Absorption of UV light | UV absorption creates excited states/radicals that initiate bond breaking and photo-oxidative chain scission. |
| X. | b | have strong C – C and C – H bonds. | Poly(alkenes) contain strong C – C and C – H bonds and lack readily hydrolysable/reactive functional groups. |

**a) Kevlar® is a thermally and mechanically very stable but flexible polymer; a section of this polymer is given below:**



**i) Name the characteristic linkage and type of polymerisation in its structure.**
**ii) Identify the two functional groups that react to form it.**
**iii) Name the monomers from which it is formed.**

**Ans.**

**(i) Characteristic linkage:**
The characteristic linkage present in Kevlar is the **amide linkage.**

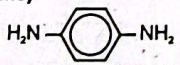
$$—CO—NH—$$

Kevlar is formed by **condensation polymerisation.**

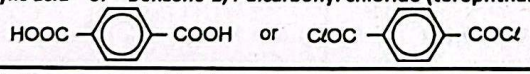
**(ii)** The two functional groups involved are:
- **Amino group** ($—NH_2$)
- **Acyl chloride group** ($—COCl$) or carboxyl group ($—COOH$)

These react together to form the amide linkage.

**(iii)** Kevlar is prepared from:
- **Benzene-1,4-diamine (p-phenylenediamine)**



- **1,4-benzenedicarboxylic acid or Benzene-1,4-dicarbonyl chloride (terephthaloyl chloride)**



**b) Explain why the reaction between an acyl chloride and ammonia is classified as a condensation reaction. Identify the small molecule that is eliminated during this reaction.**

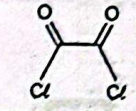
**Ans.** The reaction is called a **condensation reaction** because two molecules combine to form a larger molecule with the elimination of a small molecule.
When an acyl chloride reacts with ammonia, an amide is formed and hydrogen chloride is eliminated.
**Example:**

$$CH_3COCl + NH_3 \longrightarrow CH_3CONH_2 + HCl$$

The small molecule eliminated is: $HCl$



**c) For the following monomers:**



etanedioyl chloride



ethane-1, 2-diol

**i) Predict the type of the polymer formed.**
**ii) Draw the repeat unit and a section of the expected polymer.**
**iii) Name this polymer systematically.**

**Ans. Ethanedioyl chloride and Ethane-1,2-diol**
**i)** A polyester is formed.
**ii)** The repeat unit is:

$$[—O—CH_2—CH_2—O—CO—CO—]_n$$

A section of the polymer chain is:

$$—O—CH_2—CH_2—O—CO—CO—O—CH_2—$$

**iii)** The polymer is called poly(ethylene ethanedioate) or poly(ethane-1, 2-diyl ethanedioate).

**d) For Nylon 6,6 (from 1,6-hexanediamine and 1,4-hexandioic acid acid):**
**i) Name the linkage. ii) Name the small molecule eliminated. iii) Draw the repeating unit.**

**Ans. i)** The linkage present is the amide linkage.

$$—\overset{O}{\overset{\|\|}{C}}—NH—$$

**ii)** The small molecule eliminated during polymerisation is: $H_2O$ (Water)
**iii)** $[—NH—(CH_2)_6—NH—CO—(CH_2)_4—CO—]_n$

**e) For poly(chloroethene) (PVC)**
**i) Name the monomer. ii) Why can the monomer undergo addition polymerisation?**

**Ans. i)** The monomer of PVC is:

Chloroethene (vinyl chloride)
$CH_2 = CHCl$

**ii)** Chloroethene contains a carbon-carbon double bond (C=C).
This double bond opens during **addition polymerisation** and joins many monomer molecules together to form the polymer chain.

**f) State two properties of nylon that make it suitable for ropes and fishing nets.**

**Ans. 1.** High tensile strength.
**2.** Good resistance to abrasion and water.

**g) Give two industrial applications of PVC and two for Nylon, each.**

**Ans. Uses of PVC:** 1. Water pipes 2. Electrical cable insulation
**Uses of Nylon:** 1. Ropes 2. Fishing nets

**h) Draw the repeating unit of the polymer made from propan-1, 3-diol and benzene-1, 4-dicarboxylic acid.**

**Ans.** The repeating unit is:

$$[—O—CH_2—CH_2—CH_2—O—CO—C_6H_4—CO—]_n$$

**i) State three distinct environmental problems caused by the disposal of non-degradable polymers.**

**Ans. 1.** They accumulate in the environment for very long periods.
**2.** They pollute rivers, oceans and soil.
**3.** They can harm animals that swallow or become trapped in plastic waste.

CamScanner

**j) Name two different polymers used in artificial organs and state the specific application for each.**

**Ans.**

| Polymer | Application |
|---|---|
| Silicone rubber. | Artificial heart valves and implants. |
| Poly(ethylene). | Artificial joints and prosthetic devices. |

## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) Describe the chemical role of plasticisers in polyvinyl chloride (PVC) and explain how this modification influences the polymer's industrial applications.**

**Ans.** See Question No. 03

**b) Explain why poly(alkenes) like poly(ethene) pose a greater environmental challenge than polyesters and polyamides. Identify the chemical process that allows the latter to degrade.**

**Ans.** Poly(alkenes) such as poly(ethene) consist mainly of strong carbon-carbon and carbon-hydrogen bonds. These bonds are chemically very stable and resist attack by water, microorganisms and most chemicals. As a result, poly(alkenes) are non-biodegradable and remain in the environment for many years after disposal. Their accumulation causes several environmental problems such as:

- land pollution,
- blockage of drainage systems,
- harm to wildlife and marine organisms.

In contrast, polyesters and polyamides contain ester (—COO—) and amide (—CONH—) linkages in their polymer chains.
These linkages can be broken by water in the presence of acids, alkalis or enzymes.
Therefore, polyesters and polyamides gradually break down into smaller molecules and are more biodegradable than poly(alkenes).
The chemical process responsible for their degradation is: Hydrolysis
Hydrolysis breaks ester and amide bonds and converts the polymers back into smaller molecules such as alcohols, carboxylic acids and amines.
Hence, poly(alkenes) create a greater environmental challenge because they lack hydrolysable linkages, whereas polyesters and polyamides can degrade through hydrolysis.

## DESCRIPTIVE QUESTIONS DQs

**Q.4 Compare and contrast addition and condensation polymerisation, giving details of the specific structural requirements for the monomers in each.**

**Ans.** See Question No. 02

**Q.5 Illustrate the formation of two major condensation polymers.**

**Ans.** See Question No. 04

**Q.6 Differentiate between the environmental degradation of poly(alkenes) and polyesters.**

**Ans.**

| Poly(alkenes) | Polyesters |
|---|---|
| Contain mainly strong C – C and C – H bonds. | Contain ester linkages (— COO —) in their chains. |
| These bonds are resistant to chemical attack and hydrolysis. | Ester linkages can be broken by hydrolysis. |
| They are non-biodegradable and remain in the environment for a very long time. | They are comparatively biodegradable. |
| They accumulate in landfills and water bodies causing pollution. | They degrade more readily and produce smaller molecules. |
| Examples include poly(ethene) and PVC. | Examples include Terylene and biodegradable polyesters. |



**Explanation:**
Poly(alkenes) such as poly(ethene) and poly(propene) contain only strong carbon-carbon and carbon-hydrogen bonds. These bonds are not easily broken by water, microorganisms or chemicals. Therefore, these polymers persist in the environment for many years and create serious disposal problems.
Polyesters, on the other hand, contain ester linkages in their polymer chains.

—COO—

These ester bonds can undergo **hydrolysis** in the presence of water, acids, alkalis or enzymes.
**For example:**

Polyester + $H_2O$ ⟶ Diol + Dicarboxylic acid

As a result, polyesters break down into smaller molecules and degrade more easily in the environment.
Therefore, poly(alkenes) pose a greater environmental problem than polyesters because they lack hydrolysable linkages and are much more resistant to degradation.

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 Define polymer and monomer.**

**Ans.** A polymer is a large molecule formed by the repeated joining of many small molecules called monomers through covalent bonds. The process by which monomers combine to form polymers is called polymerization.
**Example:** $n(CH_2 = CH_2) \longrightarrow (-CH_2-CH_2-)n$

**Q.2 Differentiate between addition and condensation polymerization.**

**Ans.** In addition polymerization, monomers join together without the elimination of any small molecule, whereas condensation polymerization occurs with the elimination of molecules such as water or hydrogen chloride. Examples include poly(ethene) and nylon respectively.

**Q.3 Explain addition polymerization with an example.**

**Ans.** Addition polymerization involves the repeated addition of unsaturated monomers containing double bonds to form long chain polymers without producing by-products.

$nCH_2 = CH_2 \longrightarrow (-CH_2-CH_2-)_n$

Poly(ethene) is produced from ethene by this process.

**Q.4 Explain condensation polymerization with an example.**

**Ans.** Condensation polymerization occurs when bifunctional monomers react together with the elimination of small molecules such as water or hydrogen chloride.
**Example:** Nylon-6,6 is formed from hexane-1,6-diamine and hexanedioic acid with elimination of water.

**Q.5 Explain the formation of PVC.**

**Ans.** PVC is formed by addition polymerization of chloroethene (vinyl chloride) molecules. The carbon-carbon double bond opens and forms a long polymer chain.

$nCH_2 = CHCl \longrightarrow (-CH_2-CHCl-)_n$

PVC is widely used in pipes and insulation.

**Q.6 Explain the formation of Nylon-6,6.**

**Ans.** Nylon-6,6 is prepared by condensation polymerization between hexane-1,6-diamine and hexanedioic acid. During the reaction, water molecules are eliminated and amide linkages are formed.
The polymer belongs to the polyamide family.

**Q.7 Explain the formation of Terylene.**

**Ans.** Terylene is formed by condensation polymerization of ethane-1,2-diol and benzene-1,4-dicarboxylic acid. Ester linkages are formed with the elimination of water molecules.
Therefore, Terylene is classified as a polyester.

**Q.8 Why is PVC widely used in industry?**

**Ans.** PVC possesses high strength, chemical resistance and good electrical insulating properties. These properties make it suitable for manufacturing water pipes, window frames and electrical cable insulation.
Hence, PVC is one of the most widely used plastics.

CamScanner

**Q.9 State two uses of nylon.**

**Ans.** Nylon is strong, lightweight and resistant to wear and tear. Therefore, it is widely used in the manufacture of textiles, ropes, fishing nets and parachutes.
Its high tensile strength makes it industrially important.

**Q.10 State two uses of Terylene.**

**Ans.** Terylene is used in the textile industry for making fabrics and clothing materials. It is also blended with cotton to produce wrinkle-resistant and durable garments.
Its resistance to stretching and shrinking increases its usefulness.

**Q.11 Why are polyesters classified as condensation polymers?**

**Ans.** Polyesters are formed by the reaction of a diol with a dicarboxylic acid, accompanied by the elimination of water molecules. Since a small molecule is removed during polymer formation, they are classified as condensation polymers.

$$\text{Diol} + \text{Dicarboxylic Acid} \longrightarrow \text{Polyester} + H_2O$$

**Q.12 Why are polyamides classified as condensation polymers?**

**Ans.** Polyamides are produced by the reaction of diamines with dicarboxylic acids or acyl chlorides with the elimination of water or hydrogen chloride. The presence of amide linkages identifies them as condensation polymers. **Example:** Nylon-6,6.

**Q.13 What is the repeating unit of a polymer?**

**Ans.** The repeating unit is the smallest structural unit that repeats itself throughout the polymer chain. It is obtained by removing the double bond or end groups from the monomer molecules.
**Example for poly(ethene):** $(-CH_2-CH_2-)$

**Q.14 How can the monomer of an addition polymer be identified?**

**Ans.** The monomer of an addition polymer can be obtained by placing a double bond between the two carbon atoms of the repeating unit. This reconstructs the original alkene monomer.
**Example:** $(-CH_2 - CHCl-)n \longrightarrow CH_2 = CHCl$

**Q.15 Explain how the monomers of condensation polymers are identified.**

**Ans.** The monomers of condensation polymers are identified by breaking the ester or amide linkages present in the repeating unit. This gives the original diol, diamine or dicarboxylic acid used in polymer formation.
This method is called reverse polymerization.

**Q.16 How can the type of polymerization be predicted from monomers?**

**Ans.** If the monomer contains a carbon-carbon double bond, it usually undergoes addition polymerization. If the monomers contain two functional groups such as –OH–, –COOH– or $-NH_2-$, condensation polymerization occurs. Thus, the structure of monomers determines the polymerization process.

**Q.17 Why are polyesters biodegradable?**

**Ans.** Polyesters contain ester linkages which can be broken by acidic or alkaline hydrolysis. Microorganisms can therefore degrade these polymers more easily than poly(alkenes).
This property reduces environmental pollution.

**Q.18 Why are polyamides biodegradable?**

**Ans.** Polyamides contain amide linkages that can undergo hydrolysis in acidic or alkaline conditions. The polymer chains gradually break into smaller molecules which can be decomposed by microorganisms.
Nylon is an example of a biodegradable condensation polymer.

**Q.19 Why are poly(alkenes) difficult to biodegrade?**

**Ans.** Poly(alkenes) contain strong carbon-carbon and carbon-hydrogen bonds and lack hydrolysable functional groups. Therefore, microorganisms cannot easily break down these polymers.
As a result, they persist in the environment for many years.



**Q.20 Explain photodegradation of polymers.**

**Ans.** Photodegradation is the breakdown of polymers by sunlight, especially ultraviolet radiation. UV light weakens chemical bonds and causes the polymer chains to fragment into smaller pieces. This process helps reduce plastic waste accumulation.

**Q.21 What environmental problems are associated with non-biodegradable polymers?**

**Ans.** Non-biodegradable polymers accumulate in landfills and natural ecosystems because they decompose very slowly. Their disposal can lead to soil, water and marine pollution. Plastic waste is therefore a major environmental concern.

**Q.22 Why is recycling important for polymers?**

**Ans.** Recycling reduces environmental pollution and conserves raw materials and energy resources. It also decreases the amount of plastic waste entering landfills and oceans. Therefore, recycling is an effective method of waste management.

**Q.23 Explain hydrolysis of polyesters.**

**Ans.** Polyesters undergo hydrolysis in acidic or alkaline media due to the presence of ester linkages. The reaction breaks the polymer chain and regenerates the original alcohol and carboxylic acid components.
This property contributes to their biodegradability.

**Q.24 Explain hydrolysis of polyamides.**

**Ans.** Polyamides are hydrolysed in acidic or alkaline solutions because their amide linkages are susceptible to chemical attack. Hydrolysis produces amines and carboxylic acids or their salts.
This process causes degradation of the polymer.

**Q.25 State the advantages of biodegradable polymers.**

**Ans.** Biodegradable polymers decompose naturally through the action of microorganisms and therefore reduce environmental pollution. They minimize waste accumulation and support sustainable development.
Examples include polyesters and polyamides.

**Q.26 State the disadvantages of non-biodegradable polymers.**

**Ans.** Non-biodegradable polymers remain in the environment for long periods and contribute to land and water pollution. Their disposal often requires landfill storage or incineration.
**Examples include poly(ethene) and PVC.**

**Q.27 Explain the use of polymers in artificial organs.**

**Ans.** Biocompatible polymers are used to manufacture artificial organs because they are lightweight, durable and resistant to chemical attack. They are commonly used in artificial heart valves and blood vessels.
These materials have greatly improved biomedical technology.

**Q.28 Why are polymers suitable for biomedical applications?**

**Ans.** Polymers used in medicine are flexible, chemically stable and compatible with body tissues. These properties make them suitable for implants, artificial joints and drug delivery systems.
Hence, polymers play an important role in biomedical science.

**Q.29 Differentiate between PVC and Nylon.**

**Ans.** PVC is an addition polymer formed from chloroethene, whereas nylon is a condensation polymer formed from diamines and dicarboxylic acids. PVC contains carbon-halogen bonds while nylon contains amide linkages.
Therefore, their preparation methods and properties differ significantly.

**Q.30 Differentiate between addition and condensation polymers with examples.**

**Ans.** Addition polymers are formed from unsaturated monomers without elimination of small molecules, whereas condensation polymers are formed with elimination of molecules such as water or HCl.
Examples include poly(ethene) and PVC as addition polymers, while nylon and Terylene are condensation polymers.

CamScanner

## SELF-ASSESSMENT

Total Mark: 30

**Q.1 Encircle the correct option.** (1 × 6 = 6)

(i) **Addition polymerisation usually proceeds through a:**
(A) Neutralization reaction (B) Chain reaction (C) Hydrolysis reaction (D) Esterification reaction

(ii) **HDPE is produced using:**
(A) Concentrated $H_2SO_4$ (B) Ziegler–Natta catalyst (C) $KMnO_4$ (D) $LiAlH_4$

(iii) **Nylon is characterized by:**
(A) Low melting point and softness (B) High strength and wear resistance
(C) High electrical conductivity (D) Low durability

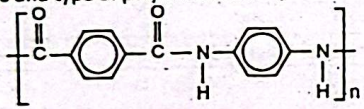
(iv) **Kevlar is classified as a:**
(A) Polyester (B) Polyamide (C) Poly(ethene) (D) PVC

(v) **What small molecule is eliminated when a diamine reacts with a dioyl chloride?**
(A) Water ($H_2O$) (B) Hydrogen chloride ($HC\ell$) (C) Ammonia ($NH_3$) (D) Ethene ($C_2H_4$)

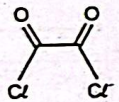
(vi) **What are the products of alkaline hydrolysis (saponification) of a polyester?**
(A) Carboxylic acid and alcohol (B) Carboxylate salt and alcohol
(C) Carboxylic acid and amine (D) Carboxylate salt and amine

**Q.2 Write short answers of the following questions.** (2 × 8 = 16)

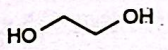
(i) Name the characteristic linkage and type of polymerisation in Kevlar. Its structure is:



(ii) For the following monomers:



etanedioyl chloride



ethane-1, 2-diol

Predict the type of the polymer formed.

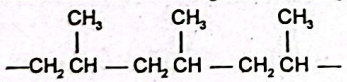
(iii) For Nylon 6, 6 (from 1, 6-hexanediamine and 1, 4-hexandioic acid acid): Name the linkage and name the small molecule eliminated.

(iv) Discuss the industrial applications of nylon.

(v) State three distinct environmental problems caused by the disposal of non-degradable polymers.

(vi) Name two different polymers used in artificial organs and state the specific application for each.

(vii) Identify the type of polymerisation and monomers forming the following polymer:



(viii) Monomers of nylon-6, 4 are given below. Draw the structure of the repeating unit of the polymer formed from these monomers.

$H_2N-(CH_2)_6-NH_2$ $HOOC-(CH_2)_2-COOH$

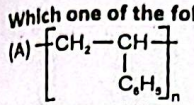
**Q.3 Extensive Questions.** (4 + 4 = 8)

(a) Compare and contrast addition and condensation polymerization.

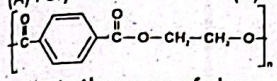
(b) Differentiate between the environmental degradation of poly(alkenes) and polyesters.



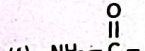
## ENTRANCE TEST MCQs

1. **Which one of the following polymer is polystyrene?** (UHS 2015)
(A)  (B)  (C)  (D) 

2. **Which one of the following polymer is called as Nylon 6, 6?** (UHS 2016, 2018)
(A) Polyester (B) Polyvinyl chloride (C) Polyamide (D) Polyvinyl acetate

3. 
**Indicate the name of above given structure:** (UHS 2016)
(A) Nylon 6,6 (B) Adipic acid (C) PVA (D) Polyester

4. **Which one of the following is an example of condensation polymer?** (UHS 2014)
(A) Polyvinylchloride (B) Polystyrene (C) Polyethene (D) Polyamide

5. **The amide linkage, present in Nylon-6,6 has the structure:** (UHS 2017)
(A)  (B)  (C)  (D) 

6. **Why is addition polymerisation often described as a chain-growth process?**
(A) Every molecule reacts stepwise with any other molecule
(B) A small molecule is eliminated at each step
(C) Only cyclic monomers can react
(D) Growth occurs rapidly at the active chain end

7. **Which application most likely requires plasticised rather than rigid PVC?**
(A) A flexible blood bag (B) A rigid window frame
(C) A drainage pipe (D) A hard floor tile

8. **Why are dioyl chlorides more reactive than dicarboxylic acids toward diamines?**
(A) They are strong bases (B) They cannot form $HC\ell$
(C) The acyl carbon is more electrophilic; $C\ell^-$ leaves readily
(D) They contain no carbonyl groups

9. **The nylon-6,6 repeat unit has formula $C_{12}H_{22}N_2O_2$. Its approximate molar mass is:**
(A) 260 g $mol^{-1}$ (B) 226 g $mol^{-1}$ (C) 113 g $mol^{-1}$ (D) 198 g $mol^{-1}$

10. **Poly(ethene): $\bar{M}$ = 280,000 g $mol^{-1}$; repeat unit = 28. Approximate degree of polymerisation?**
(A) 28 (B) 10,000 (C) 1,000 (D) 100,000

11. **PET has molecular mass 96,000 g $mol^{-1}$ and mass of its repeating unit is 192 then approximate number of repeat units are?**
(A) 500 (B) 50 (C) 1,000 (D) 192

12. **A polymer section contains repeating –NH–CO–$C_6H_4$–CO–NH–$C_6H_4$– units. It is best identified as:**
(A) PVC (B) Poly(propene)
(C) An aromatic polyamide such as Kevlar (D) A polyester such as PET

13. **A polymer is strong, low-friction, wear-resistant and used for gears and fishing line. It is most likely:**
(A) Plasticized PVC (B) PLA foam (C) Nylon (D) LDPE

**Answers Key**

| 1. A | 2. C | 3. D | 4. D | 5. C | 6. D | 7. A | 8. C | 9. B | 10. B | 11. A | 12. C | 13. C |
|---|---|---|---|---|---|---|---|---|---|---|---|---|

CamScanner

FIND US ON
Facebook
LIKE OUR PAGE TODAY
@SCHOLARPUBLICATIONS.PK

SCHOLAR PUBLICATIONS



27 CHAPTER

# BIOCHEMISTRY

## Student Learning Outcomes (SLOs)

[C-12-D-116 to C-12-D-139]

- Explain the basis of classification and structure-function relationship of carbohydrates.
- Explain the role of various carbohydrates in health and diseases.
- Identify the nutritional importance of carbohydrates and their role as energy storage.
- Explain the basis of classification and structure-function relationship of proteins.
- Describe the role of various proteins in maintaining body functions and their nutritional importance.
- Describe the role of enzyme as biocatalyst and relate this role to various functions such as digestion of food.
- Identify factors that affect enzyme activity such as the effect of temperature and pH.
- Explain the role of inhibitors of enzyme catalyzed reactions.
- Describe the basis of classification and structure-function relationship of lipids.
- Identify the nutritional and biological importance of lipids.
- Identify the structural components of DNA and RNA.
- Differentiate between the structures of DNA polymer (double strand) and RNA (single strand).
- Relate DNA sequences to its function as storage of genetic information.
- Relate RNA sequence (transcript) to its role in transfer of information to protein (translation).
- Identify the sources of minerals such as iron, calcium, phosphorus and zinc.
- Describe the role of iron, calcium, phosphorous and zinc in nutrition.
- Explain why animals and humans have large glycogen deposits for sustainable muscular activities. Hibernating animals (polar bear, reptiles and amphibians) accumulate fat to meet energy resources during hibernation.
- Identify complex carbohydrates which provide lubrication to the elbow and knee.
- Describe fibrous proteins from hair and silk.
- Explain how cholesterol and amino acid serve as hormones.
- Identify insulin as a protein hormone whose deficiency leads to diabetes mellitus.
- Explain the role of minerals in structure and function.
- Identify calcium as a requirement for coagulation.
- Identify how milk proteins can be precipitated by lowering the pH using lemon juice.

Biochemistry is the branch of science that deals with the study of chemical substances found in living organisms and the reactions they undergo. The biological compounds are complex molecules with the same types of functional groups that are found in simple organic compounds, such as alcohol, amine, aldehyde, ketone, carboxylic acid, ester, and amide groups.

This chapter focuses on the essential biomolecules such as carbohydrates, proteins, lipids, and nucleic acids, featuring their structures, functions, and roles in cellular processes. In addition to these biomolecules, the roles of minerals and enzymes in biochemical processes will also be discussed.

## CARBOHYDRATES

**Q.1 What are Carbohydrates?** S/Q

Ans. Carbohydrates are naturally occurring organic compounds including sugars, starch, cellulose, and substances found in bacterial cell walls and insect exoskeletons. These act as major sources of energy in our diet. All carbohydrates are hydrates of carbon. Chemically, carbohydrates are polyhydroxy aldehydes or ketones or their derived compounds. Three major classes of carbohydrates are being discussed here:

CamScanner

**Q.2 What are monosaccharides and disaccharides? Discuss in detail.**

Ans.

## 1. Monosaccharides

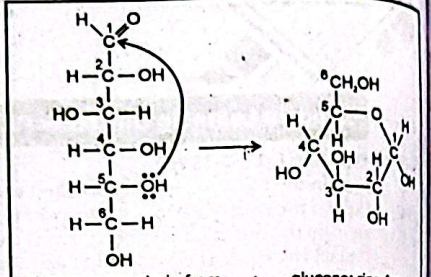
Monosaccharides are the simplest carbohydrates commonly known as sugars, e.g. glucose and fructose. They cannot be hydrolysed further into simpler compounds.

**General formula** of monosaccharides = $C_n(H_2O)_n$

Where n ranges from three to seven.

A monosaccharide with three carbon atoms is a **triose**, one with four carbon atoms is a **tetrose**; a pentose has five carbons, and a hexose contains six carbons, etc.

They are also classified according to the functional group present, such as a ketose or aldose containing ketonic and aldehydic groups respectively. For example, Glucose is an aldose, whereas fructose is a ketose.



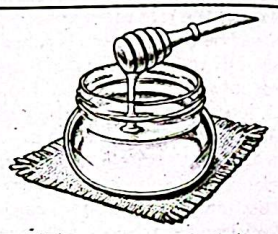
glucose open-chain from glucose: ring from

**Figure: Linear and cyclic structures of glucose**

Monosaccharides exist either as open-chains or ring-shaped molecules. Sugars with five carbon atoms (pentoses) or six carbon atoms (hexoses) are more stable and hence more abundant as cyclic structures than as open chain structures.

In their solid form, they exist in ring form and in solutions, their molecules exist as linear structures.

**Example:** Fructose forms a five membered ring known as **furanose**, whereas glucose has a six membered ring known as **pyranose**. The linear chain and cyclic structures are interconvertible. The cyclisation of glucose from its linear structure is shown in Figure.



Fructose and glucose are present in honey in high concentrations. The thickness and viscosity of honey is due to their strong and intensive hydrogen bonding.

### ➢ Hydrogen Bonding:

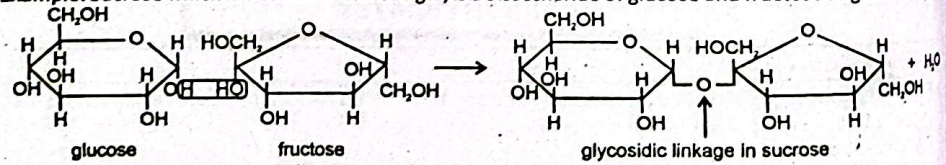
The presence of many hydroxyl groups (–OH) in the sugar molecules results in the extensive hydrogen bonding between their molecules. For this reason, monosaccharides exist in solid form in their pure form. In their solutions, they form extensive hydrogen bonding with water molecules, making them highly soluble in water.

Monosaccharides are excellent source of instant energy in the living organisms. Glucose is called blood sugar due to its presence in the human blood, while fructose is abundant in fruits and honey.

## 2. Disaccharides

Disaccharides consist of two monosaccharide units joined together via glycosidic linkage, generally with the formula $C_{12}H_{22}O_{11}$. Among the most common disaccharides are sucrose, lactose and maltose. They are formed through a condensation reaction, when the hydroxyl group of one monosaccharide combines with the hydrogen of another monosaccharide through a covalent bond, releasing a molecule of water. The bond C – O – C is known as the glycosidic bond.

**Example:** Sucrose which is a common table sugar, is a disaccharide of glucose and fructose as given in Figure.



glucose fructose glycosidic linkage in sucrose

**Figure: Formation of the Sucrose molecule**



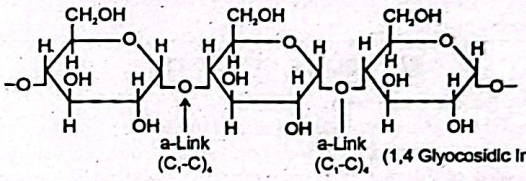
**Q.3 Classify and describe the structures of polysaccharides.** Exercise Q.4

Ans.

## 3. Polysaccharides

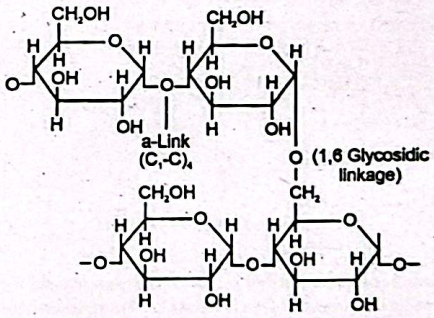
- **Polysaccharides:** Polysaccharides are large molecules consisting of a large number of monosaccharide units joined together. They have high molecular mass and their general molecular formula is $(C_6H_{10}O_5)_n$. Polysaccharides give simple sugars, i.e., monosaccharides on hydrolysis. **Common examples** are starch, glycogen, cellulose and pectin.
- **Starch:** Starch is the main storage of energy in plants, and consists of glucose units.
  **It has two components:** (i) amylose (ii) amylopectin.
  (I) **Amylose** has a long, unbranched chain with many glycosidic linkages.
  (II) **Amylopectin** is a compact highly branched structure consisting of many glucose units (Figure). Potato, sugar beet, rice, and grains have large quantities of starch in them.
- **Cellulose:** Cellulose is the major structural material found in plant cell walls. It consists of glucose units (up to 2500) linked by glycosidic bonds to form long unbranched chains linked by glycosidic bonds (Figure). These chains form strong hydrogen bonds with each other, making cellulose rigid and insoluble in water. It makes most of the plant leaves, branches, and trunk. It is very important in human food in the form of fibre, which improves the gut health.
- **Glycogen:** Glycogen, or animal starch, is a polymer of glucose that is stored in the liver and muscles of animals. It is also called the 'animal starch'. The structure of glycogen is very similar to that of amylopectin, but it is more highly branched, making it different from starch.

(a)




Structure of Amylose

(b)




Structure of Amylopectin

(c)

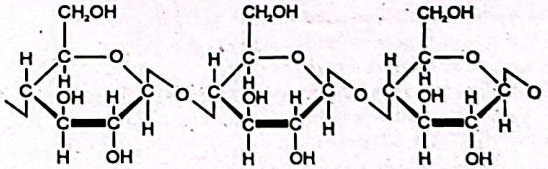


**Figure: Structure of a) amylose, b) amylopectin in starch, and c) cellulose**

CamScanner

## Nutritional Importance of Carbohydrates

**Q.4 Discuss nutritional importance of carbohydrates.** U/Q

**Ans.** Carbohydrates have a complex role in the human body. Although, they are essential for energy and nutrient intake, the type and amount consumed have a major effect on health. By selecting the right carbohydrates and balanced intake, we can reduce the risk of diseases. The following are important physiological functions of carbohydrates and the risk of imbalance in their intake.

1. Simple sugars like glucose are the primary source of energy for cells. They are easily absorbed and metabolized to release energy, with 1 g of glucose providing about 15.6 kJ. Excess glucose is stored as glycogen in the liver and muscles. Normally, blood glucose levels range between 70-110 mg/dL, though it may fluctuate slightly during the day. These levels are controlled by the hormones insulin and glucagon. If blood glucose levels rise above the normal range, it may indicate diabetes, a chronic condition that occurs when the pancreas does not produce enough insulin or when the body cannot effectively use the insulin it produces. Uncontrolled diabetes can cause hyperglycemia (high blood sugar), which, over time may damage body systems, particularly nerves and blood vessels. On the other hand, insufficient carbohydrate intake can result in fatigue and reduced physical and mental performance.
2. The main function of fructose is to provide energy during metabolism in the body. Its high intake causes obesity, resulting in an excessive accumulation of fat in the body. Diets high in refined sugars have been associated with a higher risk of chronic diseases such as diabetes, heart disease, and certain cancers. Conversely, complex carbohydrates and fibers are protective with multiple health benefits. When the body has sufficient carbohydrates for its energy needs, it utilizes these instead of breaking down proteins or fats for fuel and energy production.

### QUICK CHECK 27.1

**a) The linear structure of fructose is given here.**

**i. Show the conversion of this structure into the cyclic structure.**

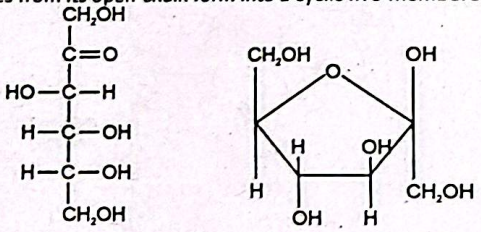
**ii. Predict whether fructose is soluble in water or not. Explain your reasoning.**

**iii. Predict the physical state of fructose in its pure form by analyzing its structure.**

**Ans. i)** Fructose is a ketohexose sugar containing a ketone group at carbon-2 and several hydroxyl groups.

Linear fructose ⇌ Cyclic fructofuranose

Thus, fructose changes from its open-chain form into a cyclic five-membered ring structure.



Fructose (open chain form)



Fructose (cyclic form)

**ii)** Yes, fructose is highly soluble in water. This is because fructose contains several hydroxyl (–OH)groups in its structure. These hydroxyl groups form hydrogen bonds with water molecules, allowing fructose to dissolve readily in water. Therefore, fructose is highly water soluble.

**iii)** Fructose exists as a **white crystalline solid** at room temperature.

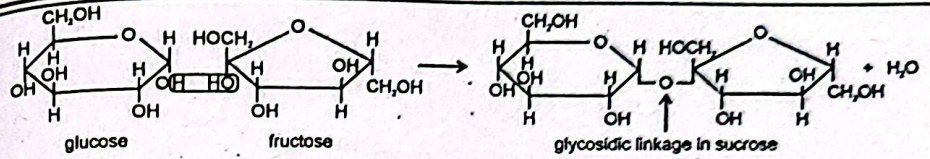
This is because fructose molecules contain many hydroxyl groups that form strong intermolecular hydrogen bonds with neighbouring molecules.

These strong intermolecular forces hold the molecules together in a crystalline solid structure.

**b) What is glycosidic linkage? Show how it is formed between fructose and glucose.**

**Ans.** A glycosidic linkage is the covalent bond formed between two monosaccharides by the elimination of a molecule of water. When glucose reacts with fructose, they combine to form sucrose through a glycosidic bond.





glucose fructose glycosidic linkage in sucrose

The bond formed between the two monosaccharides is called a **glycosidic linkage.**

**c) Briefly describe any two functions of carbohydrates and how these functions are related to their molecular structures.**

**Ans. Functions of Carbohydrates:**

1. **Source of Energy:**
   Simple carbohydrates such as glucose are used as an immediate source of energy. Their small size and high solubility allow them to be transported easily in the blood and rapidly oxidized during respiration.
2. **Energy Storage:**
   Polysaccharides such as starch and glycogen are used for energy storage. Their large polymeric structures allow many glucose units to be stored in a compact form e.g., glycogen in liver and muscles for later use. Thus, the structure of carbohydrates is closely related to their biological functions.

# PROTEINS

**Q.5 What are proteins?** S/Q

**Ans.** Proteins are large, complex macromolecules found in all living organisms abundantly. Our skin, hair, haemoglobin in blood (red pigment), and muscles, all are proteins. Proteins play key roles in the human body from building the tissue structure to various functions of the body cells and organs. Any change in the structure or function of a protein may alter the body to behave abnormally.

When proteins are completely hydrolysed, they yield amino acids. About 20 different amino acids link together in various sequences to create a wide variety of proteins.

## Structure-Based Classification

**Q.6 Define Proteins and peptide bonds.** S/Q

**Ans.** Proteins are linear chains of amino acids that are linked together by peptide bonds.

**Peptide Bond:** A peptide bond is an amide bond that forms when the –COOH group of one amino acid reacts with the $-NH_2$ group of the adjacent amino acid to form a linear polymer. The long chains of amino acids formed by many peptide linkages are called polypeptide chains. Each protein has specific polypeptide chains, which determine its structure and function.

**Q.7 How the structure of proteins support its functions. Describe at each structure level.** Exercise D/Q.5

**Ans.** To understand the complex function of a protein in an organism, it is necessary to determine the three- dimensional structure of its polypeptide chain. Proteins are organized into four structural levels: primary, secondary, tertiary, and quaternary.

### Primary Structure:

The primary structure of a protein is the specific linear sequence of amino acids linked by peptide bonds in a polypeptide chain. This sequence determines how the protein folds into its three-dimensional shape, which in turn proteins like human serum albumin (with about 585 amino acids residues) and insulin rely on their precise amino acid sequences to function properly.



Normal Red Blood Cell Sickle Cell

Sickle cell anemia is a disease caused by the deformation of normal red blood cells to cells having sickle-like shape. This is caused by abnormal formation of haemoglobin. Sickle cells clog the blood veins and disrupt the normal blood circulation.

CamScanner

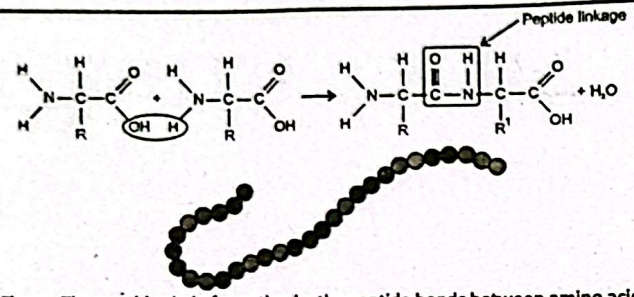



Figure: The peptide chain formation by the peptide bonds between amino acids

### Secondary Structure:

The secondary structure of a protein arises when the backbone atoms form hydrogen bonds within a polypeptide chain, producing regular patterns such as α-helices and β pleated sheets. In an α-helix, hydrogen bonds form along a single chain, creating a coiled, spiral structure (e.g., keratin). In contrast, β-pleated sheets form when hydrogen bonds occur between adjacent polypeptide strands, giving a folded, sheet-like structure (e.g., silk fibroin) as shown in Figure.

These structural arrangements provide stability and flexibility, contributing to the overall three dimensional shape of a protein, which is essential for its specific biological function.

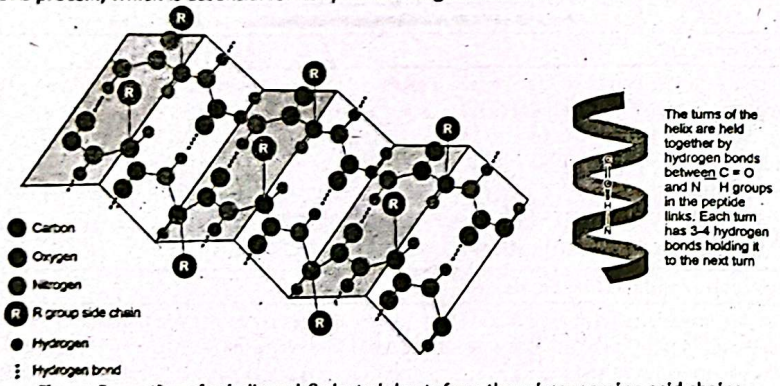



Figure: Formation of α-helix and β pleated sheets from the primary amino acid chains

### Tertiary Structure:

The tertiary structure of a protein is the overall three-dimensional shape formed when a polypeptide chain folds due to interactions between side chains (R-groups), including hydrogen bonds, ionic bonds, hydrophobic interactions, and disulphide bridges. These interactions cause the chain to twist and bend into a specific shape, often forming globular proteins. This threedimensional structure determines the protein function. For example, in enzymes, the precise shape of the active site allows specific binding to the substrate, enabling catalytic activity. Any change in this structure can affect the enzyme activity.

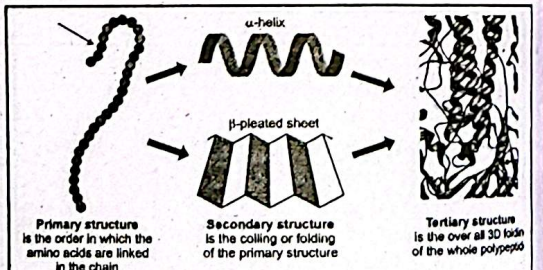



Figure: From primary amino acid chains to tertiary structure of proteins



**Keep in Mind**

Some proteins have quaternary structures too. The quaternary structure arises when two or more folded polypeptide chains (subunits) associate by interactions such as hydrogen bonds, ionic (salt) bridges, hydrophobic interactions, and sometimes disulphide bonds.

**Q.8 Describe fibrous and globular proteins.** UQ

Ans. Based on the overall shape of proteins which they take after the tertiary or quaternary structure formation, they are divided into two main classes:

i. **Fibrous Proteins:** These proteins consist of long, rod-like, or thread-like molecules with polypeptide chains running parallel and linked by strong intermolecular hydrogen bonds or disulphide bonds to form fibres. These proteins are generally insoluble in water, mechanically strong, and stable. Therefore, they serve as the structural polymers.
**Example:** collagen (connective tissue), keratin (hair, nails, skin), and myosin (muscle).

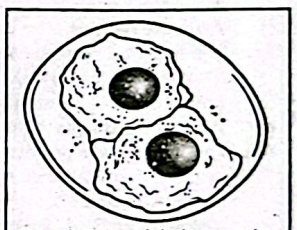
ii. **Globular Protein:** If the shape of the whole protein molecule is spherical or ovoid, it is a globular protein. Most worker proteins (functional proteins), such as enzymes, hormones, and storage proteins are globular proteins. Globular proteins are more sensitive to heat and pH.

### Denaturing of Proteins:

The disruption of structure of proteins is called denaturing of proteins. It can easily be done by:
(i) Heat (ii) Ultraviolet radiations (iii) Change in pH
(iv) Under strongly oxidizing or reducing conditions.
Under such conditions the proteins undergo denaturation.

**Examples:**

- Albumin, the principal component of egg white is hardened on heating as the hydrogen bonding between the chains is disrupted and the chains open up i.e., the helical structure of albumin is disrupted.
- Due to the same reason the milk protein casein is coagulated when the pH of the solution is changed by adding some lemon juice.
- During the formation of cheese from milk, the globular protein 'Lactalbumin' becomes fibrous.
- Denaturation can be reversible or irreversible. The denaturation of albumin is irreversible.



Egg white is a globular protein

## Biological Functions of Proteins

**Q.9 Discuss the biological functions of proteins.** UQ

Ans. Proteins can be grouped into different categories based on their biological and metabolic functions. There are some proteins which control or regulate specific physiological activities, such as growth, development, metabolism, and reproduction. These are called **Hormonal Proteins.** An example is insulin, which is produced by pancreas in our bodies and is responsible for regulating the movement of glucose from the blood into cells.

- **Storage Proteins** provide essential nutrients for the growth of the germinating seedlings or for the early development of animals. Ferritin is a storage protein found in some bacteria, and in plant and animal tissues, where it stores iron.
- **Structural Proteins** are most abundant proteins in a vertebrate body. They are fibrous, or threadlike, which maintain the shape and give structural support, such as keratin in hair, fibrin in blood clots and collagen. They also forms the matrix of skin, ligaments, tendons, and bones.
- **Contractile Proteins,** such as actin and myosin, make up the thin and thick filaments of a muscle involved in contraction and relaxation movement of the muscle fibre.
- **Defensive proteins** help organisms to fight infection and prevent injury in the body. For example, antibodies recognize and bind to specific antigens (proteins present on pathogens) with high affinity, immediately destroying the antigens.
- **Transport or Carrier Proteins** aid in the movement of molecules and ions across cell membranes. For example, iron atoms in haemoglobin bind oxygen molecules as the blood travels between the lungs and th tissues.

CamScanner

- **Receptor Proteins** are located within the cell's membrane and they receive chemical signals and responses from and to the cells.
- **Regulatory Proteins** play a role in controlling cellular and physiological activities, such as insulin, which regulates sugar metabolism and growth hormone.

## QUICK CHECK 27.2

**a) Keratin is a structural protein found in hair, nails, horn, hoofs, wool, feathers, enamel of teeth and outer layer of skin, where it gives strength and flexibility. It is not easily denatured. Which bond do you expect is responsible for this; hydrogen bond or disulphide bond? Explain.**

Ans. The bond mainly responsible for the strength and stability of keratin is the **disulphide bond (–S–S–)**. Disulphide bonds are formed between sulfur-containing amino acids such as cysteine. These are strong covalent bonds that hold different parts of the protein chain firmly together.
Hydrogen bonds are weaker and can be broken more easily by heat or chemicals, whereas disulphide bonds provide greater strength and resistance to denaturation.
Therefore, keratin is not easily denatured because it contains a large number of **disulphide bonds.**

**b) How can two peptides with identical type and number of amino acids differ in their primary structure?**

Ans. The primary structure of a protein refers to the **sequence of amino acids** in the polypeptide chain. Two peptides may contain exactly the same types and numbers of amino acids but still differ if the amino acids are arranged in a different order.
**For example, Peptide 1:** Ala–Gly–Ser–Val and **Peptide 2:** Val–Ser–Ala–Gly
Although both peptides contain the same amino acids, their primary structures are different because the sequence is different.

**c) What are the two most common types of secondary protein structures in our body?**

Ans. The two most common secondary structures of proteins are:
1. α-Helix (alpha helix) 2. β-Pleated sheet (beta sheet)
Both structures are stabilized by hydrogen bonds formed between peptide groups in the protein chain.

**d) Why does a denatured protein no longer function properly?**

Ans. The function of a protein depends upon its specific three-dimensional shape. During denaturation, heat, acids or chemicals disturb the secondary and tertiary structures of the protein and alter its shape. As a result, the active sites and binding regions change shape and the protein can no longer perform its normal biological function. Therefore, a denatured protein loses its activity because its structure is destroyed.

**e) The white of egg solidifies on heating. Explain why it happens.**

Ans. When egg white is heated **(albumin)**, the heat breaks the hydrogen bonds and other weak interactions that maintain the protein's three-dimensional structure. The protein unfolds and the molecules become entangled with one another, forming a solid network. This process is called **denaturation and coagulation of proteins.** Therefore, the white egg changes from a liquid to a solid on heating because the proteins become denatured and coagulate.

## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Carbohydrates are chemically:**
(A) Polyhydroxy alcohols (B) Polyhydroxy aldehydes or ketones
(C) Amines (D) Esters
2. **The simplest carbohydrates are called:**
(A) Polysaccharides (B) Disaccharides (C) Monosaccharides (D) Glycoproteins
3. **Glucose is classified as a:**
(A) Ketose (B) Aldose (C) Disaccharide (D) Polysaccharide
4. **Fructose is classified as a:**
(A) Aldose (B) Ketose (C) Hexitol (D) Pentose only
5. **A monosaccharide containing six carbon atoms is called a:**
(A) Triose (B) Tetrose (C) Pentose (D) Hexose
6. **Glucose mainly exists in solid form as a:**
(A) Linear chain (B) Cyclic ring (C) Triple helix (D) Branched chain
7. **The six-membered ring form of glucose is known as:**
(A) Furanose (B) Pyranose (C) Lactone (D) Pyridine



8. **Fructose forms a:**
(A) Six-membered ring (B) Five-membered ring (C) Seven-membered ring (D) Four-membered ring
9. **Monosaccharides are highly soluble in water because of:**
(A) Ionic bonding (B) Hydrogen bonding (C) Metallic bonding (D) Covalent cross-linking
10. **Glucose is commonly known as:**
(A) Fruit sugar (B) Blood sugar (C) Milk sugar (D) Malt sugar
11. **Fructose is abundant in:**
(A) Milk (B) Fruits and honey (C) Meat (D) Eggs
12. **A disaccharide consists of:**
(A) One monosaccharide (B) Two monosaccharide units
(C) Three monosaccharide units (D) Many monosaccharide units
13. **The bond joining two monosaccharides is called:**
(A) Peptide bond (B) Glycosidic linkage (C) Ester bond (D) Amide bond
14. **Sucrose is composed of:**
(A) Glucose + glucose (B) Glucose + fructose (C) Fructose + fructose (D) Glucose + galactose
15. **Formation of sucrose is a:**
(A) Hydrolysis reaction (B) Condensation reaction (C) Oxidation reaction (D) Reduction reaction
16. **Polysaccharides are formed from:**
(A) Amino acids (B) Fatty acids
(C) Large numbers of monosaccharides (D) Nucleotides
17. **The storage carbohydrate in plants is:**
(A) Glycogen (B) Cellulose (C) Starch (D) Chitin
18. **Starch consists of:**
(A) Amylose and amylopectin (B) Cellulose and glycogen
(C) Fructose and glucose (D) Keratin and collagen
19. **Amylose is:**
(A) Highly branched (B) Long and unbranched (C) Cyclic (D) Cross-linked
20. **Glycogen is stored in the:**
(A) Bones (B) Liver and muscles (C) Kidneys only (D) Lungs
21. **Cellulose is the major structural material of:**
(A) Animal cells (B) Plant cell walls (C) Blood cells (D) Muscle cells
22. **Dietary fibre mainly consists of:**
(A) Glycogen (B) Cellulose (C) Sucrose (D) Maltose
23. **Blood glucose is mainly regulated by:**
(A) Adrenaline only (B) Insulin and glucagon (C) Thyroxine (D) Growth hormone
24. **Excess glucose is stored as:**
(A) Cellulose (B) Glycogen (C) Protein (D) Fat only
25. **Proteins on complete hydrolysis produce:**
(A) Fatty acids (B) Amino acids (C) Sugars (D) Alcohols
26. **Amino acids are linked by:**
(A) Glycosidic bonds (B) Peptide bonds (C) Ester bonds (D) Ionic bonds
27. **A peptide bond is a type of:**
(A) Ether bond (B) Amide bond (C) Ester bond (D) Hydrogen bond
28. **The primary structure of a protein refers to its:**
(A) Overall shape (B) Amino acid sequence (C) Number of subunits (D) Molecular mass
29. **The α-helix is an example of:**
(A) Primary structure (B) Secondary structure (C) Tertiary structure (D) Quaternary structure
30. **β-Pleated sheets are stabilized mainly by:**
(A) Ionic bonds (B) Hydrogen bonds (C) Peptide bonds only (D) Metallic bonds
31. **Tertiary structure depends mainly on interactions between:**
(A) Sugar molecules (B) R-groups of amino acids (C) Phosphate groups (D) Water molecules
32. **Quaternary structure is formed when:**
(A) One amino acid folds (B) Two or more polypeptide chains associate
(C) DNA replicates (D) RNA is synthesized
33. **Fibrous proteins are generally:**
(A) Soluble in water (B) Insoluble and strong (C) Globular (D) Easily denatured
34. **Keratin is a:**
(A) Globular protein (B) Fibrous protein (C) Enzyme (D) Hormone
35. **Enzymes are generally:**
(A) Fibrous proteins (B) Globular proteins (C) Carbohydrates (D) Lipids
36. **Heating egg white causes protein:**
(A) Hydrolysis (B) Denaturation (C) Polymerisation (D) Hydrogenation

CamScanner

37. Insulin is an example of a:
(A) Structural protein (B) Hormonal protein (C) Storage protein (D) Contractile protein
38. Hemoglobin functions mainly as a:
(A) Storage protein (B) Transport protein (C) Defensive protein (D) Structural protein
39. Antibodies are classified as:
(A) Contractile proteins (B) Defensive proteins (C) Structural proteins (D) Storage proteins
40. Actin and myosin are examples of:
(A) Transport proteins (B) Contractile proteins (C) Hormonal proteins (D) Receptor proteins

## ENZYMES AS BIOCATALYSTS

**Q.10 Discuss the enzymes as biocatalysts.** LO

**Ans.** Enzymes are proteins that acts as biological catalysts needed for various chemical reactions that take place in living organisms. An enzyme speeds up a biochemical reaction to an extent that would be impossible without it. For example, one molecule of carbonic anhydrase in the blood can convert about one million of carbon dioxide and water molecules to carbonic acid in one second.

An enzyme has a special site on its surface, called the active site, which binds the substrate molecule and converts it into the products.

Enzymes are highly specific, each enzyme acts on only one particular substrate molecule. This specificity is due to the active site of the enzyme, which has a unique shape that allows only a specific substrate to fit into it. The random movement of enzyme and substrate molecules, allows the substrate to enter the enzyme active site. As a result of this, a temporary enzyme-substrate complex is formed. After this, the products are released, and the enzyme remains unchanged and free to bind with another substrate molecule (Figure).

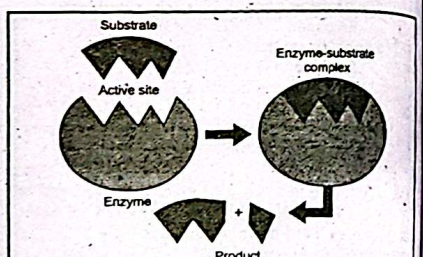


Figure: Formation of enzyme-substrate complex

This mechanism can be understood by using the lock and key model proposed by Emil Fischer in 1894. According to this model, the lock is the enzyme and the key is the substrate. Only the correctly shaped key (substrate) fits into the keyhole (active site) of the lock (enzyme).

**Q.11 Discuss the factors affecting enzyme activity and what is the role of inhibitors in enzyme-catalyzed reactions.** LO

**Ans.** ### Factors Affecting Enzyme Activity

The important factors that influence the activity of the enzyme reaction are temperature, pH and change in the substrate and enzyme concentrations. The enzyme action may also be affected in the presence of some other substances such as co-enzymes, activators and inhibitors.

- **Temperature and pH:** The temperature and pH that give maximum enzyme activity are called optimum temperature and pH, respectively. If the temperature and pH are disturbed from the optimum values, it can deactivate the enzyme action. The enzymatic reactions in the human body and other organisms occur best at or around 37°C and a pH around the neutral value (~7).
- **Concentration of Enzyme and Substrate:** The rate of an enzymatic reaction increases as the enzyme or substrate concentrations are increased. This is because with more substrate and enzyme molecules the available sites for binding to enzyme are also abundant. Therefore, the reaction rate increases due to the formation of more enzyme-substrate complex. However increasing the substrate concentration beyond a limit can slow down the reaction.

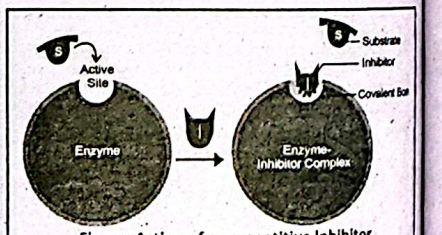


Figure: Action of a competitive inhibitor



### Role of Inhibitors in Enzyme-Catalyzed Reactions

A variety of small molecules or ions that cause enzymes to lose their catalytic activity are called inhibitors. Although, different inhibitors behave differently, but they all prevent the active site from binding with a substrate.

- **Competitive Inhibitors** (mostly reversible) are the species having the same shape as that of the substrate. The substrate and the inhibitor compete for the active site of the enzyme. The more the inhibitor, the more deactivated is the enzyme for the original substrate. For example, the substrate butanedioate (succinate ion) is oxidized by the enzyme succinate dehydrogenase. The propanedioate ion (malonate) can inhibit this enzyme due to its resemblance with the substrate butanedioate.

$^-OOC-CH_2-CH_2-COO^-$ $^-OOC-CH_2-COO^-$
succinate ion malonate ion

- **Non-competitive inhibitors** (mostly irreversible) are small ions or molecules that change the shape of the active site such that it is no longer available for the substrate. Thus, such inhibition is irreversible and it sometimes causes severe human health issues or even death. An enzyme to which a non-competitive/irreversible inhibitor, such as poisons, antibiotics, anti-metabolites and some drugs, is attached, loses enzymatic activity permanently (Figure). Penicillin is an irreversible inhibitor that blocks the enzyme trans-peptidase. This enzyme acts for the synthesis of the bacterial cell wall. Thus, penicillin kills bacteria by disrupting the cell wall enzyme.

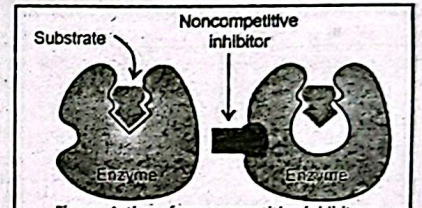


Figure: Action of non-competitive inhibitor

### QUICK CHECK 27.3

**a) How do enzymes differ from inorganic catalysts?**

**Ans. Differences between enzymes and inorganic catalysts**

| Enzymes | Inorganic Catalysts |
|---|---|
| Enzymes are biological catalysts made of proteins. | Inorganic catalysts are non-living chemical substances. |
| They are highly specific and usually catalyse only one reaction. | They are less specific and may catalyse several reactions. |
| They work best at a particular temperature and pH. | They can work over a wider range of temperature and pH. |
| High temperature can denature enzymes. | Inorganic catalysts are generally not denatured by heat. |
| **Examples:** Amylase, pepsin, catalase. | **Examples:** Iron in Haber process, $V_2O_5$ in Contact process. |

**b) What is the effect of decreasing and increasing temperature on the enzyme activity?**

**Ans. Effect of Decreasing Temperature:**

When temperature decreases, enzyme activity decreases because the molecules move more slowly and there are fewer collisions between enzyme and substrate molecules. The enzyme is not damaged and regains its activity when the temperature rises again.

**Effect of Increasing Temperature:**

As temperature increases, enzyme activity increases up to an optimum temperature (usually around **37°C** for human enzymes). Above the optimum temperature, the enzyme activity decreases rapidly because the enzyme becomes denatured and loses its specific shape.

**c) Differentiate between competitive and non-competitive inhibitors.**

**Ans.**

| Competitive Inhibitors | Non-competitive Inhibitors |
|---|---|
| They compete with the substrate for the active site of the enzyme. | They bind to a site other than the active site. |
| Their structure resembles that of the substrate. | Their structure does not need to resemble the substrate. |
| They block the active site and prevent substrate binding. | They change the shape of the active site indirectly. |
| Their effect can be reduced by increasing substrate concentration. | Increasing substrate concentration does not overcome inhibition. |

CamScanner

**d) An enzyme is a protein. When the pH is changed, the function of the enzyme is disturbed. In terms of the protein structure, explain how and why it happens so?**

**Ans.** Enzymes are proteins whose activity depends upon their specific three-dimensional structure. A change in pH changes the concentration of $H^+$ ions in the solution, which affects the ionic bonds and hydrogen bonds responsible for maintaining the secondary and tertiary structures of the protein. As these bonds are disturbed, the shape of the enzyme changes, especially the shape of its active site. As a result, the substrate can no longer fit or bind properly into the active site and the enzyme activity decreases or stops completely.

## LIPIDS

**Q.12 What are lipids?** S/Q

**Ans.** Lipids are a class of organic compounds found in animals and plants that include fats and phospholipids (such as those in the cellular membrane), steroids, and terpenes (essential oils). Unlike polysaccharides and proteins, lipids are not polymers and lack repeating monomeric units. They are hydrophobic but soluble in organic solvents. Lipids perform many different functions in living systems as fuel molecules, signal molecules, components of membranes, hormones and intracellular messengers.

**Q.13 Write an account of classification of lipids with suitable examples.** Exercise D/Q.6

**Ans. Classification of Lipids:**

Lipids are broadly classified into:

i) Simple lipids ii) Complex lipids

iii) Derived lipids based on their chemical composition.

**Interesting Information**

The cobra venom has an enzyme PLA2, which can disrupt the cell wall of the red blood cell. This result in hemolysis, which causes swelling of the affected organ and ultimately death.



### i. Simple Lipids

These are esters of fatty acids with different types of alcohols. Simple lipids are sub-classified based on the type of alcohols, such as fats, oils, and waxes.

➢ **Triglycerides:**

Animal fats and vegetable oils are esters formed from one glycerol molecule and three fatty acids, are called triglycerides as shown in figure. The fatty acids may be similar or different.

Saturated fatty acids make lipids that are solid at room temperature and are called **fats**. On the other hand, oils contain unsaturated fatty acids with one or more double bonds. The hydrophobic structure makes them efficient energy storage molecules and also provides insulation, protection of organs, and a source of fat-soluble vitamins.

***Saturated fatty acids make lipids that are solid at room temperature and are called fats.***

**Oils contain** unsaturated fatty acids with one or more double bonds. The hydrophobic structure makes them efficient energy storage molecules and also provides insulation, protection of organs, and a source of fat-soluble vitamins. The hydrophobic nature of fatty acid chains makes fats insoluble in water but soluble in organic solvents. In the body, this property allows them to form insulating layers under the skin and cushioning around organs such as the kidneys, helping in temperature regulation and protection.

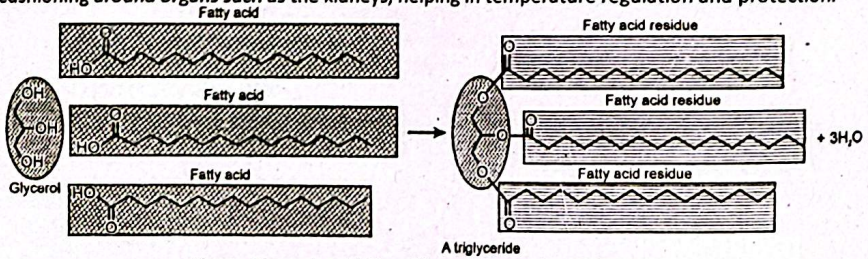


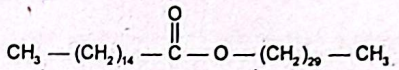

Figure: Glycerol and fatty acids combine to give triglycerides.



➢ **Waxes:**

Most waxes are made up of long fatty acid chains esterified to long-chain alcohols. Both chains are nonpolar and hydrophobic (water-repelling). Because of the hydrophobic nature of waxes, they serve as barriers by forming protective coatings, which prevents water from sticking on the surface.

For example, seen in nature include beeswax, the oil in a whale's head, the feathers of some aquatic birds and plant waxes. These are widely used in pharmaceutical, cosmetic and other industries in the manufacture of lotions, ointments and polishes, etc.



$$CH_3-(CH_2)_{14}-\overset{O}{\overset{\|}{C}}-O-(CH_2)_{29}-CH_3$$

Beeswax

### ii. Compound Lipids

These are esters of fatty acids with alcohols containing an additional group, such as phosphate, nitrogenous base, carbohydrate, protein etc. A phospholipid is similar to a fat molecule but has only two fatty acids attached to glycerol instead of three. The third hydroxyl group of glycerol is linked to a phosphate group, which makes the molecule polar. The hydrocarbon tails are hydrophobic, while the phosphate group and its attached components form a hydrophilic head that has an affinity for water (Figure).

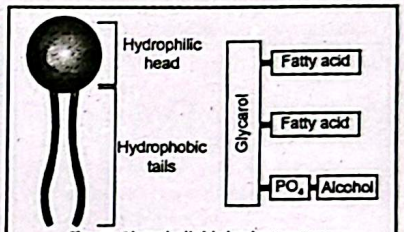



Figure: Phospholipids basic structure

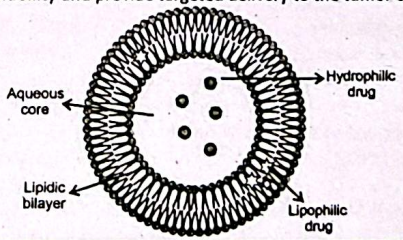
When phospholipids are added to water, they turn into a double-layered sheet called a "bilayer". The polar ends face outward and the non-polar ends cluster together in their own layer. It forms the structure of all cell membranes. Some liposomes are artificial phospholipids that are used for hydrophilic drug delivery.

Lipoproteins are complexes of lipids and proteins that transport hydrophobic lipids (like cholesterol and triglycerides) in the bloodstream.

Glycolipids are lipids with carbohydrate (sugar) groups attached, mostly found in nervous tissue.

**Did You Know?**

Liposomes are ideal for delivering hydrophilic (water-loving) cancer drugs because their structure, a lipid bilayer surrounding a watery core, allows them to encapsulate water-soluble agents, shielding them from degradation and enabling cellular uptake. They improve solubility and provide targeted delivery to the tumor cells.




### iii. Derived or Associated Lipids

Derived lipids are the hydrolytic products of simple and compound lipids, which have the same characteristics as of lipids, e.g. fatty acids, glycerol, steroids, lipid soluble vitamins, etc. They are not fats themselves, but come from fats. They perform important roles in the body including energy and hormone production, cell structure, nerve health, and vitamin function.

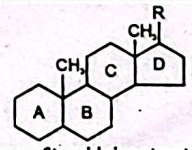



Figure: Steroid ring structure

CamScanner

➤ **Steroids:**

Steroids are not formed from fatty acids but have some lipid like properties. They consist of three cyclohexane rings and one cyclopentane ring fused together making the steroid nucleus (Figure). The four rings in the steroid nucleus are named as A, B, C, and D. Many steroids also have the -OH functional group, which put them into the alcohol class (sterols). There are numerous steroids in the biological systems, including cholesterol, bile salts, vitamin D and steroid hormones.

➤ **Terpenes:**

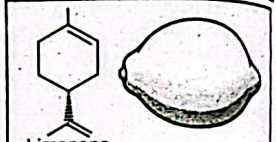
***Lipids present in plants include a wide variety of hydrocarbons called terpenes, which are built from isoprene*** ($CH_2 = C(CH_3) - CH = CH_2$) ***units.*** These hydrocarbons and their oxygenated derivatives have fewer than 40 carbon atoms. Terpenes that contain 40 carbon atoms (8 isoprene units) are known as carotenoids.

## ➲ Nutritional and Biological Importance of Lipids

**Q.14 Discuss the nutritional and biological importance of lipids.** S/Q

**Ans.** A major function of lipids is to serve as a primary source of energy storage in living organisms. They provide more energy per gram than carbohydrates, because when oxidised to carbon dioxide and water, they give a higher caloric value.

Lipids act as solvents for the transport of fat soluble vitamins (A, D, E and K) and help in their absorption in the intestinal cells and later into the bloodstream. We can meet our vitamin requirements by consuming foods that contain these fat-soluble vitamins. These vitamins should be eaten with a bit of healthy fat. Fats provide insulation to the body from water, heat, and electricity due to their non-polar nature.



Limonene, a terpene in lemon

**Did You Know?**

Animals, such as polar bears, reptiles, and amphibians, store extra fat when hibernating. Hibernation is a condition when animals significantly slow down their metabolic rate, body temperature, heart rate and breathing to save energy for the periods when food is scarce. During this period, metabolic rates decrease extremely. Fat is a more concentrated source of energy compared to glycogen, allowing animals to utilize stored fat effectively while minimizing energy consumption.as

### ☑ QUICK CHECK 27.4

**a) Why lipids are not soluble in water?**

**Ans.** Lipids are not soluble in water because they consist mainly of long **non-polar hydrocarbon chains.** Water is a polar solvent and cannot form strong interactions with these non-polar molecules. Therefore, lipids do not dissolve in water but dissolve in non-polar organic solvents such as ether, benzene and chloroform.

**b) What are three major functions of lipids in the human body?**

**Ans.** 1. **Energy Storage:** Lipids act as a long-term energy reserve and provide more energy per gram than carbohydrates.
2. **Thermal Insulation:** A layer of fat beneath the skin helps reduce heat loss and maintains body temperature.
3. **Protection of Organs:** Lipids surround and cushion important organs such as the kidneys and heart, protecting them from physical damage.

**c) What type/s of lipid do/does not contain fatty acids? Give examples.**

**Ans.** Derived the lipids that do not contain fatty acids and may be are called **non-saponifiable lipids.**

**Examples include:**

- **Cholesterol**
- **Steroid hormones** such as testosterone and estrogen.

These lipids do not undergo hydrolysis to produce fatty acids.



**d) Vegetable oil and vegetable ghee both are triglycerides. What is the major structural difference between the two?**

**Ans.** The major difference lies in the degree of saturation of the fatty acids.

**Ans.**

| Vegetable oil | Vegetable ghee |
|---|---|
| • Contains mainly unsaturated fatty acids. | • Contains mainly **saturated fatty acids** or hydrogenated fatty acids. |
| • These fatty acids contain one or more carbon-carbon double bonds (C = C). Therefore, vegetable oils are usually liquids at room temperature. | • These fatty acids contain only **single bonds** (C – C). Therefore, vegetable ghee is usually solid or semi-solid at room temperature. |
| • Thus, the main structural difference is that vegetable oils contain more double bond. | • Thus, vegetable ghee contains fewer or no double bonds due to hydrogenation. |

# NUCLEIC ACIDS

**Q.15 What are nucleic acids?** S/Q

**Ans.** **Nucleic acids are large biomolecules that store and transmit genetic information.** They are polymers made up of smaller units called nucleotides. Nucleic acids are formed from the nucleotide chains containing alternating sugar and phosphate groups with organic bases attached to the sugar molecules. The sugars are ribose in RNA and deoxyribose in DNA; these are five membered sugar molecules. Nucleotides are joined together by a phosphodiester linkage with the '5' and '3' carbon atoms of the sugar to form nucleic acids (Figure). The process is repeated up to several million times to make a polynucleotide. Phosphodiester linkages are strong covalent bonds, which gives strength and stability to the polynucleotide chain.

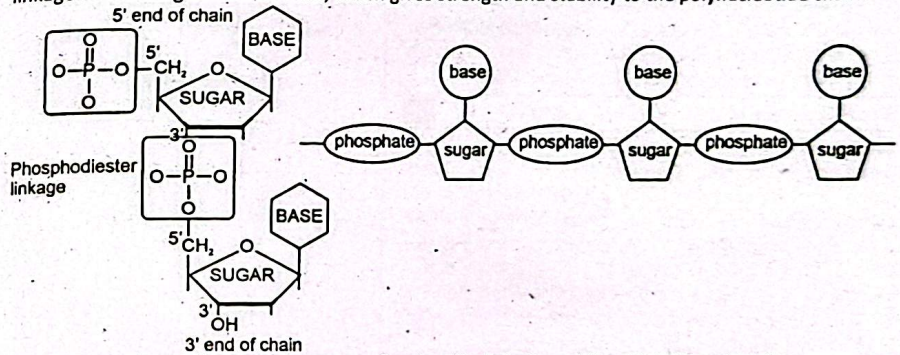


Figure: The general structure of nucleotide chains in nucleic acids (DNA and RNA)

## ➲ Deoxyribonucleic Acid (DNA)

**Q.16 Write note on deoxyribonucleic acid (DNA). Also explain Watson and Crick model of DNA.** L/Q

**Ans.** DNA is present in the nucleus of most living cells. It is a coded plan (or 'blueprint') for making proteins, which are, in turn, vital for life. Each specific protein is made by a specific gene; a section of DNA (Figure). The genetic information of an organism is stored in DNA molecules that carries the genetic instructions for the development, functioning, growth, and reproduction of all living organisms. The double helix structure of DNA allows for the storage of information through the sequence of its four different nitrogenous bases and transmit genetic information efficiently and accurately for the synthesis of proteins.

**Chromosomes:** These genes are organised into larger units called chromosomes. In humans, we receive 23 pairs of these from our parents. While nearly every cell in the body carries the full set of 23 pairs, each cell type expresses a different specific protein. For instance, a red blood cell activates the gene for **haemoglobin** while keeping the gene for keratin switched off.

CamScanner

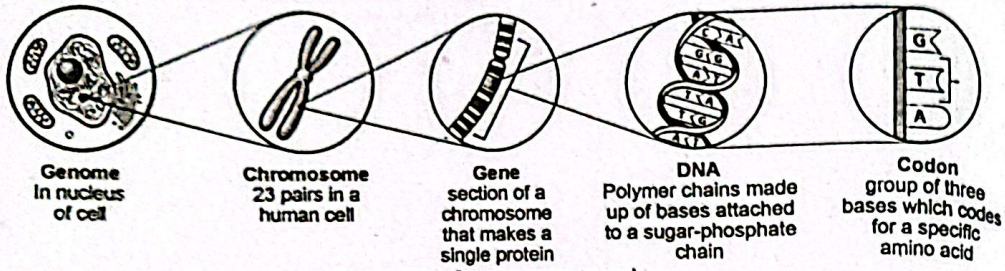



**Figure: DNA; from genome to codon**

## ➲ The Structure and function of DNA

### Watson and Crick Mode:

In 1953, James Watson and Francis Crick showed that DNA consists of two polynucleotide chains. Each chain forms a right-handed helical spiral and the two chains coil around each other to form a double helix. The two polynucleotide chains are not identical but opposite to each other due to base pairing i.e. ' 3 ' end of one faces the ' 5 ' end of the other. Each chain has a sugar-phosphate backbone with bases which project at right-angles and held by weak hydrogen bonds with bases of the opposite chain across the double helix. Adenine (A) is always opposite to thymine (T), and guanine (G) and cytosine (C) are opposite to each other. There are two hydrogen bonds between A and T pair, and three hydrogen bonds between G and C pair **(Figure)**.

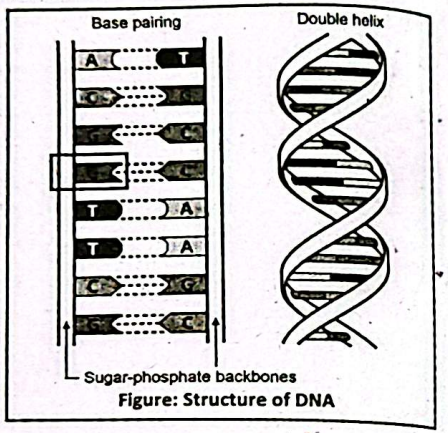



**Figure: Structure of DNA**

**Q.17 What is the Role of DNA in Protein Synthesis?** S/Q

**Ans. Role of DNA in Protein Synthesis:**

Genes are the specific regions of DNA that carry genetic information. They provide instructions for the cell to make a particular protein. One important process of DNA is its self-replication. Replication is the process during the cell cycle in which DNA is copied, so that when the cell division occurs, each new cell receives a complete set of genetic material. In this way, the genetic information is transmitted from one cell to the daughter cells and to the next generation.

## ➲ Structure of RNA

**Q.18 Briefly discuss structure of RNA and its types** S/Q

**Ans.** RNA is usually single stranded unlike DNA, but the chain can fold back to itself to form a helical loop. A ribonucleotide chain in the RNA contains ribose, four nitrogenous bases (A, U, G, and C), and the phosphate group as given in Figure. There are three major types of RNA in the cells.

**Messenger RNA (mRNA):** it carries the genetic blueprint copied from the DNA in the nucleus.

**Ribosomal RNA (rRNA):** it helps to make up the ribosome.

**Transfer RNA (tRNA):** it translates the nucleotide sequence in mRNA into the corresponding sequence of amino acids in a protein.

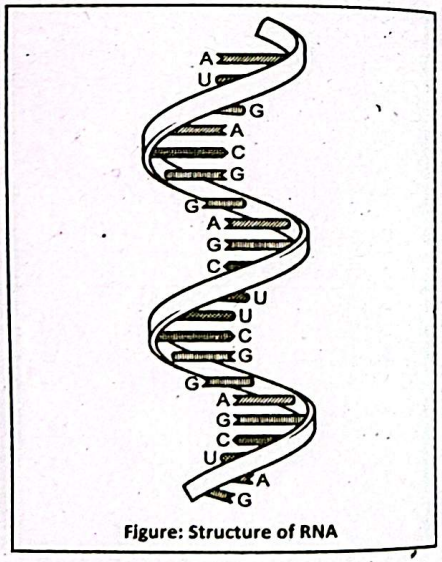


**Figure: Structure of RNA**



## ➲ "Genetic Code and Protein Synthesis"

**Q.19 Discuss genetic code and protein synthesis.** U/Q

**Ans.** Protein synthesis is a complex process involved in transferring genetic information encoded in the DNA. Two processes required for transmitting genetic information for the synthesis of numerous proteins in living organisms: i) Transcription ii) Translation

**I. Transcription:**

The process starts with making copies, i.e. making copies of DNA in the nucleus, the genetic instructions for making a protein are copied from a DNA gene into mRNA; this process is called **transcription.**

**II. Translation:**

When the mRNA strand is complete, it detaches from DNA and enters the cytoplasm, where it attaches to ribosomes. At the ribosomes, the code carried by mRNA is read and converted into a specific sequence of amino acids, forming a protein through the process called **translation.**

***Amino acids are arranged according to the sequence of bases in the RNA.*** The tRNA molecules release their amino acids, which join together in a chain, forming a polypeptide chain. The polypeptide chain grows as bonds form between the amino acids, and finally the complete protein molecule is formed.

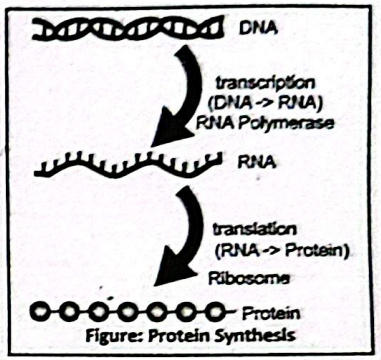



**Figure: Protein Synthesis**

### ☑ QUICK CHECK 27.5

**a) Compare the stability provided by the sugar-phosphate backbone versus the inter-chain base pairing. In your answer, refer to the specific types of bonds and the number of bonds formed between:**

- **Adenine (A) and Thymine (T)**
- **Guanine (G) and Cytosine (C)**

**Ans.** The stability of DNA is provided by both

i) **sugar-phosphate backbone**

ii) **base pairing between the two strands**

**Note:** Their types of bond and strength of bonding are different.

i) **Sugar-phosphate backbone** (Strong and Permanent):

The sugar-phosphate backbone forms the sides of the DNA double helix. The sugar and phosphate groups are joined by strong covalent phosphodiester bonds. These covalent bonds provide the main structural stability to each DNA strand.

ii) **Inter-chain base pairing** (Weak and temporary):

The two DNA strands are held together by hydrogen bonds between complementary nitrogenous bases but the bonds are weak this allows the strands to separate easily during replication and transcription. The number of hydrogen bonds depends upon the type of base pair:

- Adenine (A) pairs with Thymine (T) through two hydrogen bonds: A = TA = TA = T
- Guanine (G) pairs with Cytosine (C) through three hydrogen bonds: G ≡ CG

Because G-C pairs contain three hydrogen bonds, they are more stable than A-T pairs.

**b) How the DNA and RNA are chemically different? What are the similarities between these two?**

**Ans. Differences between DNA and RNA**

| DNA | RNA |
|---|---|
| Contains deoxyribose sugar | Contains ribose sugar |
| Contains thymine (T) | Contains uracil (U) instead of thymine |
| Usually double stranded | Usually single stranded |
| More chemically stable | Less chemically stable |
| Stores genetic information | Involved in protein synthesis |

CamScanner

**Similarities between DNA and RNA**

- Both are nucleic acids.
- Both are made up of nucleotides.
- Both contain a sugar-phosphate backbone.
- Both contain the nitrogenous bases adenine, guanine and cytosine.
- Both play important roles in genetic information and protein synthesis.

**c) Nearly every cell in the human body contains the exact same 23 pairs of chromosomes, yet a red blood cell produces haemoglobin while a skin cell produces keratin. Explain why.**

**Ans.** Although body cells contain the same genetic information, not all genes are active in every cell. Different types of cells switch on different sets of genes according to their functions. This process is called **differential gene expression.**
In red blood cells, the genes responsible for haemoglobin production are active, so haemoglobin is synthesized.
In skin cells, the genes responsible for keratin production are active, so keratin is synthesized.
Therefore, cells with the same DNA can produce different proteins because different genes are expressed in different cell types.

## MINERALS

**Q.20 What are minerals? How they are classified? Give sources and functions of some important minerals.** L/O

**Ans.** **Minerals** are inorganic substances, necessary for the maintenance of certain physiochemical life processes vital for living organism. Although, they produce no energy, they have important functions to perform in various activities.

### ➢ Classes of Minerals:

Minerals may be broadly classified as macro (major) or micro (trace) elements on the basis of the amount required by the body.

**i) Macrominerals**
**The macrominerals** include calcium, phosphorus, sodium and chloride, potassium, magnesium and sulphur. The macro-minerals are required in amounts greater than 100 mg/dL.

**ii) Microminerals**
The microminerals include iron, copper, cobalt, iodine, zinc, manganese, molybdenum, fluoride, chromium, selenium and sulfur. The micro-minerals are required in amounts less than 100 mg/dL.

**Table: Sources and role of minerals**

| Mineral | Sources | Role in Nutrition |
|---|---|---|
| Iron | Liver, meat, egg yolks, nuts, enriched or whole grains, beans, peas and lentils. | Hemoglobin synthesis found in red blood and myoglobin in muscle cells. Needed to carry oxygen. |
| Calcium | Milk and other dairy products, greens, broccoli, and salmon, sardines, beans, peas and lentils. | Helps in the formation of bones and teeth, normal blood clotting, muscle contraction and relaxation, heart function and nerve function. |
| Phosphorus | Meat, fish, poultry, eggs, milk, cereal products. | Aids in the formation of bones and teeth. Regulates the release and use of body energy (ATP). It helps to carry fat in the body as a part of phospholipids. Maintains normal acid/base balance in the body. |
| Zinc | Meat, seafood, whole grains. | Component of many enzyme systems e.g. involved in growth, immune function, etc. Found in the hormone insulin. |
| Sodium, potassium, and chloride | Salt, meat, sea food, fruit juices, vegetables, lentil | Maintaining fluid balance, nerve transmission, and muscle function |



## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Enzymes are:**
(A) Carbohydrates (B) Proteins acting as biological catalysts
(C) Lipids (D) Minerals

2. **The main function of an enzyme is to:**
(A) Stop chemical reactions (B) Speed up biochemical reactions
(C) Produce ATP (D) Store energy

3. **The specific region of an enzyme where the substrate binds is called the:**
(A) Binding chain (B) Active site (C) Catalyst center (D) Reaction pocket

4. **The temporary complex formed between enzyme and substrate is the:**
(A) Protein complex (B) Enzyme-substrate complex (C) Peptide complex (D) ATP complex

5. **According to Emil Fischer's model, the enzyme acts as the:**
(A) Key (B) Lock (C) Catalyst (D) Product

6. **In the lock and key model, the substrate acts as the:**
(A) Lock (B) Key (C) Enzyme (D) Inhibitor

7. **Enzymes are highly:**
(A) Reactive (B) Specific (C) Acidic (D) Basic

8. **After a reaction, the enzyme:**
(A) Is permanently changed (B) Remains unchanged (C) Is destroyed (D) Becomes a product

9. **The optimum temperature for most human enzymes is approximately:**
(A) 0°C (B) 25°C (C) 37°C (D) 100°C

10. **The optimum pH for many human enzymes is approximately:**
(A) 2-3 (B) 4-5 (C) 6.4-6.9 (D) 10-11

11. **Deviating from optimum temperature generally:**
(A) Increases activity indefinitely (B) Decreases enzyme activity
(C) Produces new enzymes (D) Has no effect

12. **Increasing enzyme concentration generally:**
(A) Decreases reaction rate (B) Increases reaction rate (C) Stops the reaction (D) Denatures the enzyme

13. **Increasing substrate concentration initially:**
(A) Decreases reaction rate (B) Increases reaction rate (C) Stops enzyme activity (D) Denatures the enzyme

14. **Competitive inhibitors are also called:**
(A) Irreversible inhibitors (B) Reversible inhibitors (C) Permanent inhibitors (D) Toxic inhibitors

15. **Competitive inhibitors compete with the substrate for the:**
(A) Product (B) Active site (C) Cell membrane (D) Ribosome

16. **Competitive inhibitors usually resemble the:**
(A) Product (B) Substrate (C) Enzyme (D) Hormone

17. **Non-competitive inhibitors:**
(A) Bind like substrates (B) Change the shape of the active site
(C) Increase enzyme activity (D) Form products

18. **Non-competitive inhibition is generally:**
(A) Reversible (B) Irreversible (C) Temporary (D) Catalytic

19. **Penicillin acts as a:**
(A) Competitive inhibitor (B) Non-competitive inhibitor (C) Coenzyme (D) Activator

20. **Lipids are generally:**
(A) Hydrophilic (B) Hydrophobic (C) Water soluble (D) Ionic compounds

21. **Lipids are soluble mainly in:**
(A) Water (B) Organic solvents (C) Dilute acids (D) Salt solution

22. **Lipids are not considered polymers because they:**
(A) Lack repeating monomer units (B) Contain nitrogen
(C) Are acidic (D) Contain peptide bonds

23. **Triglycerides consist of:**
(A) One glycerol and three fatty acids (B) Two glycerol molecules
(C) Three glycerol molecules (D) One fatty acid only

24. **Saturated fatty acids usually form:**
(A) Oils (B) Fats (C) Waxes (D) Steroids

25. **Unsaturated fatty acids mainly form:**
(A) Oils (B) Fats (C) Waxes (D) Proteins

CamScanner

26. Waxes are esters of fatty acids with:
(A) Sugars (B) Long-chain alcohols (C) Amino acids (D) Glyceraldehyde
27. Phospholipids differ from triglycerides because they contain:
(A) Four fatty acids (B) A phosphate group (C) Two glycerol molecules (D) No alcohol
28. Phospholipids form the basic structure of:
(A) Bones (B) Cell membranes (C) Hair (D) Muscles
29. Lipoproteins mainly transport:
(A) Carbohydrates (B) Hydrophobic lipids (C) Minerals (D) Amino acids
30. Glycolipids are abundant in:
(A) Blood plasma (B) Nervous tissue (C) Bones (D) Liver only
31. Steroids possess:
(A) A peptide chain (B) Four fused rings (C) Glycosidic linkage (D) Phosphodiester linkage
32. Cholesterol belongs to the class of:
(A) Proteins (B) Steroids (C) Waxes (D) Triglycerides
33. Terpenes are mainly found in:
(A) Animals only (B) Plants (C) Fungi only (D) Bacteria only
34. Lipids provide:
(A) Less energy than carbohydrates (B) More energy per gram than carbohydrates
(C) No energy (D) Equal energy as minerals
35. Vitamins A, D, E and K are:
(A) Water-soluble vitamins (B) Fat-soluble vitamins (C) Mineral salts (D) Proteins
36. Lipids help in the absorption of:
(A) Vitamin C (B) Vitamin $B_{12}$ (C) Fat-soluble vitamins (D) Glucose
37. Body fat helps in:
(A) Photosynthesis (B) Insulation and protection (C) Oxygen transport (D) Blood clotting only
38. Liposomes are useful for:
(A) Oxygen transport (B) Drug delivery (C) Protein synthesis (D) Blood clotting
39. During hibernation, animals mainly utilize stored:
(A) Glycogen only (B) Fat (C) Proteins (D) Minerals
40. The major energy-storage lipid in animals is:
(A) Phospholipid (B) Triglyceride (C) Steroid (D) Glycolipid

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

**BLOCK # 01**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. B | 4. B | 5. D | 6. B | 7. B | 8. B | 9. B | 10. B | 11. B | 12. B | 13. B | 14. B | 15. B |
| 16. C | 17. C | 18. A | 19. B | 20. B | 21. B | 22. B | 23. B | 24. B | 25. B | 26. B | 27. B | 28. B | 29. B | 30. B |
| 31. B | 32. B | 33. B | 34. B | 35. B | 36. B | 37. B | 38. B | 39. B | 40. B | | | | | |

**BLOCK # 02**

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. B | 4. B | 5. B | 6. B | 7. B | 8. B | 9. C | 10. C | 11. B | 12. B | 13. B | 14. B | 15. B |
| 16. B | 17. B | 18. B | 19. B | 20. B | 21. B | 22. A | 23. A | 24. B | 25. A | 26. B | 27. B | 28. B | 29. B | 30. B |
| 31. B | 32. B | 33. B | 34. B | 35. B | 36. C | 37. B | 38. B | 39. B | 40. B | | | | | |

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. Glucose is a building block for all, except:
a) cellulose b) glycogen c) insulin d) starch
II. Which one of the following is not an aldose?
a) glucose b) galactose c) mannose d) fructose
III. Which one of the following elements is not present in all proteins?
a) carbon b) hydrogen c) nitrogen d) sulphur
IV. In DNA, the linkages between different nitrogenous bases are:
a) phosphate linkage b) hydrogen bonding c) glycosidic linkage d) peptide linkage
V. Which one of the following nitrogenous bases is unique to RNA?
a) cytosine b) adenine c) thiamine d) uracil



VI. Waxes are the esters of:
a) glycerols b) sterols c) ethanol d) long-chain fatty acids and alcohols.
VII. A cell membrane is made up of:
a) phospholipid bilayer b) lipid c) phospholipid d) only protein
VIII. The covalent backbone bond in protein structure that is not broken on denaturation:
a) hydrogen bonds b) peptide bonds c) ionic bond d) disulfide bonds
IX. The backbone of nucleic acid structure is constructed by:
a) peptide bonds b) glycosidic bonds c) phosphodiester bridges d) all of them
X. Which element prevents the development of tooth decay:
a) fluorine b) calcium c) phosphorus d) sodium

### Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | c | inulin | Inulin is a polymer of fructose, whereas cellulose, glycogen and starch are polymers of glucose. |
| II. | d | fructose | Fructose contains a ketone group, so it is a ketose rather than an aldose. |
| III. | d | sulphur | Carbon, hydrogen and nitrogen are present in all proteins, but sulphur is found only in some amino acids such as cysteine and methionine. |
| IV. | b | hydrogen bonding | Nitrogenous bases of opposite DNA strands are held together by hydrogen bonds. |
| V. | d | uracil | Uracil is present only in RNA, while thymine is present only in DNA. |
| VI. | d | long-chain fatty acids and alcohols. | Waxes are esters formed from long-chain fatty acids and long-chain alcohols. |
| VII. | a | phospholipid bilayer | The cell membrane mainly consists of a phospholipid bilayer with proteins embedded in it. |
| VIII. | b | peptide bonds | Denaturation destroys secondary and tertiary structures but does not break the peptide bonds of the primary structure. |
| IX. | c | phosphodiester bridges | The sugar and phosphate groups of nucleic acids are linked through phosphodiester bonds, forming the backbone of DNA and RNA. |
| X. | a | fluorine | Fluorine strengthens tooth enamel and helps protect teeth from decay and cavities. |

## Q 2. SHORT ANSWER QUESTIONS SAQs

a) What role does glycogen play in the human body?

Ans. Glycogen is the storage form of glucose in animals. It is mainly stored in the liver and muscles and serves as an energy reserve. When the body needs energy, glycogen breaks down into glucose to maintain blood sugar level and supply energy to cells.

b) Point out the main structural difference between the compounds in each of the following pairs.
i) Glucose and fructose ii) Cellulose and starch
iii) Competitive and non-competitive inhibition iv) Glycolipids and lipoproteins

Ans. Main structural difference between the compounds:

| | |
|---|---|
| **i) Glucose and Fructose**<br>• Glucose is an aldohexose and contains an aldehyde group (–CHO).<br>• Fructose is a ketohexose and contains a ketone group (>C=O). | **ii) Cellulose and Starch**<br>• Cellulose contains β-glucose units joined by β(1→4) glycosidic bonds.<br>• Starch contains α-glucose units joined mainly by α(1→4) glycosidic bonds and some α(1→6) bonds in branched chains. |
| **iii) Competitive and Non-competitive Inhibition**<br>• Competitive inhibitors bind to the active site and compete with the substrate. | **iv) Glycolipids and Lipoproteins**<br>• Glycolipids consist of lipids attached to carbohydrates. |

CamScanner

| | |
|---|---|
| • Non-competitive inhibitors bind at a different site and change the shape of the active site. | • Lipoproteins consist of lipids attached to proteins. |

**c) Which class of biomolecule contains each of the following linkages? Describe the function of each linkage.**
**i) Glycosidic ii) Peptide iii) Ester iv) Phosphodiester**

**Ans.**

| | |
|---|---|
| **i) Glycosidic Linkage**<br>**Found in:** Carbohydrates<br>**Function:** It joins monosaccharides together to form disaccharides and polysaccharides such as starch and cellulose. | **ii) Peptide Linkage**<br>**Found in:** Proteins<br>**Function:** It joins amino acids together to form polypeptide chains and proteins. |
| **iii) Ester Linkage**<br>**Found in:** Lipids<br>**Function:** It joins fatty acids with glycerol to form fats and oils. | **iv) Phosphodiester Linkage**<br>**Found in:** Nucleic acids<br>**Function:** It joins nucleotides together to form the sugar-phosphate backbone of DNA and RNA. |

**d) How the tertiary structure of proteins is formed?**

**Ans.** The tertiary structure is formed by the folding and twisting of a polypeptide chain into a three-dimensional shape. This structure is stabilized by hydrogen bonds, ionic bonds, disulphide bonds and hydrophobic interactions. These interactions maintain the specific shape required for protein function.

**e) In what way fats and oils are different?**

**Ans.**

| Fats | Oils |
|---|---|
| Usually solid at room temperature. | Usually liquid at room temperature. |
| Contain more saturated fatty acids. | Contain more unsaturated fatty acids. |
| Mostly obtained from animals. | Mostly obtained from plants. |

**f) Describe the structure of steroids. Write a note on the functions of cholesterol.**

**Ans.**

| Structure of Steroids | Functions of Cholesterol |
|---|---|
| Steroids consist of four fused carbon rings:<br>• Three six-membered rings.<br>• One five-membered ring.<br>This fused ring system is called the steroid nucleus. | • It is a component of cell membranes.<br>• It helps maintain membrane fluidity.<br>• It is the precursor of steroid hormones.<br>• It is used for the synthesis of vitamin D.<br>• It is involved in the formation of bile salts. |

**g) Describe the mechanism of enzyme action.**

**Ans.** According to the lock and key model, the substrate fits into the active site of the enzyme.

$$E + S \longrightarrow ES \longrightarrow E + PE + S$$

Where:
• E = Enzyme • S = Substrate • ES = Enzyme-substrate complex • P = Product
The enzyme lowers the activation energy of the reaction and converts the substrate into products without being consumed.

**h) Why does an enzyme catalyze a reaction of only a specific substrate?**

**Ans.** Each enzyme has a specific active site with a particular shape.
Only the substrate with a complementary shape can fit into the active site and form an enzyme-substrate complex. Therefore, enzymes are highly specific in their action.

**i) Name different RNAs and discuss their function.**

**Ans.** 1. **Messenger RNA (mRNA):** Carries genetic information from DNA to ribosomes for protein synthesis.
2. **Transfer RNA (tRNA):** Transfers amino acids to the ribosome during protein synthesis.
3. **Ribosomal RNA (rRNA):** Forms part of ribosomes and helps in protein synthesis.



**j) What are some sources of potassium, iron, calcium, magnesium and zinc in our diet?**

**Ans.**

| Mineral | Common Sources |
|---|---|
| Potassium (k) | Bananas, potatoes, oranges |
| Iron (Fe) | Red meat, spinach, liver |
| Calcium (Ca) | Milk, cheese, yogurt |
| Magnesium (Mg) | Nuts, whole grains, green vegetables |
| Zinc (Zn) | Meat, eggs, seafood, beans |

**k) What is the role of iron in the body?**

**Ans.** Iron is an essential component of haemoglobin in red blood cells.
Its main function is to transport oxygen from the lungs to body tissues.
Iron is also important for enzyme activity and normal metabolism.

**l) How enzyme inhibitors are important in our body and medicine?**

**Ans.** Enzyme inhibitors regulate metabolic reactions in the body by controlling enzyme activity.
In medicine, many drugs act as enzyme inhibitors to treat diseases.
**Examples include:**
• Aspirin inhibits enzymes involved in pain and inflammation.
• Penicillin inhibits bacterial enzymes required for cell wall synthesis.
• Some anticancer drugs inhibit enzymes needed for the growth of cancer cells.
Thus, enzyme inhibitors play an important role in both normal body functions and medical treatment.

**m) Differentiate between the primary and secondary structure of proteins.**

**Ans.**

| Primary Structure | Secondary Structure |
|---|---|
| It is the exact linear sequence of amino acids in a polypeptide chain. | It is the regular local folding or coiling of the polypeptide backbone into structures like α-helix and β-pleated sheet. |
| Amino acids are joined together by covalent peptide bonds (–CO–NH–). | Stabilized mainly by hydrogen bonds between the backbone C = O (carbonyl) and N – H (amide) groups. |
| It determines the type and number of amino acids in the protein. | It provides the local 3D shape and stability to the polypeptide chain. |

## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a. How condensation of sugars and condensation of amino acid are same?**

**Ans.** Both reactions are examples of **condensation reactions** in which two smaller molecules combine to form a larger molecule with the elimination of a small molecule, usually water.
• In sugars, two monosaccharides combine to form a disaccharide by removing a molecule of water and forming a **glycosidic linkage.**

$$\text{Glucose} + \text{Glucose} \longrightarrow \text{Maltose} + H_2O$$

• In amino acids, two amino acids combine to form a dipeptide by removing a molecule of water and forming a **peptide linkage.**

$$\text{Amino acid} + \text{Amino acid} \longrightarrow \text{Dipeptide} + H_2O$$

Thus, both processes involve the removal of water and formation of a covalent bond between monomer units.

**b. Why is cholesterol included in the lipid family?**

**Ans.** Cholesterol is included in the lipid family because it is **insoluble in water** but soluble in non-polar organic solvents such as ether and chloroform. Like other lipids, cholesterol is hydrophobic in nature and plays important roles in cell membranes and hormone production. Therefore, despite having a different structure from fats and oils, cholesterol is classified as a lipid.

**c. Why fats and oils are also called triacylglycerides?**

**Ans.** Fats and oils are called **triacylglycerides** because one molecule of glycerol is attached to **three molecules of fatty acids** through ester linkages.
The prefix **"tri"** means three, while **"acyl"** refers to the fatty acid residues attached to glycerol.
Hence, fats and oils are known as triacylglycerols.

CamScanner

**d. How hydrogen bonding is important in the double helix of DNA?**

**Ans.** Hydrogen bonds hold the two strands of DNA together and maintain the double helical structure.
The complementary base pairs are joined by hydrogen bonds:
- Adenine (A) pairs with Thymine (T) through **two hydrogen bonds.**
- Guanine (G) pairs with Cytosine (C) through **three hydrogen bonds.**

These hydrogen bonds provide stability to the DNA molecule while still allowing the strands to separate during replication and protein synthesis.
Therefore, hydrogen bonding is essential for maintaining the structure and function of DNA.

**e. If the sequence T-A-C-C-G-A located on one strand of DNA, what sequence is seen opposite to it on the other strand?**

**Ans.** In DNA:
- Adenine (A) pairs with Thymine (T)
- Guanine (G) pairs with Cytosine (C)

Therefore,
T–A–C–C–G–A
will pair with:
A–T–G–G–C–T
Hence, the sequence on the opposite strand will be:
A–T–G–G–C–T

## DESCRIPTIVE QUESTIONS DQs

**Q.4 Classify and describe the structures of polysaccharides.**

**Ans.** See Question No. 03

**Q.5 How the structure of proteins support its functions. Describe at each structure level.**

**Ans.** See Question No. 07

**Q.6 Write an account of classification of lipids with suitable examples.**

**Ans.** See Question No. 13

**Q.7 What are nucleic acids? Describe the role of DNA and RNA in the protein synthesis.**

**Ans.** Nucleic acids are large biomolecules made up of repeating units called nucleotides.
Each nucleotide consists of:
• A pentose sugar • A phosphate group • A nitrogenous base
The two main types of nucleic acids are DNA and RNA.

➢ **Role of DNA in Protein Synthesis**

DNA contains the genetic information required for the synthesis of proteins.
The sequence of nitrogenous bases in DNA determines the sequence of amino acids in a protein.
During protein synthesis, the required information is copied from DNA into messenger RNA in a process called transcription.
Thus, DNA acts as the master blueprint for protein synthesis.

➢ **Role of RNA in Protein Synthesis**

Three types of RNA participate in protein synthesis.
1. **Messenger RNA (mRNA):** mRNA carries genetic information from DNA to the ribosome in the form of codons.
2. **Transfer RNA (tRNA):** tRNA carries specific amino acids to the ribosome and places them according to the codons present on mRNA.
3. **Ribosomal RNA (rRNA):** rRNA forms the major part of ribosomes and provides the site where proteins are synthesized.

➢ **Steps of Protein Synthesis**

**Step 1: Transcription:** The genetic information in DNA is copied into mRNA inside the nucleus.

**Step 2: Translation:** The mRNA moves to the ribosome where tRNA brings amino acids according to the sequence of codons on mRNA. The amino acids join together by peptide bonds to form a polypeptide chain.

**Conclusion:** DNA stores genetic information, while RNA transfers and uses this information for the synthesis of proteins. Together they control the production of proteins required for the growth, repair and functioning of the body.



## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 Classify carbohydrates with examples.**

**Ans.** Carbohydrates are classified into monosaccharides, disaccharides and polysaccharides depending on the number of sugar units present. Glucose and fructose are monosaccharides, sucrose is a disaccharide, while starch and glycogen are polysaccharides.

**Q.2 Why are carbohydrates important in human nutrition?**

**Ans.** Carbohydrates are the primary source of energy for the human body. Glucose produced during digestion is oxidized during respiration to release energy required for various metabolic activities.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + Energy$$

**Q.3 Differentiate between starch and glycogen.**

**Ans.** Starch is the storage polysaccharide in plants, whereas glycogen is the storage polysaccharide in animals. Glycogen possesses a more highly branched structure, allowing rapid release of glucose when energy is required.

**Q.4 Explain the importance of glycogen in animals.**

**Ans.** Glycogen acts as an energy reserve in animals and is mainly stored in the liver and muscles. During periods of high activity or fasting, glycogen is broken down to glucose to provide energy.

**Q.5 What are proteins?**

**Ans.** Proteins are natural polymers composed of amino acids joined together by peptide bonds. They perform structural, catalytic and transport functions in living organisms.

$$Amino\ Acid + Amino\ Acid \longrightarrow Dipeptide + H_2O$$

**Q.6 Differentiate between fibrous and globular proteins.**

**Ans.** Fibrous proteins possess long thread-like structures and mainly perform structural functions, whereas globular proteins have compact spherical shapes and perform functional roles such as transport and catalysis. Examples are keratin and hemoglobin respectively.

**Q.7 Explain the role of proteins in the body.**

**Ans.** Proteins are required for growth, repair and maintenance of body tissues. They also function as enzymes, hormones, antibodies and transport molecules in living organisms.

**Q.8 Why are enzymes called biological catalysts?**

**Ans.** Enzymes increase the rate of biochemical reactions without being consumed during the reaction. They lower activation energy and enable reactions to occur rapidly under mild biological conditions.

**Q.9 State two factors affecting enzyme activity.**

**Ans.** Temperature and pH are the most important factors affecting enzyme activity. Each enzyme has an optimum temperature and pH at which it shows maximum activity.

**Q.10 Explain the effect of temperature on enzyme activity.**

**Ans.** The rate of enzyme-catalyzed reactions increases with temperature up to the optimum temperature due to increased molecular collisions. Above the optimum temperature, enzymes become denatured and lose their activity.

**Q.11 Explain the effect of pH on enzyme activity.**

**Ans.** Every enzyme functions best at a specific pH called its optimum pH. A change in pH alters the shape of the active site and decreases enzyme activity. Extreme pH values may denature the enzyme permanently.
**Examples:** Pepsin works best at pH 2, while trypsin shows maximum activity at pH 8.

**Q.12 What are enzyme inhibitors?**

**Ans.** Enzyme inhibitors are substances that decrease or stop enzyme activity by interfering with the active site or enzyme structure. They play an important role in regulating biochemical reactions.
Examples include competitive and non-competitive inhibitors.

**Q.13 Explain competitive inhibition.**

**Ans.** In competitive inhibition, the inhibitor resembles the substrate and competes for the enzyme's active site. This reduces the number of enzyme molecules available for substrate binding and decreases the reaction rate.
**Example:** Malonate acts as a competitive inhibitor of succinate dehydrogenase.

CamScanner

**Q.14 What are lipids?**

**Ans.** Lipids are naturally occurring organic compounds composed mainly of glycerol and fatty acids. They are insoluble in water but soluble in organic solvents such as ether and benzene.
Fats and oils are common examples of lipids.

**Q.15 State the biological importance of lipids.**

**Ans.** Lipids act as an energy reserve, provide thermal insulation and protect internal organs from mechanical injury. They also form an important part of cell membranes. Thus, lipids perform both structural and storage functions.

**Q.16 Differentiate between saturated and unsaturated fats.**

**Ans.** Saturated fats contain only single carbon-carbon bonds, whereas unsaturated fats contain one or more carbon-carbon double bonds. Saturated fats are usually solids while unsaturated fats are generally liquids at room temperature. Examples include butter and vegetable oil respectively.

**Q.17 Differentiate between DNA and RNA.**

**Ans.** DNA is a double-stranded molecule containing deoxyribose sugar and thymine, whereas RNA is single-stranded and contains ribose sugar and uracil instead of thymine. DNA stores genetic information while RNA participates in protein synthesis.

**Q.18 Explain the function of DNA.**

**Ans.** DNA stores and transmits genetic information from one generation to the next. It controls protein synthesis and regulates the activities of living cells. Therefore, DNA is known as the molecule of heredity.

**Q.19 Explain the role of RNA in protein synthesis.**

**Ans.** RNA carries genetic information from DNA to ribosomes where proteins are synthesized. Messenger RNA acts as a template for arranging amino acids in the correct sequence. Thus, RNA plays a central role in translation.

**Q.20 Why is DNA double stranded whereas RNA is single stranded?**

**Ans.** DNA is double stranded to provide stability and protection for genetic information during storage and replication. RNA is single stranded because it mainly functions in protein synthesis and transport of genetic information.

**Q.21 State the importance of calcium in the human body.**

**Ans.** Calcium is essential for the formation of bones and teeth and is also required for muscle contraction and blood clotting. A deficiency of calcium may lead to weak bones and osteoporosis.

**Q.22 Explain the role of phosphorus in nutrition.**

**Ans.** Phosphorus is an important constituent of bones, teeth, DNA and ATP molecules. It plays a vital role in energy transfer and cellular metabolism. Therefore, phosphorus is essential for growth and development.

**Q.23 State the importance of iron in the body.**

**Ans.** Iron is an essential component of hemoglobin, the oxygen-carrying pigment of blood. It is responsible for transporting oxygen from the lungs to body tissues. Iron deficiency may cause anemia.

**Q.24 Explain the role of zinc in nutrition.**

**Ans.** Zinc acts as a cofactor for many enzymes and is essential for growth, wound healing and immune function. It also plays an important role in protein synthesis.

**Q.25 Why do animals store glycogen instead of glucose?**

**Ans.** Glycogen is insoluble and does not affect the osmotic pressure of cells, whereas glucose is soluble and would disturb water balance if stored in large amounts. Therefore, animals store carbohydrates in the form of glycogen.

**Q.26 Why do hibernating animals accumulate large fat reserves?**

**Ans.** Hibernating animals store fats because lipids provide more energy per gram than carbohydrates. During hibernation, these fat reserves supply energy for survival when food is unavailable.



**Q.27 Explain the role of cholesterol in the body.**

**Ans.** Cholesterol is an important component of cell membranes and acts as a precursor for steroid hormones, vitamin D and bile acids. However, excessive cholesterol may increase the risk of cardiovascular diseases.

**Q.28 Why is insulin considered a protein hormone?**

**Ans.** Insulin is a protein hormone composed of amino acids linked through peptide bonds. It regulates blood glucose levels by promoting the uptake and storage of glucose in body cells.

**Q.29 How does insulin deficiency lead to diabetes mellitus?**

**Ans.** Insulin deficiency reduces the uptake of glucose by cells, causing an increase in blood glucose concentration. This condition results in diabetes mellitus, characterized by excessive thirst and frequent urination.

**Q.30 Explain how milk proteins can be precipitated using lemon juice.**

**Ans.** Lemon juice lowers the pH of milk and causes the protein casein to coagulate and precipitate. This occurs because proteins lose their solubility near their isoelectric point.
This principle is used in the preparation of cottage cheese and yogurt.

## SELF-ASSESSMENT

**Total Mark: 30**

**Q.1 Encircle the correct option.** **(1 × 6 = 6)**

(i) **Fructose is classified as a:**
(A) Aldose (B) Ketose (C) Hexitol (D) Pentose only

(ii) **Cellulose is the major structural material of:**
(A) Animal cells (B) Plant cell walls (C) Blood cells (D) Muscle cells

(iii) **In the lock and key model, the substrate acts as the:**
(A) Lock (B) Key (C) Enzyme (D) Inhibitor

(iv) **Vitamins A, D, E and K are:**
(A) Water-soluble vitamins (B) Fat-soluble vitamins
(C) Mineral salts (D) Proteins

(v) **The covalent backbone bond in protein structure that is not broken on denaturation:**
(A) hydrogen bonds (B) peptide bonds (C) ionic bond (D) disulfide bonds

(vi) **Which one of the following element is not present in all proteins?**
(A) carbon (B) hydrogen (C) nitrogen (D) sulphur

**Q.2 Write short answers of the following questions.** **(2 × 8 = 16)**

(i) What is glycosidic linkage? Show how it is formed between fructose and glucose.
(ii) What are the two most common types of secondary protein structures in our body?
(iii) How do enzymes differ from inorganic catalysts?
(iv) Vegetable oil and vegetable ghee both are triglycerides. What is the major structural difference between the two?
(v) Which class of biomolecule contains each of the following linkages? Describe the function of each linkage.
i) Ester ii) Phosphodiester
(vi) Describe the mechanism of enzyme action.
(vii) What are some sources of potassium, iron, calcium, magnesium and zinc in our diet?
(viii) Name different RNAs and discuss their function.

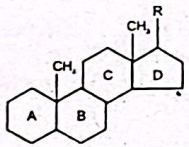
**Q.3 Extensive Questions.** **(4 + 4 = 8)**

(a) What are nucleic acids? Describe the role of DNA and RNA in the protein synthesis.
(b) Write an account of classification of lipids with suitable examples.

CamScanner

## ENTRANCE TEST MCQs

1. Which one of the following is an exact composition of a carbohydrates? (UHS 2016)
   (A) Carbon and Hydrogen (C) Carbon and Oxygen
   (B) Carbon, Hydrogen and Oxygen (D) Hydrogen and Oxygen
2. Collagen is a fibrous protein present most abundantly in: (UHS 2015)
   (A) Hair (B) Nail (C) Tendons (D) Arteries
3. Polyamide is formed due to the condensation of hexane-dioic acid with: (UHS 2018)
   (A) Hexane-1,5-diamine (B) Hexane-1,6-diamine (C) Hexane-1,4-diamine (D)Hexane-2,5-diamine
4. Two or more amino acids condensed to form protein by a peptide linkage which is present between two atoms: (UHS 2015)
   (A) C and C (B) C and N (C) O and C (D) C and H
5. Which of the following nitrogenous base is not present in RNA? (UHS 2014)
   (A) Cytosine (B) Adenine (C) Thiamine (D) Uracil
6. Out of these which nitrogen base is NOT present in DNA? (UHS 2019)
   (A) Adenine (B) Uracil (C) Guanine (D) thymine
7. Which of the following is the main function of DNA: (UHS 2017)
   (A) Making of proteins (B) Breaking of ribose sugar (C) Making of amino acids (D) Carries genetic information
8. Which of the following is a natural polymer? (ECAT 2016)
   (A) Terylene (B) Polysaccharide (C) Nylon (D) Polyethene
9. Following is the structure of: (NET 2019)




   (A) Glucose (B) Lysine (C) Steroid (D) Androgens
10. Formation of sucrose from glucose and fructose is a condensation reaction because:
    (A) Hydrogen gas is produced (B) The carbon chain is oxidized
    (C) No covalent bond is formed (D) Water is eliminated during glycosidic-bond formation
11. A disulfide bridge forms by oxidation between side chains of two residues of:
    (A) Valine (B) Cysteine (C) Glycine (D) Alanine
12. The covalent sugar-phosphate backbone gives a polynucleotide chain:
    (A) Enzyme catalytic activity (B) Mechanical strength and chemical stability
    (C) Base-pair specificity only (D) Hydrophobic lipid character
13. Transcription makes RNA from DNA; translation makes:
    (A) A polypeptide from an mRNA sequence (B) DNA from lipid
    (C) Glucose from protein (D) A mineral from RNA
14. The displayed dipeptide contains how many peptide bonds?
    (A) Zero (B) Two (C) Three (D) One
15. The displayed molecule is uracil. It is characteristic of:
    (A) DNA only (B) Proteins (C) Triglycerides (D) RNA
16. A molecule contains glycerol, two fatty acids and phosphate. It is most likely a:
    (A) Steroid (B) Disaccharide (C) Phospholipid (D) Triglyceride
17. Why is cellulose strong and insoluble despite being made from glucose?
    (A) It contains peptide bonds (B) It is highly branched and ionic
    (C) It contains steroid rings (D) Linear chains form extensive interchain hydrogen bonds
18. A molecule stores genetic information, uses deoxyribose and normally forms a double helix. It is:
    (A) Protein (B) Glycogen (C) DNA (D) RNA
19. A molecule contains ribose, uracil and phosphate. It is a component of:
    (A) Proteins (B) RNA (C) DNA only D. Triglycerides

**Answers Key**

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1.B | 2.C | 3.B | 4.B | 5.C | 6.B | 7.D | 8.B | 9. C | 10. D |
| 11.B | 12.B | 13.A | 14.D | 15.D | 16.C | 17.D | 18.C | 19.B | |



28 CHAPTER

# CHROMATOGRAPHY

### Student Learning Outcomes (SLOs)

[C-12-E-29 to C-12-E-33]

- Describe the terms stationary phase, mobile phase, $R_f$ value, baseline, and solvent front.
- Explain the principles and applications of thin-layer chromatography in forensic chemistry and analysis of unknown materials.
- Interpret $R_f$ values and retention times in chromatograms to determine the composition of a mixture.
- Explain the importance of selecting the appropriate stationary and mobile phases in chromatography and their impact on the separation of compounds.
- Describe the use of mass spectrometry in combination with chromatography for identifying and quantifying small amounts of unknown materials in forensic analysis.

## INTRODUCTION

We can separating one or two components from a simple mixture needs simple techniques such as filtration, distillation, and solvent extraction. However, complex mixtures require advanced techniques. Chromatography is a versatile and important analytical technique that allows chemists to separate the individual components of a complex mixture based on their varying affinities for two different phases. Complex mixtures, such as dyes in blooming flowers, pollutants in a water body, or medicinal extracts from the plant leaves, can be separated using chromatography. Use of chromatography allows for the identification, purification, and quantification of substances with high precision, making chromatography an efficient modern chemical analytical tool in medicine, forensic, environmental science, etc. Most chromatographic techniques are based on the principle of adsorption or partition.

**Q.1 What is Adsorption? Give an example.** S/Q

**Ans. Adsorption:**

Adsorption is a surface phenomenon in which particles accumulate only on the outer surface.

**For example**, activated charcoal adsorbs gases and impurities onto its surface, which is why it's used in filters and purification systems.

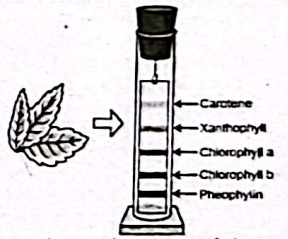



Figure: The complex mixture of pigments in leave can be efficiently separated using chromatography

**Q.2 Name any three important types of Chromatography.** S/Q

**Ans.** Among many types of chromatography, the three important types are:

i. Paper chromatography (PC)
ii. Gas chromatography (GC)
iii. Thin layer chromatography (TLC)

## PAPER CHROMATOGRAPHY

**Q.3 Describe the principle and working of paper chromatography.** Exercise D/Q.4

**Ans.** The technique of using a solvent to separate a mixture into its components is called paper chromatography.

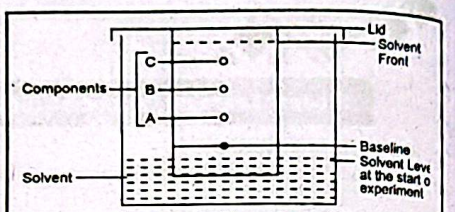
➢ **Principle of Paper Chromatography:**

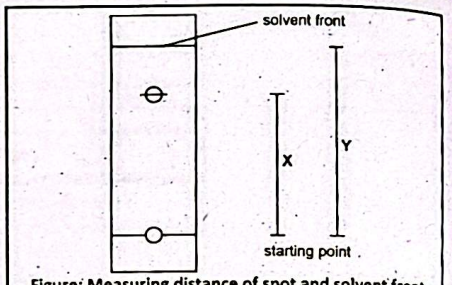
The separating principle depends on relative solubility of the components.

CamScanner

### Procedure:

- The piece of paper used in chromatography contains water combined with cellulose of the paper.
- A small spot of the sample is put on the base line near the bottom of the paper by capillary tube.
- The paper is dipped in a suitable solvent which will soak up the paper. The solvent level must be below the spot of the sample.
- The solutes present in the sample dissolve in the solvent to different extents. Some are more soluble in the solvent **(mobile phase)** moving up the paper. Others dissolve better in the water trapped in the paper **(stationary phase)**, therefore, they do not travel very far up the paper.
- This difference in the solubility allows the different components in the sample to be separated.
- Chromatography is used to separate both coloured and colourless substances.
- Colourless substances can be visualised by spraying them with a **locating agent** which give colour to them. The components are identified by their retardation factor ($R_f$).




### Retardation Factor or Retention Factor ($R_f$) Value:

- The $R_f$ value of a substance is calculated by dividing the distance traveled by the component with the distance travelled by the solvent.

$$R_f = \frac{\text{Distance travelled by the stubstance}}{\text{Distance travelled by the solvent}} = \frac{x}{y}$$

- **Unit:** $R_f$ has no unit because it is ratio.
- **Advantage:** The $R_f$ value of a substance does not change under same conditions (same solvent and same temperature).

## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Chromatography is mainly used to:**
   (A) Prepare compounds (B) Separate components of mixtures
   (C) Measure density (D) Determine melting point
2. **Chromatography separates substances based on their:**
   (A) Colour only (B) Affinity for two different phases
   (C) Molecular formula (D) Boiling point only
3. **Chromatography is widely used in:**
   (A) Medicine (B) Forensic science (C) Environmental science (D) All of these
4. **Adsorption is a phenomenon that occurs:**
   (A) Throughout the bulk of a material (B) Only on the surface
   (C) Only in liquids (D) Only in gases
5. **Activated charcoal purifies substances mainly due to:**
   (A) Absorption (B) Adsorption (C) Neutralization (D) Oxidation
6. **Which of the following is not a type of chromatography?**
   (A) Paper chromatography (B) Thin-layer chromatography
   (C) Gas chromatography (D) Ion-exchange chromatography
7. **Paper chromatography mainly separates substances based on differences in:**
   (A) Density (B) Solubility (C) Boiling point (D) Melting point
8. **In paper chromatography, the stationary phase is:**
   (A) Water trapped in cellulose paper (B) Alcohol
   (C) Silica gel (D) Nitrogen gas
9. **In paper chromatography, the mobile phase is:**
   (A) Water (B) Solvent (C) Air (D) Paper



10. **The sample is applied to the paper using a:**
    (A) Pipette (B) Capillary tube (C) Syringe (D) Burette
11. **During paper chromatography, the solvent level should be:**
    (A) Above the sample spot (B) Equal to the sample spot (C) Below the sample spot (D) At the top of the paper
12. **A substance more soluble in the mobile phase will:**
    (A) Not move (B) Move farther up the paper (C) Stay at the baseline (D) Decompose
13. **Colourless compounds can be visualized using:**
    (A) Indicator paper (B) Locating agents (C) Litmus solution (D) Dilute acid
14. **The $R_f$ value is calculated as:**
    (A) Distance travelled by solvent ÷ distance travelled by substance
    (B) Distance travelled by substance ÷ distance travelled by solvent
    (C) Height × width (D) Time ÷ distance
15. **The $R_f$ value has:**
    (A) Unit of cm (B) Unit of m (C) No unit (D) Unit of second
16. **Under identical conditions, the Rf value of a substance:**
    (A) Changes randomly (B) Remains constant (C) Always increases (D) Always decreases

## THIN-LAYER CHROMATOGRAPHY

**Q.4 Explain the principle and working process of thin layer chromatography (TLC) in detail.** Exercise Q.Q.5

**Ans. Principle**

Thin Layer Chromatography (TLC) is based on the principle of adsorption.

### Stationary Phase:

- The stationary phase is a thin layer of silica gel or aluminium oxide coated on a glass, plastic or aluminium plate.
- In thin layer chromatography (TLC), alumina ($Al_2O_3$) or silica ($SiO_2$) is mixed in water to make slurry which is then spread evenly onto a glass slide. This layer is dried in an oven to make a white solid layer **(stationary phase)** on the glass slide.

### Advantages

- An advantage of TLC is that it is faster than paper chromatography.
- TLC provides **better resolution** and clearer separation of spots (as compared to paper chromatography).

### Mobile Phase

- The mobile phase is a suitable solvent or mixture of solvents.
- Different substances have different degrees of adsorption on the stationary phase and different solubilities in the mobile phase, so they move at different speeds and become separated.
- TLC is faster than paper chromatography.

### Working Process/Procedure of TLC

- A straight baseline is drawn by pencil and ruler near the bottom of the glass slide.
- A spot of sample is put on the baseline by the capillary tube. More than one samples can be spotted at different places on the same glass slide.
- The solvent is taken in a chromatography tank. The glass slide is dipped in the solvent (mobile phase) in such a way that baseline is above solvent level.

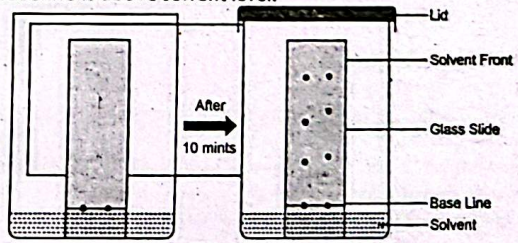



Figure: Thin layer chromatography

- The components present in the sample dissolve in the solvent and adsorb the stationary phase differently.
- **Adsorption:** Some are more soluble in the mobile phase while some are more adsorbed onto the solid stationary phase.

CamScanner

- **Polar Substances:** Polar substances have greater attraction for polar solid stationary phase and are adsorbed more strongly. Therefore, they travel more slowly up the stationary phase.
- **Non-polar substances:** non-polar substances are more soluble in the nonpolar solvent, and they move up the slide farther. This difference allows the substances in the sample to separate.
- **Solvent Front:** After the solvent has moved up to a certain height, the glass slide is removed from the chromatographic chamber. Solvent front, the highest point reached by the solvent, is marked. The glass slide is dried by dryer.
- **Calculation of $R_f$ Values:** $R_f$ values of different coloured spots are calculated.
- By comparing these $R_f$ values with standard values, the components present in the sample are identified.
- **Visualizing Colourless Substances:** Sometime the components are colourless, locating agent is sprayed to visualise them.
- **Example:** Ninhydrin spray give purple colour to colourless amino acids.
- Some colourless substances glow when irradiated with ultra-violet light.
- Some colourless substances turn brown with iodine vapours.

➢ **Applications:**

i) TLC identify unknown compounds by comparing their $R_f$ values with standard known values.
ii) The purity of a substance can be checked by TLC.
iii) The progress of reaction whether reactants are consumed or products are made, can be checked by TLC.
iv) In pharmaceutical and food industry, purity of drugs and presence of preservatives, colourants, sweeteners in food can be checked by TLC.
v) TCL can also detect pollutants, pesticides, toxic substances in soil, water, food and air.
vi) TLC is useful in forensic science where it is used to identify drugs, post blast debris, blood, sweat, semen at crime scene.

➢ **Limitations:**

i) TLC is mainly a qualitative technique and can only give an idea about the amount of a substance. So, TLC is not accurate and precise quantitative technique.
ii) TLC cannot clearly separate compounds having close $R_f$ values. Hence resolution of spots is not always high and sharp.
iii) In TLC, only small amounts of sample can be applied and analysed. It is not suitable for largescale separation.
iv) This technique is sensitive to humidity, temperature and cleanliness of working environment which reduces reproducibility.

### ☑ QUICK CHECK 28.1

**a) A mixture contains butanone and pentane. How can they be separated by using thin layer chromatography using aluminium oxide as stationary phase and benzene as solvent?**

**Ans.** In thin layer chromatography, the components separate because of their different attractions for the stationary phase and the mobile phase.

Aluminium oxide is a **polar stationary phase**, while benzene is a **non-polar solvent**.

- **Butanone** is a polar compound because it contains a carbonyl group ((C=O)). Therefore, it is strongly attracted to the polar aluminium oxide and moves slowly up the plate.
- **Pentane** is a non-polar compound and has weaker attraction for aluminium oxide but greater attraction for benzene. Therefore, it moves further up the plate.

**Result:** pentane will have a larger ($R_f$) value than butanone, and the two compounds will appear as distinct and separate spots on the chroma+togram.

**b) A mixture of two substances X and Y is analysed by thin-layer chromatography. The $R_f$ value of substance X is larger than that of substance Y. Suggest why substance X has a larger $R_f$ value.**

**Ans.** A larger ($R_f$) value means that substance X travelled a greater distance up the chromatogram.

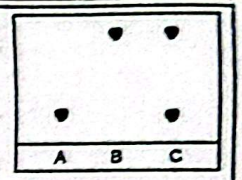
This may be because:

- X has a weaker attraction for the stationary phase, or
- X has a stronger attraction for the solvent (mobile phase).

**Result:** substance X moves more quickly with the solvent and produces a larger ($R_f$) value than substance Y.



**c) A separate thin layer chromatography experiment was done using the hair dyes A, B and C. The chromatogram obtained is shown. State three conclusions about the hair dyes A, B and C which vcan be deduced from the chromatogram.**




**Ans.** From the chromatogram, the following conclusions can be drawn:

- **Dye A** gives only one spot, it is a pure substance or contains only one colouring component.
- **Dye B** produces a single spot at a different height from dye A, showing that it is also pure but different from dye A.
- **Hair dye C** is a mixture of two components. Dye C gives two spots, indicating that it contains two different colouring substances. One spot of C is at the same height as the spot of A and the other is at the same height as the spot of B. Therefore, dye C contains the same colouring components that are present in both dyes A and B.

## GAS CHROMATOGRAPHY

**Q.5 Describe the main components of gas chromatography.** Exercise Q.Q.5

**Ans.** Gas chromatography (GC) is used to separate and analyze volatile compounds.

➢ **Stationary and Mobile Phase:**

**Stationary Phase:**

- In GC, the stationary phase is a non-volatile, long chain, non-polar hydrocarbon liquid having high boiling-point bonded to small particles of silica ($SiO_2$) or alumina ($Al_2O_3$).

➢ **Carrier Gas / Mobile Phase:**

- In GC, the mobile phase is an inert gas (carrier gas) such as: Helium or Nitrogen.

➢ **Injector Port:**

- The sample is injected into injector port, where sample is quickly vapourised by an oven.

➢ **Chromatographic Column:**

- The carrier gas carries the vapours of the sample through a long-coiled column packed with tiny silica particles having large surface area over which separation occurs.

➢ **Separation Principle:**

- The **non-polar substances** in the mixture have greater interaction with **non-polar** liquid on the solid particles of stationary phase.
- Therefore, these nonpolar substances are carried through the column more slowly.
- Thus, substances that interact more strongly move slower while other move faster, resulting in separation.

➢ **Detector:**

- As the separated substances exit the column, they pass through a detector which identify and record them as peaks on a graph called a **chromatogram.**
- Detector also records retention time of each component. The time taken by a substance to pass through the column is retention time.

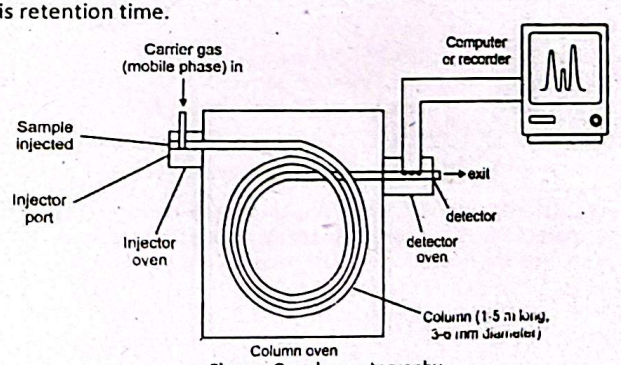



Figure: Gas chromatography

### Main Features of Gas Chromatography:

Gas chromatography has high sensitivity, good resolution, fast analysis and accurate quantification. Mixture of gases can easily be separated by GC at room temperature. GC is also a quantitative technique. The peaks obtained are first identified and then area of each peak is measured which will give the proportion of each component in the mixture. The peaks are similar to triangles, therefore, the area of peak can be calculated by the following formula.

$$\text{Area of a peak} = \frac{1}{2} \times \text{base} \times \text{height}$$

The percentage of an ester A in the mixture of three esters A, B and C is given by,

$$\% \text{ of A} = \frac{\text{peak area of A}}{\text{sum of peak areas of A, B and C}} \times 100$$

If the peaks are very narrow or have similar base widths then peak height is used instead of area to estimate the proportion of components in a mixture. GC is used to check the presence of steroids in competing athletes. This is also used to test the components of fuel used in car racing.

### Applications of GC:

i) In the industrial sector, GC is vital for quality control and environmental protection. For example, Petrochemical plants use it to analyse the composition of fuels, and for detecting trace amounts of organic pollutants in environmental samples.

ii) Forensic laboratories rely heavily on gas chromatography to provide evidence in legal investigations. It is frequently used to perform blood alcohol content (BAC) tests. Additionally, GC is used to detect illegal drugs, poisons, or performance enhancing substances in biological samples.

iii) The food and beverage industry utilises GC to ensure the consistency and safety of products. It can detect spoilage by identifying metabolic byproducts of bacteria or fungi before they are visible to the eye. Furthermore, GC is used to analyse the complex aromatic profiles of perfumes, essential oils, and food flavourings.

iv) In clinical settings, gas chromatography is used to diagnose metabolic disorders by analysing specific compounds in a patient's breath or urine. It also plays a role in pharmaceutical research, where it is used to test the purity of newly synthesized drugs, ensuring that no harmful residual solvents or impurities remain in the final medication before it reaches the patient.

v) GC is used to check the presence of steroids in competing athletes. This is also used to test the components of fuel used in car racing.

**Interesting Information**

Chromatography is important in forensic science. A man in China, namely Nian Bin, was accused of murdering two neighbouring children by mixing rat poison (a fluoroacetate) in their food in 2006. However, after 8 years, in 2014, he was proven innocent and released. The food sample was tested using gas chromatography, which proved no mixing of the poison.

### Limitations of GC:

i) GC works only for volatile (easily vaporised) substances.

ii) Samples must be thermally stable. Compounds that decompose at high temperatures cannot be used.

iii) Large biomolecules e.g., proteins and polymers cannot be analysed by GC because they do not vaporise easily.

iv) Instruments and maintenance costs for GC are high.

### QUICK CHECK 28.2

**An impure sample of lactic acid, $CH_3CH(OH)COOH$ contains butanone as the only contamination. The mixture is analysed using gas chromatography. Butanone is found to have a longer retention time than lactic acid.**

**i) Suggest suitable substances that could be used as the mobile and stationary phases.**

**Ans.** In gas chromatography:

- The **mobile phase** is an inert carrier gas e.g., helium, nitrogen.
- The **stationary phase** is a high-boiling non-volatile hydrocarbon liquid which is coated on an inert solid support.



**Suitable stationary phase:**

- A high-boiling liquid such as silicone oil or a similar non-volatile liquid coated on an inert support.

**ii) Describe how the percentage composition of the mixture can be determined from the gas chromatogram.**

**Ans.** When the mixture passes through the gas chromatograph, separate peaks are obtained for lactic acid and butanone.

The area under each peak is proportional to the amount of that component present in the mixture.

The percentage composition can therefore be calculated using:

$$\text{Percentage of component} = \frac{\text{Area of its peak}}{\text{Total area of all peaks}} \times 100$$

$$\text{Percentage of lactic acid} = \frac{\text{Area of lactic acid peak}}{\text{Total peaks area}} \times 100$$

$$\text{Percentage of butanone} = \frac{\text{Area of butanone peak}}{\text{Total peaks area}} \times 100$$

Therefore, the percentage composition of the mixture is determined by comparing the areas under the peaks in the chromatogram.

## COMPARISON OF THREE TYPES OF CHROMATOGRAPHY

**Q.6 Compare Paper chromatography, thin layer chromatography and gas chromatography.** S/Q

**Ans.**

| Feature | Paper Chromatography | TLC (Thin-Layer) | GC (Gas Chromatography) |
|---|---|---|---|
| Principle | Partition | Adsorption + solubility | Partition (gas-liquid) |
| Mobile Phase | Liquid | Liquid | Gas |
| Stationary Phase | Water in paper | Silica/alumina | Non-volatile liquid |
| Speed | Slow | Faster | Very fast |

## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **In TLC, the stationary phase is commonly:**
   (A) Water (B) Silica or alumina (C) Ethanol (D) Nitrogen
2. **TLC is generally _____ than paper chromatography.**
   (A) Slower (B) Faster (C) Less accurate (D) More expensive only
3. **In TLC, the sample is spotted on a:**
   (A) Plastic sheet (B) Glass slide (C) Filter paper (D) Test tube
4. **In TLC, the baseline is drawn using a:**
   (A) Pen (B) Pencil (C) Marker (D) Ink
5. **Polar substances in TLC:**
   (A) Travel farther (B) Are adsorbed more strongly
   (C) Vaporize quickly (D) Do not separate
6. **Non-polar substances generally:**
   (A) Move farther up the TLC plate (B) Remain at the baseline
   (C) React with silica (D) Decompose
7. **The highest point reached by the solvent is called the:**
   (A) Origin (B) Solvent front (C) Baseline (D) Chromatogram
8. **TLC is commonly used to:**
   (A) Check purity (B) Identify compounds (C) Monitor reactions (D) All of these
9. **One limitation of TLC is that it:**
   (A) Is only quantitative
   (B) Cannot separate compounds with very similar $R_f$ values effectively
   (C) Cannot separate coloured substances
   (D) Uses no stationary phase

CamScanner

10. **Gas chromatography is mainly used for:**
(A) Insoluble solids (B) Gases and volatile compounds
(C) Proteins (D) Polymers

11. **The mobile phase in gas chromatography is:**
(A) Water (B) Carrier gas (C) Alcohol (D) Silica

12. **A common carrier gas used in GC is:**
(A) Oxygen (B) Helium (C) Carbon dioxide (D) Chlorine

13. **The stationary phase in GC is:**
(A) Water (B) Non-volatile liquid (C) Ethanol (D) Silica gel only

14. **The injected sample in GC is first:**
(A) Frozen (B) Vaporized (C) Neutralized (D) Condensed

15. **The detector in GC records:**
(A) pH (B) Chromatogram peaks (C) Density (D) Colour

16. **The time taken by a substance to pass through the GC column is called:**
(A) $R_f$ value (B) Retention time (C) Residence time (D) Elution factor

17. **Gas chromatography is a:**
(A) Qualitative technique only (B) Quantitative technique
(C) Volumetric technique (D) Gravimetric technique

18. **Percentage composition in GC is determined using:**
(A) Peak area (B) Melting point (C) Boiling point (D) Density

19. **GC has:**
(A) Low sensitivity (B) High sensitivity (C) Low resolution (D) Poor accuracy

20. **GC is commonly used for:**
(A) Blood alcohol testing (B) Drug detection (C) Fuel analysis (D) All of these

21. **One limitation of GC is that samples must be:**
(A) Water soluble (B) Thermally stable (C) Ionic (D) Coloured

22. **Which of the following cannot usually be analysed by GC?**
(A) Helium (B) Proteins (C) Volatile liquids (D) Gases

23. **Among the three techniques, the fastest is:**
(A) Paper chromatography (B) Thin-layer chromatography
(C) Gas chromatography (D) All are equally fast

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

**BLOCK # 01**

| 1. B | 2. B | 3. D | 4. B | 5. B | 6. D | 7. B | 8. A | 9. B | 10. B | 11. C | 12. B | 13. B | 14. B | 15. C | 16. B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

**BLOCK # 02**

| 1. B | 2. B | 3. B | 4. B | 5. B | 6. A | 7. B | 8. D | 9. B | 10. B | 11. B | 12. B | 13. B | 14. B | 15. B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 16. B | 17. B | 18. A | 19. B | 20. D | 21. B | 22. B | 23. C | | | | | | | |

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. **Why must the solvent level be below the spot of the dye?**
a) To increase temperature b) To prevent the dye from dissolving directly into the solvent
c) To speed up chromatography d) To increase adsorption

II. **Why do some components of a dye travel further up the paper than others?**
a) They are more soluble in the water trap in paper (stationary phase)
b) They are more soluble in the solvent (mobile phase)
c) They react with the paper d) They have higher density

III. **A substance has a very low $R_f$ value. What does this indicate?**
a) It is insoluble in the solvent b) It is highly soluble in the solvent
c) It strongly sticks to the water inside paper d) It has a high density

IV. **Which statement best explains adsorption?**
a) Substance dissolves completely in another b) Substance sticks only to the surface of another material
c) Substance changes its state d) Substance reacts chemically



V. **A polar compound in TLC will usually:**
a) Travel farther up the plate b) Stay near the baseline
c) Evaporate quickly d) Dissolve completely

VI. **Why is TLC considered faster than paper chromatography?**
a) It uses more solvent b) It has a solid stationary phase that allows quicker separation
c) It requires higher temperature d) It uses colored substances only

VII. **What is the role of the carrier gas in gas chromatography?**
a) To react with the sample b) To act as stationary phase
c) To carry vaporized sample through the column d) To detect the substances

VIII. **Why must the stationary phase in GC have a high boiling point?**
a) To evaporate quickly b) To increase pressure
c) To remain in liquid form during the process d) To react with gases

IX. **What does the area under a peak in a chromatogram indicate?**
a) Amount (proportion) of the substance b) Retention time
c) Temperature of column d) Color of compound

X. **If two peaks have similar base width but different heights, how can composition be estimated?**
a) By color b) By retention time c) By pressure d) By peak height

**Answer Key With Explanations**

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | b | To prevent the dye from dissolving directly into the solvent. | The solvent level should remain below the sample spot so that the dye does not dissolve directly into the solvent reservoir. |
| II. | b | They are more soluble in the solvent (mobile phase) | Components that are more soluble in the mobile phase move faster and travel further up the chromatogram. |
| III. | c | It strongly sticks to the water inside paper. | A very low $R_f$ value means the substance has a strong attraction for the stationary phase and moves only a short distance. |
| IV. | b | Substance sticks only to the surface of another material. | Adsorption means the particles of a substance stick only to the surface of another material rather than entering its interior. |
| V. | b | Stay near the baseline. | In TLC, the stationary phase is usually polar. Therefore, polar compounds are strongly adsorbed and remain close to the baseline. |
| VI. | b | It has a solid stationary phase that allows quicker separation. | TLC uses a finely divided solid stationary phase such as silica or alumina, which allows faster separation of components. |
| VII. | c | To carry vaporized sample through the column. | The carrier gas transports the vaporized sample through the chromatographic column without reacting with it. |
| VIII. | c | To remain in liquid form during the process. | The stationary phase must have a high boiling point so that it does not evaporate during the chromatographic process. |
| IX. | a | Amount (proportion) of the substance. | The area under a chromatographic peak is proportional to the amount of that component present in the mixture. |
| X. | d | By peak height. | When peak widths are nearly the same, the relative amounts of components can be estimated from their peak heights. |

## Q 2. SHORT ANSWER QUESTIONS SAQs

a) **What is the principle of paper chromatography?**

Ans. Paper chromatography works on the principle of partition of substances between a stationary phase and a mobile phase. The components of a mixture separate because they have different solubilities in the mobile phase (solvent) and different attractions for the stationary phase water entrapped in cellulose fibers of paper (separation of components).

b) **Why is pencil used instead of ink in chromatography to mark the baseline?**

Ans. Pencil is used because graphite in pencil is insoluble in the solvent and does not move during chromatography. Ink used in pens often (frequently) contains dyes that dissolve in the solvent and interfere with the results.

CamScanner

**c) State two advantages of TLC over paper chromatography.**

**Ans.** 1. TLC gives faster separation of components.
2. TLC provides better resolution and clearer separation of spots (as compared to paper chromatography).

**d) Why do polar substances move slowly in TLC?**

**Ans.** Polar substances are strongly attracted to the polar stationary phase such as silica gel or aluminium oxide. Therefore, they are adsorbed more strongly and held back and move slowly up the TLC plate relative to the solvent front.

**e) Why is TLC not suitable for large-scale separation?**

**Ans.** TLC is mainly a small scale analytical technique used for identification and purity testing. Only a small amount of sample can be applied, so it is not suitable for separating large quantities of substances.

**f) What is the function of injector port in GC?**

**Ans.** The injector port introduces the sample in precise volume into the gas chromatograph and rapidly vaporizes it without decomposition before it enters the column.

**g) Why must samples be volatile in GC?**

**Ans.** In gas chromatography, the sample must be completely converted into vapours so that the carrier gas can carry it through the column. Therefore, only volatile substances can be analysed by GC.

**h) State two limitations of gas chromatography.**

**Ans.** 1. Only volatile compounds can be analysed.
2. Thermally unstable substances cannot be analysed because they decompose on heating.

**i) What information does a chromatogram provide?**

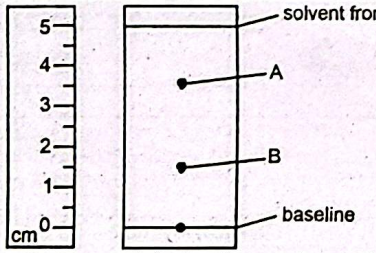
**Ans.** A chromatogram provides information about:
- the number of peaks show the number of components present in a mixture.
- the identity of the components (from $R_f$ values or retention times).
- and the relative amount of each component (peak area).

**j) What is adsorption? Give one example.**

**Ans.** Adsorption is the process in which molecules of a substance (gas, liquid, dissolved solved) accumulate only on the surface of another substance (solid or liquid).
It is a surface phenomenon.
**Examples:** In TLC, dye molecules are adsorbed on the surface of silica gel or aluminium oxide. Moreover, activated charcoal adsorbs colour and toxic gases (on its surface). Animal charcoal adsorbs coloured impurities from a sugar solution.

## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) A mixture of amino acids is analysed using thin layer chromatography. The chromatogram obtained is shown. The table shows some $R_f$ values for different amino acids in the same solvent.**




| amino acid | $R_f$ value |
|---|---|
| alanine | 0.40 |
| glutamic acid | 0.29 |
| leucine | 0.71 |
| valine | 0.61 |

**i) Use the chromatogram and the $R_f$ values to deduce the amino acid responsible for spot A and spot B.**



**ii) A second chromatogram of the same mixture is taken using a more polar solvent. Predict the effect on the $R_f$ values of the amino acids. Explain your reasoning.**

**Ans.** (i) From the chromatogram:
Distance travelled by solvent front = 5 cm

**Spot A:**
Distance travelled by A ≈ 3.5 cm, $R_f = \frac{3.5}{5} = 0.70$
This value is closest to 0.71, therefore,
Spot A = Leucine

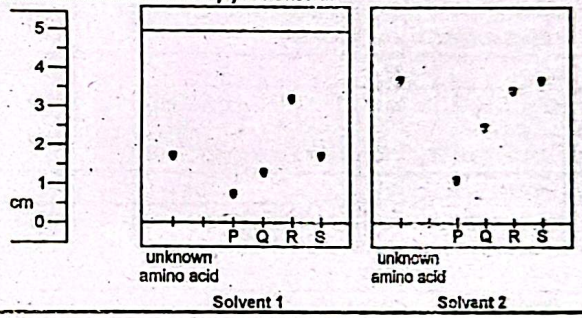
**Spot B:**
Distance travelled by B ≈ 1.5 cm, $R_f = \frac{1.5}{5} = 0.30$
This value is closest to 0.29, therefore,
Spot B = Glutamic acid

**Ans.** (ii) The $R_f$ values of the amino acids will increase. A more polar solvent will dissolve polar amino acids more readily and will have higher $R_f$ values.

**b) Gas chromatography involves a stationary phase and a mobile phase. Name a suitable substance that could be used for each phase.**

**Ans.** Gas Chromatography:
- **Mobile Phase:** Helium gas (or nitrogen)
- **Stationary Phase:** A high boiling non-volatile liquid such as silicone oil coated on an inert solid support.

**c) An unknown amino acid is analysed by thin-layer chromatography. Two chromatographs of the unknown amino acid and four reference amino acids, P, Q, R and S, are obtained using two different solvents. Identify the unknown amino acid. Justify your answer.**




**Ans.** **Solvent 1:** The unknown amino acid gives a spot at approximately the same height as amino acid S.
**Solvent 2:** The unknown amino acid again gives a spot at approximately the same height as amino acid S.
Since the unknown amino acid has the same position and therefore the same $R_f$ value as Q in both solvents, the unknown amino acid is:

Unknown amino acid = S

**Justification:** Identification using two different solvents is more reliable because two substances may have similar $R_f$ values in one solvent but are unlikely to have identical $R_f$ values in two different solvents

## DESCRIPTIVE QUESTIONS DQs

**Q.4 Describe the principle and working of paper chromatography.**

**Ans.** See Question No. 03

**Q.5 Explain the principle and working process of thin layer chromatography (TLC) in detail.**

**Ans.** See Question No. 04

**Q.6 Describe the main components of gas chromatography.**

**Ans.** See Question No. 05

CamScanner

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 Define chromatography.**

**Ans.** Chromatography is a separation technique used to separate, identify and analyze the components of a mixture based on their different affinities for stationary and mobile phases. It is widely used in analytical and forensic chemistry.

**Q.2 What is meant by stationary phase?**

**Ans.** The stationary phase is the phase that remains fixed during chromatography and does not move with the solvent. Components having stronger attraction for the stationary phase move more slowly.
**Example:** Silica gel in TLC acts as the stationary phase.

**Q.3 What is meant by mobile phase?**

**Ans.** The mobile phase is the phase that moves through the stationary phase carrying the mixture components along with it. Components having greater affinity for the mobile phase travel faster.
**Example:** Organic solvents are commonly used as mobile phases in TLC.

**Q.4 Define baseline in chromatography.**

**Ans.** The baseline is the line drawn near the bottom of the chromatographic plate where the sample is initially applied. It serves as the reference point for measuring distances travelled by the sample components.

**Q.5 What is meant by solvent front?**

**Ans.** The solvent front is the furthest point reached by the solvent during chromatographic separation. It is marked immediately after removing the chromatographic plate from the solvent chamber.
The solvent front is required for calculating $R_f$ values.

**Q.6 Define $R_f$ value.**

**Ans.** The $R_f$ value or retention factor is the ratio of the distance travelled by the solute to the distance travelled by the solvent front.

$R_f$ = Distance travelled by solute /Distance travelled by solvent

**Q.7 Why is the $R_f$ value always less than one?**

**Ans.** The solvent front always moves further than any component of the mixture because it carries the substances along the stationary phase. Therefore, the numerator is always smaller than the denominator.
Hence, the $R_f$ value is always less than one.

**Q.8 What is Thin Layer Chromatography (TLC)?**

**Ans.** Thin Layer Chromatography is a chromatographic technique in which a thin layer of silica gel or alumina acts as the stationary phase while a solvent acts as the mobile phase. It is widely used for separation and identification of compounds.

**Q.9 How can TLC distinguish between a pure substance and a mixture?**

**Ans.** A pure substance produces a single spot on the chromatogram, whereas a mixture gives two or more spots because it contains more than one component. Therefore, TLC can be used to check the purity of compounds.

**Q.10 State two applications of TLC.**

**Ans.** Thin Layer Chromatography is used for identifying unknown compounds and checking the purity of substances. It is also used in forensic science for the analysis of drugs, poisons and inks.

**Q.11 Explain the principle of Thin Layer Chromatography (TLC).**

**Ans.** Thin Layer Chromatography works on the principle of different affinities of compounds for the stationary and mobile phases. Components that are more strongly adsorbed on the stationary phase move slowly, whereas those with greater solubility in the mobile phase move faster.
Thus, the mixture components become separated.



**Q.12 Why do different compounds move different distances in TLC?**

**Ans.** Different compounds have different attractions for the stationary phase and different solubilities in the mobile phase. Therefore, each compound travels at a different rate and moves a different distance on the chromatographic plate.
This difference enables separation of mixture components.

**Q.13 How is the $R_f$ value calculated?**

**Ans.** The $R_f$ value is calculated by dividing the distance travelled by the substance by the distance travelled by the solvent front from the baseline.

$R_f$ = Distance travelled by solute/Distance travelled by solvent

The value always lies between 0 and 1.

**Q.14 What information can be obtained from an $R_f$ value?**

**Ans.** The $R_f$ value helps in identifying compounds by comparing their values with those of known standards under identical experimental conditions. Similar compounds generally possess similar $R_f$ values.
Thus, $R_f$ values are useful for qualitative analysis.

**Q.15 Why must $R_f$ values be compared under identical conditions?**

**Ans.** The $R_f$ value depends upon the nature of the stationary phase, mobile phase and temperature. Therefore, valid comparisons can only be made when the experimental conditions are the same.
Otherwise, different $R_f$ values may be obtained for the same compound.

**Q.16 Why is the solvent front marked immediately after development?**

**Ans.** The solvent evaporates rapidly after removing the chromatographic plate from the chamber. Marking the solvent front immediately ensures accurate measurement of the solvent distance for calculating $R_f$ values.

**Q.17 Why should the sample spot be placed above the solvent level?**

**Ans.** If the sample spot is submerged in the solvent, it will dissolve directly into the solvent reservoir instead of moving up the plate with the mobile phase. This will prevent proper separation of the components.

**Q.18 Why is silica gel commonly used in TLC?**

**Ans.** Silica gel is highly porous and strongly adsorbs many organic compounds, making it an effective stationary phase. Its large surface area improves separation efficiency.

**Q.19 Define retention time.**

**Ans.** Retention time is the time taken by a compound to pass through the chromatographic column and reach the detector in gas chromatography. Each compound has a characteristic retention time under fixed conditions.

**Q.20 How can retention time help identify a compound?**

**Ans.** The retention time of an unknown compound is compared with the retention times of known standard substances under identical conditions. Matching values indicate the likely identity of the compound.

**Q.21 What is a chromatogram?**

**Ans.** A chromatogram is the graphical record produced by a chromatographic analysis. In gas chromatography, it consists of peaks representing different compounds present in the sample.

**Q.22 What does each peak in a chromatogram represent?**

**Ans.** Each peak in a chromatogram corresponds to a different component of the mixture. The position of the peak gives the retention time, while the area under the peak indicates the quantity of the compound.

**Q.23 How can the amount of a compound be determined from a chromatogram?**

**Ans.** The quantity of a compound is proportional to the area under its chromatographic peak. Larger peak areas indicate greater amounts of that compound in the sample.

CamScanner

**Q.24 What is GC-MS?**

**Ans.** GC-MS stands for Gas Chromatography-Mass Spectrometry, a technique that combines separation by gas chromatography with identification by mass spectrometry. It provides highly accurate qualitative and quantitative analysis.

**Q.25 Why is GC-MS considered a powerful analytical technique?**

**Ans.** GC-MS first separates the components of a mixture and then identifies them from their mass spectra. This combination provides highly reliable identification even for complex mixtures containing very small quantities of substances.

**Q.26 State two forensic applications of chromatography.**

**Ans.** Chromatography is used in forensic science for the detection of drugs, poisons and explosive residues. It is also used in ink analysis and toxicological investigations.

**Q.27 How is chromatography used in forensic investigations?**

**Ans.** Chromatography separates and identifies substances present in crime scene samples such as blood, urine and unknown powders. This information helps forensic scientists determine the presence of drugs or poisons.

**Q.28 Why is GC-MS suitable for detecting trace amounts of substances?**

**Ans.** GC-MS possesses very high sensitivity and can detect substances present in extremely small quantities. Therefore, it is particularly useful in forensic and environmental analysis.

**Q.29 Explain the importance of selecting suitable stationary and mobile phases.**

**Ans.** Efficient separation depends on the difference in affinity of compounds for the stationary and mobile phases. Proper selection improves resolution and allows accurate identification of mixture components.

**Q.30 Why is chromatography an important analytical technique?**

**Ans.** Chromatography allows the separation, identification and quantification of mixture components with high accuracy. Therefore, it has become an essential tool in chemistry, medicine, pharmaceuticals and forensic science.



## SELF-ASSESSMENT

Total Mark: 30

**Q.1 Encircle the correct option.** (1 × 6 = 6)

(i) **The $R_f$ value is calculated as:**
(A) Distance travelled by solvent ÷ distance travelled by substance
(B) Distance travelled by substance ÷ distance travelled by solvent
(C) Height × width (D) Time ÷ distance

(ii) **During paper chromatography, the solvent level should be:**
(A) Above the sample spot (B) Equal to the sample spot
(C) Below the sample spot (D) At the top of the paper

(iii) **In TLC, the sample is spotted on a:**
(A) Plastic sheet (B) Glass slide (C) Filter paper (D) Test tube

(iv) **Percentage composition in GC is determined using:**
(A) Peak area (B) Melting point (C) Boiling point (D) Density

(v) **What does the area under a peak in a chromatogram indicate?**
(A) Amount (proportion) of the substance (B) Retention time
(C) Temperature of column (D) Color of compound

(vi) **A polar compound in TLC will usually:**
(A) Travel farther up the plate (B) Stay near the baseline
(C) Evaporate quickly (D) Dissolve completely

**Q.2 Write short answers of the following questions.** (2 × 8 = 16)

(i) A mixture of two substances X and Y is analysed by thin-layer chromatography. The $R_f$ value of substance X is larger than that of substance Y. Suggest why substance X has a larger $R_f$ value.
(ii) State two advantages of TLC over paper chromatography.
(iii) Why is TLC not suitable for large-scale separation?
(iv) Why must samples be volatile in GC?
(v) State two limitations of gas chromatography.
(vi) What is adsorption? Give one example.
(vii) Gas chromatography involves a stationary phase and a mobile phase. Name a suitable substance that could be used for each phase.
(viii) How can the amount of a compound be determined from a chromatogram?

**Q.3 Extensive Questions.** (4 + 4 = 8)

(a) Write a detailed note on experimental procedure of paper chromatography.
(b) Write a detailed note on experimental procedure of thin layer chromatography.

CamScanner

## ENTRANCE TEST MCQs

1. A component having small value of k (distribution coefficient) mostly remains in:
(A) stationary phase (B) Mobile phase (C) Chromatographic tank (D) None of these
2. Chromatography in which the stationary phase is a solid is classified as:
(A) Partition chromatography (B) Gas chromatography
(C) Adsorption chromatography (D) Thin layer chromatography
3. In paper chromatography, the rate at which solute moves depend on:
(A) distribution law (B) distribution co-efficient (C) law of partial pressure (D) law of definite proportion
4. The solvent used in chromatographic tank is called:
(A) effluent (B) residue (C) chromatogram (D) eluent
5. Chromatography is not used for:
(A) separation (B) isolation (C) purification (D) sublimation
6. If no component moves from the baseline, the solvent is probably:
(A) Too volatile only (B) Too strongly coloured
(C) Always nonpolar enough (D) Too weak or inappropriate
7. One limitation of paper chromatography compared with TLC is that it is generally:
(A) More quantitative than GC (B) Unable to use liquids
(C) Faster than GC (D) Slower
8. A spot travels 5.5 cm while the solvent front travels 10.0 cm. Its $R_f$ is:
(A) 0.75 (B) 0.55 (C) 15.50 (D) 1.82
9. Unknown U shows two spots matching standards P and R. The best conclusion is:
(A) U contains only P (B) U contains no known component
(C) U contains P and R (D) U is pure Q
10. The best solvent system for TLC usually gives target $R_f$ values:
(A) Exactly 1 for all spots (B) Greater than 1
(C) Neither too close to 0 nor too close to 1 (D) Exactly 0 for all spots
11. A longer GC column usually improves separation but may:
(A) Increase analysis time and pressure drop (B) Make all samples nonvolatile
(C) Remove the need for carrier gas (D) Eliminate peaks
12. A later TLC sample shows only the product spot. The reaction is:
(A) Not started (B) Contaminated necessarily
(C) A GC analysis (D) Complete or nearly complete
13. To improve separation of two TLC spots with nearly identical $R_f$ values, first try:
(A) Submerging the spots (B) Ignoring the solvent front
(C) Changing solvent composition (D) Using ink for baseline
14. Which combination best screens several nonvolatile dyes rapidly?
(A) GC without derivatization (B) Mass spectrometry alone
(C) Distillation only (D) TLC with standards
15. Why can one solvent not separate every mixture well?
(A) $R_f$ never changes (B) Stationary phases are irrelevant
(C) Mixtures differ in polarity and selectivity (D) All compounds have identical affinities
16. If the baseline is below solvent level in TLC, the sample may:
(A) Gain a larger true $R_f$ (B) Become a GC peak
(C) Move normally with capillary action (D) Dissolve into the solvent reservoir and be lost
17. Why can chromatography both separate and help identify mixture components?
(A) Components separate and can be compared with standards
(B) It changes every component into a different compound
(C) It relies only on colour differences (D) It measures only total sample mass

**Answers Key**

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. B | 4. A | 5. C | 6. D | 7. D | 8. B | 9. C | 10. C | 11. A | 12. D | 13. C | 14. D |
| 15. C | 16. D | 17. A | | | | | | | | | | | |



29 CHAPTER

# SPECTROSCOPY-1

### Student Learning Outcomes (SLOs)

[C-12-E-03 to C-12-E-18]

- Explain that the degree of unsaturation or index of hydrogen deficiency (IHD) can be used to determine from a molecular formula, the number of rings or multiple bonds in a molecule.
- Explore how Mass spectrometry (MS), proton nuclear magnetic resonance spectroscopy ($^1$H NMR), infrared spectroscopy (IR) are techniques that can be used to help identify compounds and to determine their structure.
- Interpret an infrared (spectrum of a simple molecule to identify functional groups.
- Deduce possible structures for organic compounds using IR spectrum and molecular formula (Examples: phenol, acetone, ethanol).
- Predict whether a given molecule will absorb in the UV/visible region.
- Predict the colour of a transition metal complex form its UV/visible spectrum.
- Explain atomic emission and atomic absorption spectrum.
- Explain how a mass spectrometer can be used to determine the relative atomic mass of an element from its isotopic composition.
- Perform calculations involving non-integer relative atomic masses and abundance of isotopes from given data, including mass spectra.
- Explain the concept of emission spectra. Use the concept of emission spectra to deduce the electronic configuration of elements.
- Analyze mass spectra in terms of m/e values and isotopic abundances (knowledge of the working of the mass spectrometer is not required).
- Calculate the relative atomic mass of an element given the relative abundances of its isotopes, or its mass spectrum.
- Deduce the molecular mass of an organic molecule from the molecular ion peak in a mass spectrum.
- Suggest the identity of molecules formed by simple fragmentation in a given mass spectrum.
- Deduce the number of carbon atoms, n, in a compound using the $M^+$ peak and the formula:

$$n = \frac{100 \times \text{abundance of } (M+1)^+}{1.1 \times \text{abundance of } (M)^+}$$

- Deduce the presence of bromine and chlorine atoms in a compound using the M peak.

Light and other forms of electromagnetic radiation travel in the form of waves, which consist of oscillating electric and magnetic fields. These waves are defined by their wavelength (λ) and frequency (ν), and they travel at the speed of light ($c = 3.0 \times 10^8$ m/s).

**Q.1 What is the relationship between wavelength and Frequency?** S/Q

**Ans. Relationship between Wavelength and Frequency:**

$$c = \lambda\nu$$

Where λ is the wavelength (in meters), ν is the frequency (in Hertz or $s^{-1}$), and c is the speed of light (in $ms^{-1}$). The electromagnetic spectrum comprises of different radiations, including radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays, and gamma rays.

CamScanner

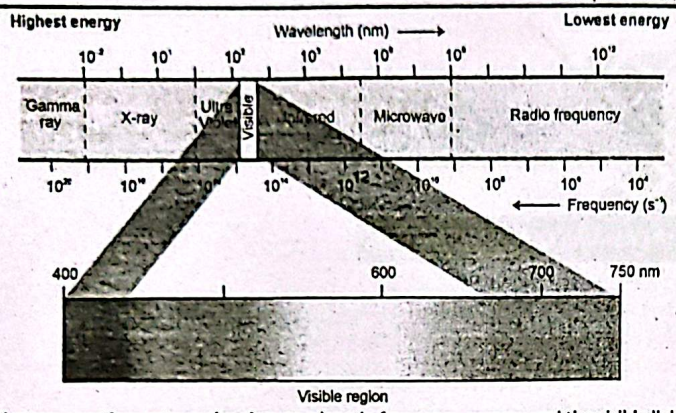



**Figure: Electromagnetic spectrum showing wavelength, frequency, energy, and the visible light region.**

**Q.2 Give postulates of Planck's quantum theory.** S/Q

**Ans. According to Planck's Quantum Theory:**

1. Only discrete amounts of energy may be emitted or absorbed by various atoms and molecules. Quantum energy is the smallest quantity of electromagnetic radiation that can be released or absorbed.
2. The frequency of a radiation and the energy it carries are directly proportional to each other.

The energy of radiation is expressed as,

Where,

E = Energy of the radiation

h = Planck's constant ($6.626 \times 10^{-34}$ J.s)

v = Frequency of radiation

$$E = \frac{hc}{\lambda} \quad (J.s,\ m/s,\ m) \qquad J \longrightarrow E = hc\bar{\upsilon} \longrightarrow cm^{-1}$$

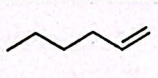
## INDEX OF HYDROGEN DEFICIENCY (IHD)

**Q.3 Write a note on Index of Hydrogen Deficiency (IHD).** L/Q

**Ans.** ***The degree of unsaturation (U), or index of hydrogen deficiency (IHD), is defined as the difference in the number of pairs of hydrogen atoms between the compound and the acyclic alkane with the same number of carbon atoms.***

Each double bond or ring costs two hydrogen atoms compared to a saturated analog and results in one degree of unsaturation. For example, if a compound has the molecular formula $C_4H_6$, it has four hydrogen atoms less than the saturated, compound $C_4H_{10}$. Therefore, this compound has two degrees of unsaturation (IHD = 2).

These compounds have the same molecular formula but different structures, i.e. these are two isomers. However, there is one more similarity between these two compounds. Both these have two hydrogens less than a saturated alkane. It means they have a deficiency of two hydrogen atoms.



1-Hexene ($C_6H_{12}$) Cyclohexane ($C_6H_{12}$)

**Example:** Consider the 1-Hexene and cyclohexane

The deficiency of hydrogen corresponds to the degree of unsaturation of a compound. The index of hydrogen deficiency (IHD) is a measure of the degrees of unsaturation in a compound. A compound is said to have one degree of unsaturation for every two hydrogen atoms that are missing.

This is why the above two compounds have an IHD equal to 1.

### ➲ Importance of IHD

Knowing the IHD of a molecule gives information or about its composition and structure. For example, if the IHD is 0, it is certain that the chemical has no rings and no double bonds. This is very helpful because you can find this number easily just by looking at the chemical formula.

**Keep in Mind**

A double bond and ring each counts as one IHD. A triple bond counts as two IHD.



If the IHD is 1, the chemical must have either one ring or one double bond, but it cannot have both. If the IHD is 2, there are a few choices: it could have two rings, two double bonds, one of each, or one triple bond. Thus, IHD can give us very useful information about a chemical without using complex analytical techniques. Also, before using an analytical technique, IHD helps to assess which technique would be better for the compound under study. The IHD for hydrocarbons can be calculated using the data given in Table.

**Table: Index of Hydrogen Deficiency of Hydrocarbons**

| Formula | Index of Hydrogen Deficiency (IHD) | Structure Unit Involved |
|---|---|---|
| $C_nH_{2n+2}$ | 0 | open chain alkane only |
| $C_nH_{2n}$ | 1 | 1 double bond or 1 unsaturated ring |
| $C_nH_{2n-2}$ | 2 | 2 double bonds or 2 rings<br>or 1 double bond plus 1 ring<br>or 1 triple bond |

### ☑ QUICK CHECK 29.1

**a) Calculate the IHD for each of the following.**

**i) $C_6H_6$ ii) $C_6H_{12}$ iii) $C_4H_4$**

**Ans.** The formula for IHD (Index of Hydrogen Deficiency) is:

$$IHD = \frac{2C+2-H}{2}$$

i) $C_6H_6$: $IHD = \frac{2(6)+2-6}{2} = \frac{12+2-6}{2} = \frac{8}{2} = 4$

ii) $C_6H_{12}$: $IHD = \frac{2(6)+2-12}{2} = \frac{12+2-12}{2} = \frac{2}{2} = 1$

iii) $C_4H_4$: $IHD = \frac{2(4)+2-4}{2} = \frac{8+2-4}{2} = \frac{6}{2} = 3$

**b) Propose the structure of the above compounds given in (a).**

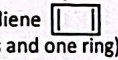
**Ans.** Since many structures are possible, one suitable structure for each formula is:

i) $C_6H_6$: **Structure:** Benzene 

(IHD = 4, one ring + three double bonds)

ii) $C_6H_{12}$: **Structure:** Cyclohexane 

(IHD = 1, one ring)
Another possible structure is hexene containing one double bond. e.g., 1-Hexene

iii) $C_4H_4$: **Structure:** Cyclobutadiene 

(IHD = 3, two double bonds and one ring)

Another possible structure is 1-buten-3-yne.

$H_2C = CH - C \equiv CH$ (one double and one triple bond)

**c) Hopanes are the waxy solids found in petroleum products as residues after refining the crude oil. A hopane has the formula $C_{30}H_{52}$,**

**i) Find its IHD. ii) Predict whether this compound is saturated or not.**

**Ans.** Hopane has the formula $C_{30}H_{52}$.

i) $IHD = \frac{2(30)+2-52}{2} = \frac{60+2-52}{2} = \frac{10}{2} = 5$

ii) Hopane is a saturated pentacyclic compound with IHD = 5. It is because of the presence of five rings and not due to C – C double bonds. Only single C – C bonds are present in it.

## ATOMIC SPECTRUM

**Q.4 Explain two types of atomic spectrum.** Exercise D/Q.5

**Ans.** Atomic spectra are observed when atoms emit or absorb light of a certain wavelength. They are of two types:

(i) Atomic emission spectra (ii) Atomic absorption spectra

Atomic spectra provide evidence that electrons in atoms can only transition between discrete atomic energy levels.

CamScanner

### (i) Atomic Emission Spectra

When energy is absorbed by electrons of an atom, electrons move from lower energy levels to higher energy levels. These excited electrons radiate energy to return from the excited state to ground states and form emission spectra.

Emission spectra can be produced by heating a low-pressure gas. Heating provides energy to excite electrons to higher energy levels.

When an electron transitions back to a lower energy level, it emits a photon. Each transition corresponds to a specific wavelength of light which appears as an observable spectral line. The resulting emission spectrum contains a set of distinct wavelengths, represented by coloured lines on a black background.

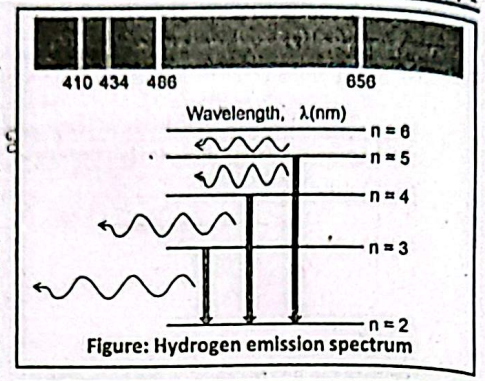


Figure: Hydrogen emission spectrum

### (ii) Atomic Absorption Spectra

An absorption spectrum contains the frequencies of light transmitted in the form of dark bands when energy is absorbed by the electrons in the ground state to reach higher energy states. Absorption spectra can be produced by passing white light through a cool, low-pressure gas. Only photons with the exact energy required to excite electrons will be absorbed. Each absorbed photon corresponds to a specific wavelength of light which appears as a dark line on a coloured background. These lines correspond to the same lines observed on an emission spectrum for the same element. However, an absorption spectrum is like a photographic negative of an emission spectrum.

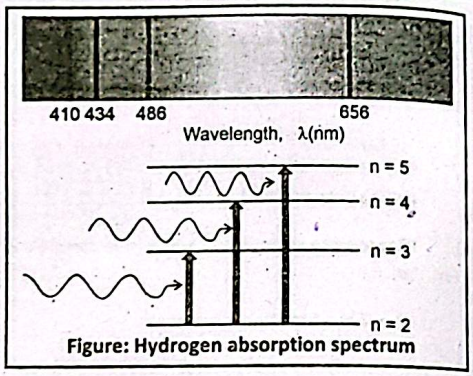


Figure: Hydrogen absorption spectrum

## SPECTROSCOPY

**Q.5 What is spectroscopy and spectrum? Give example of hydrogen.** LQ

**Ans. Spectroscopy:**

Spectroscopy deals with the production, measurement, and interpretation of spectra arising from the interaction of electromagnetic radiation with matter.

➢ **Spectrum:**

A spectrum can be used to obtain information about atomic and molecular energy levels, molecular geometries, interactions of molecules and the nature of chemical bonds. A spectroscopic measurement can also be used for measuring the amount of a specific substance in a sample (quantitative analysis) or even just to identify an unknown sample (qualitative analysis).

The chemical composition of a substance can be investigated using emission and absorption spectra. Each element produces a unique pattern of spectral lines. No two elements produce the same set of spectral lines, therefore, elements can be identified by their atomic spectra. Emission line spectra are unique to each element, like a fingerprint.

**Did You Know?**

Atomic spectra can also help astronomers to determine the chemical composition of stars. By analyzing the light emitted from these celestial bodies, scientists can uncover the mysteries of the universe.






**Example:** Hydrogen is known to produce strong spectral lines in the red portion of the visible spectrum, at 656 nm. When sodium is burned, a characteristic yellow flame is observed due to the strong spectral lines in the yellow portion of the spectrum, at 589 nm. When mercury is burned, most of the emission lines are below 450 nm, which produce a characteristic blue light.

## UV/VISIBLE SPECTROSCOPY

**Q.6 Describe various possible electronic transitions in a compound having sigma, pi bonds, and non-bonding electrons.** Exercise Q.Q.4

**OR What is UV/Visible Spectroscopy? Explain with conjugated system.**

**Ans.** Ultraviolet-visible (UV-Vis) spectroscopy is one of the most popular analytical techniques because it is very versatile and easy to use. In UV-Vis spectroscopy, the UV-Vis light is passed through a sample and the transmittance of light is measured. The absorbance (A) can be determined from the transmittance (T) using the formula $A = -\log(T)$. A UV-Vis spectrum displays the absorbance of a substance at various wavelengths. The amount of absorbance at any wavelength is due to the electronic structure of the molecule.

**Types of electrons in a compound can be:**

- $\sigma$ electrons ($\sigma$-bonds)
- $\pi$ electrons (in unsaturated compounds only)
- $n$ electrons (non-bonded electrons)

Sigma bonding orbitals are lower in energy than $\pi$ bonding orbitals, which in turn, are lower in energy than non-bonding orbitals. When electromagnetic radiation of the correct frequency is absorbed, a transition occurs from one of these orbitals (or n) to an empty orbital, usually an antibonding orbital, $\sigma^*$ or $\pi^*$. UV-Vis spectroscopy uses the wavelengths from 200 – 800 nm to study the changes in electronic energy levels. These changes are due to the transfer of electrons from $\pi$ - or non-bonding orbitals as shown in Figure.

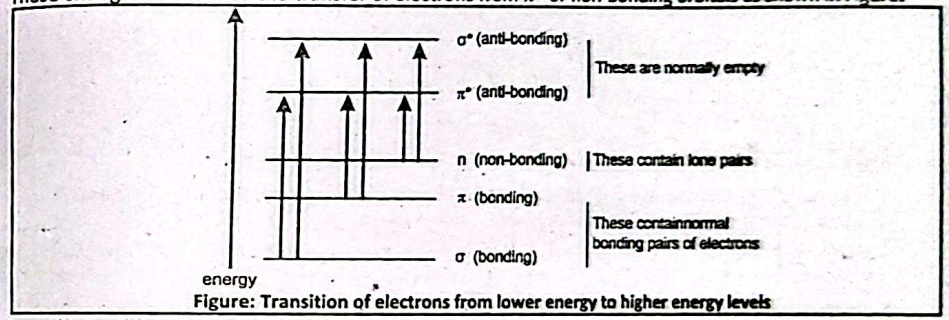


Figure: Transition of electrons from lower energy to higher energy levels

In each possible case, an electron is excited; light from a filled orbital into an empty anti-bonding orbital. Each jump takes energy from the light of a specific wavelength is absorbed.

**The important electronic transitions are:**

- from pi bonding orbitals to pi anti-bonding orbitals ($\pi$ to $\pi^*$).
- from non-bonding orbitals to pi anti-bonding orbitals (n to $\pi^*$).
- from non-bonding orbitals to sigma anti-bonding orbitals (n to $\sigma^*$).

The diagram below shows a simple UV-visible absorption spectrum for buta-1,3-diene, $CH_2 = CH - CH = CH_2$. The absorption peak at a value of 217 nm corresponds to the wavelength absorbed maximum and is called $\lambda_{max}$. This is in the UV region and so there would be no visible sign of any light being absorbed the compound is colourless. There are no non-bonding electrons so the only electron jumps taking place (within the range that the spectrometer can measure) are from pi bonding to pi anti-bonding orbitals.

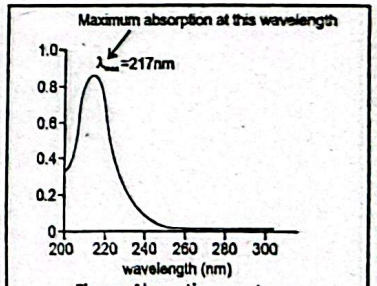
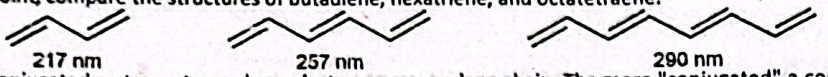


Figure: Absorption spectrum

CamScanner

The value of $\lambda_{max}$ for a particular compound is highly dependent on the extent of conjugation. To illustrate this point, compare the structures of butadiene, hexatriene, and octatetraene.



217 nm 257 nm 290 nm

In a conjugated system, atoms share electrons across a long chain. The more "conjugated" a compound is, the more energy levels it has, and the gaps between these levels become smaller. Because these gaps are smaller, it takes less energy to push an electron from a low level to a higher one. Since the energy of light depends on its frequency, these smaller energy gaps allow the compound to absorb light with less energy (lower frequency), that is why highly conjugated compounds often have bright colours. Because longer light waves have less energy, these chemicals absorb light with a longer wavelength, called the $\lambda_{max}$. This means that the more double bonds a compound has connected together, the higher its $\lambda_{max}$ number will be. Usually, with every addition of a double bond to the chain, that number increases by about 30 to 40 nm. By looking at this number, the extent of conjugation in a compound can be determined.

## QUICK CHECK 29.2

**a) Which type of electronic transitions require least energy in UV/Vis spectroscopy? Explain.**

**i)** $\sigma \rightarrow \sigma^*$ **ii)** $\pi \rightarrow \pi^*$ **iii)** $n \rightarrow \sigma^*$ **iv)** $n \rightarrow \pi^*$

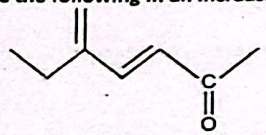
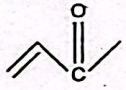
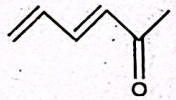
**Ans.** The energy required for electronic transitions decreases in the following order:

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

Therefore, the transition requiring the **least energy** is: $n \rightarrow \pi^*$

**Explanation:** In an $n \rightarrow \pi^*$ transition, an electron from a non-bonding orbital (lone pair) is promoted to an antibonding $\pi^*$ orbital. The energy difference between these orbitals is small, so less energy and longer wavelength light are required.

**b) Arrange the following in an increasing order of $\lambda_{max}$.**

**(i)**  **(ii)**  **(iii)** 

**Ans.** The wavelength of absorption increases with increasing conjugation.

**Compound (i):** This is a simple α, β-unsaturated ketone with the least conjugation. i.e., one C = C bond conjugate with carbonyl group so, $\lambda_{max}$ = lowest

**Compound (ii):** This compound contains a longer conjugated system than (ii), i.e., two C = C bonds conjugated with carbonyl group. So it absorbs at a longer wavelength.

**Compound (iii):** This compound contains the greatest degree of conjugation because the carbonyl group and multiple double bonds are conjugated over a larger region, additionally it has more alkyl groups.

Therefore, ii < iii < i

Increasing order of $\lambda_{max}$: ii < iii < i

**c) Will $CH_3CHOHCH_3$ show a significant absorption in the UV-Vis region? Explain.**

**Ans.** No, $CH_3CHOHCH_3$ is **2-propanol**, which contains only σ bonds, an oxygen atom with lone pairs and no π bond or conjugated system

The possible transitions are: $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma^*$

But these transitions require high energy and occur mainly in the far UV region.

So, $CH_3CHOHCH_3$ will not show significant absorption in the UV-visible region will not show significant absorption in the UV-Vis region.

**Interesting Information**

Green tomato and a red ripe tomato both have different colours. Green tomato has chlorophyll in higher quantities, while red tomato contains lycopene. Both these compounds have different $\lambda_{max}$ and a specific colour in the visible range.



## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. Electromagnetic radiation travels in the form of:
(A) Particles only (B) Waves (C) Molecules (D) Ions
2. Electromagnetic waves consist of oscillating:
(A) Electric fields only (B) Magnetic fields only (C) Electric and magnetic fields (D) Gravitational fields
3. The SI unit of wavelength is:
(A) cm (B) nm (C) m (D) Å
4. Frequency is measured in:
(A) Joules (B) Hertz ($s^{-1}$) (C) Newton (D) Pascal
5. The speed of light in vacuum is approximately:
(A) $3 \times 10^8$ m $s^{-1}$ (B) $3 \times 10^7$ m $s^{-1}$ (C) $3 \times 10^8$ m $s^{-1}$ (D) $3 \times 10^9$ m $s^{-1}$
6. The relationship between wavelength and frequency is:
(A) $c = \lambda v$ (B) $c = \lambda / v$ (C) $\lambda = cv$ (D) $v = c\lambda$
7. According to Planck's quantum theory, energy is emitted or absorbed in:
(A) Continuous amounts (B) Discrete packets (C) Infinite quantities (D) Random quantities
8. The smallest quantity of electromagnetic radiation is called a:
(A) Photon (B) Quantum (C) Electron (D) Proton
9. The energy of radiation is directly proportional to:
(A) Wavelength (B) Frequency (C) Density (D) Pressure
10. The equation relating energy and frequency is:
(A) $E = mc^2$ (B) $E = hv$ (C) $PV = nRT$ (D) $F = ma$
11. Which radiation has the highest energy?
(A) Radio waves (B) Infrared (C) X-rays (D) Gamma rays
12. Visible light lies between:
(A) Radio and microwaves (B) Infrared and ultraviolet
(C) X-rays and gamma rays (D) Microwaves and radio waves
13. IHD stands for:
(A) Internal Hydrogen Density (B) Index of Hydrogen Deficiency
(C) Ideal Hydrogen Distribution (D) Ionization Heat Difference
14. IHD measures the degree of:
(A) Saturation (B) Unsaturation (C) Ionization (D) Hydration
15. A saturated alkane has an IHD of:
(A) 0 (B) 1 (C) 2 (D) 3
16. An IHD value of 1 indicates:
(A) One ring or one double bond (B) One triple bond only
(C) Two double bonds (D) Three rings
17. A triple bond contributes:
(A) Zero IHD (B) One IHD (C) Two IHD (D) Three IHD
18. A compound with formula $C_6H_6$ has an IHD of:
(A) 0 (B) 1 (C) 2 (D) 3
19. Atomic spectra provide evidence that electrons occupy:
(A) Continuous energy levels (B) Discrete energy levels
(C) Random energy levels (D) Infinite energy levels
20. When electrons absorb energy, they move to:
(A) Lower energy levels (B) Higher energy levels (C) The nucleus (D) Another atom
21. Emission spectra are produced when electrons:
(A) Gain protons (B) Return to lower energy levels
(C) Lose neutrons (D) Form molecules
22. Emission spectra appear as:
(A) Dark lines on a coloured background (B) Coloured lines on a black background
(C) White lines on a red background (D) Continuous rainbow only
23. Absorption spectra are produced by passing:
(A) UV light through hot gas (B) White light through cool low-pressure gas
(C) Gamma rays through solids (D) X-rays through liquids
24. Absorption spectra contain:
(A) Bright coloured lines (B) Dark lines (C) No lines (D) Continuous black bands
25. Every element has:
(A) The same spectrum (B) A unique spectrum (C) Two spectra only (D) No spectrum

CamScanner

26. Hydrogen shows a strong emission line at approximately:
(A) 410 nm (B) 486 nm (C) 589 nm (D) 656 nm
27. Sodium produces a characteristic:
(A) Green flame (B) Yellow flame (C) Blue flame (D) Red flame
28. Spectroscopy is used for:
(A) Qualitative analysis (B) Quantitative analysis
(C) Both qualitative and quantitative analysis (D) None of these
29. UV–Visible spectroscopy measures:
(A) Magnetic field (B) Light absorbance (C) Pressure (D) Conductivity
30. UV–Visible spectroscopy commonly uses wavelengths between:
(A) 100–200 nm (B) 200–800 nm (C) 800–1200 nm (D) 1200–2000 nm
31. Sigma bonding orbitals are:
(A) Higher in energy than π orbitals (B) Lower in energy than π orbitals
(C) Equal in energy to π orbitals (D) Empty orbitals
32. Which electronic transition is common in unsaturated compounds?
(A) $\sigma \rightarrow \sigma^*$ (B) $\pi \rightarrow \pi^*$ (C) Nuclear transition (D) Proton transition
33. $\lambda_{max}$ refers to:
(A) Minimum wavelength (B) Maximum absorbance wavelength
(C) Maximum frequency (D) Lowest energy
34. Buta-1,3-diene has a $\lambda_{max}$ of approximately:
(A) 150 nm (B) 217 nm (C) 350 nm (D) 589 nm
35. Increasing conjugation generally causes $\lambda_{max}$ to:
(A) Decrease (B) Increase (C) Remain constant (D) Become zero
36. Highly conjugated compounds absorb:
(A) Shorter wavelengths (B) Longer wavelengths (C) Gamma rays only (D) Radio waves only
37. More conjugation means:
(A) Larger energy gap (B) Smaller energy gap (C) No energy gap (D) No electron transition
38. Colour in many organic compounds is mainly due to:
(A) Nuclear transitions (B) Extensive conjugation (C) Ionic bonding (D) Hydrogen bonding
39. UV–Visible spectroscopy mainly studies changes in:
(A) Nuclear energy levels (B) Electronic energy levels
(C) Vibrational energy only (D) Rotational energy only
40. The absorbance in UV–Visible spectroscopy depends primarily on the molecule's:
(A) Density (B) Electronic structure (C) Melting point (D) Solubility

## INFRARED SPECTROSCOPY

**Q.7 What is Infrared Spectroscopy? Discuss IR Absorption ranges of functional groups.** L/Q

**Ans.** All covalent bonds act rather like springs, vibrating in a number of different ways. The frequencies of vibrations occur in the infra-red region of the electromagnetic spectrum. If an organic molecule is irradiated with the infra-red energy that matches the natural vibration frequency of its bonds, it absorbs some of that energy and the amplitude of vibration increases.

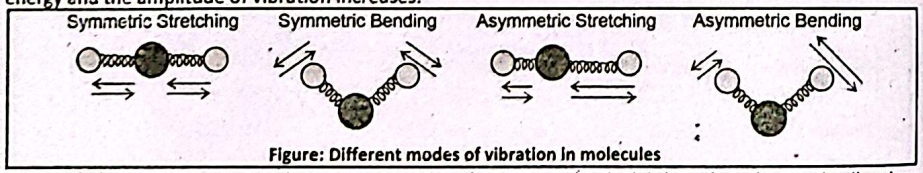



**Figure: Different modes of vibration in molecules**

Infrared (IR) spectroscopy is a technique used to identify compounds which is based on changes in vibrations of atoms when they absorb IR of specific frequencies. A spectrophotometer irradiates the sample with IR radiation and then detects the absorption of radiation by the molecule. Symmetrical and nonpolar molecules such as $O_2$ or $H_2$, are, therefore, IR inactive. Polar bonds such as O – H, N – H, etc. show absorption at higher wavenumbers. Similarly, bonds with smaller bond length and those with multiple bonds (e.g., HC ≡ CH also absorb at higher wavenumbers. The reason for these observations is that these bonds are stronger and require higher energy.



An IR spectrum consists of two regions. The fingerprint region below 1500 $cm^{-1}$ and the functional group region above 1500 $cm^{-1}$. Only functional region is discussed here which is enough to interpret the nature of organic compound. The table below gives information about infrared absorption frequencies (wave numbers).

**Did You Know?**

Infrared spectroscopy can be used to measure alcohol levels using modern roadside breathalyser. A ray of infrared radiation is passed through the breath that is exhaled into the breathalyser chamber. The characteristic bonds of ethanol are detected and measured - the higher the absorbance of infrared radiation, the more ethanol in the person's breathe.

**Table: IR Absorption ranges of functional groups ($cm^{-1}$)**

| Bond | Functional groups containing the bond | Characteristic infrared absorption range (in wavenumbers)/$cm^{-1}$ |
|---|---|---|
| C – O | Alcoholic, ester | 1040-1300 |
| C = C | aromatic compound, alkene | 1500-1680 |
| C = O | amide | 1640-1690 |
| | carbonyl, carboxyl | 1670-1740 |
| | ester | 1710-1750 |
| C ≡ N | nitrile | 2200-2250 |
| C – H | alkane | 2850-2950 |
| N – H | amine, amide | 3300-3500 |
| O – H | carboxyl | 2500-3300 |
| | hydroxy | 3200-3600 |

### Interpreting and Predicting Infrared Spectra

**Q.8 Discuss how infrared spectrum is interpreted with an example.** L/Q

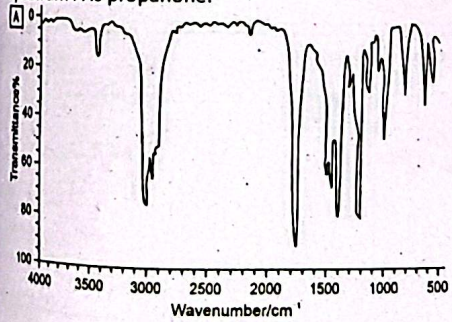
**Ans.** The best way to understand how to interpret an IR spectrum is by looking at solved examples and becoming familiar with the characteristic features of an IR spectrum.

**Example 29.1**

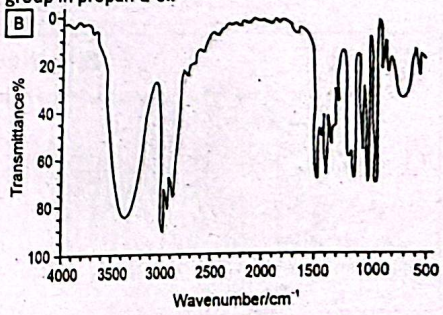
**Examine the two spectra shown and determine which one belongs to propan-2-ol and which one belongs to propanone.**

**Ans.**

The presence of a strong, sharp absorption around 1710 cm corresponds to the characteristic C = O, carbonyl, the functional group in a ketone. IR spectrum A is propanone.




In spectrum B the presence of a strong, absorption around 3200-3600 cm suggests that there is an alcohol group present, which corresponds to the –OH group in propan-2-ol.



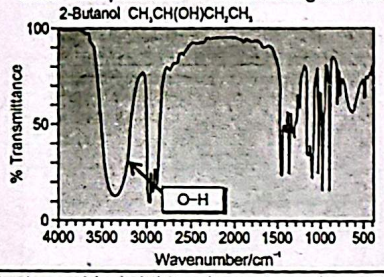

CamScanner

## IR Spectra of Important Functional Groups

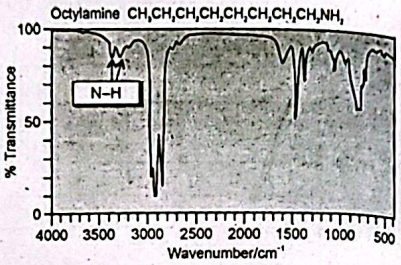
**Q.9 Discuss how infrared spectra of important functional group OH group of alcohol, The N – H bond in an amine, N – H and C = O groups of amide and CO group of carboxylic group?** L/Q

**Ans.**

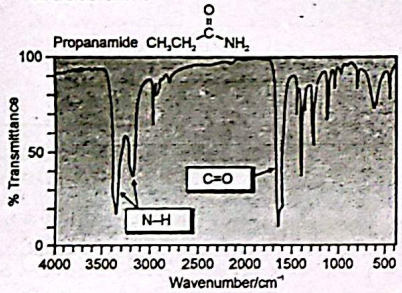
**(i)** The OH group of the alcohol shows a strong absorption at 3600-3200 $cm^{-1}$. The peak at 3000 $cm^{-1}$ is due to $sp^3$ hybridized C – H bonds as in the spectrum of butan-2-ol given here.



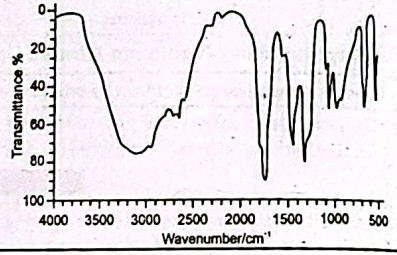

**(ii)** The N – H bond in an amine gives rise to two weak absorptions at 3300 and 3400 $cm^{-1}$.




**(iii)** An amide exhibits absorptions above 1500 $cm^{-1}$ for both its N – H and C = O groups: N – H (two peaks) at 3200 and 3400 $cm^{-1}$; C = O at 1660 $cm^{-1}$.




**(iv)** The C = O group in the carboxylic acids shows a strong absorption at 1700 $cm^{-1}$ along with broad and deep absorption of the O – H bond of a carboxylic acid between 2500 and 3300 $cm^{-1}$. This right hand side of this peak is often distorted by the peaks from C – H bonds.



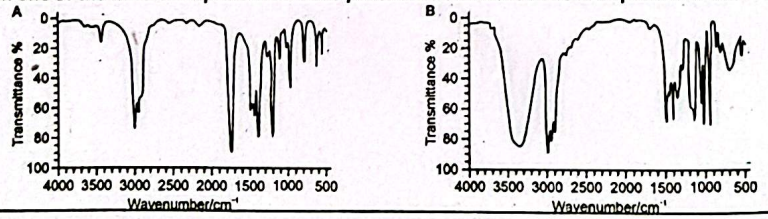

**NOTE: N – H signal in amines is broad but it is not broader than O – H signal in alcohols.**

**Did You Know?**

Infrared spectroscopy is used to identify pollutants in vehicle emissions. The air sensors detect and measure the amount of pollutants such as carbon monoxide, carbon dioxide and unburnt hydrocarbons. This commonly occurs on motorways and in busy town centres to monitor localised pollution.

### QUICK CHECK 29.3

**I. Which one of the infra-red spectra is that of pentanone and which one is of pentan-2-ol?**

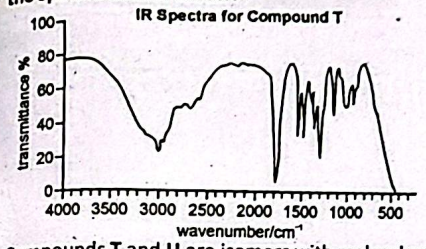


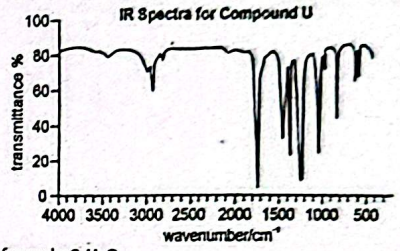



**Ans.** To identify the compounds, look for their characteristic IR absorption peaks.

- **Spectrum A is Butanone**
- **Reason:** Spectrum A shows a strong sharp absorption near 1715 $cm^{-1}$. This peak is due to the C = O (carbonyl) stretching vibration of a ketone. There is no broad O – H peak present.
- **Spectrum B is Butan-2-ol**
- **Reason:** Spectrum B shows a broad absorption band between 3200–3600 $cm^{-1}$. This broad peak is characteristic of the O–H stretching vibration of an alcohol. There is no strong carbonyl peak near 1700 $cm^{-1}$.

**II. Compounds T and U are isomers with the molecular formula $C_3H_6O_2$. Suggest their structures based on the spectra shown below:**




**Ans.** Compounds T and U are isomers with molecular formula $C_3H_6O_2$.
We identify them from their IR spectra.

- **Compound T**
  - A very broad absorption from about 2500–3300 $cm^{-1}$ → characteristic of O–H of a carboxylic acid.
  - A strong absorption near 1700 $cm^{-1}$ → C = O stretching.

  These two peaks together confirm the presence of a **carboxylic acid group (–COOH).**

  Therefore, compound T is: $CH_3 — CH_2 — COOH$ (Propanoic acid)

- **Compound U**
  - There is strong C = O absorption near 1740 $cm^{-1}$, showing that C = O group present.
  - It does not show broad O – H absorption between 2500–3500 $cm^{-1}$ it means that it is not an alcohol nor a carboxylic acid.

  This indicates that compound U is an **ester.**

  A suitable ester with molecular formula $C_3H_6O_2$ is: $CH_3COOCH_3$ (Methyl ethanoate)

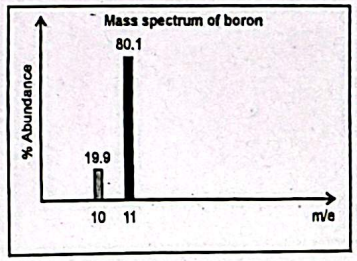
## MASS SPECTROMETRY

**Q.10 How mass spectrometry is used to determine the isotopic mass and average atomic masses of elements? Explain giving an example.** Exercise D/Q.6

**Ans.** Mass spectrometry is an analytical technique used to identify unknown compounds. The molecules/atoms in the small sample are bombarded with high energy electrons which can cause a molecule/atom to lose an electron. As a result, a positive ion is formed which is detected by detector and recorded as m/e (mass to charge ratio of the ion) versus percentage of ion.

### Isotopic Mass and Abundance

Mass spectrometry can be used to find the relative abundance of the isotopes experimentally. The relative abundance is the proportion of a particular isotope in a mixture of isotopes found in nature.




**Example:**

The relative abundance of Cl-35 and Cl-37 is 75% and 25% respectively. The heights of the peaks in mass spectroscopy show the proportion of each isotope present.

CamScanner

For example, in the graph below, the peak heights show the relative abundance of the boron isotopes: boron-10 has a relative abundance of 19.9% and boron-11 has a relative abundance of 80.1%.

### ➲ Calculating Relative Atomic Mass

The relative atomic mass, $A_r$ by using the average mass of the isotopes. The relative atomic mass of an element can be calculated by using the relative abundance and isotopic masses. The relative abundance of an isotope is either given or can be read the mass spectrum.

$$\text{Relative Atomic Mass } (A_r) = \frac{\Sigma(\text{isotopic mass} \times \text{isotopic abundance})}{100}$$

**Example 29.2**

**Calculate the relative atomic mass, $A_r$, of oxygen to 2 decimal point.**

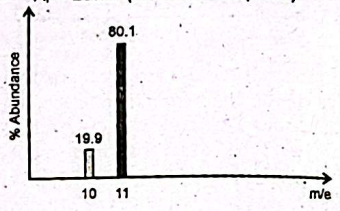
Ans.
- $A_r = \frac{(99.76\times16)+(0.04\times17)+(0.20\times18)}{100}$
- $A_r = 16.0044$
- Ar = 16.00 (to 2 d.p.)

| Isotope | Percentage abundance |
|---|---|
| $^{16}O$ | 99.76 |
| $^{17}O$ | 0.04 |
| $^{18}O$ | 0.20 |

**Example 29.3**

**Calculate the relative atomic mass of boron using its mass spectrum, to 2 decimal point.**

Ans.
- $A_r = \frac{(19.9\times10)+(80.1\times11)}{100}$
- $A_r = 10.801$
- $A_r = 10.80$ (to 2 decimal point)




### ➲ Molecular Ion Peak and Fragmentation

**Q.11 Discuss molecular ion peak and fragmentation in mass spectrometry.** L/O

Ans. When molecules in a sample compound are bombarded with highly accelerated electrons it causes the molecules to lose electrons. This results in the formation of a positively charged molecular ion with one unpaired electron. One of the electrons in the pair has been removed by the beam of electrons.

$$\text{Molecule} \xrightarrow{\text{electron bombardment}} \text{Molecule}^{+\bullet} + e^-$$

$\text{Molecule}^{+\bullet}$ represents the molecular ion. The molecular ion can further fragment to form new ions, molecules, and free radicals.

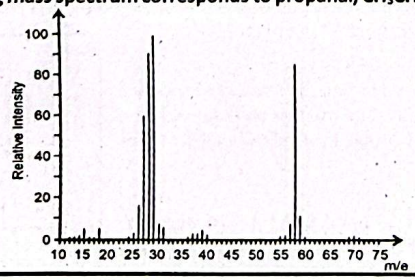
**a) Deducing Molecular Formula**

Each peak in the mass spectrum corresponds to a certain fragment with a particular m/e value. The peak mostly with the highest m/e value is the molecular ion ($M^+$) peak which gives information about the molecular mass of the compound. The molecular ion is the entire molecule that has lost one electron when bombarded with a beam of electrons.

$$\text{Molecule} \xrightarrow{\text{electron bombardment}} \text{Molecule}^{+\bullet} + e^-$$

**Example 29.4**

**Determine whether the following mass spectrum corresponds to propanal, $CH_3CH_2CHO$ or butanal, $CH_3CH_2CH_2CHO$.**






Ans. The mass spectrum corresponds to propanal as the molecular ion peak is at m/e = 58. The molecular ion mass of $CH_3CH_2CHO^+$ ion is 58 and butanal arises from the $CH_3CH_2CH_2CHO^+$ ion which has a m/e of 72.

**b) Identifying Molecules Using Fragmentation**

The molecular ion peak can be used to identify a compound by its molecular mass. However, different compounds may have the same molecular mass. To further determine the structure of the unknown compound, fragmentation is used. Fragments may appear due to the formation of characteristic smaller ions or the loss of small molecules. For example, loss of small molecules/fragments give rise to peaks at 18($H_2O$), 29($C_2H_5^+$) and 44($CO_2$).

**➢ Alkanes**

Simple alkanes are fragmented in mass spectroscopy by breaking the C – C bonds. m/e values of some of the common alkane fragments are given in the Table.

The fragmentation of the straight chain hexane: 86, 71, 57, 43, 29 and 15, which is due to the fragmentation at different location.

- $CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ (Mass:86)
- $CH_3-CH_2-CH_2-CH_2^+$ (Mass:57)
- $CH_3-CH_2^+$ (Mass:29)
- $CH_3-CH_2-CH_2-CH_2-CH_2^+$ (Mass:71)
- $CH_3-CH_2-CH_2^+$ (Mass:43)
- $CH_3^+$ (Mass:15)

**Table: Common fragments of hexane**

| Fragment | m/e |
|---|---|
| $CH_3^+$ | 15 |
| $C_2H_5^+$ | 29 |
| $C_3H_7^+$ | 43 |
| $C_4H_9^+$ | 57 |
| $C_5H_{11}^+$ | 71 |
| $C_6H_{13}^+$ | 85 |

**c) The M + 1 & M + 2 Peaks**

**i. Determine the Number of Carbon Atoms Using M + 1 Peak**

The [M + 1] peak is a smaller peak which is due to the natural abundance of the isotope carbon-13. The height of the [M+1] peak for a particular ion depends on how many carbon atoms are present in that molecule; the more carbon atoms, the larger the [M+1] peak is. For example, the height of the [M+1] peak for hexane (containing six carbon atoms) ion will be greater than the height of the [M+1] peak of ethane (containing two carbon atoms) ion.

Carbon-13 makes up approximately 1.1% of all carbon atoms. Therefore, the [M+1] peak is much smaller than the M peak as the isotope is less common. The ratio of $^{13}C$ to $^{12}C$ is approximately 1:99. Thus, the greater the number of carbon atoms present in a molecule the greater the height of the [M+1] peak. The number of carbon atoms, n, in a compound can be deduced using the [M + 1] peak and the following formula:

$$n = \frac{100\times\text{abundance of [M+1]}}{1.1\times\text{abundance of } M^+ \text{ ion}}$$

**Example 29.5**

**i. Determine the number of carbon atoms of compound X with the following mass spectrum:**

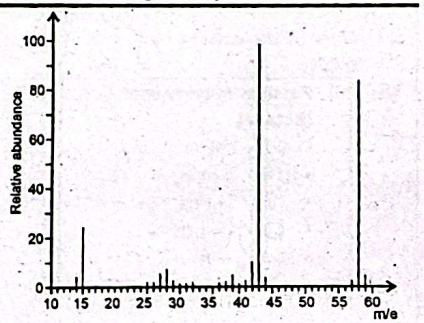
Ans. The M ion peak is at m/e 58 with a relative abundance of around 85.

The [M + 1] peak is at m/e 59 with a relative abundance of 3.

**Therefore**, the number of carbon atoms (n) is:

$$n = \frac{100\times3}{1.1\times85} = 3.21$$

There are, therefore, 3 carbon atoms present in compound X.




CamScanner

**ii. Detecting Bromine and Chlorine Atoms Using M + 2 Peak**

**Ans.** The presence of bromine or chlorine atoms in a compound gives rise to a [M + 2] and possibly [M + 4] peak.

**Chlorine**

Chlorine exists as two isotopes, $^{35}Cl$ and $^{37}Cl$. A compound containing one chlorine atom will, therefore, have two molecular ion peaks due to the two different isotopes, it contain,

$^{35}Cl$ = $M^+$ peak

$^{37}Cl$ = [M + 2] peak

The ratio of the peak heights is 3 : 1 (as the relative abundance of $^{35}Cl$ is 3 × greater than that of $^{37}Cl$.

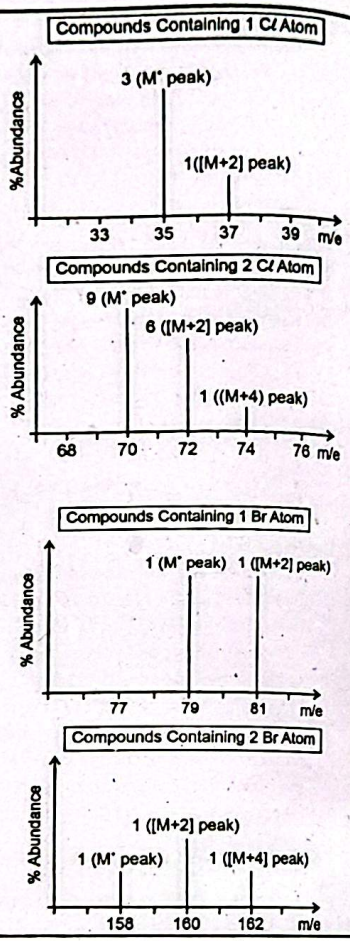
A compound containing two chlorine atoms will have three molecular ion peaks due to the different combinations of chlorine isotopes they can contain

$^{35}Cl + {}^{35}Cl = M^+$ peak

$^{35}Cl + {}^{37}Cl$ = [M + 2] peak

$^{37}Cl + {}^{37}Cl$ = [M + 4] peak

The ratio of the peak heights is 9 : 6 : 1.




**Bromine**

Bromine also exists as two isotopes, $^{79}Br$ and $^{81}Br$. A compound containing one bromine atom will have two molecular ion peaks.

$^{79}Br$ = $M^+$ peak

$^{81}Br$ = [M + 2] peak

The ratio of the peak heights is 1 : 1 (they are of similar heights as their relative abundance is the

A compound containing two bromine atoms will have three molecular ion peaks.

$^{79}Br + {}^{79}Br$ = M peak

$^{79}Br + {}^{81}Br$ = [M + 2] peak

$^{81}Br + {}^{81}Br$ = [M + 4] peak

The ratio of the peak heights is 1 : 2 : 1.

## ☑ QUICK CHECK 29.4

**a) Show all the possible fragments of:**

**i) $C_4H_{10}$ ii) $C_5H_{12}$ iii) $C_7H_{16}$**

**Ans.**

**i) Possible fragments of $C_4H_{10}$ (Butane)**

Possible fragments are:

- $CH_3^+ \rightarrow m/e = 15$
- $C_2H_5^+ \rightarrow m/e = 29$
- $C_3H_7^+ \rightarrow m/e = 43$
- $C_4H_9^+ \rightarrow m/e = 57$

**ii) $C_5H_{12}$ (Pentane)**

Possible fragments are:

- $CH_3^+ \rightarrow m/e = 15$
- $C_2H_5^+ \rightarrow m/e = 29$
- $C_3H_7^+ \rightarrow m/e = 43$
- $C_4H_9^+ \rightarrow m/e = 57$
- $C_5H_{11}^+ \rightarrow m/e = 71$

**iii) $C_7H_{16}$ (Heptane)**

Possible fragments are:

- $CH_3^+ \rightarrow m/e = 15$
- $C_2H_5^+ \rightarrow m/e = 29$
- $C_3H_7^+ \rightarrow m/e = 43$
- $C_4H_9^+ \rightarrow m/e = 57$
- $C_5H_{11}^+ \rightarrow m/e = 71$
- $C_6H_{13}^+ \rightarrow m/e = 85$
- $C_7H_{15}^+ \rightarrow m/e = 99$



**b) The mass spectrum of $CH_3Br$ is given below.**

**i) Identify the fragment against each peak.**

**Ans.**

| m/e value | Fragment |
|---|---|
| 15 | $CH_3^+$ |
| 94 | $CH_3{}^{79}Br^+$ |
| 96 | $CH_3{}^{81}Br^+$ |

**ii) What is the justification of two peaks at 94 and 96?**

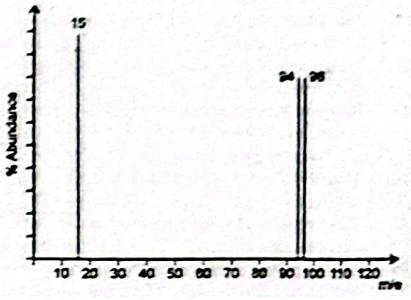
**Ans.** Bromine exists naturally as two isotopes:

- $^{79}Br$ (about 50%)
- $^{81}Br$ (about 50%)

Therefore, methyl bromide forms two molecular ions:

$CH_3{}^{79}Br^+$ with m/e = 12+3+79 = 94 and $CH_3{}^{81}Br^+$ with m/e = 12 + 3 + 81 = 96

Hence, two molecular ion peaks appear at **m/e = 94 and 96,** usually with almost equal intensity because both bromine isotopes are present in nearly equal abundance and also appear on mass spectrum as peaks of similar heights.




## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Infrared spectroscopy is based on changes in:**
   (A) Nuclear spin (B) Molecular vibrations (C) Electron spin (D) Atomic mass
2. **IR radiation is absorbed when molecules:**
   (A) Rotate only (B) Vibrate (C) Ionize (D) Condense
3. **A molecule absorbs IR radiation only if it has:**
   (A) A permanent dipole that changes during vibration (B) A triple bond
   (C) A ring structure (D) High molecular mass
4. **Which molecule is IR inactive?**
   (A) $H_2O$ (B) $NH_3$ (C) $O_2$ (D) HCl
5. **The fingerprint region of an IR spectrum lies:**
   (A) Above 4000 $cm^{-1}$ (B) Above 3000 $cm^{-1}$ (C) Below 1500 $cm^{-1}$ (D) Between 1500-2000 $cm^{-1}$
6. **The functional group region is:**
   (A) Below 1000 $cm^{-1}$ (B) Above 1500 $cm^{-1}$ (C) Between 500-1000 $cm^{-1}$ (D) Between 1000-1500 $cm^{-1}$
7. **The O–H stretching absorption of alcohols appears around:**
   (A) 1500-1700 $cm^{-1}$ (B) 2200-2300 $cm^{-1}$ (C) 3200-3600 $cm^{-1}$ (D) 400-800 $cm^{-1}$
8. **Carboxylic acids show a broad O–H absorption between:**
   (A) 1000-1500 $cm^{-1}$ (B) 1700-1800 $cm^{-1}$ (C) 2500-3300 $cm^{-1}$ (D) 3600-4000 $cm^{-1}$
9. **The C=O stretching vibration generally appears near:**
   (A) 1000 $cm^{-1}$ (B) 1700 $cm^{-1}$ (C) 2500 $cm^{-1}$ (D) 3300 $cm^{-1}$
10. **The N–H absorption of amines occurs around:**
    (A) 1000-1500 $cm^{-1}$ (B) 1700-1800 $cm^{-1}$ (C) 2200-2300 $cm^{-1}$ (D) 3300-3500 $cm^{-1}$
11. **The C≡N stretching vibration appears approximately at:**
    (A) 1200 $cm^{-1}$ (B) 1700 $cm^{-1}$ (C) 2200–2250 $cm^{-1}$ (D) 3400 $cm^{-1}$
12. **Alkane C–H stretching occurs around:**
    (A) 2850-2950 $cm^{-1}$ (B) 1700 $cm^{-1}$ (C) 2200 $cm^{-1}$ (D) 3600 $cm^{-1}$
13. **IR spectroscopy is mainly used to identify:**
    (A) Functional groups (B) Isotopes (C) Atomic numbers (D) Crystal structures
14. **The broadest absorption peak in IR spectra is generally due to:**
    (A) C–H (B) N–H (C) O–H (D) C=C
15. **Roadside breathalyzers commonly use:**
    (A) UV spectroscopy (B) IR spectroscopy (C) NMR spectroscopy (D) Mass spectrometry
16. **Mass spectrometry is mainly used to:**
    (A) Measure pressure (B) Identify unknown compounds
    (C) Measure density (D) Determine colour

CamScanner

17. In mass spectrometry, molecules are bombarded with:
(A) Alpha particles (B) High-energy electrons (C) Neutrons (D) UV photons

18. Electron bombardment produces:
(A) Negative ions (B) Positive ions (C) Neutral atoms (D) Molecules only

19. Mass spectra are plotted as:
(A) Frequency vs wavelength (B) m/e vs relative abundance
(C) Pressure vs volume (D) Time vs distance

20. The molecular ion is represented by:
(A) $M^-$ (B) $M^+$ (C) $M^{2+}$ (D) $H^+$

21. The molecular ion peak usually has the:
(A) Lowest m/e value (B) Highest m/e value (C) Lowest intensity (D) Same intensity as all peaks

22. Fragmentation in mass spectrometry produces:
(A) Smaller ions (B) Larger molecules (C) Electrons only (D) Neutrons

23. Relative atomic mass is calculated using:
(A) Atomic number only (B) Isotopic masses and abundances
(C) Mass number only (D) Density

24. The M+1 peak mainly arises due to:
(A) Hydrogen-2 (B) Carbon-13 (C) Oxygen-18 (D) Chlorine-37

25. The height of the M+1 peak increases with increasing number of:
(A) Hydrogen atoms (B) Carbon atoms (C) Oxygen atoms (D) Nitrogen atoms

26. The M+1 peak helps determine the number of:
(A) Oxygen atoms (B) Carbon atoms (C) Nitrogen atoms (D) Sulfur atoms

27. A compound containing one chlorine atom gives M and M+2 peaks in the ratio:
(A) 1 : 1 (B) 3 : 1 (C) 9 : 6 : 1 (D) 1 : 2 : 1

28. A compound containing two chlorine atoms shows molecular ion peaks in the ratio:
(A) 1 : 1 (B) 3 : 1 (C) 9 : 6 : 1 (D) 1 : 2 : 1

29. One bromine atom gives M and M+2 peaks in the ratio:
(A) 3 : 1 (B) 1 : 1 (C) 9 : 6 : 1 (D) 1 : 2 : 1

30. Two bromine atoms give M : M+2 : M+4 peaks in the ratio:
(A) 3 : 1 : 1 (B) 1 : 2 : 1 (C) 9 : 6 : 1 (D) 1 : 1 : 1

31. The relative abundance of $^{35}Cl$ : $^{37}Cl$ is approximately:
(A) 1 : 1 (B) 2 : 1 (C) 3 : 1 (D) 9 : 1

32. The relative abundance of $^{79}Br$ : $^{81}Br$ is approximately:
(A) 3 : 1 (B) 1 : 1 (C) 9 : 6 (D) 2 : 1

33. The fragment ion $CH_3^+$ has an m/e value of:
(A) 15 (B) 29 (C) 43 (D) 57

34. The fragment ion $C_2H_5^+$ has an m/e value of:
(A) 15 (B) 29 (C) 43 (D) 71

35. The molecular ion peak provides information about the:
(A) Molecular mass (B) Melting point (C) Boiling point (D) Density

36. Gas chromatography and mass spectrometry are both used for:
(A) Compound identification (B) Measuring pH (C) Determining colour (D) Measuring viscosity

37. Which technique can determine isotopic abundance experimentally?
(A) UV spectroscopy (B) IR spectroscopy (C) Mass spectrometry (D) Flame test

38. The base peak in a mass spectrum represents the:
(A) Lightest ion (B) Most abundant ion (C) Molecular ion only (D) Smallest fragment

39. Fragmentation helps in determining the:
(A) Colour of compounds (B) Structure of compounds (C) Solubility (D) Density

40. Mass spectrometry is most useful for determining:
(A) Molecular mass and structural information (B) Boiling point only
(C) Melting point only (D) Surface area only

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

BLOCK # 01

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. C | 4. B | 5. C | 6. A | 7. B | 8. B | 9. B | 10. B | 11. D | 12. B | 13. B | 14. B | 15. A |
| 16. A | 17. C | 18. C | 19. B | 20. B | 21. B | 22. B | 23. B | 24. B | 25. B | 26. D | 27. B | 28. C | 29. B | 30. B |
| 31. B | 32. B | 33. B | 34. B | 35. B | 36. B | 37. B | 38. B | 39. B | 40. B | | | | | |



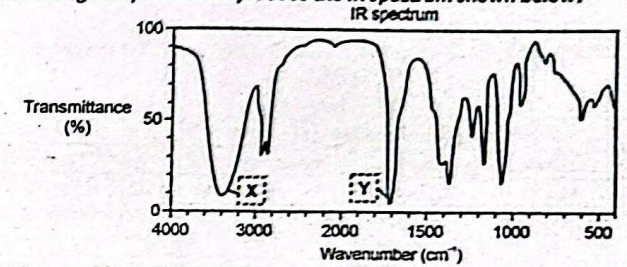
BLOCK # 02

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. A | 4. C | 5. C | 6. B | 7. C | 8. C | 9. B | 10. D | 11. C | 12. A | 13. A | 14. C | 15. B |
| 16. B | 17. B | 18. B | 19. B | 20. B | 21. B | 22. A | 23. B | 24. B | 25. B | 26. B | 27. B | 28. C | 29. B | 30. B |
| 31. C | 32. B | 33. A | 34. B | 35. A | 36. A | 37. C | 38. B | 39. B | 40. A | | | | | |

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I) Which of the following compounds can produce the IR spectrum shown below?




a) propanoic acid b) 4-hydroxybutanone c) pentan-1-ol d) 2-hydroxybut-1-ene

II. What is the wavelength range of the UV spectrum?
a) 100 nm to 500 nm b) 200 nm to 800 nm c) 300 nm to 1000 nm d) 400 nm to 1600 nm

III. The λ of $\sigma$ to $\sigma^*$ transitions lies in the
a) IR region b) Visible region c) UV region d) None of the above

IV. The types of transitions possible in UV-visible region for a compound with molecular formula $C_4H_8$ are:
a) $n \rightarrow \pi^*$ b) $n \rightarrow \sigma^*$ c) $\sigma \rightarrow \sigma^*$ d) $\pi \rightarrow \pi^*$

V. What is index of hydrogen deficiency of $C_4H_8$?
a) 2 b) 3 c) 4 d) 5

VI. Which of the following statements about the mass spectrum of $CH_3Cl$ is correct?
a) There is one peak for the molecular ion with an m/e value of 45.
b) There is one peak for the molecular ion with an m/e value of 52.
c) The last two peaks have abundances in the ratio 3:1 and occur at m/e values of 50 and 52.
d) The last two peaks are of equal size and occur at m/e values of 50 and 52.

VII. The average atomic mass of Ne having isotopes $^{20}Ne$, $^{21}Ne$, $^{22}Ne$, with natural abundance is:
a) 20.50 amu b) 20.18 amu c) 30.70 amu d) 20.00 amu

VIII. Which of the following fragments will not be produced in the fragmentation of hexane ($C_6H_{14}$)?
a) $M^{\cdot+}$ b) M + 1 c) M − 1 d) M + 4

IX. The IR spectrum of a compound X contains peak at 1560 $cm^{-1}$, 1690 $cm^{-1}$, and a broad peak between 2500-3200 $cm^{-1}$, Thus X is most likely:
a) An unsaturated ketone b) An alkene
c) An unsaturated carboxylic acid d) An alcohol

### Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | b | 4-hydroxybutanone | The spectrum shows:<br>A broad O–H peak around 3200–3600 $cm^{-1}$. (Indicating –OH group)<br>A strong C=O peak near 1700 $cm^{-1}$. (Indicating carbonyl group)<br>So, 4-hydroxybutanone contains both an alcohol group and a carbonyl group. |

CamScanner

| | | | |
|---|---|---|---|
| II. | b | 200 nm to 800 nm | The UV-visible region generally extends from about 200 nm to 800 nm. |
| III. | c | UV region | The $\sigma \rightarrow \sigma^*$ transition requires very high energy and therefore occurs in the UV region. |
| IV. | d | $\pi \rightarrow \pi^*$ | $C_2H_4$ (ethene) contains a C = C double bond, so the characteristic transition is: $\pi \rightarrow \pi^*$ |
| V. | d | 5 | $IHD = \frac{2C+2-H}{2} = \frac{2(8)+2-8}{2} = \frac{16+2-8}{2} = \frac{10}{2} = 5$ |
| VI. | d | The last two peaks are of equal size and occur at m/e values of 50 and 52. | Chlorine exists as two isotopes:<br>$35Cl$ (75%)<br>$37Cl$ (25%)<br>Therefore, $CH_3Cl$ gives two molecular ion peaks:<br>$CH_3{}^{35}Cl^+$ at m/e = 50<br>$CH_3{}^{37}Cl^+$ at m/e = 52<br>**Hence option (d) is correct.** |
| VII. | b | 20.18 amu | The abundance-weighted mean of $^{20}Ne$, $^{21}Ne$ and $^{22}Ne$ is about 20.18 amu. |
| VIII. | d | M + 4 | Normal hexane fragmentation/isotope patterns include M, small M+ isotope peaks and lower-mass fragments; M+4 is not a normal fragmentation product. |
| IX. | c | An unsaturated carboxylic acid | A broad 2500-3200 $cm^{-1}$ O – H band plus C = O near 1690 $cm^{-1}$ and C = C absorption indicates an unsaturated carboxylic acid. |

## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) Bromobutane, $CH_3CH_2CH_2CH_2Br$, can be reacted with hot aqueous sodium hydroxide to prepare butan-1-ol.**

$$CH_3CH_2CH_2CH_2Br + OH^- \longrightarrow CH_3CH_2CH_2CH_2OH + Br^-$$

**Butan-1-ol produced can be analysed by mass spectrometry.**

**i. Predict the formula of the fragment ion with a m/e value of 17.**

**ii. Predict two other fragment ions that you would expect to see in the mass spectrum of butan-1-ol and state the m/e value of each ion.**

**Ans.**

i) The fragment having m/e = 17 is: $OH^+$
Since, 16 + 1 = 17
**Answer: $OH^+$**

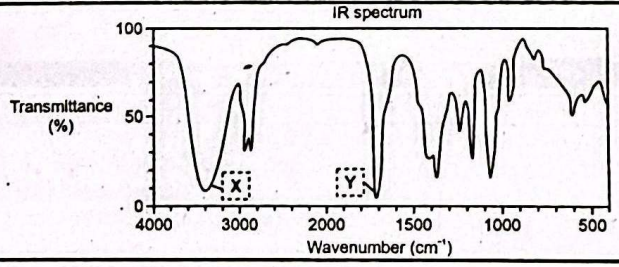
ii)

| Fragment ion | m/e value | Process |
|---|---|---|
| $[CH_2OH]^+$ | 31 | α-cleavage, base peak for p-alcohols |
| $[C_4H_8]^+$ | 56 | Loss of water, M-18 peak |

**Other acceptable fragments include:**

| Fragment ion | m/e value |
|---|---|
| $CH_3^+$ | 15 |
| $C_2H_5^+$ | 29 |

**b) Identify the functional groups responsible for the peaks labelled X and Y.**






**Ans.**

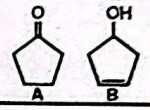
**Peak X:**
The broad absorption around 3200–3600 $cm^{-1}$ is due to:
- O–H stretching of alcohol stretching of alcohol

**Peak Y:**
The strong absorption near 1700 $cm^{-1}$ is due to:
C = O stretching of carbonyl group

**Answer:**

| Peak | Functional Group |
|---|---|
| X | O–H (alcohol) |
| Y | C=O (carbonyl) |

**c) Explain how the two isomers shown in the diagram can be distinguished using the IR spectroscopy.**




**Ans. Compound A (Cyclopentanone)**
Compound A contains a ketone group (C = O).
Its IR spectrum will show a strong absorption near: 1740 $cm^{-1}$

**Compound B (Cyclopent-2-en-1-ol)**
Compound B contains an alcohol group (O–H).
Its IR spectrum will show a broad absorption near: 3200–3600 $cm^{-1}$

**Conclusion:**
A gives a strong C = O peak near 1700 $cm^{-1}$.
B gives a broad O–H peak near 3200–3600 $cm^{-1}$.
Therefore, the two compounds can easily be distinguished by the presence of these characteristic peaks.

**d) The molecular formulas of the following compounds are given below:**
**but-1-ene: $C_4H_8$ but-1,3-diene: $C_4H_6$**

**i. Fine out the IHD of both of these compounds.**

**ii. Compare the UV absorption spectrum of but-1-ene to that of but-1, 3-diene by stating the difference in their $\lambda_{max}$ qualitatively.**

**Ans.**

i) The formula is: $IHD = \frac{2C+2-H}{2}$

For but-1-ene ($C_4H_8$): $IHD = \frac{2(4)+2-8}{2} = \frac{8+2-8}{2} = \frac{2}{2} = 1$

**Answer: IHD = 1**

For but-1,3-diene ($C_4H_6$): $IHD = \frac{2(4)+2-6}{2} = \frac{8+2-6}{2} = \frac{4}{2} = 2$

**Answer: IHD = 2**

ii) But-1, 3-diene contains a conjugated system of double bonds, while but-1-ene contains only one double bond. Conjugation lowers the energy required for electronic transition.
**Therefore:**
- But-1-ene absorbs at a shorter wavelength.
- But-1,3-diene absorbs at a longer wavelength and has a higher $\lambda_{max}$.

**Conclusion:**
$\lambda_{max}$(but-1,3-diene) > $\lambda_{max}$(but-1-ene)
because conjugation shifts absorption towards longer wavelengths (bathochromic shift)

**e) Show all the possible fragments of $C_5H_{12}$ and their (m/e) values in its mass spectrum.**

**Ans. $C_5H_{12}$ (Pentane)**
Possible fragments are:

CamScanner

- $CH_3^+ \rightarrow m/e = 15$
- $C_2H_5^+ \rightarrow m/e = 29$
- $C_3H_7^+ \rightarrow m/e = 43$
- $C_4H_9^+ \rightarrow m/e = 57$
- $C_5H_{11}^+ \rightarrow m/e = 71$

However, molecular ion has m/e

## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) Compound X is an atmospheric pollutant emitted from combustion of petrol and diesel vehicles. Compound X is a potent human carcinogen. Analysis of compound X showed the following percentage composition by mass: C, 88.89% and H, 11.1%. Mass spectrometry showed a molecular ion peak at m/e = 54. Compound X reacts with $H_2$ in the presence of a nickel catalyst in a 1:2 molar ratio. Analyse and interpret this information to determine a possible structure for compound X. Show all your working.**

**Ans. Find the Empirical Formula**

**Assume 100 g of compound:**

| Element | % Composition | Moles |
|---|---|---|
| C | 88.9 | $\frac{88.9}{12} = 7.41$ |
| H | 11.1 | $\frac{11.1}{1} = 1.5$ |

**Divide by the smallest value:**

| Element | Moles |
|---|---|
| C | $\frac{7.41}{7.41} = 1$ |
| H | $\frac{11.1}{7.41} = 1.5$ |

Multiply by 2: $C_2H_3$

Therefore, the empirical formula is: $C_2H_3$

➢ **Determine Molecular Formula**

Empirical formula mass: $(2\times12) + 3 = 27$

Given molecular mass from mass spectrum:

$$M = 54$$

$$\frac{54}{27} = 2$$

Therefore, $(C_2H_3) \times 2 = C_4H_6$

Hence the molecular formula is: $C_4H_6$

➢ **Calculate IHD**

$$IHD = \frac{2C+2-H}{2} = \frac{2(4)+2-6}{2} = \frac{8+2-6}{2} = \frac{4}{2} = 2$$

Thus compound X has two double bonds or one triple bond or one ring and one double bond.

➢ **Use Hydrogenation Information**

Compound X reacts with hydrogen in a 1 : 2 molar ratio. This means:

1 mol X + 2 mol $H_2$

Therefore compound X contains two π bonds that can be hydrogenated. Hence X contains two double bonds.

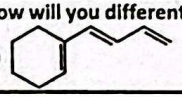
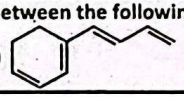
➢ **Possible Structure**

A possible structure for X: $CH_2 = CH — CH = CH_2$ which is buta-1,3-diene.

This compound is a component of automobile exhaust and is a known human carcinogen.

**(Note:** but-1-yne and but-2-yen can be other options).

**b) How will you differentiate between the following using the UV visible spectroscopy.**

**(i)**  **(ii)** 

**Ans.** These two compounds show $\pi \longrightarrow \pi^*$ transitions in the UV-visible spectrum compound:
(i) absorbs at a longer wavelength ($\lambda_{max}$) than compound (ii) as it has greater conjugation.

**Compound (i):** It contains 3 conjugated C = C bonds, so it absorbs at a shorter wavelength at about 255-260 nm.

**Compound (ii):** It contains 4 conjugated C = C bonds it has greater conjugation, absorbs longer wavelength at about 320 nm and shows bathchromic shift.



## DESCRIPTIVE QUESTIONS DQs

**Q.4 Describe various possible electronic transitions in a compound having sigma, pi bonds, and non-bonding electrons.**

**Ans.** See Question No. 06

**Q.5 Explain two types of atomic spectrum.**

**Ans.** See Question No. 04

**Q.6 How mass spectrometry is used to determine the isotopic mass and average atomic masses of elements? Explain giving an example.**

**Ans.** See Question No. 10

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 What is Index of Hydrogen Deficiency (IHD)?**

**Ans.** Index of Hydrogen Deficiency (IHD) is the number of rings and multiple bonds present in a molecule. It helps chemists estimate the degree of unsaturation and predict possible structures of organic compounds.

$$IHD = \frac{2C+2-H+N-X}{2}$$

**Q.2 What information does IHD provide about a molecule?**

**Ans.** IHD provides information about the number of rings, double bonds and triple bonds present in a molecule. Each double bond or ring contributes one unit, whereas a triple bond contributes two units to IHD.

**Q.3 What is mass spectrometry?**

**Ans.** Mass spectrometry is an analytical technique used to determine the molecular mass and fragmentation pattern of compounds. It helps in identifying unknown compounds and determining their structures.

**Q.4 What is a molecular ion peak?**

**Ans.** The molecular ion peak ($M^+$) corresponds to the intact molecule after losing one electron during ionization. Its m/z value gives the molecular mass of the compound.

**Q.5 What is a base peak?**

**Ans.** The base peak is the tallest peak in a mass spectrum and is assigned a relative intensity of 100%. It corresponds to the most stable and abundant fragment ion.

**Q.6 What is infrared spectroscopy?**

**Ans.** Infrared spectroscopy is a technique used to identify functional groups present in organic molecules by measuring the absorption of infrared radiation at characteristic frequencies.

**Q.7 How does IR spectroscopy identify functional groups?**

**Ans.** Different functional groups absorb infrared radiation at characteristic frequencies because their bonds vibrate at different energies. By analyzing these absorption peaks, the functional groups present in a molecule can be identified.

**Q.8 What IR absorption indicates the presence of an alcohol?**

**Ans.** Alcohols show a broad O-H stretching absorption band in the region of approximately 3200–3600 $cm^{-1}$. This broad peak is characteristic of hydroxyl-containing compounds such as ethanol.

**Q.9 What IR absorption indicates the presence of a carbonyl group?**

**Ans.** Carbonyl compounds such as aldehydes, ketones and carboxylic acids show a strong absorption peak near 1700 $cm^{-1}$ due to C=O stretching vibrations.
This peak is one of the most important diagnostic absorptions in IR spectroscopy.

**Q.10 Why do compounds containing π bonds absorb UV light?**

**Ans.** Compounds containing π electrons absorb UV radiation because electrons can be promoted from lower energy π orbitals to higher energy π* orbitals. Therefore, molecules containing double bonds often absorb in the UV region.

CamScanner

**Q.11 Explain why transition metal complexes are coloured?**

**Ans.** Transition metal complexes contain partially filled d-orbitals which split into different energy levels in the presence of ligands. Electrons absorb visible light and move from lower to higher energy d-orbitals. The colour observed is the complementary colour of the light absorbed.

**Q.12 What is meant by complementary colour?**

**Ans.** The complementary colour is the colour observed when a compound absorbs a particular colour of visible light. For example, if a compound absorbs red light, it appears green, which is the complementary colour of red.

**Q.13 Differentiate between atomic emission and atomic absorption spectra.**

**Ans.** Atomic emission spectra consist of bright coloured lines produced when excited electrons return to lower energy levels. Atomic absorption spectra consist of dark lines formed when electrons absorb specific wavelengths and move to higher energy levels.

**Q.14 Explain the origin of line spectra.**

**Ans.** Line spectra arise because electrons can occupy only specific energy levels in an atom. When electrons move between these energy levels, radiation of specific wavelengths is emitted or absorbed, producing discrete spectral lines.

**Q.15 How can a mass spectrometer determine relative atomic mass?**

**Ans.** A mass spectrometer measures the masses and relative abundances of isotopes of an element. The relative atomic mass is then calculated as the weighted average of the isotopic masses.

$$\text{RAM} = \frac{\sum(\text{Isotopic mas} \times \%\text{abundance})}{100}$$

**Q.16 Why are relative atomic masses often non-integer values?**

**Ans.** Most elements exist as mixtures of isotopes having different masses and abundances. Therefore, the relative atomic mass is a weighted average of isotopic masses and is usually not a whole number.
**Example:** Chlorine has a relative atomic mass of 35.5.

**Q.17 Explain the significance of the molecular ion peak.**

**Ans.** The molecular ion peak ($M^+$) represents the intact molecule after ionization and provides the molecular mass of the compound. It is often the first step in identifying an unknown compound using mass spectrometry.

**Q.18 What information can be obtained from fragmentation peaks?**

**Ans.** Fragmentation peaks arise due to the breakdown of the molecular ion into smaller ions. These peaks provide information about the structure and arrangement of atoms in the molecule.
Thus, fragmentation patterns help in structure determination.

**Q.19 How can the number of carbon atoms be estimated from the M+1 peak?**

**Ans.** The M+1 peak mainly arises due to the presence of the carbon-13 isotope. The approximate number of carbon atoms can be estimated using:

$$n = \frac{\%M+1}{1.1}$$

where n is the number of carbon atoms.

**Q.20 Explain the origin of the M+1 peak.**

**Ans.** The M+1 peak is mainly produced due to the presence of the naturally occurring isotope carbon-($^{13}C$). Since approximately 1.1% of carbon atoms exist as $^{13}C$, compounds containing carbon show an M+1 peak.

**Q.21 How can chlorine be identified from a mass spectrum?**

**Ans.** Compounds containing chlorine show molecular ion peaks at M and M+2 with an intensity ratio of approximately 3:1. This pattern arises due to the natural abundances of $^{35}Cl$ and $^{37}Cl$.

$$^{35}Cl : {}^{37}Cl = 3 : 1$$

**Q.22 How can bromine be identified from a mass spectrum?**

**Ans.** Compounds containing bromine show M and M+2 peaks of almost equal intensity because bromine exists as two isotopes, $^{79}Br$ and $^{81}Br$, in nearly equal abundances.



$$^{79}Br : {}^{81}Br = 1 : 1$$

**Q.23 Why do bromine-containing compounds show equal M and M+2 peaks?**

**Ans.** Bromine has two naturally occurring isotopes, 79Br and 81Br, each having approximately 50% abundance. Therefore, both isotopes contribute equally to the molecular ion peaks, producing a 1:1 ratio.

**Q.24 Why do chlorine-containing compounds show a 3:1 peak ratio?**

**Ans.** Chlorine consists mainly of $^{35}Cl$ (75%) and $^{37}Cl$ (25%) Consequently, the molecular ion peaks corresponding to these isotopes appear in an approximate ratio of 3 : 1.

**Q.25 How can IR spectroscopy distinguish ethanol from ethanal?**

**Ans.** Ethanol shows a broad O–H absorption peak around 3200-3600 $cm^{-1}$, whereas ethanal shows a strong C=O absorption near 1700 $cm^{-1}$. Therefore, IR spectroscopy can easily distinguish between these compounds.

**Q.26 How can IR spectroscopy distinguish acetone from ethanol?**

**Ans.** Acetone contains a carbonyl group and therefore shows a strong absorption peak near 1700 $cm^{-1}$. Ethanol shows a broad O–H absorption band near 3300 $cm^{-1}$ but lacks the carbonyl peak.

**Q.27 How can IR spectroscopy identify phenol?**

**Ans.** Phenol shows a broad O–H absorption band around 3200-3600 $cm^{-1}$ due to the hydroxyl group attached to the aromatic ring. Aromatic C=C absorptions may also appear near 1600 $cm^{-1}$.

**Q.28 Why is spectroscopy important in organic chemistry?**

**Ans.** Spectroscopy provides information about molecular mass, functional groups and molecular structure. Therefore, it allows chemists to identify unknown compounds quickly and accurately.

**Q.29 Why are MS, IR and NMR often used together?**

**Ans.** Mass spectrometry provides molecular mass, IR spectroscopy identifies functional groups and NMR spectroscopy provides information about the arrangement of hydrogen atoms. Together, these techniques allow complete structure determination.

**Q.30 Explain the importance of spectroscopy in modern chemistry.**

**Ans.** Spectroscopy is an essential analytical tool used in research, medicine, pharmaceuticals and forensic science. It enables rapid identification and characterization of compounds with high accuracy and reliability.

## SELF-ASSESSMENT

**Total Mark: 30**

**Q.1 Encircle the correct option.** **(1 × 6 = 6)**

**(i) The speed of light in vacuum is approximately:**
(A) $3 \times 10^6$ m $s^{-1}$ (B) $3 \times 10^7$ m $s^{-1}$ (C) $3 \times 10^8$ m $s^{-1}$ (D) $3 \times 10^9$ m $s^{-1}$

**(ii) An IHD value of 1 indicates:**
(A) One ring or one double bond (B) One triple bond only
(C) Two double bonds (D) Three rings

**(iii) The O–H stretching absorption of alcohols appears around:**
(A) 1500-1700 $cm^{-1}$ (B) 2200-2300 $cm^{-1}$ (C) 3200-3600 $cm^{-1}$ (D) 400-800 $cm^{-1}$

**(iv) A compound containing two chlorine atoms shows molecular ion peaks in the ratio:**
(A) 1 : 1 (B) 3 : 1 (C) 9 : 6 : 1 (D) 1 : 2 : 1

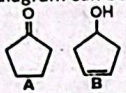
**(v) The types of transitions possible in UV-visible region for a compound with molecular formula $C_4H_8$ are:**
(A) $n \rightarrow \pi^*$ (B) $n \rightarrow \sigma^*$ (C) $\sigma \rightarrow \sigma^*$ (D) $\pi \rightarrow \pi^*$

**(vi) The IR spectrum of a compound X contains peak at 1560 $cm^{-1}$, 1690 $cm^{-1}$, and a broad peak between 2500-3200 $cm^{-1}$, Thus X is most likely:**
(A) An unsaturated ketone (B) An alkene
(C) An unsaturated carboxylic acid (D) An alcohol

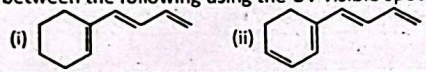
CamScanner

**Q.2 Write short answers of the following questions.** (2 × 8 = 16)

(i) Calculate the IHD for each of the following: I) $C_6H_6$ II) $C_6H_{12}$
(ii) Will $CH_3CHOHCH_3$ show a significant absorption in the UV-Vis region? Explain.
(iii) The mass spectrum of $CH_3Br$ is given: Identify the fragment against each peak.
(iv) Explain how the two isomers shown in the diagram can be distinguished using IR spectroscopy.




(v) The molecular formulas of the following compounds are given below:
but-1-ene: $C_4H_8$ but-1,3-diene: $C_4H_6$
(vi) Fine out the IHD for both of these compounds.
(vii) Show all the possible fragments of $C_7H_{16}$ and their (m/e) values in its mass spectrum.
(viii) How will you differentiate between the following using the UV visible spectroscopy.




**Q.3 Extensive Questions.** (4 + 4 = 8)

(a) Describe various possible electronic transitions in a compound having sigma, pi bonds, and non-bonding electrons.
(b) Explain two types of atomic spectrum.

## ENTRANCE TEST MCQs

1. **Halogen atoms are treated like hydrogen atoms in IHD calculations because they are:**
(A) Trivalent (B) Tetravalent (C) Monovalent D. Divalent
2. **A compound becomes visibly coloured when its absorption extends into approximately:**
(A) 1000-3000 nm (B) 4000-500 $cm^{-1}$ (C) 400-750 nm (D) 1-10 nm
3. **In a transmittance IR spectrum, a strong absorption is shown as:**
(A) A tall upward peak necessarily (B) No feature
(C) A mass-spectral line (D) A deep downward trough
4. **An element shows peaks at m/e 10 and 11 with heights 1 and 4. Its Ar is:**
(A) 10.5 (B) 11.0 (C) 10.8 (D) 10.2
5. **$C_3H_6O$, IHD 1, IR C=O at 1715 $cm^{-1}$, $M^+$ 58. Best structure?**
(A) Propene (B) Propanone (C) Propan-1-ol (D) Propane-1,2-diol
6. **$C_2H_6O$, broad IR at 3300 $cm^{-1}$, $M^+$ 46. Most likely compound?**
(A) Ethanol (B) Ethanal (C) Ethanoic acid (D) Ethene
7. **$C_6H_6O$, IHD 4, broad O – H IR, aromatic UV absorption. Likely structure?**
(A) Cyclohexanol (B) Hexanone (C) Ethane-1,2-diol (D) Phenol
8. **$C_3H_6O_2$ shows broad 2500–3300 $cm^{-1}$ and C = O near 1710 $cm^{-1}$. Likely compound?**
(A) Propanone (B) Propanamide (C) Propanoic acid (D) Propan-1-ol
9. **The $C_4H_6$ compound in the previous question consumes 2 mol $H_2$ per mol. A possible structure is:**
(A) Butane (B) Cyclobutane (C) But-2-ene (D) Buta-1,3-diene
10. **$M^+$ 58, strong C = O near 1715 $cm^{-1}$, no $M^{+2}$ pair. Most likely compound?**
(A) Chloromethane (B) Phenol (C) Propanone (D) Bromomethane

**Answers Key**

| 1. C | 2. C | 3. D | 4. C | 5. B | 6. A | 7. D | 8. C | 9. D | 10. C |
|---|---|---|---|---|---|---|---|---|---|



30 CHAPTER

# SPECTROSCOPY-2
# NMR

**Student Learning Outcomes (SLOs)**

[C-12-E-19 to C-12-E-28]
- Explain the use of tetramethylsilane, TMS, as the standard for chemical shift measurement.
- Recognize the need for deuterated solvents, e.g., $CDCl_3$, when obtaining a proton NMR spectrum.
- Analyze the different environments of protons present in a simple molecule using a $^1H$ (proton) NMR spectrum.
- Predict the chemical shifts and splitting patterns of the protons in a given molecule.
- Use a $^1H$ (proton) NMR spectrum to deduce relative numbers of each type of proton present, the number of equivalent protons on the carbon atom adjacent to the one to which the given proton is attached.
- Describe the identification of O–H and N–H protons by proton exchange using $D_2O$.
- Deduce possible structures for the molecule.
- Predict the number of peaks in a $^{13}C$ NMR spectrum for a given molecule.
- Analyze the different environments of carbon atoms present in a simple molecule using a $^{13}C$ NMR spectrum.
- Use a $^{13}C$ NMR spectrum to deduce possible structures of a simple molecule.

### Common Types of NMR Spectroscopy:

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful analytical technique which is extensively used in chemistry, polymer industry, study of proteins and natural products, environment monitoring, and medical field. In chemistry, this technique is particularly used for the identification of organic compounds and determination of their structures. Proton ($^1H$) NMR and carbon-13 ($^{13}C$) NMR are two most commonly used methods in this regard.

## PRINCIPLE OF PROTON (1H) NMR

**Q.1 Discuss the principle of proton ($^1H$) NMR with the help of methanol as an example.** S/Q

**Ans.** NMR spectroscopy is based on the magnetic properties (nuclear spin) of nuclei. Atoms with odd mass numbers usually show signals on NMR. The atomic nuclei of these atoms, like hydrogen ($^1H$) and carbon-13 ($^{13}C$) behave like a tiny magnets. In the absence of a magnetic field, all the nuclei have random orientation and have the same energy. When placed in a strong magnetic field, these nuclei align themselves either with or against the field and give rise to two spin states i.e., low energy state and high energy state **(Figure)**.

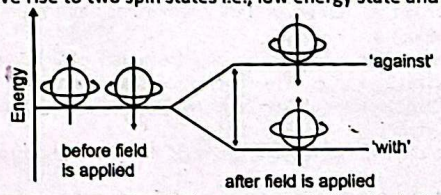



**Figure: Alignment of nuclei in a magnetic field and spin flipping**

**Did You Know?**
The atoms with even atomic and mass numbers have generally equal number of protons and neutrons in their nuclei. As their magnetic fields cancel out each other, there is no net magnetic field of such nuclei e.g., $^{12}C$.

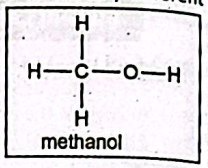
CamScanner

**Q.2 What is spin flipping and NMR spectrum?** L/Q

**Ans.** Every nucleus has its own characteristic resonance frequency depending upon the applied magnetic field. By irradiating with radio waves, the nuclei at low energy state can absorb energy and move to higher energy state (spin flipping). When they return to their original states, they emit energy which is detected and converted into an NMR spectrum (plural spectra).

➢ **Factor:**

The exact energy required to flip a nucleus depends upon its position in a compound and the surrounding atoms, collectively known as the molecular environment. Thus, NMR can be used to identify different hydrogen atoms lying in different environments within one molecule.



methanol

➢ **Example: Methanol**

In the methanol ($CH_3-OH$) molecule there are two types of hydrogen atoms.

i. three hydrogen atoms are attached to a carbon atom

ii. one hydrogen atom is bonded to an oxygen atom.

➢ **Inference:**

These methyl ($-CH_3$) hydrogens and hydroxyl (O – H) hydrogen lie in different environment, so they absorb different amount of energy (different frequency of radio waves) for flipping.

By irradiating with radio waves, the nuclei in the lower energy state can absorb energy and move to the higher energy state (spin flipping). When they return to their original states, they emit energy which is detected and converted to an NMR spectrum (plural spectra).

## SOLVENTS FOR NMR SPECTROSCOPY

**Q.3 Describe the solvents used for NMR spectroscopy.** S/Q

**Ans.** In the $^1H$ NMR analysis the sample to be analyzed is dissolved in excess solvent to prepare a solution.

➢ **Solvents:**

- Ordinary solvents contain hydrogen atoms which produce strong signals and cause interference in the spectrum of the sample. To avoid this problem, deuterated solvents such as $CDCl_3$ (deuterated chloroform) or $CD_3OD$ (deuterated methanol), are used.
- If regular $CHCl_3$ is used as a solvent, the signal from its single proton ($^1H$) would be intense enough to completely overlap and mask the weaker signals arising from the protons in the actual sample.
- In $CHCl_3$, hydrogen (H) is replaced with its isotope Deuterium (D). Deuterium requires a different frequency of radio waves for flipping, hence it neither absorbs radio frequency provided to the sample solution nor its peak appears in the $^1H$ NMR spectrum. This makes the solvent "silent", and only the signals of the sample are observed in the spectrum.

## CHEMICAL ENVIRONMENT AND CHEMICAL SHIFT (δ)

**Q.4 Describe chemical environment and chemical shift (δ)?** L/Q

**Ans.** Chemical shift is an important parameter in NMR spectroscopy and represents the position of a signal relative to a reference compound.

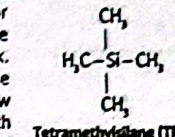
(OR) Chemical shift is the difference in resonance energy frequency of a nucleus in a compound relative a standard reference compound, due to its different electronic environment.

- Tetramethylsilane, $Si(CH_3)_4$ (commonly known as TMS) is used as the standard reference and its signal is assigned a value of 0.0 ppm.
- All other signals due to the hydrogen nuclei (protons) in the sample compounds are measured relative to this **TMS zero point.**
- **Chemical shift, Definition:** *The position of a peak in a $^1H$ NMR spectrum relative to TMS peak is called the chemical shift (δ).*
- **Unit:** It is measured in parts per million (ppm) unit. Chemical shift indicates the electronic environment of a proton.
- Protons in different environments have different δ values, while those lying in same environment have same δ value.



**Did You Know?**

TMS is particularly suitable as a standard compound for NMR because all 12 of its protons have the same chemical environment and produce a single sharp peak. Moreover, the protons on TMS appear at the extreme right region of the spectrum (due to the low electronegativity of silicon) and do not overlap with most organic proton signals. TMS is chemically inert and volatile, which makes it easy to remove after use.



Tetramethylsilane (TMS)

➢ **Example: $^1H$ NMR Spectrum of Methanol**

In the $^1H$ NMR spectrum of methanol (Figure), the relative position of peak for methyl ($-CH_3$) hydrogens at 3.35 ppm compared to 0.0 ppm of TMS is the chemical shift of these protons. Similarly, O – H hydrogen of methanol has a chemical shift of 4.80 ppm.

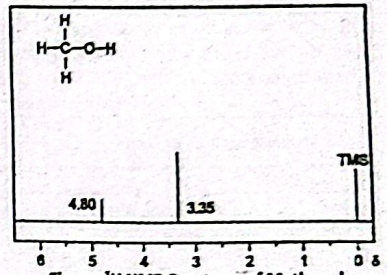


Figure: $^1H$ NMR Spectrum of Methanol

➢ **Observation:**

Protons ($^1H$) in a molecule are surrounded by electrons and this electron density affects the appearance of an NMR spectrum. Protons in different parts of a molecule are in different "**environments**" because of the atoms and bonds near them.

➢ **Case I:**

***All the protons ($^1H$) found in chemically identical environments within a molecule are chemically equivalent, and they exhibit the same chemical shift in the $^1H$ NMR spectra of that molecule.*** All the protons in TMS, methane, ethane, benzene and propanone (acetone) are chemically equivalent. Methane gives rise to a single absorption peak in its $^1H$ NMR spectrum **(Figure).**

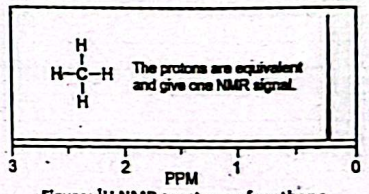
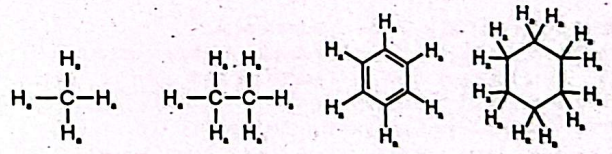


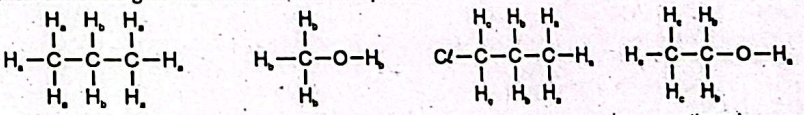
Figure: $^1H$ NMR spectrum of methane


methane ethane benzene cyclohexane

**All the hydrogen atoms in these molecules have same chemical environment**

➢ **Case II:**

Consider a molecule which has sets of protons that are chemically different from one another, have different chemical shift and give rise to more than one peaks.


propane methanol 1-chloropropane ethanol

Molecules having two different chemical environments for protons

Molecules having three different chemical environments for protons

CamScanner

➢ **Example: Ethanol ($C_2H_5OH$)**

A proton on a $-CH_3$ group is different from the one on $-CH_2-$ and O – H in **ethanol ($C_2H_5OH$)** molecule. The chemical shift of a proton ($^1H$) is affected by the electron density of its surrounding chemical environment. Protons surrounded by high electron density (alkyl groups) have lower chemical shift values, whereas protons surrounded by a low electron density (near electronegative atoms like F, O, N, Cl etc.) appear at high chemical shift values.

➢ **Example: Methyl ($-CH_3$) Protons in the $^1H$ NMR Spectrum of Methanol**

Methyl ($-CH_3$) protons in the $^1H$ NMR spectrum of methanol appear at 3.35 ppm due to a higher electron density around them as compared to O – H proton, which appears at 4.80 ppm due to the presence of electronegative oxygen next to it (Figure).

A $^1H$ NMR spectrum has a **chemical shift (δ) range of (0–13 ppm)**. The chemical shifts for different environments of protons have been given in Table. This data table is helpful in identifying and predicting the environment of protons in $^1H$ NMR spectrum of an unknown compound.

**Table: Chemical Shifts of Some Common Types of Protons**

| Environment of Proton | Examples | Chemical Shift Range δ (ppm) |
|---|---|---|
| Alkyl (alkanes) | $-CH_3$, $-CH_2-$, > CH – | 0.5-1.5 |
| Alkyl next to C = O (ketone/ester) | $CH_3-C=O$, $-CH_2-C=O$, > CH – C = O | 2.0-2.6 |
| Alkyl next to aromatic ring | $CH_3-Ar$, $-CH_2-Ar$, > CH – Ar | 2.3-3.0 |
| Alkyl next to electronegative atom (halogenoalkanes, alcohols) | $CH_3-O$, $-CH_2-O$, $CH_3-Cl$, $-CH_2-Cl$ | 3.0-4.5 |
| Vinylic (alkenes) (C = C–) | > C = CHR | 4.5-6.0 |
| Aromatic (attached to aromatic ring) | Ar – H | 6.5-9.0 |
| Aldehyde | RCHO | 9.0-10.0 |
| Alcohol | ROH | 0.5-6.0 |
| Phenol | Ar – OH | 4.5-7.0 |
| Carboxylic acid | RCOOH | 9.0-13.0 |
| Alkyl amine | R – NH – | 1.0-5.0 |
| Aryl amine | $Ar-NH_2$ | 3.0-6.0 |
| Amide | RCONHR | 5.0-12.0 |

## QUICK CHECK 30.1

**a) Explain why the 12 protons in TMS produce only a single peak.**

**Ans.** TMS **(tetramethylsilane)**, i.e., $Si(CH_3)_4$ contains four identical methyl groups attached symmetrically to the silicon atom. Thus, All **12 hydrogen** atoms are in exactly the same chemical environment and absorb at the same magnetic field strength (radiofrequency).

Hence, all 12 protons give **one single signal (peak)** in the 1H NMR spectrum.

So, TMS gives a single peak because all 12 protons are chemically equivalent.

**b) Identify how many chemical environments are there for protons in the following molecules. Also predict the expected chemical shift of the protons in each environment.**

**i) 1,2-dichloroethane ii) propane iii) propan-2-ol iv) butan-2-one**

**Ans.**

**i) 1,2-dichloroethane**

**Structure:** $ClCH_2-CH_2Cl$

The molecule is symmetrical, so both hydrogen atoms are equivalent.

Number of proton environments: 1

**Chemical shift:**

Hydrogens attached to carbons bearing chlorine atoms are strongly deshielded. δ ≈ 3.7 ppm

**ii) Propane**

**Structure:** $CH_3-CH_2-CH_3$

There are two proton environments:

1. Terminal $CH_3$ groups (equivalent)
2. Central $CH_2$ group

**Number of proton environments, Chemical shifts:**

| Proton type | Chemical shift |
|---|---|
| $CH_3$ (6 H) | 0.9 ppm |
| $CH_2$ (2 H) | 1.3 ppm |



**iii) Propan-2-ol**

**Structure:** $CH_3CHOHCH_3$

**Proton environments:**

1. Two equivalent $CH_3$ groups
2. Methine proton (CH)
3. Hydroxyl proton (OH)

**Number of proton environments:** 3

**Chemical shifts:**

| Proton type | Chemical shift |
|---|---|
| $CH_3$ | 0.9–1.0 ppm |
| CH attached to OH | 3.8–4.2 ppm |
| OH | 1–5 ppm (variable) |

**iv) Butan-2-one**

**Structure:** $CH_3COCH_2CH_3$

**Proton environments:**

1. $CH_3CO-$
2. $CH_2$
3. Terminal $CH_3$

**Number of proton environments:** 3

**Chemical shifts:**

| Proton type | Chemical shift |
|---|---|
| $CH_3CO-$ | 2.1 ppm |
| $CH_2$ | 2.4–2.6 ppm |
| Terminal $CH_3$ | 0.9–1.0 ppm |

**e) What proton environment does a signal at δ 7.5 ppm likely represent?**

**Ans.** Signals around **7–8 ppm** are characteristic of **aromatic protons** attached to a benzene ring. Therefore, a signal at **7.5 ppm** most likely corresponds to, aromatic proton (Ar-H) of a benzene ring

**Examples include:** Benzene, Toluene, Phenol.

# INTERPRETATION OF $^1H$ NMR SPECTRA

## Chemical Shift and Relative Number of Protons

**Q.5 Describe the low resolution $^1H$ NMR spectrum interpretation.** Exercise D/Q.4

**Ans.** A low-resolution $^1H$ NMR spectrum provides three main pieces of information about the structure of a compound; the number of different proton environments in the molecule, types of these environments, and the relative number of protons in each environment. To extract this information from a $^1H$ NMR spectrum, three parameters are carefully analysed; total number of peaks in the spectrum, position of each peak (chemical shift), and the area under each peak. ***The number of peaks in a $^1H$ NMR spectrum corresponds to the number of different chemical environments for protons present in the molecule.*** Each peak in the spectrum stands for a different chemical environment.

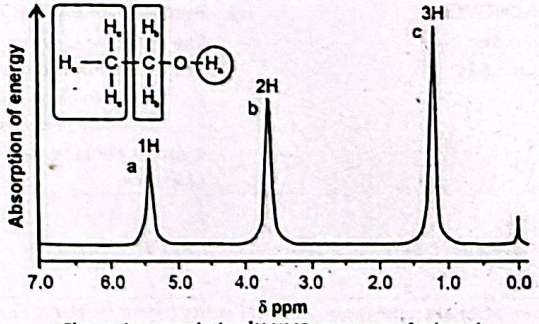



**Figure: Low-resolution $^1H$ NMR spectrum of ethanol**

➢ **Low-Resolution $^1H$ NMR Spectrum of Ethanol ($CH_3CH_2OH$):**

As illustrated in above Figure, the spectrum of ethanol ($CH_3CH_2OH$) has three peaks which shows that there are three different proton environments in ethanol molecule i.e., the $CH_3$ protons, the $CH_2$ protons, and the OH proton.

***Chemical shift of each peak corresponds to the type of chemical environment of protons giving rise to that peak.*** The type of proton environment can be identified by comparing the chemical shifts to standard values (Table).

CamScanner

In the spectrum of ethanol (Figure), the peak at 5.4 ppm represents the O – H proton in a low electron density (deshielded) environment (OH). The peak having chemical shift 3.7 ppm can be identified as $-CH_2-$ next to oxygen, while the signal at 1.2 ppm can be identified as methyl group ($-CH_3$ protons).
**The area under each peak is proportional to the number of protons giving rise to that peak.**

➢ **Relative Peaks of $^1H$ NMR Spectrum of Ethanol:**
In the $^1H$ NMR spectrum of ethanol (Figure), peaks are labeled $^1H$, $^2H$ and $^3H$ to show relative deshielded environment peak areas in 1:2:3 ratio. This ratio matches with the number of protons in each environment ($-OH$ has 1, $-CH_2$ has 2 and $-CH_3$ has 3 protons).

➢ **Conclusion:**
Analysis of the above spectrum shows that there are three kinds of chemical environments for protons, so three signals are observed. The intensity ratio shows that they are present in the ratio of 1:2:3. The sum of number of each type of protons gives the total number of protons present in the molecule. Hence, there are total 6 hydrogen (1+2+3) atoms in an ethanol ($C_2H_5OH$) molecule.

## ☑ QUICK CHECK 30.2

**a) What does the number of signals in a $^1H$ NMR spectrum represent?**

**Ans.** The number of signals in a $^1H$ NMR spectrum represents the number of **different proton (hydrogen) environments** present in the molecule.
Number of signals = Number of chemically non-equivalent proton environments
**e.g.,** $CH_3-CH_2-OH$ has three proton environments i.e. $CH_3$, $CH_2$ and OH and gives three peaks.

**b) Predict the number of peaks that will appear in the $^1H$ NMR spectra of the following molecules?**
**(i) 1,1,2,2-dichloroethane (ii) butane (iii) propan-2-ol (iv) pentan-3-one (v) benzene**

**Ans.**

**i) 1,1,2,2-Dichloroethane ($CHCl_2$)**
The molecule is symmetrical, so both hydrogen atoms are equivalent.
1 signal

**ii) Butane ($CH_3CH_2CH_2CH_3$)**
There are two proton environments: Terminal two $CH_3$ groups = 6 H and Internal two $CH_2$ groups = 4 H.
2 signals

**iii) Propan-2-ol ($CH_3CHOHCH_3$)**
Three proton environments:
- Two $CH_3$ groups = 6 H
- CH = 1 H
- OH = 1 H

3 signals

**iv) Pentan-3-one ($CH_3CH_2COCH_2CH_3$)**
The molecule is symmetrical.
**Proton environments:**
- Two equivalent $CH_3$ groups = 6 H
- Two equivalent $CH_2$ groups = 4 H

2 signals because carbonyl group is the center of ketone.

**v) Benzene ($C_6H_6$)**
All six aromatic protons are equivalent because of the symmetry of benzene.
**1 signal**

**c) Predict the number of peaks and their chemical shifts in the $^1H$ NMR spectrum of bromoethane ($CH_3-CH_2-Br$).**

**Ans.**
**Proton Environments:**
1. $CH_3$ group
2. $CH_2Br$ group

Therefore, 2 signals (due to two different proton environments)

**Approximate chemical shifts:**

| Proton Environment | Chemical Shift |
|---|---|
| $CH_3^-$ | ~ 1.2 ppm |
| $-CH_2Br$ | ~ 3.4 ppm |



The $CH_2Br$ protons appear further downfield because bromine is electronegative and causes deshielding.

**d) How many signals will be observed in the $^1H$ NMR spectrum of 2-chlorobutane. Draw its structure and identify the hydrogen atoms which will showing different values of chemical shift.**

**Ans.** **Structure:** $CH_3-CH(Cl)-CH_2-CH_3$

**Proton Environments:**
1. Left $CH_3$ = 3 H
2. CH attached to Cl = 1 H
3. $CH_2$ = 2 H
4. Right $CH_3$ = 3 H

Thus, 4 signals

| Proton Environment | Chemical Shift |
|---|---|
| Left $CH_3$ | 1.5 ppm |
| CH attached to Cl | 3.9 ppm |
| $CH_2$ | 1.7 ppm |
| Right $CH_3$ | 1.0 ppm |

**Highest Chemical Shift:**
The proton attached directly to the carbon bearing chlorine experiences maximum deshielding.
CH(Cl)

**e) Arrange the different protons in $CH_3CH_2CH(CH_3)OH$, in increasing order of their peak areas in its NMR spectrum.**

**Ans.** **Molecule:**

$$\underset{(a)}{CH_3}-\underset{(b)}{CH_2}-\underset{\underset{CH_3}{|}\ (c)\ (d)}{CH}-\underset{(e)}{OH}$$

**Nominal Integrations (Number of equivalent protons):**

| Proton Type | Label | No. of H | Expected Itegration |
|---|---|---|---|
| Hydroxyl proton | OH | 1 | 1 |
| Methine proton | CH (bearing OH) | 1 | 1 |
| Methylene protons | $CH_2$ | 2 | 2 |
| Methyl protons (on CH) | $CH_3$ | 3 | 3 |
| Methyl protons (terminal) | $CH_3$ | 3 | 3 |

**Increasing order of peak area (integration):**

$$OH\ (1H) = CH\ (1H) < CH_2\ (2H) < CH_3\ (3H) = CH_3\ (3H)$$

Same number of protons (1H each) | Two protons | Both methyl groups have three equivalent atoms

**Note:** OH proton (exchangeable may sometimes show a smaller or broader signal, so its integration can be less reliable.)

a = $CH_3$ (terminal) b = $CH_2$ c = CH(bearing OH) d = $CH_3$ (on CH) e = OH

## ➲ Splitting of Peaks

**Q.6 Discuss the splitting of peaks with examples: Case I: Ethanol. Case II: Ethane** L/Q

**Ans.** The NMR signals of protons are not only affected by the nearby electrons, but also by protons on the adjacent atomic nuclei.

### ➲ Explanation of Splitting of Peaks:

This effect can be observed by a high-resolution NMR. When a high resolution $^1H$ NMR spectrum of a molecule is studied, it reveals that each peak is often made up of a cluster of sub-peaks. This is due to the splitting of each signal due to the presence of protons ($^1H$) on adjacent carbon atoms.
*The splitting of signals into multiple peaks (e.g., doublets, triplets, quartets) indicates the number of protons ($^1H$) on the adjacent (neighbouring) carbon atom.*
Number of sub-peaks can be calculated by using ' n + 1 ' rule. A signal usually splits into n + 1 subpeaks, where n is the number of protons on adjacent carbon atoms.

CamScanner

Number of sub-peaks = n + 1

(Where n = the number of protons on the adjacent carbon atom).

### Case I: Ethanol

In the high-resolution $^1H$ NMR spectrum of ethanol,

(i) The $-CH_3$ peak is split into three sub-peaks (known as triplet) because the number of protons on adjacent carbon is 2(2 + 1 = 3).

(ii) $CH_2$ - peak is split into four sub-peaks (known as a quartet) because there are 3 protons on its adjacent carbon (3 + 1 = 4).

(iii) The –OH signal is not split because hydrogen is bonded to an oxygen atom instead of carbon atom (Figure).

**Note:** This is important to note that – OH and – NH protons usually do not show splitting, so these appear as singlet peak. Similarly, chemically equivalent protons do not cause splitting of their neighbouring protons.

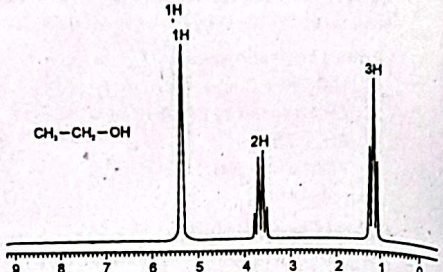



Figure: High-resolution $^1H$ NMR spectrum of ethanol

### Case II: Ethane ($CH_3 - CH_3$)

The ethane ($CH_3 - CH_3$) molecule has two methyl groups attached to each other. Peak does not show splitting because all the hydrogen atoms in ethane are chemically equivalent (Figure).

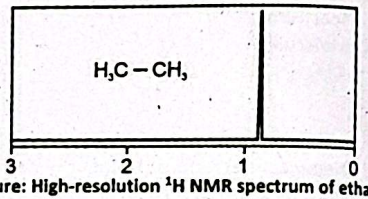



Figure: High-resolution $^1H$ NMR spectrum of ethane

### Sub-Peaks

The number of sub-peaks for different number of neighbouring protons and their appearance given in Table is useful to recognise splitting patterns in high-resolution $^1H$ NMR spectra.

**Table: Common splitting patterns in high-resolution $^1H$ NMR spectra**

| No. of Protons on Adjacent Carbon Atom (n) | Number of Sub-Peaks (n + 1) | Splitting Pattern | Abbreviation | Appearance of Split Peak |
|---|---|---|---|---|
| 0 | 1 | Singlet | s |  |
| 1 | 2 | Doublet | d |  |
| 2 | 3 | Triplet | t |  |
| 3 | 4 | Quartet | q |  |



## QUICK CHECK 30.3

a) Calculate the number of sub-peaks for each signal in the high-resolution spectra of the following compounds?
i) butan-2-ol ii) 1-chloropropane iii) propanone iv) 2,2-dimethylpropane
v) methanol vi) 2-methylpropan-2-ol

Ans.

**i) butan-2-ol**

Structure: $CH_3 — CH(OH) — CH_2 — CH$

Proton environments and splitting:

| Proton Environment | Adjacent H (n) | Multiplicity |
|---|---|---|
| Left $CH_3$ | 1 | Doublet (2 peaks) |
| CH | 5 (3 + 2) | Sextet (6 peaks) |
| $-CH_2$ | 4 (1 + 3) | Quintet (5 peaks) |
| Right $CH_3$ | 2 | Triplet (3 peaks) |
| OH | Usually no coupling (Zero) | Singlet (1 peak) |

Result: 2, 6, 5, 3, 1

**ii) 1-chloropropane**

Structure: $CH_3CH_2CH_2Cl$

Splitting:

| Proton Environment | Adjacent H | Multiplicity |
|---|---|---|
| $CH_3$ | 2 | Triplet (3 peaks) |
| Middle $CH_2$ | 5 | Sextet (6 peaks) |
| $CH_2Cl$ | 2 | Triplet (3 peaks) |

Result: 3, 6, 3

**iii) Propanone**

Structure: $CH_3COCH_3$

Both methyl groups are equivalent and adjacent carbonyl carbon contains no hydrogens.

n = 0

Thus, 1 signal as a singlet.

Result: 1

**iv) 2,2-dimethylpropane**

Structure: $(CH_3)_4C$

All twelve hydrogens are equivalent and there are no adjacent hydrogens (All $CH_3$ groups, n = 0).

Therefore, 1 signal as a singlet.

Result: 1

**v) Methanol**

Structure: $CH_3OH$

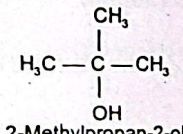
In most cases, the OH proton exchanges rapidly and does not couple.

| Proton Environment | Multiplicity |
|---|---|
| $CH_3$ | Singlet (1 peak) |
| OH | Singlet (1 peak) |

Result: 1,1

**vi) 2-methylpropan-2-ol**

Structure:




2-Methylpropan-2-ol
(tert-butanol)

Molecular formula: $C_4H_{10}O$
Total signals: 2

| Proton | Number of H | Adjacent (n) hydrogens | Multiplicity (n+1) | Number of sub-peaks |
|---|---|---|---|---|
| $(CH_3)_3C-$ | 9 (all equivalent) | 0 (on adjacent C There are no H's) | Singlet (0 + 1 = 1) | 1 |
| –OH | 1 | 0 (rapid exchange, no coupling) | Singlet (0 + 1 = 1) | 1 |

CamScanner

## ➲ Identification of O – H and N – H Protons in $^1H$ NMR Spectrum

**Q.7 How O – H and N – H proton in $^1H$ NMR spectrum are identified?** LO

**Ans.** The hydrogen atoms in O – H (alcohols or carboxylic acids) and N – H (amines or amides) are easily exchangeable, due to which they show a wide range of chemical shift value for their singlet peak.

$$CH_3—CH_2—O—H^a + H^b—O—H^b \rightleftharpoons CH_3—CH_2—O—H^b + H^a—O—H^b$$

Sometimes, it becomes very difficult to identify these peaks in spectra.

➢ **Deuterium Exchange or $D_2O$ Shake:**

- A technique known as 'deuterium exchange' or '$D_2O$ shake' is used to detect whether the singlet in a $^1H$ NMR spectrum is actually due to the presence of an O – H or N – H hydrogen.
- In this method, the $^1H$ NMR spectrum of the compound is recorded which shows all the H atoms in the molecule including the O – H or N – H proton(s).
- A few drops of $D_2O$ are then added to the NMR sample tube, the solution is shaken well and its spectrum is recorded again.
- The peak belonging to O – H or N – H proton disappears in the second spectrum.

➢ **Comparison:**

Comparing both spectra confirms the identity of the peak arising due to N – H or O – H.

➢ **Explanation:**

The reason for this observation is that protons ($^1H$) attached to highly electronegative atoms like O or N are easily exchanged. When $D_2O$ is added to the sample solution, these hydrogens are quickly exchanged with the deuterium (D) atoms.

$$R—O—H + D_2O \rightleftharpoons R—O—D + HOD$$

➢ **Conclusion:**

As deuterium atom requires different energy for spin flipping as compared to $^1H$, it does not show a peak in the $^1H$ NMR spectrum making it 'invisible'.

### ☑ QUICK CHECK 30.4

**a) Why do O – H or N – H peaks disappear after a $D_2O$ shake in the NMR spectroscopy?**

**Ans.** When a sample is shaken with **$D_2O$ (deuterium oxide or heavy water)**, the hydrogen atom of the **O–H** or **N–H** group exchanges with deuterium (D).

➢ **For Alcohols:**

$$R—OH + D_2O \longrightarrow R—OD + HOD$$

➢ **For Amines:**

$$R—NH_2 + D_2O \longrightarrow R—NHD + HOD$$

or

$$R—NHD + D_2O \longrightarrow R—ND_2 + HOD$$

Since **deuterium ($^2H$)** does not give a signal in ordinary **$^1H$ NMR spectroscopy**, the original **O–H** or **N–H** proton peak disappears after the $D_2O$ shake.

Therefore, Disappearance of a peak after $D_2O$ shake confirms the presence of O – H or N – H protons.

**b) State the expected peak area and splitting patterns for ($-CH_2CH_2NH_2$).**

**Ans.** Structure: $—CH_2—CH_2—NH_2$

There are **three proton environments:**

1. $CH_2$ attached to carbon chain
2. $CH_2$ attached to $NH_2$
3. $NH_2$

➢ **Peak Areas (Integration ratio)**

| Proton Environment | Number of H | Relative Area |
|---|---|---|
| $CH_2$ | 2 | 2 |
| $CH_2NH_2$ | 2 | 2 |
| $NH_2$ | 2 | 2 |

Hence the integration ratio is: 2 : 2 : 2 or simply 1:1:1



➢ **Splitting Patterns:**

First $CH_2$ is adjacent to **2 protons** on the neighboring $CH_2$:

$n + 1 = 2 + 1 = 3$

- **Triplet**

Second $CH_2$ is adjacent to **2 protons** on the first $CH_2$:

$n + 1 = 2 + 1 = 3$

- **Triplet**

$NH_2$ protons usually undergo rapid exchange and generally do not couple with neighboring protons.

- **Broad singlet**

➢ **Final Answer:**

| Proton Environment | Peak Area | Splitting Pattern |
|---|---|---|
| First $CH_2$ | 2 | Triplet |
| Second $CH_2$ | 2 | Triplet |
| $NH_2$ | 2 | Broad singlet |

➢ **Integration ratio:** 2:2:2

## PREDICTION OF $^1H$ NMR SPECTRUM FOR A GIVEN MOLECULE

**Q.8 Write down the four step to predict $^1H$ NMR spectrum for a given molecule. Explain this $^1H$ NMR spectrum of chloroethane ($CH_3 – CH_2 – Cl$).** LO

**Ans.** After understanding the concepts of chemical environment, chemical shift and splitting of peaks, one can predict the $^1H$ NMR spectrum of a given molecule by analyzing its structure. This can be done in the following steps:

- **Step I: No. of Peaks:** Identify different proton environments in the molecule.
  Number of different environments = Number of peaks expected in spectrum
- **Step II: Chemical Shift:** Estimate the chemical shift (δ) for each set of protons having same chemical environment by using known ranges from the data table (Table 30.1). If the data table is not available, check the nearest bonds and atoms. The protons near electronegative elements have higher chemical shift (δ), while those with alkyl groups generally have lower chemical shift.
- **Step III: Splitting of Peaks:** Predict the splitting pattern of each peak by applying the ' n + 1 ' rule.
- **Step IV: Relative Peak Area:** Assign integration ratios according to the number of hydrogen atoms in each environment.

**Example 30.1:**

**Predict the $^1H$ NMR spectrum of chloroethane ($CH_3 – CH_2 – Cl$).**

**Solution:**

➢ **No. of Peaks**

Two different chemical environments are present in the molecule.

No. of peaks in the $^1H$ NMR spectrum of chloroethane = 2

➢ **Chemical Shift**

The $–CH_2–$ is attached to an electronegative element, it will show a higher value of chemical shift (3.0-4.5 ppm). The methyl protons will show lower value of chemical shift (0.5-1.5ppm).

➢ **Splitting of Peaks**

No. of sub-peaks for $–CH_3 = 2 + 1 = 3$ (The carbon adjacent to $–CH_3$ has 2 protons)

$–CH_3$ signal will split into a triplet.

No. of sub-peaks for $–CH_2– = 3 + 1 = 4$ (The carbon adjacent to $–CH_2–$ has 3 protons)

$–CH_2–$ signal will split into a quartet.

➢ **Relative Peak Area**

The ratio of peak area for $–CH_3$ and $–CH_2–$ will be 3:2.

CamScanner

## QUICK CHECK 30.5

For the compound $(CH_3)_2CHOH$, predict the following:

a) The number of peaks
b) The type of proton and chemical shift
c) The relative peak areas
d) The splitting pattern

**Ans.** For the compound:

$(CH_3)_2CHOH$

This is propan-2-ol (isopropyl alcohol).

➢ Structure: $CH_3 — CH(OH) — CH_3$

**a) Number of peaks**

There are three different proton environments:

1. Two equivalent $CH_3$ groups
2. One CH proton attached to OH
3. One OH proton

Therefore, 3 peaks

**b) Type of proton and chemical shift**

| Proton Type | Number of H | Approximate Chemical Shift |
|---|---|---|
| $CH_3$ | 6 | 0.9–1.3 ppm |
| CH attached to OH | 1 | 3.8–4.2 ppm |
| OH | 1 | 1–51 ppm (variable) |

**c) Relative peak areas**

The integration ratio corresponds to the number of protons in each environment:

- Two equivalent methyl groups = 6 H
- Methine proton = 1 H
- Hydroxyl proton = 1 H

Thus, 6:1:1

**d) Splitting pattern**

$CH_3$ Protons

Each $CH_3$ group is adjacent to the central CH proton (1 H).

Using the n + 1 rule:

1 + 1 = 2

Therefore, $CH_3$ gives a: **Doublet**

➢ **CH Proton**

The central CH proton is adjacent to six equivalent methyl protons (6 H).

6 + 1 = 7

Therefore, the CH proton gives a: **Septet (7 peaks)**

➢ **OH Proton**

The OH proton usually undergoes rapid exchange and generally does not couple with neighboring protons.

Therefore, it appears as a: **Broad singlet**

## DETERMINATION OF THE POSSIBLE STRUCTURE OF A MOLECULE FROM $^1$H NMR

**Q.9 How the structure of a compound is determined from the $^1$H NMR spectrum?** Exercise Q.5

**(OR) Describe the general rules for determination of the possible structure of a molecule from $^1$H NMR and discuss the ester according to these rules.** LQ

**Ans.** The structure of an unknown compound can also be deduced by analyzing its $^1$H NMR spectrum. It can be done by putting together the following key pieces of information like a puzzle. To determine the structure:

1. Count the number of peaks in the spectrum.

   No. of peaks = No. of different proton environments

2. Use the chemical shift of each peak to identify the nature and environment of protons (use data table).
3. Use peak area to find the actual number of hydrogen atoms for each peak (this gives the no. of hydrogen atoms present in each environment).
4. Analyze the splitting pattern and calculate the number of adjacent protons.

   No. of sub-peaks = n + 1

   n = No. of sub-peaks – 1

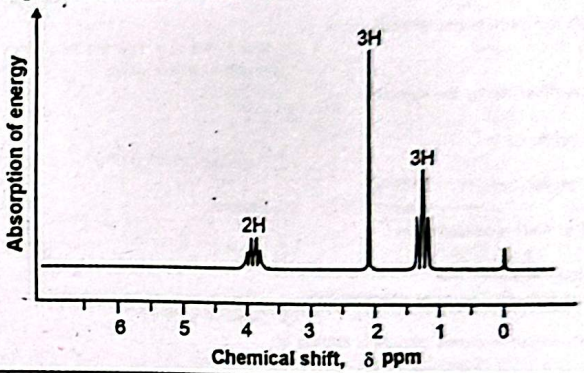
5. Combine this information to assemble the complete molecular structure.



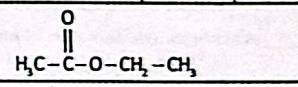
**Example 30.2**

**The $^1$H NMR spectrum of an ester is given below. Deduce the structure of the ester.**

**Solution:** The solution is given in the table below.




| No. | Peak Chemical Shift (ppm) | No. of Equivalent protons | Responsible Group | Splitting | No. of Neighbouring Protons |
|---|---|---|---|---|---|
| 1 | 1.3 | 3 H | $-CH_3$ next to $-CH_2$ | Triplet | 3 – 1 = 2H($CH_3$ . $CH_2$–) |
| 2 | 2.2 | 3 H | $-CH_3$ next to C = O | Singlet | 1 – 1 = 0($CH_3$ – C = O) |
| 3 | 3.9 | 2 H | $CH_2$ - next to an electronegative O atom | Quartet | 4 – 1 = 3($CH_3$ – $CH_2$ – O) |
| Overall Structure | | | | | |




## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Proton NMR spectroscopy is based on the magnetic properties of:**
   (A) Electrons (B) Atomic nuclei (C) Molecules (D) Ions
2. **Nuclei with odd mass numbers generally:**
   (A) Are NMR inactive (B) Show NMR signals (C) Have no nuclear spin (D) Are chemically inert
3. **Which isotope of carbon is NMR active?**
   (A) $^{12}$C (B) $^{13}$C (C) $^{14}$C (D) All isotopes
4. **In the absence of a magnetic field, nuclei have:**
   (A) Two spin states (B) Random orientation (C) Fixed orientation (D) No energy
5. **In a magnetic field, nuclei align:**
   (A) Randomly (B) Parallel or antiparallel to the field
   (C) Only parallel (D) Only antiparallel
6. **The transition from the low-energy state to the high-energy state is called:**
   (A) Resonance (B) Spin flipping (C) Fragmentation (D) Ionization
7. **Spin flipping occurs by absorbing:**
   (A) Infrared radiation (B) Radio waves (C) X-rays (D) Ultraviolet light
8. **The exact energy required for spin flipping depends on the:**
   (A) Colour of the compound (B) Molecular environment
   (C) Molecular mass only (D) Boiling point
9. **In methanol, the $-CH_3$ and $-OH$ protons:**
   (A) Have identical environments (B) Have different chemical environments
   (C) Produce no signals (D) Are chemically equivalent

CamScanner

10. **Ordinary solvents are avoided in $^1$H NMR because they:**
(A) Are expensive (B) Produce interfering proton signals
(C) Evaporate quickly (D) React with TMS

11. **A commonly used deuterated solvent is:**
(A) $CHCl_3$ (B) $CDCl_3$ (C) $CCl_4$ (D) $H_2O$

12. **Deuterated solvents are used because deuterium:**
(A) Gives a stronger proton signal (B) Resonates at a different frequency
(C) Is radioactive (D) Is chemically reactive

13. **Chemical shift is represented by the symbol:**
(A) λ (B) ν (C) δ (D) μ

14. **Chemical shift is measured in:**
(A) Hertz (B) Tesla (C) Parts per million (ppm) (D) Joules

15. **The reference compound used in $^1$H NMR is:**
(A) Benzene (B) Tetramethylsilane (TMS) (C) Ethanol (D) Methane

16. **The chemical shift of TMS is assigned as:**
(A) 1 ppm (B) 10 ppm (C) 0 ppm (D) 12 ppm

17. **Chemically equivalent protons have:**
(A) Different chemical shifts (B) The same chemical shift
(C) No signal (D) Different splitting

18. **Protons near electronegative atoms generally appear at:**
(A) Lower δ values (B) Higher δ values (C) Zero ppm (D) Negative ppm

19. **Alkyl protons usually resonate between:**
(A) 0.5–1.5 ppm (B) 3.0–4.5 ppm (C) 6.5–9.0 ppm (D) 9.0–13.0 ppm

20. **Aromatic protons generally appear between:**
(A) 0–2 ppm (B) 2–4 ppm (C) 6.5–9.0 ppm (D) 10–12 ppm

21. **The number of peaks in a low-resolution $^1$H NMR spectrum indicates the number of:**
(A) Carbon atoms (B) Different proton environments
(C) Double bonds (D) Functional groups only

22. **The area under an NMR peak represents the:**
(A) Molecular mass (B) Relative number of protons
(C) Number of carbon atoms (D) Boiling point

23. **Ethanol gives _____ peaks in its low-resolution $^1$H NMR spectrum.**
(A) One (B) Two (C) Three (D) Four

24. **High-resolution NMR reveals:**
(A) Molecular weight (B) Signal splitting (C) Density (D) Colour

25. **Signal splitting occurs due to:**
(A) Adjacent protons (B) Adjacent oxygen atoms (C) Molecular mass (D) Pressure

26. **The number of sub-peaks is determined by the:**
(A) Molecular formula (B) n+1 rule (C) Beer-Lambert law (D) Rf value

27. **If a proton has two equivalent neighbouring protons, its signal appears as a:**
(A) Singlet (B) Doublet (C) Triplet (D) Quartet

28. **A proton with three neighbouring protons appears as a:**
(A) Singlet (B) Doublet (C) Triplet (D) Quartet

29. **A singlet corresponds to:**
(A) No neighbouring protons (B) One neighbouring proton
(C) Two neighbouring protons (D) Three neighbouring protons

30. **The –OH proton usually appears as a:**
(A) Doublet (B) Triplet (C) Quartet (D) Singlet

31. **The –NH proton generally appears as a:**
(A) Quartet (B) Doublet (C) Singlet (D) Triplet

32. **The $D_2O$ shake test is used to identify:**
(A) Alkyl protons (B) Aromatic protons (C) O–H and N–H protons (D) Aldehyde protons

33. **After adding $D_2O$, O–H peaks:**
(A) Increase (B) Split (C) Disappear (D) Shift to 0 ppm

34. **During $D_2O$ exchange, hydrogen is replaced by:**
(A) Carbon (B) Oxygen (C) Deuterium (D) Nitrogen

35. **In predicting an NMR spectrum, the first step is to identify:**
(A) Functional groups only (B) Different proton environments
(C) Carbon atoms only (D) Molecular mass



36. **The splitting pattern mainly provides information about:**
(A) Molecular weight (B) Number of neighbouring protons
(C) Functional groups only (D) Number of carbon atoms

37. **Peak integration helps determine:**
(A) Molecular formula (B) Relative number of equivalent protons
(C) Bond angle (D) Hybridization

38. **Which of the following does not usually cause splitting?**
(A) $-CH_3$ (B) $-CH_2-$ (C) $-OH$ (D) $-CH-$

39. **The complete interpretation of a $^1$H NMR spectrum involves:**
(A) Number of peaks only (B) Chemical shift only
(C) Peak area only (D) Number of peaks, chemical shift, integration and splitting

40. **Proton NMR is primarily used to determine the:**
(A) Crystal structure (B) Structure of organic compounds
(C) Melting point (D) Density

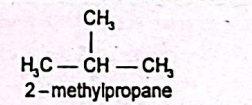
## $^{13}$C NMR SPECTROSCOPY

**Q.10 Discuss $^{13}$C NMR spectroscopy with chemical environment of carbon.** UQ

**Ans.** The nucleus of $^{12}C$ does not have magnetic properties because of even number of protons and neutrons (even mass number), and is, therefore, NMR inactive. However, the $^{13}C$ nucleus possesses magnetic spin due to its odd number of neutrons. On the basis of the magnetic properties of carbon-13 isotope, $^{13}C$ NMR spectra can be recorded for carbon compounds. Like $^1$H NMR, chemical shift (in ppm) in $^{13}C$ NMR is compared to the reference molecule TMS (δ = 0.0 ppm). However, the $^{13}C$ NMR has a range of chemical shift from 0–220 ppm. The deuterated chlorofom ($CDCl_3$) is usually used as a solvent which produces a small signal near 77 ppm.

### Chemical Environment of Carbon

The environment of a carbon atom determined by the types of atoms directly attached to it. Carbon atoms that are in the same environment are chemically equivalent, and show the same chemical shift. For example, both carbon atoms in ethane have the same environment. Carbon atoms in different environments are chemically non-equivalent and they will appear at different positions (chemical shifts) in $^{13}C$ NMR spectra. For example, all three methyl carbon atoms in 2-methylpropane have the same environment, while the tertiary carbon has different environment than these three carbon atoms.



2–methylpropane

The type of environment can be predicted by looking at atoms or bonds around carbon atoms. The chemical shifts of different carbon environments are given in Table.

**Table: Chemical shifts of different carbon environments**

| Hybridization of carbon atom | Environment of carbon atom | Examples | Chemical Shift Range δ (ppm) |
|---|---|---|---|
| $sp^3$ | Alkyl | $CH_3$, $-CH_2-$, > CH–, > C < | 0-50 |
| $sp^3$ | Carbon atom next to alkene or aryl ring | $-C-C=C$,  | 25-50 |
| $sp^3$ | Carbon atom next to carbonyl or carboxyl | $-C-COR$, $-C-COOR$ | 30-65 |
| $sp^3$ | Carbon atom next to halogen | $C-X$ | 30-60 |
| $sp^3$ | Carbon atom next to oxygen | $C-O$ | 50-70 |
| $sp^2$ | Alkene or aryl carbon |  > C = C < | 110-160 |
| $sp^2$ | Carboxyl carbon | $R-COOH$, $-COOR$ | 160-185 |
| $sp^2$ | Carbonyl carbon | $R-CHO$, $R-CO-R$ | 190-220 |
| sp | Nitrile | $R-C\equiv N$ | 100-125 |

CamScanner

## ➲ Predicting $^{13}C$ NMR Spectra

**Q.11 How $^{13}C$ NMR spectra predict?** L/Q

**Ans.** The $^{13}C$ NMR spectrum is simpler than $^{1}H$ NMR in which each peak (or signal) corresponds to a single, different environment or type of carbon atom. Chemical shift of each peak tells about its environment.

**The number of peaks = The number of different carbon environments**

$^{13}C$ NMR spectrum of ethane shows only one peak as both the carbon atoms have the same environment.

➢ **In Propane ($CH_3 - CH_2 - CH_3$):**

There are two types of carbon environments, the two terminal $-CH_3$ carbons have the same environment while the middle $-CH_2-$ carbon has a different environment.

The $^{13}C$ NMR spectrum of propane shows two peaks, one for the methyl carbon atoms while the other for $-CH_2-$ carbon atom.

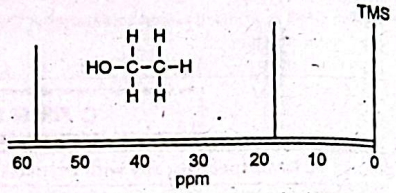



**Figure: $^{13}C$ NMR spectrum of ethanol**

➢ **In Ethanol:**

Two peaks are observed in the $^{13}C$ spectrum of ethanol ($CH_3 - CH_2 - OH$), due to the presence of two types of environments in this molecule (Figure). Analyzing the $^{13}C$ NMR spectrum of ethanol by using the data given in Table, it is evident that the peak at 18 ppm is for $-CH_3$ carbon, while the peak near 57 ppm is due to $-CH_2-$ carbon atom.

**Q.12 Differences between $^{13}C$ NMR and $^{1}H$ NMR.** S/Q

**Ans.** There are two main differences between $^{1}H$ NMR and $^{13}C$ NMR spectra.

i. The relative peak area in $^{13}C$ NMR is usually not proportional to the number of carbon atoms unlike $^{1}H$ NMR in which peak area shows the number of protons.

ii. The peaks do not show splitting, hence these appear as vertical lines.

### ☑ QUICK CHECK 30.6

**a) How many signals do you expect to observe in the $^{13}C$ NMR spectrum of butane? Justify your answer.**

**Ans. Structure of Butane:** $CH_3 — CH_2 — CH_2 — CH_3$

Because butane is symmetrical:

- The two terminal $CH_3$ carbons are equivalent.
- The two middle $CH_2$ carbons are equivalent.

Therefore, there are only **two different carbon environments.** So, 2 signals

**Signals:**

| Carbon Type | Equivalent Positions | Number of Equivalent Carbons |
|---|---|---|
| $CH_3$ (terminal) | C1 and C4 (equivalent) | 2 |
| $CH_2$ (middle) | C2 and C3 (equivalent) | 2 |

**b) Predict the $^{13}C$ NMR spectrum of butan-2-ol.**

**Ans. Structure:** $CH_3 — CH(OH) — CH_2 — CH_3$

All four carbon atoms are in different environments.

Therefore, 4 signals

Approximate chemical shifts:

| Carbon Atom | Carbon Type | Chemical Shift (ppm) |
|---|---|---|
| $CH_3 — CH(OH)$ | Methyl | 20–25 |
| $CH(OH)$ | Carbon attached to O | 65–75 |
| $CH_2$ | Methylene | 30–40 |
| Terminal $CH_3$ | Methyl | 10–15 |



Thus the $^{13}C$ NMR spectrum consists of four peaks approximately at: 10, 25, 35, 70 ppm

**c) Predict the chemical shift of carbon atoms in propanoic acid.**

**Ans. Structure:** $CH_3CH_2COOH$

There are three different carbon environments.

| Carbon Atom | Environment | Approximate Chemical Shift |
|---|---|---|
| $CH_3$ | Alkyl carbon, (most shielded) | 10–15 ppm |
| $CH_2$ | Carbon adjacent to carbonyl | 20–35 ppm |
| COOH carbon | Carboxylic acid carbonyl carbon | 160–185 ppm |

Therefore, the expected signals occur approximately at: 12 ppm, 30 ppm, 180 ppm

## ➲ Determination of Structure of a Molecule

**Q.13 Write a detailed note on the determination of the structure of a compound from its $^{13}C$ NMR spectrum.** Exercise Q.5

**(OR) How determination of structure of a molecule is done?** L/Q

**Ans.** The $^{13}C$ NMR a spectrum can be used to figure out the structure of a molecule. The steps during the analysis of a spectrum are:

**i. Count the Peaks**

The number of peaks in the spectrum tells the number of different types (environments) of carbon atoms in the molecule. If a molecule has 5 carbon atoms but only 3 peaks, it means there are 2 pairs of carbons, which are identical (chemically equivalent).

**ii. Look at the Positions of Peak (Chemical Shift δ)**

The position (ppm value) of each peak tells whether the carbon atom is present in an alkane, alkene, alkyne, aromatic or carbonyl compound. The assignment of the chemical shift value can be made according to the data provided in Table.

**iii. Work out the spectrum for possible structures**

Use the information from the peak count and positions to draw possible structures that fit the molecular formula of the compound. If the formula of a compound is $C_4H_{10}O$ and its $^{13}C$ NMR spectrum shows 3 peaks (Figure).

It means that 3 different carbon environments are present in the molecule. The three possible molecules for this formula are butan-1-ol, butan-2-ol and 2methoxypropane. The structure of the unknown compound cannot be butan-1-ol or butan-2-ol (which are expected to show 4 peaks). It must be a more symmetrical structure with 3 peaks: 2-methylpropan-1-ol with two equivalent methyl ($CH_3$) groups at 19.0 ppm, one methane (CH) carbon, slightly de-shielded due to branching at 30.5 ppm and one methylene ($CH_2$) bonded directly to the hydroxyl group at 69.0 ppm

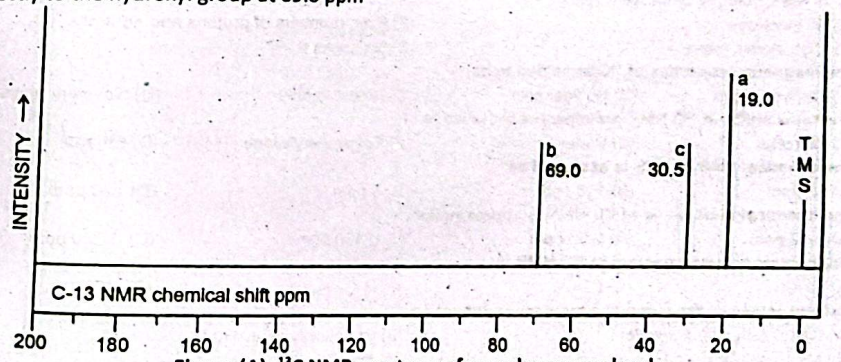



**Figure (A): $^{13}C$ NMR spectrum of an unknown molecule**

CamScanner

## QUICK CHECK 30.7

**Draw the structures of butan-1-ol and butan-2-ol.**

**i) Using the spectrum given in Figure (A), explain why this spectrum does not match with the structures of these two molecules.**

**ii) Which peaks (mention chemical shift) would you expect in the spectra of butan-1-ol and butan-2-ol?**

**Ans. Structures of Butan-1-ol and Butan-2-ol**

**Butan-1-ol:** $CH_3—CH_2—CH_2—CH_2—OH$

**Butan-2-ol:** $CH_3—CH(OH)—CH_2—CH_3$

**i)** Both **butan-1-ol** and **butan-2-ol** are alcohols and therefore their spectra should contain:

- A **broad O–H absorption** at approximately: 3200–3600 cm
- A carbon attached to oxygen giving signals around: 50–75 ppm ($^{13}C$ NMR) or 3–4 ppm ($^1H$ NMR)

If the spectrum in Figure (A) **does not show an O–H peak** (or does not contain signals corresponding to a carbon attached to oxygen), then the compound cannot be either butan-1-ol or butan-2-ol. Moreover,

- **Butan-1-ol** contains **4 different carbon environments** in $^{13}C$ NMR (4 peaks).
- **Butan-2-ol** also contains **4 different carbon environments** in $^{13}C$ NMR (4 peaks).

If the spectrum shows a different number of signals, it cannot correspond to either molecule.

**ii) Butan-1-ol (Approximate 4 peaks)**

| Proton Environment | Approximate Chemical Shift |
|---|---|
| C – OH | ~ 61 ppm |
| Internal $CH_2$ group | ~ 34 ppm |
| $CH_2$ attached next to $CH_3$ | ~ 18 ppm |
| Terminal $CH_3$ | ~ 13 ppm |

**Butan-2-ol (Approximate 4 peaks)**

| Proton Environment | Approximate Chemical Shift |
|---|---|
| C – OH | ~ 69 ppm |
| $CH_2$ carbon | ~ 31 ppm |
| $CH_3$ adjacent to C – OH | ~ 22 ppm |
| Terminal $CH_3$ Carbon | ~ 9 ppm |

## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Which isotope of carbon is NMR active?**
   (A) $^{12}C$ (B) $^{13}C$ (C) $^{14}C$ (D) Both $^{12}C$ and $^{14}C$
2. **$^{12}C$ is NMR inactive because it has:**
   (A) No electrons (B) Even numbers of protons and neutrons
   (C) High atomic mass (D) No nucleus
3. **The magnetic properties of $^{13}C$ arise due to its:**
   (A) Electron cloud (B) Nuclear spin (C) Atomic radius (D) Covalent bonding
4. **Chemical shifts in $^{13}C$ NMR are measured relative to:**
   (A) Benzene (B) Water (C) Tetramethylsilane (TMS) (D) Ethanol
5. **The chemical shift of TMS is assigned as:**
   (A) 12 ppm (B) 100 ppm (C) 0 ppm (D) 220 ppm
6. **The chemical shift range of $^{13}C$ NMR is approximately:**
   (A) 0-12 ppm (B) 0-50 ppm (C) 0-100 ppm (D) 0-220 ppm
7. **The commonly used solvent in $^{13}C$ NMR is:**
   (A) $CHCl_3$ (B) $CDCl_3$ (C) $H_2O$ (D) $CCl_4$
8. **Carbon atoms in the same chemical environment are:**
   (A) Chemically non-equivalent (B) Chemically equivalent
   (C) Magnetically inactive (D) Invisible



9. **Chemically equivalent carbon atoms produce:**
   (A) Different peaks (B) The same peak (C) No peak (D) Doublets only
10. **Carbon atoms in different environments appear at:**
    (A) The same chemical shift (B) Different chemical shifts
    (C) Zero ppm (D) Negative ppm
11. **The number of peaks in a $^{13}C$ NMR spectrum equals the number of:**
    (A) Carbon atoms (B) Different carbon environments
    (C) Hydrogen atoms (D) Functional groups
12. **Ethane shows _____ peak(s) in its $^{13}C$ NMR spectrum.**
    (A) One (B) Two (C) Three (D) Four
13. **Propane shows _____ peaks in its $^{13}C$ NMR spectrum.**
    (A) One (B) Two (C) Three (D) Four
14. **Ethanol gives _____ peaks in its $^{13}C$ NMR spectrum.**
    (A) One (B) Two (C) Three (D) Four
15. **Alkyl carbon atoms generally resonate between:**
    (A) 0-50 ppm (B) 50-100 ppm (C) 100-150 ppm (D) 150-220 ppm
16. **Carbon attached directly to oxygen generally appears between:**
    (A) 0-20 ppm (B) 20-40 ppm (C) 50-70 ppm (D) 150-180 ppm
17. **Alkene carbon atoms usually appear between:**
    (A) 0-50 ppm (B) 50-70 ppm (C) 110-160 ppm (D) 190-220 ppm
18. **Carbonyl carbons of aldehydes and ketones appear around:**
    (A) 20-40 ppm (B) 50-70 ppm (C) 110-160 ppm (D) 190-220 ppm
19. **Carboxyl carbon atoms generally resonate between:**
    (A) 30-60 ppm (B) 80-100 ppm (C) 110-150 ppm (D) 160-185 ppm
20. **Nitrile carbon atoms generally appear between:**
    (A) 20-40 ppm (B) 50-70 ppm (C) 100-125 ppm (D) 190-220 ppm
21. **Carbon atoms adjacent to halogens usually resonate between:**
    (A) 0-20 ppm (B) 30-60 ppm (C) 80-100 ppm (D) 180-220 ppm
22. **Carbon atoms adjacent to carbonyl groups generally appear between:**
    (A) 0-20 ppm (B) 30-65 ppm (C) 100-150 ppm (D) 180-220 ppm
23. **Carbon atoms adjacent to alkene or aryl groups generally appear between:**
    (A) 0-20 ppm (B) 25-50 ppm (C) 100-125 ppm (D) 190-220 ppm
24. **Which statement is correct regarding $^{13}C$ NMR peak area?**
    (A) It is proportional to the number of carbon atoms.
    (B) It is usually not proportional to the number of carbon atoms.
    (C) It always equals molecular mass.
    (D) It represents proton count.
25. **Unlike $^1H$ NMR, peaks in $^{13}C$ NMR generally:**
    (A) Are quartets (B) Are triplets (C) Show no splitting (D) Always appear as doublets
26. **$^{13}C$ NMR is less sensitive than $^1H$ NMR because:**
    (A) Carbon has no electrons. (B) Peaks do not split and $^{13}C$ is less abundant.
    (C) TMS is absent. (D) Carbon has lower mass.
27. **The chemical shift mainly indicates the:**
    (A) Molecular weight (B) Carbon environment (C) Boiling point (D) Density
28. **The first step in interpreting a $^{13}C$ NMR spectrum is to count:**
    (A) Functional groups (B) Carbon atoms (C) Number of peaks (D) Hydrogen atoms
29. **Two peaks in a $^{13}C$ NMR spectrum indicate:**
    (A) Two carbon atoms only (B) Two different carbon environments
    (C) Two hydrogen atoms (D) Two double bonds
30. **Which compound contains chemically equivalent carbon atoms?**
    (A) Ethane (B) Ethanol (C) Propanol (D) Propanone
31. **The carbon atom of an alcohol bonded directly to oxygen generally resonates near:**
    (A) 10 ppm (B) 25 ppm (C) 60 ppm (D) 200 ppm
32. **The carbonyl carbon of a ketone gives a signal at approximately:**
    (A) 15 ppm (B) 60 ppm (C) 120 ppm (D) 200 ppm
33. **The chemical shift of alkene carbon atoms is greater than that of:**
    (A) Carbonyl carbons (B) Alkyl carbons (C) Carboxyl carbons (D) Nitrile carbons
34. **$^{13}C$ NMR is primarily used to study the environments of:**
    (A) Hydrogen atoms (B) Oxygen atoms (C) Carbon atoms (D) Nitrogen atoms

CamScanner

35. Which technique is especially useful for determining the carbon skeleton of organic compounds?
(A) UV Spectroscopy (B) IR Spectroscopy (C) $^{13}$C NMR Spectroscopy (D) Flame Test

36. Carbon atoms in different chemical environments produce:
(A) One signal (B) Identical signals (C) Different signals (D) No signals

37. TMS is used in both $^1$H and $^{13}$C NMR because it:
(A) Has many different signals (B) Provides a reference at 0 ppm
(C) Is radioactive (D) Reacts with samples

38. $^{13}$C NMR helps determine the:
(A) Number of carbon environments (B) Number of neutrons only
(C) Molecular colour (D) Boiling point

39. $^{13}$C NMR spectroscopy is mainly used for:
(A) Determining carbon environments and molecular structure
(B) Measuring pH
(C) Determining melting point (D) Measuring conductivity

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

### BLOCK # 01

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. B | 4. B | 5. B | 6. B | 7. B | 8. B | 9. B | 10. B | 11. B | 12. B | 13. C | 14. C | 15. B |
| 16. C | 17. B | 18. B | 19. A | 20. C | 21. B | 22. B | 23. C | 24. B | 25. A | 26. B | 27. C | 28. D | 29. A | 30. D |
| 31. C | 32. C | 33. C | 34. C | 35. B | 36. B | 37. B | 38. C | 39. D | 40. B | | | | | |

### BLOCK # 02

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. B | 4. C | 5. C | 6. D | 7. B | 8. B | 9. B | 10. B | 11. B | 12. A | 13. B | 14. B | 15. A |
| 16. C | 17. C | 18. D | 19. D | 20. C | 21. B | 22. B | 23. B | 24. B | 25. C | 26. B | 27. B | 28. C | 29. B | 30. A |
| 31. C | 32. D | 33. B | 34. C | 35. C | 36. C | 37. B | 38. A | 39. A | | | | | | |

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. NMR relies on the magnetic properties of nuclei known as:
a) Chemical shift b) Nuclear density c) Nuclear spin d) Signal intensity

II. Chemical shift (δ) in the $^1$H NMR spectroscopy is measured relative to TMS and is expressed in:
a) Tesla (T) b) Hertz (Hz) c) Parts per million (ppm) d) Degrees Celsius (°C)

III. Deuterated solvents ($CDCl_3$) are used in $^1$H NMR to:
a) Increase magnet strength b) Split the signals
c) Provide a reference signal d) Avoid solvent signal interference

IV. The primary purpose of measuring the peak area in $^1$H NMR is to find the:
a) Chemical shift b) Number of neighboring protons
c) Total carbon atoms d) Relative number of protons

V. Splitting is typically not observed for O – H or N – H protons because of:
a) NMR-inactivity b) Longer bond c) Deuterated solvent d) Rapid chemical exchange

VI. In the n + 1 splitting rule, ' n ' represents the number of protons on:
a) the entire molecule b) the carbon being analyzed
c) adjacent carbon atoms d) the signal's total area

VII. The chemical shift (δ) of a $^{13}$C peak identifies the:
a) Number of adjacent carbons b) Functional group envlronment (C = C, C = O, etc.)
c) Molecule's symmetry d) Number of protons

VIII. The number of peaks in a $^{13}$C NMR spectrum equals the number of:
a) Total carbon atoms b) Chemically non-equivalent carbons
c) Adjacent hydrogen atoms d) $^{12}$C atoms

IX. How many $^1$C peaks does propane ($CH_3CH_2CH_3$) show?
a) 1 b) 2 c) 3 d) 4

X. What is the splitting pattern for a proton with 2 neighbouring protons (n = 2)?
a) Singlet b) Doublet c) Triplet d) Quartet



## Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| i) | c | Nuclear spin | NMR spectroscopy is based on the magnetic property called nuclear spin possessed by nuclei such as $^1$H and $^{13}$C. |
| ii) | c | Parts per million (ppm) | Chemical shift values are measured relative to TMS and reported in ppm. |
| iii) | d | Avoid solvent signal interference | Deuterated solvents do not produce proton signals and therefore prevent interference from the solvent. |
| iv) | d | Relative number of protons | The integrated area under a peak gives the relative number of equivalent hydrogens producing that signal. |
| v) | d | Rapid chemical exchange | O–H and N–H protons exchange rapidly between molecules and usually do not show splitting. |
| vi) | c | Adjacent carbon atoms | According to the n + 1 rule, splitting depends on the number of equivalent neighbouring protons on adjacent carbons. |
| vii) | b | Functional group environment (C=C, C=O, etc.) | The position of a $^{13}$C signal indicates the type of carbon environment or functional group present. |
| viii) | b | Chemically non-equivalent carbons | Each unique carbon environment produces one signal in the $^{13}$C NMR spectrum. |
| ix) | b | 2 | Propane contains two carbon environments: terminal $CH_3$ carbons and the central $CH_2$ carbon. |
| x) | c | Triplet | A proton with two neighbouring equivalent protons follows the n+1 rule and gives a triplet (2 + 1 = 3 peaks). |

## Q 2. SHORT ANSWER QUESTIONS SAQs

a) State two reasons why TMS is a standard for $^1$H NMR.

Ans. 1. All 12 protons in TMS are chemically equivalent, so it gives a single sharp peak.
2. Its signal appears at 0 ppm, far away from most organic proton signals, so it does not interfere with the sample spectrum.
Other acceptable reason:
TMS is chemically inert and volatile, so it can be easily removed after analysis.

b) Why does deuterium (D) not appear in a $^1$H NMR spectrum?

Ans. Deuterium (2H or D) does not appear in a 1H NMR spectrum because the instrument detects only protons (1H). Deuterium resonates at a different frequency and is therefore invisible in proton NMR.

c) A compound ($C_4H_{10}O$) has a $^1$H NMR peak area ratio of 1:3:6. How many protons does each signal represent?

Ans. Total number of protons: 10
Sum of ratio numbers: 1 + 3 + 6 = 10
Therefore the ratio directly corresponds to the number of protons.

| Peak Area Ratio | Number of Protons |
|---|---|
| 1 | 1 proton |
| 3 | 3 protons |
| 6 | 6 protons |

Answer: 1 H, 3 H, 6 H

CamScanner

**d) What is the purpose of the $D_2O$ shake test in $^1H$ NMR?**

**Ans.** The $D_2O$ shake test is used to identify **exchangeable protons** such as:

- O — H protons
- N — H protons

These hydrogens exchange with deuterium from $D_2O$ and their peaks disappear from the 1H NMR spectrum.

**Example:** $ROH + D_2O \longrightarrow ROD + HOD$

Thus, disappearance of a peak after $D_2O$ addition confirms the presence of an **O – H or N – H group.**

**e) List the key features used to interpret a $^1H$ NMR spectrum.**

**Ans.** The main features are:

1. **Number of signals:** Gives the number of chemically different proton environments.
2. **Chemical shift (δ):** Indicates the chemical environment of protons.
3. **Peak area (integration):** Gives the relative number of protons in each environment.
4. **Splitting pattern (multiplicity):** Gives the number of neighbouring protons using the n+1 rule.

**f) State two differences between $^1H$ NMR and $^{13}C$ NMR spectroscopies.**

**Ans. Nuclei observed and natural abundance (sensitivity)**

| $^1H$ NMR | $^{13}C$ NMR |
|---|---|
| Observes hydrogen ($^1H$) nuclei. | Observes carbon-13 ($^{13}C$) nuclei. |
| $^1H$ is 99% naturally abundant. | $^{13}C$ is only about 1.1% naturally abundant (low abundance). |
| Therefore, $^1H$ NMR is very sensitive (signals are strong; small sample needed). | Therefore, $^{13}C$ NMR is much less sensitive (signals are weak; larger sample needed). |
| Chemical shift range is 0-12 ppm. | Chemical shift ranges are 0-200 ppm (much wider range). |

## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) A – $CH_2$ – group is lying between a – $CH_3$ and a – CH < group. What is the splitting pattern for the – $CH_2$ – signal? Show your calculation.**

**Ans.** The – $CH_2$ – group has neighboring protons on both sides:

- **On one side:** $CH_3 \rightarrow$ 3 protons
- **On the other side:** CH → 1 proton

Total adjacent protons: n = 3 + 1 = 4

Using the **n + 1 rule:**

Number of peaks = n + 1

Number of peaks = n + 1 = 4 + 1 = 5

Therefore, the – $CH_2$ signal appears as a: Quintet (5 peaks)

**b) Predict the $^1H$ NMR spectrum of butanoic acid.**

**Ans. Structure:** $CH_3CH_2CH_2COOH$

There are four proton environments.

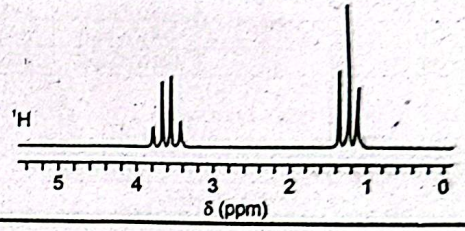
| Proton Environment | Number of H | Chemical Shift (ppm) | Splitting |
|---|---|---|---|
| $CH_3$ | 3 | 0.9 | Triplet |
| Middle $CH_2$ | 2 | 1.3-1.6 | Sextet |
| $CH_2$ adjacent to COOH | 2 | 2.2-2.5 | Triplet |
| COOH proton | 1 | 10-12 | Broad singlet |

**Integration ratio:** 3:2:2:1

Thus, the spectrum contains: triplet at **0.9 ppm**, sextet at **1.4 ppm**, triplet at **2.3 ppm**, broad singlet at **10–12 ppm.**



**c) An organic compound has a molecular formula, Chloroethane $C_2H_5Cl$. The $^1H$ NMR of the compound is given below. Deduce the structure of the compound by using its spectrum. Explain your working in detail.**




**Ans. Molecular formula:** $C_2H_5Cl$ **Possible structure:** chloroethane $CH_3CH_2Cl$

**Expected $^1H$ NMR Spectrum:**

| Proton Environment | Number of H | Chemical Shift | Splitting |
|---|---|---|---|
| $CH_3$ | 3 | 1.0-1.3 ppm | Triplet |
| $CH_2Cl$ | 2 | 3.3-3.8 ppm | Quartet |

**Integration ratio:** 3:2

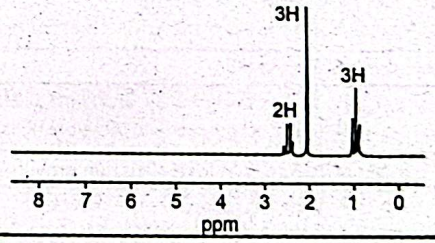
Since:

- $CH_3$ is adjacent to $CH_2 \rightarrow$ triplet
- $CH_2$ is adjacent to $CH_3 \rightarrow$ quartet
- $CH_2$ attached to chlorine appears downfield near 3.5 ppm

Therefore, the structure is: $CH_3CH_2Cl$

**Name:** Chloroethane

**d) An organic compound has a formula $C_4H_8O$. In laboratory, the compound gives 2,4-DNPH and iodoform tests positive but Fehling's test shows a negative result. The $^1H$ NMR of the compound is shown below. Deduce the structure of the compound and justify your answer.**




**Ans. Step 1: Interpretation of tests**

- **Positive 2,4-DNP test:** Indicates presence of Carbonyl group (C = O)
- **Positive Iodoform test:** Indicates presence of CH3CO – (a methyl ketone)
- **Negative Fehling's test:** Indicates compound is not an aldehyde.

Therefore the compound must be a **ketone.**

**Step 2: Use molecular formula $C_4H_8O$**

The ketone with this formula containing a $CH_3CO-$ group is:

$CH_3COCH_2CH_3$

Butan-2-one

CamScanner

**Expected $^1H$ NMR spectrum of Butan-2-one**

| Proton Environment | Number of H | Chemical Shift | Splitting |
|---|---|---|---|
| $COCH_3$ | 3 | 2.1 ppm | Singlet |
| $CH_2$ | 2 | 2.4-2.6 ppm | Quartet |
| $CH_3$ | 3 | 0.9-1.0 ppm | Triplet |

**Integration ratio:** 3:2:3

Therefore, the structure is: $CH_3COCH_2CH_3$ (Butan-2-one)

## DESCRIPTIVE QUESTIONS DQs

**Q.4 Describe the low resolution $^1H$ NMR spectrum interpretation.**

**Ans.** See Question No. 05

**Q.5 How the structure of a compound is determined from the $^1H$ NMR spectrum?**

**Ans.** See Question No. 09

**Q.6 Write a detailed note on the determination of the structure of a compound from its $^{13}C$ NMR spectrum.**

**Ans.** See Question No. 13

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 What is NMR spectroscopy?**

**Ans.** Nuclear Magnetic Resonance (NMR) spectroscopy is an analytical technique used to study the environments of hydrogen and carbon atoms in organic compounds. It helps determine molecular structure and distinguish between different isomers.

**Q.2 Why is TMS used as a standard in NMR spectroscopy?**

**Ans.** Tetramethylsilane (TMS) is used as an internal standard because all twelve hydrogen atoms are equivalent and produce a single sharp signal. It is chemically inert and its signal is assigned a chemical shift of 0 ppm.

**Q.3 What is chemical shift?**

**Ans.** Chemical shift is the position of an NMR signal relative to the TMS standard and is measured in parts per million (ppm). It provides information about the electronic environment surrounding a nucleus.

**Q.4 Why are deuterated solvents used in proton NMR?**

**Ans.** Ordinary solvents contain hydrogen atoms that would produce additional peaks in the spectrum. Deuterated solvents such as $CDCl_3$ contain deuterium instead of hydrogen and therefore do not interfere with proton signals.

**Q.5 What information does the number of peaks in a $^1H$ NMR spectrum provide?**

**Ans.** The number of peaks in a proton NMR spectrum represents the number of chemically different hydrogen environments present in the molecule. Equivalent protons produce only one signal.

**Q.6 What information is provided by peak integration?**

**Ans.** The area under an NMR peak is proportional to the number of equivalent protons responsible for that signal. Integration therefore gives the relative ratio of hydrogen atoms in different environments.

**Q.7 State the n+1 rule.**

**Ans.** The n+1 rule states that a proton signal is split into n+1 peaks, where n is the number of equivalent hydrogen atoms on adjacent carbon atoms.

**For example,** two neighbouring protons produce a triplet.



**Q.8 Explain the origin of splitting in NMR spectra.**

**Ans.** Splitting occurs because magnetic interactions exist between neighbouring non-equivalent hydrogen atoms. These interactions divide a signal into multiple peaks called multiplets.

**Q.9 What is meant by a proton environment?**

**Ans.** Hydrogen atoms having identical chemical surroundings are said to belong to the same proton environment and produce a single NMR signal.

**Example:** All four hydrogen atoms in methane belong to one environment.

**Q.10 Explain the proton environments present in ethanol.**

**Ans.** Ethanol contains three different proton environments corresponding to $CH_3$, $CH_2$ and OH protons. Therefore, ethanol produces three signals in its proton NMR spectrum.

$CH_3CH_2OH$

**Q.11 Explain the splitting pattern of the $CH_3$ group in ethanol.**

**Ans.** The $CH_3$ group in ethanol is attached to a carbon containing two hydrogen atoms ($CH_2$). According to the n+1 rule, the $CH_3$ signal is split into three peaks.

$$n + 1 = 2 + 1 = 3$$

Therefore, the $CH_3$ group appears as a **triplet.**

**Q.12 Explain the splitting pattern of the $CH_2$ group in ethanol.**

**Ans.** The $CH_2$ group in ethanol is adjacent to a $CH_3$ group containing three hydrogen atoms. According to the n+1 rule, the $CH_2$ signal appears as four peaks.

$$n + 1 = 3 + 1 = 4$$

Hence, the $CH_2$ group produces a **quartet.**

**Q.13 Why does the OH proton in alcohol usually appear as a singlet?**

**Ans.** The OH proton undergoes rapid proton exchange with nearby molecules and therefore does not couple with neighbouring protons. As a result, its signal generally appears as a singlet in the proton NMR spectrum.

**Q.14 Explain the $D_2O$ exchange test.**

**Ans.** The $D_2O$ exchange test is used to identify O-H and N-H protons in proton NMR spectroscopy. When $D_2O$ is added, exchangeable protons are replaced by deuterium and their signals disappear from the spectrum.

**Example:** $R-OH + D_2O \longrightarrow R-OD + HOD$

**Q.15 Why do O–H and N–H signals disappear after addition of $D_2O$?**

**Ans.** Hydrogen atoms attached to oxygen and nitrogen can easily exchange with deuterium atoms from $D_2O$. Since deuterium is not detected in proton NMR spectroscopy, these peaks disappear after the exchange reaction.

**Q.16 What information does the chemical shift provide?**

**Ans.** Chemical shift provides information about the electronic environment surrounding a proton or carbon atom. Protons near electronegative atoms experience deshielding and appear at higher chemical shift values.

**Q.17 What is meant by shielding and deshielding?**

**Ans.** Shielding occurs when surrounding electrons protect the nucleus from the external magnetic field, causing signals to appear upfield. Deshielding occurs when electron density decreases, causing signals to move downfield.

**Q.18 Why do protons attached to electronegative atoms appear downfield?**

**Ans.** Electronegative atoms such as oxygen and chlorine withdraw electron density from nearby protons. This deshields the protons and shifts their signals to higher chemical shift values.

**Example:** $CH_3Cl$ absorbs further downfield than $CH_4$.

CamScanner

**Q.19 How many proton environments are present in propanone?**

**Ans.** Propanone contains only one proton environment because both methyl groups are chemically equivalent due to molecular symmetry. $CH_3COCH_3$
Therefore, propanone produces a single proton NMR signal.

**Q.20 How many carbon environments are present in propanone?**

**Ans.** Propanone contains two carbon environments: one for the carbonyl carbon and one for the two equivalent methyl carbons. Therefore, propanone gives two peaks in its $^{13}C$ NMR spectrum.

**Q.21 What information does the number of peaks in a $^{13}C$ NMR spectrum provide?**

**Ans.** The number of peaks in a carbon-13 NMR spectrum corresponds to the number of chemically different carbon environments present in the molecule. Equivalent carbons give only one signal.

**Q.22 Explain the carbon environments present in ethanol.**

**Ans.** Ethanol contains two different carbon environments: one methyl carbon ($CH_3$) and one methylene carbon ($CH_2$).
$CH_3CH_2OH$
Therefore, ethanol gives two peaks in its $^{13}C$ NMR spectrum.

**Q.23 How can NMR spectroscopy distinguish between ethanol and dimethyl ether?**

**Ans.** Both compounds have the molecular formula $C_2H_6O$, but ethanol shows three proton environments while dimethyl ether contains only one proton environment because both methyl groups are equivalent.
Thus, NMR can distinguish structural isomers.

**Q.24 Explain the proton NMR spectrum of methane.**

**Ans.** All four hydrogen atoms in methane are chemically equivalent and have identical surroundings. Therefore, methane produces a single unsplit signal in its proton NMR spectrum. $CH_4$

**Q.25 Explain the proton NMR spectrum of chloromethane.**

**Ans.** All three hydrogen atoms in chloromethane are chemically equivalent and have no neighbouring hydrogen atoms on adjacent carbons. Therefore, chloromethane gives a single singlet signal. $CH_3Cl$

**Q.26 How many proton environments are present in propane?**

**Ans.** Propane contains two proton environments: one for the two equivalent terminal $CH_3$ groups and one for the central $CH_2$ group. $CH_3CH_2CH_3$
Hence, propane gives two proton NMR signals.

**Q.27 How can $^1H$ NMR help in structure determination?**

**Ans.** Proton NMR provides information about the number of proton environments, relative number of protons and neighbouring hydrogen atoms. This information allows chemists to determine molecular structure accurately.

**Q.28 How can $^{13}C$ NMR help in structure determination?**

**Ans.** Carbon-13 NMR reveals the number of chemically distinct carbon atoms present in a molecule. It is especially useful for distinguishing compounds with similar molecular formulas.

**Q.29 Why are $^1H$ NMR and $^{13}C$ NMR used together?**

**Ans.** $^1H$ NMR provides information about hydrogen environments and splitting patterns, whereas $^{13}C$ NMR provides information about carbon environments. Combining both techniques allows complete structural analysis of organic compounds.

**Q.30 Explain the importance of NMR spectroscopy in modern chemistry.**

**Ans.** NMR spectroscopy is one of the most powerful techniques for determining molecular structures and identifying unknown compounds. It is extensively used in research laboratories, pharmaceuticals, medicine and forensic science for accurate structural analysis.



## SELF-ASSESSMENT

Total Mark: 30

**Q.1 Encircle the correct option.** (1 × 6 = 6)

(i) **The transition from the low-energy state to the high-energy state is called:**
(A) Resonance (B) Spin flipping (C) Fragmentation (D) Ionization

(ii) **Aromatic protons generally appear between:**
(A) 0–2 ppm (B) 2–4 ppm (C) 6.5–9.0 ppm (D) 10–12 ppm

(iii) **Propane shows _____ peaks in its $^{13}C$ NMR spectrum.**
(A) One (B) Two (C) Three (D) Four

(iv) **The chemical shift of alkene carbon atoms is greater than that of:**
(A) Carbonyl carbons (B) Alkyl carbons (C) Carboxyl carbons (D) Nitrile carbons

(v) **Chemical shift (δ) in the $^1H$ NMR spectroscopy is measured relative to TMS and is expressed in:**
(A) Tesla (T) (B) Hertz (Hz) (C) Parts per million (ppm) (D) Degrees Celsius (°C)

(vi) **Splitting is typically not observed for O – H or N – H protons because of:**
(A) NMR-inactivity (B) Longer bond (C) Deuterated solvent (D) Rapid chemical exchange

**Q.2 Write short answers of the following questions.** (2 × 8 = 16)

(i) Explain why the 12 protons in TMS produce only a single peak.
(ii) What proton environment does a signal at δ 7.5 ppm likely represent?
(iii) What does the number of signals in a $^1H$ NMR spectrum represent?
(iv) Calculate the number of sub-peaks for each signal in the high-resolution spectra of the following compounds? i) butan-2-ol ii) 1-chloropropane
(v) State the expected peak area and splitting patterns for $(-CH_2CH_2NH_2)$.
(vi) How many signals do you expect to observe in the $^{13}C$ NMR spectrum of butane? Justify your answer.
(vii) What is the purpose of the $D_2O$ shake test in $^1H$ NMR?
(viii) State two differences between $^1H$ NMR and $^{13}C$ NMR spectroscopies.

**Q.3 Extensive Questions.** (4 + 4 = 8)

(a) Describe the low resolution $^1H$ NMR spectrum interpretation.
(b) Write a detailed note on the determination of the structure of a compound from its $^{13}C$ NMR spectrum.

CamScanner

## ENTRANCE TEST MCQs

1. **The displayed propan-2-ol contains how many proton environments in the simplified model?**
   (A) 1 (B) 2 (C) 4 (D) 3
2. **A signal with two equivalent neighbouring protons is normally a:**
   (A) Triplet (B) Singlet (C) Doublet (D) Quartet
3. **If a signal contains five lines, the simple n+1 rule indicates:**
   (A) Four equivalent neighbouring protons (B) Five neighbouring protons
   (C) Three neighbouring protons (D) No neighbours
4. **A $CH_2$ group between a $CH_3$ group and a CH group may show complex splitting because:**
   (A) It has no adjacent protons (B) The n+1 rule is never valid
   (C) It is a carbon-13 signal (D) It couples to two non-equivalent neighbour sets
5. **When interpreting a $^1H$ NMR spectrum, the first step is usually to:**
   (A) Count the number of signals (B) Ignore integration
   (C) Remove TMS (D) Convert ppm to nm
6. **A structure proposal is strongest when it agrees with:**
   (A) Peak count, shifts, integration, splitting & formula (B) Only one peak position
   (C) Only colour (D) Only boiling point
7. **$^1H$ NMR: aldehyde 9.8 ppm, 2H multiplet 2.4, 3H triplet 1.0. Compound?**
   (A) Propanoic acid (B) Propanal (C) Propanone (D) Ethanol
8. **The displayed neopentane structure is expected to give how many $^1H$ signals?**
   (A) 2 (B) 3 (C) 4 (D) 1
9. **For identifying an unknown compound, the most suitable workflow is:**
   (A) Use one peak only (B) Combine formula, NMR shifts, integration and splitting
   (C) Guess from colour, then ignore spectra (D) Use integration one peak

**Answers Key**

| 1. D | 2. A | 3. A | 4. D | 5. A | 6. A | 7. B | 8. D | 9. B |
|---|---|---|---|---|---|---|---|---|



31 CHAPTER

# MATERIALS AND ENERGY

### Student Learning Outcomes (SLOs)

[C-12-E-34 to C-12-E-49]

- Explain the properties of different materials and how they can be applied to desired structures.
- Explain the process of extracting metals from ores and alloying them to achieve desired characteristics.
- Explain the mechanism of catalysts and how they increase the rate of reaction while remaining unchanged at the end.
- Explain the challenges associated with recycling and toxicity of some materials produced through materials science.
- Explain the use of X-ray crystallography in analyzing structures.
- Differentiate between petrochemicals and chemicals derived from them.
- Identify the various raw materials for the petrochemical industry.
- Explain the process of fractional distillation and refining of petroleum.
- Describe the major chemical processes involved in the petrochemical industry.
- Identify major petrochemicals and their applications.
- Differentiate between energy density and specific energy.
- Describe the nature, uses, and impact of fossil fuels.
- Describe the processes of nuclear fission and fusion and their energy significance.
- Explain the working and significance of solar panels as a source of energy.
- Explain the environmental impact of energy consumption, particularly in relation to global warming and its relation to the importance of reducing carbon footprint and moving towards sustainable energy sources.
- Evaluate different energy sources based on cost, efficiency, impact, and sustainability.

**Q.1 Discuss historical background of materials.** S/Q

**Ans. Historical Background:**

- Humans have long benefited from the natural resources for their daily needs. The most ancient materials are wood, metals, and those obtained from animals, such as clothes.
- With increase in the human population and limited natural resources, new materials and machines were needed to fulfill the human needs.
- A large number of materials from metal alloys to nanomaterial, from large electric cells to very efficient miniature batteries, etc. were invented.
- The new machines like computers, mobiles, construction machinery, aircrafts, etc., all involve a combination of modern materials and energy devices.

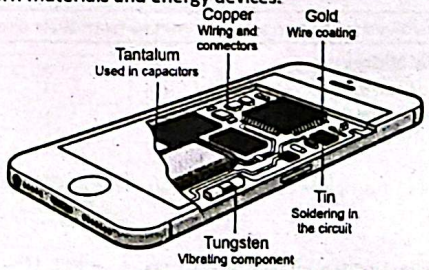



**Figure: This mobile contains a variety of metals, plastic, their composites, and a small but efficient energy device, i.e., Li-ion battery**

CamScanner

**Q.2 What is the role of chemistry in modern materials and energy sources?** S/Q

**Ans.** The role of chemistry is in the preparation, properties, and uses of a variety of materials, such as metals, alloys, polymers and ceramics, as well as the analytical techniques used for their analysis, such as X-ray crystallography. Chemistry deals with energy density, specific energy, and efficiency of the source, e.g., fossil fuel, nuclear and solar energy. The environmental effects of the energy consumption, the sustainable energy sources, such as photochemical energy devices.

## MATERIALS

**Q.3 What is a material?** S/Q

**Ans.** ***A material is any substance or mixture of substances that makes up a physical object of daily-life or industrial importance, for example, plastics, metals, ceramics, building material, etc.*** Materials have superior thermal, mechanical (e.g., hardness, elasticity, etc.) and chemical properties. They are understood by their composition, the nature of chemical bonds, and the microstructure. The selection of a material for a certain application is made depending on its physical, chemical, mechanical, electrical and thermal characteristics. Different materials and their properties.

### ➲ Metals and Alloys

**Q.4 What are metals?** S/Q

**Ans.** Metals are hard, rigid substances that are good conductors of heat and electricity. They are malleable and ductile and thus can be easily rolled into sheets or easily drawn into wires without fracture. These characteristics allow the use of metals in indoor applications, **construction and industries.** Steel is utilized in bridges and can be found in several buildings due to its strength. Aluminum is utilized in the bodies of aircrafts, because it is light-weight, and copper is normally used in electric wires since it has amazing conductivity. Metals are mostly found in the earth's crust. Less reactive metals, such as gold and platinum can be found in the free state, i.e., they exist in the metallic state in nature and do not form compounds with other elements frequently.

**Q.5 What is a need for metallurgy?** S/Q

**Ans. Need for Metallurgy:**
More reactive metals, e.g., sodium, aluminium, iron, copper, etc., exist in the combined state in the form of ores. **Example:** Haematite ($Fe_2O_3$) is an ore of iron and it is found in certain parts of the world. Metal ores are distributed in the earth's crust in different quantities.

**Q.6 Define Ore and Gangue.** S/Q

**Ans. Ore:**
**Definition:** An ore is a naturally occurring mineral (rock) from which a metal can be extracted profitably and conveniently. Ores are not pure compounds. Ores are mixtures of the desired metal compound impurities, and earthly materials.
**Gangue:**
Unwanted impurities in the ore are called **gangue.**
Metals are extracted from their ores through a series of physical and chemical processes.

**Q.7 Describe the main steps involved in the extraction of metals from their ores.** Exercise D/Q.6

**Ans. Extraction of Metals (Metallurgy)**
***Metallurgy is the science of extracting metals out of their ores and making them pure for better use.***
The reactivity and the nature of the metal defines the extraction procedure.
Metallurgy involves a series of processes to finally obtain the purest form of a metal.

**i. Mining:**
Mining is the process of acquiring the metal ores that are buried deep in the earth. e.g., iron ores.

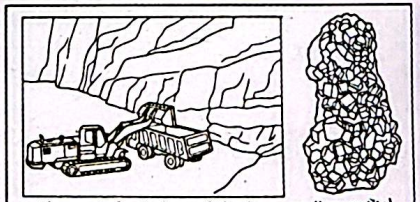


Figure: Left; A view of the iron ore (haematite) mining, right; A lump of haematite



**ii. Ore Concentration:**
Ore Concentration is the process in which the ore of a metal is made free from impurities as much as possible.

**iii. Conversion of Concentrated ore to Metal Oxide:**
This can be done in two ways, mostly. The first method is roasting which involves heating a sulphide ore of a metal with excess supply of air.

$$2ZnS_{(s)} + 3O_{2(g)} \longrightarrow 2ZnO_{(s)} + 2SO_{2(g)}$$

Another method is calcination in which a metal carbonate ore is heated in a limited or no air environment to convert it into its oxide.

$$ZnCO_{3(s)} \longrightarrow ZnO_{(s)} + CO_{2(g)}$$

**iv. Reduction of Metal Oxides to Metal:**
The reduction of metal oxides is the most important step of the metal extraction. Different techniques are used for different metals depending on their reactivity. For less reactive metals (below carbon in the reactivity series), carbon is used as a reducing agent. Carbon is first converted into CO, which then reacts with the metal oxide. Carbon monoxide displaces the oxygen from the metal oxide to form a free metal. An example is the reduction of the enriched iron ore as follows:

$$C + \frac{1}{2}O_2 \longrightarrow CO$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

However, the above method cannot be used for metals that are more reactive than carbon as carbon is not able to reduce their oxides.
For such metals, an **electrolytic method** is used, which requires significant energy to melt the metal compounds and pass an electric current through them. This method is crucial for extracting highly reactive metals (e.g., Na, K, Al as they are not easily reduced with carbon), or for achieving very high purity in less reactive metals (e.g. Cu). The positive metal ions move to the cathode (negative electrode), where they gain electrons to form the metal.

**v. Refining the Metal:**
Most of metals have high percentages in the samples obtained after reduction. However, some metals need very high purity for special applications.
For example, copper needs to be 99.99% pure in the electrical wiring. The final step is the purification to get the pure metal, which is then used for practical purposes. A metal can be refined by thermal, chemical or electrochemical methods.

**vi. Alloying of Metals:**
Alloying involves the mixing of any two or more metals to give a homogeneous solution or mixing of a metal with a non-metal. This is done to alter the microstructure of the metal to enhance the properties, such as strength, corrosion resistance, and electrical or magnetic properties. Common alloys and their uses are provided in Table.

**Table: Properties and Uses of Common Alloys**

| Alloy | Constituent Elements | Properties | Common Uses |
|---|---|---|---|
| Brass | Copper (60 – 90%) + Zinc (10 – 40%) | Strong, corrosion-resistant | Electrical fittings |
| Bronze | Copper (88%) + Tin (12%) | Hard, wear resistant | Medals, statues |
| Steel | Iron (98 – 99%) + Carbon (0.1 – 2%) (and other elements: Cr , Ni , Mn, Si, S) | Tough, durable, strong | Buildings, tools |
| Duralumin | Aluminium (93-95%) + Copper (3.54.5%) + Magnesium (0.4-0.7%) + Manganese (0.4-0.7%) | Lightweight, strong, but less corrosion-resistant | Aircraft body |

### ➲ Ceramics

**Definition:** Ceramics are inorganic, nonmetallic solids made up of compounds of metals and non-metals. Ceramics are hard but brittle materials that have high melting temperatures and very good insulating capabilities, which make them fit in high temperature and electrical applications.

CamScanner

Chemically, they contain a blend of silicates and oxides of alkali and alkaline earth metals, and aluminium, such as $K_2O$, $Na_2O$, CaO, $Al_2O_3$, etc. They may also contain $ZrO_2$ (Zirconia), carbides like SiC, TIC (tungsten carbide), The strong bonds and fixed structures give ceramics unique and highly desirable properties such as strength, durability, and resistance to corrosion and heat. Due to these characteristics, they are useful in pottery, furnaces, tiles and sanitary ware (porcelain), windows and optical fibres (glass), spark plugs (alumina), etc. A summary of various properties of ceramics and their applications is provided in Table.

**Table: Properties of Ceramics and Their Applications**

| Property | Description | Application Example |
|---|---|---|
| High Melting Point | Remain solid at very high temperatures. | Refractory bricks lining steel furnaces. |
| Hardness and Wear Resistance | Extremely difficult to scratch or abrade. | Abrasives (e.g., silicon carbide in sandpaper) and cutting tools. |
| Electrical Insulator | Do not conduct electricity (most). | Porcelain insulators on power lines. |
| Chemical Inertness | Highly resistant to corrosion and chemical attack. | Ceramic coatings on chemical processing equipment. |

## ➲ Polymers

Polymers are large inorganic or organic molecules having unique properties. Although, organic polymers are much more common, inorganic polymers are essentially more significant in certain applications than organic polymers. Polymers are prepared from a variety of small molecules of choice.

## ➲ Composites

**Q.8 Explain composite materials by describing and differentiating the roles of the matrix and the reinforcement in them.** Exercise D/Q.4

**Ans.** Composites are very efficient and useful modern day materials. A composite is a combination of two or more materials to form a product which has better properties.

One component is called the matrix, while the others, which are caged in the matrix, are called reinforcement agents. Some composites may have more than one reinforcement agent. An example is fibre glass, which is composed of a polymer as the matrix, and the reinforcement agent may be the fibres of a fabric, glass, or carbon-based materials. The matrix holds the reinforcement, whereas the reinforcement provides high strength to the material. Composites possess good strength to weight ratio and strong resistance to corrosion and are, therefore, suitable in demanding applications. As an example, boat hulls and car bodies are made of fibre glass, whereas carbon fibre is widely used in the aircraft and sports gear industry because of its lightness and strong durability.

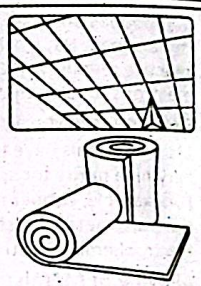


Figure: Fibre glass is used for insulating walls and ceiling from heat and cold

## ➲ Semiconductors

Semiconductors are substances that conduct electricity only in special conditions and are light, heat, and voltage sensitive. Due to these characteristics, they are important in modern electronic applications. The difference between conductors and semiconductors is that the current passing through a semiconductor can be controlled as demanded in an application. The most common semiconductor is silicon, which is used in microchips and solar panels since it is highly effective and abundant. A mobile SIM card is composed of a silicon chip with some other minor components, such as copper connectors. Silicon can be used to conduct, store and process data in a device. Another major semiconductor is gallium arsenide (GaAs), which is used in wireless communication, e.g. 5G internet devices. Gallium nitride (GaN) is used in electric cars for fast charging due to its advanced characteristics.

### ☑ QUICK CHECK 31.1

**i. Why ceramics are used as insulators on power lines.**

**Ans.** Ceramics are used as insulators on power lines because they:

- Have **very low electrical conductivity** (do not allow electric current to pass).
- Possess **high dielectric strength**, enabling them to withstand high voltages.
- Are **resistant to heat, weathering, and corrosion.**



Therefore,

Ceramics prevent leakage of electricity from power lines to supporting structures.

**ii. Why is silicon preferred for use in microchips and solar panels?**

**Ans.** **Silicon is preferred because:**

- It is a **semiconductor**, so its electrical conductivity can be controlled by doping.
- It forms a stable **oxide layer ($SiO_2$)** that protects electronic devices.
- It is abundant, inexpensive, and chemically stable.
- It efficiently converts sunlight into electrical energy in solar cells.

Therefore, Silicon is widely used because of its excellent semiconductor properties.

**iii. What do reinforcement agents provide in composite materials?**

**Ans.** Reinforcing agents such as **glass fibres, carbon fibres, or Kevlar fibres provide:**

- **High strength**
- **Increased stiffness**
- **Improved toughness**
- **Better resistance to cracking and deformation**

The matrix binds the material together, while the reinforcement bears most of the load. Therefore, Reinforcing agents increase the mechanical strength and durability of composites.

# TOXICITY AND RECYCLING IN MATERIAL SCIENCE

**Q.9 Discuss the toxicity and recycling in material science.** LO

**Ans.**

## Toxicity of Materials:

Toxicity is the extent to which a substance can harm an organism or the environment. A material may be toxic during its production, use, and final disposal. The toxicity is measured by the extent and type of hazard that a material may cause. Hazards posed by a material are of many types. At first place are health hazards, i.e., a substance can cause damage to health upon exposure?

**Example:** Metals like chromium are carcinogens (cause cancer), mutagens (change DNA and genes), and cause respiratory issues. Another example is some additives in plastics, which can cause hormonal problems in the body.

Some materials can cause physical hazards due to their physical or chemical properties.

The physical hazards may happen to buildings, humans, ecosystems, and the environment.

**Example:** A flammable or an explosive material can harm humans, forests, or damage a building. Environmental hazards are by the substances that can cause long-term harm to aquatic life or the environment. Heavy metals, such as lead, mercury, and cadmium can leach into soil and groundwater. Heavy metals are dangerous to plants, animals on ground, as well as fish and other aquatic organisms.

## ➲ Major Toxic Materials

Although, there are a number of toxic materials that are becoming the part of the environment. Plastics and heavy metals are two major concerns that are being discussed here as examples. These materials are commonly used due to their superior properties. However, their long-term effects are lethal.

- **Heavy Metals:** Lead (Pb), mercury (Hg) and cadmium (Cd) are the common metals found in electronics, batteries, and fluorescent lights. They can get into the ground water from where they can transfer to the living organisms.
- **Plastics:** A lot of plastics have toxic additives such as phthalates or bisphenol A(BPA), which can interfere with the hormones in the body. Microplastics can now be found in oceans, soil, and even in food which have a long-term effects on the human life and the ecosystems. In humans, microplastics are a growing health concern.

## ➲ Recycling

**Q.10 Explain the importance and challenges to the process of recycling.** Exercise D/Q.7

**Ans.** Recycling is an important aspect of waste management, conservation of resources and energy saving. Yet, in materials science, modern materials are experiencing severe technical, economic, and environmental limitations to recycling and reuse. With more complex synthetic products, toxicity and the waste disposal have become a rising concern.

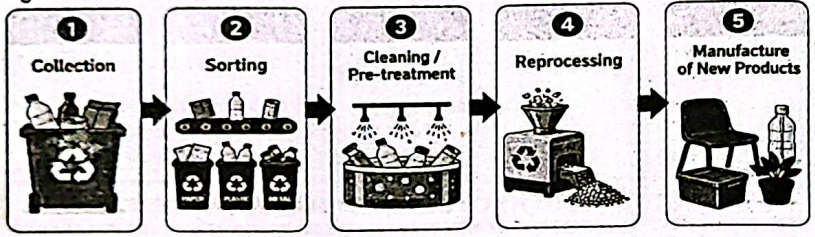
CamScanner

Recycling minimizes the solid waste in the landfills and preserves the limited natural resources, such as metals, oil and timber. One of its other advantages is energy saving e.g., the recycling of aluminium consumes 95 percent less energy as compared to the recovery of aluminium by using the raw ore.

➢ **Importance:**

- Conserves finite raw materials such as metals, petroleum feedstocks, timber and minerals.
- Reduces the amount of waste sent to landfill or incineration.
- Often saves energy compared with extracting and processing virgin materials.
- Reduces pollution and, in many cases, greenhouse-gas emissions.
- Recovers valuable materials and can reduce production costs and dependence on imported resources.

➢ **Main stages:**




➢ **Challenges Associated with Recycling:**

i. The first challenge is material separation. Most of the present day products (e.g., mobile phones, laptops) are assembled using mixed materials which are not easily separated, such as plastic coating on metals or multi layered packaging films.

ii. The second major challenge to recycling is expensive reprocessing. Reprocessing waste involves sorting, cleaning, and inshort usually expensive. Reprocessing of plastic, electronics, and other materials requires a lot of energy. Excessive use of energy is uneconomical, especially when these materials are available elsewhere at a lower price.

iii. Most often, reprocessing results in the contamination of the product material, posing the contamination challenges. The recycled metals and plastics can be contaminated by dye, chemicals, or biological materials that decrease their quality and safety for reuse. In food-grade use, recycling of contaminated plastic is not possible.

**Table: Principles and Methods of Recycling of some Important Materials**

| Material | Recycling Method | Chemical Principles/Focus |
|---|---|---|
| Plastics | Mechanical Recycling (Reprocessing) | Sorting, cleaning, melting, and reforming the plastic. Limited by contamination and degradation of polymer chains. |
| | Chemical Recycling (Depolymerization) | Breaking down the polymer chains into the original monomers or simpler chemicals using heat, solvents, or catalysts. This produces purer reactants. |
| Metals (Steel, Aluminum) | Thermal and Chemical Refining (Metallurgy) | Melting and refining processes to remove impurities. Requires significant energy, but much less than the primary production. |
| Paper | Pulping and Deinking | Chemical and mechanical separation of fibres. Pulp is treated with chemicals (like NaOH or $Na_2CO_3$) to remove inks and dyes. |
| Glass | Cullet Preparation and Melting | Cleaning, crushing, and melting the scrap glass (cullet) to form new glass easily melts. |

### ☑ QUICK CHECK 31.2

**a) Name two types of hazards caused by toxic materials.**

**Ans.** Toxic materials can cause:

1. **Health hazards** such as poisoning, cancer, respiratory diseases, and damage to organs.
2. **Environmental hazards** such as contamination of soil, water, and air, affecting plants and animals.



**b) Which methods will you use for the recycling of:**
**i) empty metal food cans ii) empty beverage glass bottles iii) shopping bags and toys**

**Ans.**
i) **Method:** Melting and reprocessing
The cans are collected, sorted, melted, and remade into new metal products.
ii) **Method:** Crushing and remelting
Glass bottles are crushed into cullet and melted to produce new bottles or glass products.
iii) **Method:** Plastic recycling by melting and remoulding
Plastic materials are collected, sorted by type, melted, and moulded into new plastic products.

**c) Name the types of hazards posed by:**
**i) poly(ethene) ii) Hg metal iii) water glass bottles iv) hospital waste**

**Ans. Types of Hazards:**
i) **Poly(ethene):** Mainly a fire/environmental hazard - it is combustible and persists as non-biodegradable plastic waste.
ii) **Hg Metal:** Toxic chemical hazard - mercury and especially its vapour can cause serious poisoning.
iii) **Glass Water Bottles:** Physical/sharps hazard - broken glass can cause cuts and injuries.
iv) **Hospital Waste:** Biological/infectious hazard (and often sharps hazard) because it may contain pathogens, contaminated needles and body fluids.

**d) How does recycling help conserve natural resources?**

**Ans.** Recycling helps conserve natural resources by:

- Reducing the need for raw materials such as ores, petroleum, and timber.
- Saving energy required for manufacturing from raw materials.
- Reducing landfill waste and environmental pollution.
- Preserving non-renewable resources for future generations.

Therefore, recycling reduces resource consumption and protects the environment.

## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **A material is best defined as:**
(A) A naturally occurring element only (B) Any substance or mixture used to make physical objects
(C) A pure metal (D) A synthetic polymer only

2. **Metals are generally good conductors of:**
(A) Heat only (B) Electricity only (C) Heat and electricity (D) Sound only

3. **The property that allows metals to be drawn into wires is:**
(A) Malleability (B) Ductility (C) Brittleness (D) Elasticity

4. **The property that allows metals to be rolled into sheets is:**
(A) Ductility (B) Malleability (C) Conductivity (D) Toughness

5. **Which metal is commonly used in aircraft bodies because of its low density?**
(A) Iron (B) Copper (C) Aluminium (D) Zinc

6. **Copper is widely used in electrical wiring because of its:**
(A) High melting point (B) Excellent conductivity (C) Low density (D) Hardness

7. **Less reactive metals such as gold are generally found:**
(A) As oxides (B) As sulphides (C) In the free state (D) As carbonates

8. **Hematite is an ore of:**
(A) Copper (B) Zinc (C) Iron (D) Aluminium

9. **Unwanted earthy impurities present in ores are called:**
(A) Flux (B) Slag (C) Gangue (D) Coke

10. **Metallurgy is the science of extracting and:**
(A) Purifying metals (B) Manufacturing plastics (C) Refining petroleum (D) Producing ceramics

11. **Mining is the process of:**
(A) Refining metals (B) Extracting ores from the earth
(C) Alloy formation (D) Roasting ores

12. **Ore concentration is carried out to remove:**
(A) Water (B) Impurities (C) Oxygen (D) Carbon dioxide

13. **Roasting is mainly used for:**
(A) Carbonate ores (B) Sulphide ores (C) Oxide ores (D) Native metals

14. **Calcination is generally carried out for:**
(A) Sulphide ores (B) Carbonate ores (C) Oxide ores (D) Halide ores

CamScanner

15. During roasting, sulphide ores are converted into:
(A) Sulphates (B) Metal oxides (C) Carbonates (D) Chlorides
16. During calcination, zinc carbonate produces:
(A) ZnS (B) ZnO (C) $ZnCl_2$ (D) $ZnSO_4$
17. Carbon is used to reduce the oxides of metals that are:
(A) More reactive than carbon (B) Less reactive than carbon
(C) Noble gases (D) Alkali metals only
18. Highly reactive metals such as sodium are extracted by:
(A) Roasting (B) Calcination (C) Electrolysis (D) Carbon reduction
19. During electrolysis, metal ions move towards the:
(A) Anode (B) Cathode (C) Salt bridge (D) Electrolyte surface
20. The final purification of metals is known as:
(A) Smelting (B) Alloying (C) Refining (D) Mining
21. Alloying means mixing two or more metals or:
(A) A purifying metals only (B) A metal with a non-metal (C) An extracting metals (D) An oxidizing metals
22. Brass is an alloy of:
(A) Copper and Tin (B) Copper and Zinc (C) Iron and Carbon (D) Aluminium and Copper
23. Bronze is an alloy of:
(A) Copper and Zinc (B) Copper and Tin (C) Iron and Carbon (D) Aluminium and Magnesium
24. Steel mainly consists of:
(A) Iron and Carbon (B) Copper and Zinc (C) Aluminium and Copper (D) Iron and Tin
25. Ceramics are generally:
(A) Soft and flexible (B) Hard and brittle (C) Good conductors (D) Elastic
26. Most ceramics are excellent:
(A) Electrical conductors (B) Electrical insulators (C) Semiconductors (D) Superconductors
27. Which of the following is a ceramic application?
(A) Spark plugs (B) Electric wires (C) Aircraft bodies (D) Batteries
28. A composite is formed by combining:
(A) Two or more materials (B) Two metals only (C) Two polymers only (D) Two ceramics only
29. In a composite, the material that holds everything together is called the:
(A) Reinforcement (B) Matrix (C) Catalyst (D) Binder
30. Reinforcement agents mainly provide:
(A) Colour (B) Strength (C) Conductivity (D) Transparency
31. Fibreglass is an example of:
(A) Alloy (B) Composite (C) Ceramic (D) Semiconductor
32. The most widely used semiconductor is:
(A) Copper (B) Silicon (C) Iron (D) Zinc
33. Gallium arsenide (GaAs) is mainly used in:
(A) Cement (B) 5G communication devices (C) Aircraft, (D) Water purification
34. Gallium nitride (GaN) is widely used for:
(A) Fast charging in electric vehicles (B) Glass manufacture
(C) Fertilizers (D) Paints
35. Which heavy metal is carcinogenic and may damage DNA?
(A) Chromium (B) Sodium (C) Magnesium (D) Calcium
36. Recycling aluminium saves approximately:
(A) 25% energy (B) 50% energy (C) 75% energy (D) 95% energy

## X-RAY CRYSTALLOGRAPHY AND STRUCTURE ANALYSIS

**Q.11 Explain how X-rays interact with crystals to produce diffraction patterns and how these patterns help determine atomic positions?** Exercise Q.5

**Ans.** X-ray crystallography is a very strong analytical tool used to identify three dimensional positions of atoms in a crystalline solid. It is important in material science, biochemistry, and pharmaceutical chemistry as it enables scientists to visualize material structures.

X-rays have very small wavelength, comparable to the distance between atoms. Therefore, this electromagnetic radiation can be used to find the position of electrons and atoms in a molecule or an ionic compound. The solid materials consist of layers or strands of atoms.



When the X-rays from the source fall on a crystal, they are diffracted after hitting the atoms at specific angles as shown in Figure.

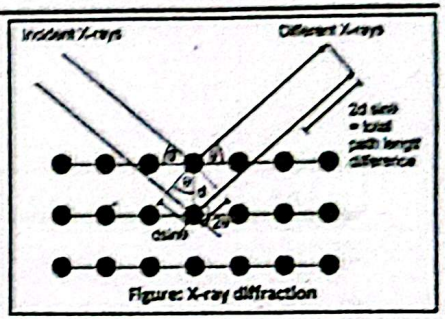


Figure: X-ray diffraction

### Diffraction Patterns:

These diffracted rays make patterns on a screen called the diffraction patterns. A diffraction pattern spots the location of atoms and electrons in a molecule by drawing maps and determining the distance between atoms. With the help of mathematical models and the analysis of this pattern, scientists are able to draw a detailed map of atomic position and bond angles in the crystal. Thus, a complete pattern of atoms and their electron density can be mapped to determine the overall structure of the molecule or the crystal.

The structure of the naphthalene molecule is presented in Figure.

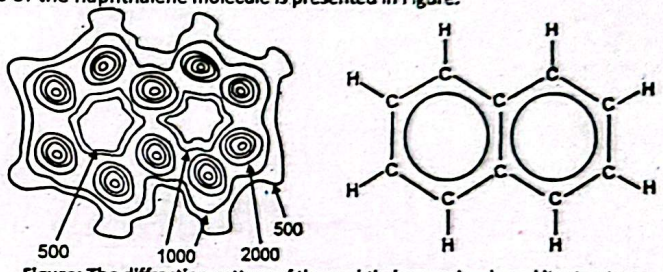


Figure: The diffraction pattern of the naphthalene molecule and its structure

**Double Helix Structure of DNA:** The most well-known use of XRD (X-ray diffraction) is the determination of the double helix structure of DNA. The method of X-ray crystallography is still applicable in analyzing complex biomolecules like enzymes and proteins.

### Applications:

i. It can also be used for the pharmaceutical drug development. During the drug development, designers employ this method to realize how a drug molecule attaches to its target.
ii. The analyses of materials and minerals. Here, it is used to analyze the minerals, synthetic crystals and nanomaterial. This is helpful to enhance material performance in the fields of electronics, optics and constructions.

## FOSSIL FUELS

**Q.12 What are fossil fuels and discuss their uses?** S.Q

**Ans. Fossil Fuels:**

Petroleum (crude oil), coal, and natural gas are collectively called **fossil fuels.**

- **Crude oil** is extracted from underground reservoirs and refined in large size plants through fractional distillation. Major products from petroleum are naphtha, gasoline, kerosene and diesel.
- **Methane ($CH_4$):** Methane ($CH_4$) is the major component of natural gas, in mixtures with ethane, propane, and butane. Methane is mainly employed in the production of ammonia (used in fertilizers) and methanol (utilized in solvents and fuel).
- **Coal:** Coal is not as useful as it was before, but it still represents a petrochemical raw material, especially in areas where reserves are high. The primary use is to obtain some aromatic compounds benzene, toluene, and xylene that are vital in the manufacture of dyes, resins, and explosives.

**Keep in Mind**
Despite the fact that fossil fuels are highly efficient sources of energy, combustion of these products produces greenhouse gases such as carbon dioxide ($CO_2$) and others. This leads to air pollution, global warming, and climate change.

CamScanner

Table: Forms and uses of fossil fuels

| Fossil Fuel | Main Uses |
|---|---|
| Petroleum | Transportation fuels (petrol, diesel), lubricants. |
| Natural Gas | Cooking, heating, electricity, and fertilizer production. |
| Coal | Electricity generation, cement, and steel industries. |

## FRACTIONAL DISTILLATION AND REFINING OF PETROLEUM

**Q.13 Describe fractional distillation and refining of petroleum.** U/Q

**Ans.** Crude oil is a complicated mixture of hydrocarbons and it needs separation into simpler and useful hydrocarbons. This separation process is done physically by a method known as **fractional distillation** which depends on the difference in boiling points of different hydrocarbons. During this process, the crude oil is heated inside a furnace until it is vapourized. The vapour is then passed to a fractionating column, a tall tower through which the temperature drops slowly going up.

Since the vapour travels upwards, various hydrocarbon constituents condense at various points in the column based on their boiling points. Hydrocarbons that are heavier and have higher boiling point are condensed closer to the bottom, whereas lighter hydrocarbons with low boiling point rises further. The process enables the extraction of useful fractions of crude oil, which are given below with their uses in Figure.

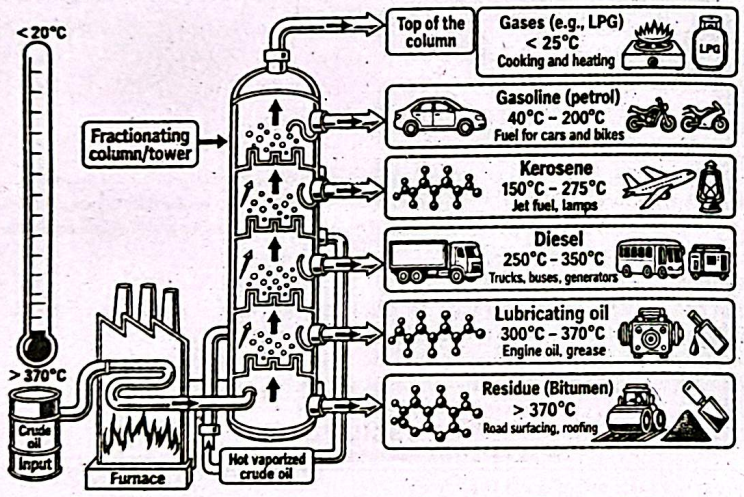



Figure: Fractional distillation of crude oil into useful hydrocarbons

Fractional distillation is an important process as it provides petrochemicals having applications in industries, and for domestic, and transportation purposes.

### QUICK CHECK 31.3

**a) If fossil fuels are non-renewable resources, why are they still heavily used worldwide?**

**Ans.** Fossil fuels are still heavily used because:

- They provide a **large amount of energy per unit mass** (high calorific value).
- The technology and infrastructure for their extraction, transport, and use are already well developed.
- They are relatively **cheap and readily available** in many countries.
- They are used extensively in **transportation, electricity generation, and industries.**

Therefore, Fossil fuels remain widely used because they are economical, energy-rich, and easily accessible.



**b) Can XRD be used to find the structure of liquids?**

**Ans.** No, X-ray diffraction (XRD) is mainly used to determine the structure of crystalline solids because they have a regular and repeating arrangement of particles that produces clear diffraction patterns. Liquids do not have a long-range ordered structure, so they do not produce sharp diffraction patterns required for structural determination. Therefore, XRD is suitable for crystalline solids but not for liquids.

## PETROCHEMICALS

**Q.14 What are petrochemicals? Give some examples. What chemicals derived from them with uses?** S/Q

**Ans.** **Petrochemicals:**

Petrochemicals are compounds (chemicals) obtained primarily by means of crude oil and natural gas through refining and transformation. They are used to make diverse daily items found in several industries including packaging, construction, textile, electronics, and medical sectors.

Synthetic chemicals or substances manufactured from petrochemicals are the derivatives of petrochemicals and these are v... important industrial products. The derivatives of petrochemicals are subjected to chemical transformation, such as polymerization, oxidation, or substitution to obtain materials of immense daily-life significance. Some petrochemicals, their derivatives, and their uses are tabulated in below Table.

Table: Derivatives of Petrochemicals and their Uses

| Petrochemical | Derived Chemical/Product | Uses |
|---|---|---|
| Ethene | Poly(ethene) (Plastic) | Bags, bottles, packaging |
| Propene | Poly(propene) | Containers, automotive parts |
| Benzene | Styrene ⟶ Polystyrene / Poly(phenylethene) | Disposable cups, insulation |
| Toluene | TNT (Trinitrotoluene) | Explosives |
| Xylene | Polyester Fibres | Textiles, clothing (fleece, jerseys), and upholstery. |
| Butadiene | Synthetic Rubber (e.g., Styrene Butadiene Rubber) | Tires, footwear |

### ➲ Petrochemical Process Technology

**Q.15 Define cracking and discuss its two types.**

**Ans.** **Cracking**

A petrochemical industry involves a number of very important processes, which are discussed here. Cracking is a chemical process involving the breaking of large hydrocarbon (typically a naphtha or heavy oils) molecules into smaller, more useful molecules, such as alkenes. The process is necessary since ethene and propene, which are smaller hydrocarbons, are the major raw materials used in the production of plastics and artificial rubber.

There are two primary methods used to achieve this: (i) Thermal Cracking (ii) Catalytic Cracking.

**i. Thermal Cracking**

This process is based on very high temperatures (usually between 450°C and 750°C) and high pressure to physically open the carbon-carbon bonds. Since no catalyst is involved, the process needs high energy input. It normally generates a high percentage of alkenes, which is important in the plastic industry. For example, a long-chain alkane, such as decane ($C_{10}H_{22}$) can be thermally cracked to produce octane and ethene:

$$C_{10}H_{22} \longrightarrow C_8H_{18} + C_2H_4$$

**ii. Catalytic Cracking**

Catalytic Cracking on the other hand is more efficient, and is more commonly used in modern refineries. This is done by adding a catalyst (usually **zeolites:** aluminosilicates or silicaalumina), which reduces the activation energy of the reaction significantly. This enables the process to occur at reduced temperatures (approximately 500°C) and pressures, saving energy and better control over the final products.

CamScanner

**Example:**

- The cracking of a heavy fraction naphtha in the presence of a catalyst produces high-demand petrochemicals. The reaction normally gives a blend of short chain alkenes (lower hydrocarbons):

$$\text{Naphtha (Heavy Hydrocarbons)} \xrightarrow{\text{Catalyst}} \underset{\text{ethene}}{C_2H_4} + \underset{\text{propene}}{C_3H_6}$$

**Q.16 What is reforming? Discuss the reactions during reforming.**

**Ans. Reforming**

Reforming is a refining process that rearranges the molecular structure of hydrocarbons. In contrast to cracking (where the molecules are broken down), reforming rearranges straight-chain alkanes into a branched or cyclic (aromatic) structure.

The main purpose of reforming is to enhance the quality of fuel by converting low octane straight chains to high-octane branched or aromatic fuels to avoid engine knocking.

➢ **Reactions during reforming are given below:**

1. **Isomerisation: (Formation of Branched Hydrocarbons)**

The straight chain hydrocarbons are converted into branched-chain isomers of higher-octane numbers e.g.

$$CH_3-(CH_2)_4-CH_3 \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3 \qquad \text{(n-hexane to iso-hexane)}$$

2. **Cyclization: (Cyclic Hydrocarbons Formation)**

Cyclic compounds are prepared by the conversion of straight-chain hydrocarbons e.g.

$$CH_3-(CH_2)_4-CH_3 \longrightarrow \text{⬡} + H_2 \qquad \text{(hexane to cyclohexane)}$$

3. **Dehydrogenation: (Aromatization)**

Hydrogen is lost by cycloalkanes to produce aromatic compounds. It is used to generate important chemical base materials e.g., BTX (benzene, toluene and xylene) that are the building blocks of plastics, dyes and synthetic fibres. For example, hexane, a straight 6 carbon chain is transformed into a stable aromatic ring through cyclohexane, releasing hydrogen gas as a valuable byproduct.

$$\text{⬡} \xrightarrow[\text{heat}]{\text{Pt catalyst}} \text{⬡} + 3H_2 \qquad \text{(cyclohexane to benzene)}$$

**QUICK CHECK 31.4**

**a) Why is catalytic cracking more commonly used in modern petroleum refineries?**

**Ans.** Catalytic cracking is preferred because it:

- Produces a **higher yield of useful products** such as petrol and alkenes.
- Occurs at **lower temperatures and pressures**, reducing energy consumption.
- Is **faster and more economical** than thermal cracking.
- Produces **branched hydrocarbons**, which have higher octane numbers and improve fuel quality.

Therefore,

Catalytic cracking is more efficient, economical, and gives better-quality products.

**b) If more alkenes such as ethene and propene are desired to be produced from higher hydrocarbons, such as diesel or kerosine, which cracking method should be preferred and why?**

**Ans.** Thermal cracking is preferred due to following reasons:

- Thermal cracking operates at **very high temperatures and pressures.**
- It favors the formation of **smaller molecules with a higher proportion of alkenes** such as ethene and propene.
- These alkenes are important raw materials for the **petrochemical industry** and polymer production.

**c) During reforming, give one example of the straight chain hydrocarbon.**

**Ans. Example: n-hexane**

In catalytic reforming, straight-chain hydrocarbons such as n-hexane or n-heptane are converted into branched, cyclic or aromatic hydrocarbons with improved fuel properties.



**d) Hexane is converted into benzene and hydrogen through reforming. Explain why hydrogen can be considered a valuable by-product.**

**Ans. Reaction:**

$$C_6H_{14} \longrightarrow C_6H_6 + 4H_2$$

Hydrogen is considered a valuable by-product because it is used:

In the **Haber process** for ammonia manufacture, in **hydrogenation of vegetable oils** and in **hydrocracking and desulfurization** processes in refineries.

As a **clean fuel** in fuel cells and hydrogen-powered vehicles.

Therefore, hydrogen is a useful industrial chemical and clean energy source, making it a valuable by-product.

## ENERGY DENSITY AND SPECIFIC ENERGY

**Q.17 Discuss the two aspects used to evaluate a fuel.**

**Ans. There are two key aspects used to evaluate a fuel:**

**(I) Energy Density. (II) Specific Energy.**

I. **Energy density** is the energy capacity of a substance, generally expressed by the quantity of energy that can be stored per unit volume of a fuel, typically in megajoules per liter (MJ/L). High energy density fuels allow the use of a relatively small volume to store with large energy potential. These are useful in stationary applications and storage, e.g., in power plants, generators, etc. For example, diesel is more energy dense (~37 MJ/L) in comparison to gasoline (~34.2 MJ/L), i.e., it contains more energy per liter.

II. **Specific energy** can be defined as the amount of energy contained in a mass. It is typically measured in megajoules per kilogram (MJ/kg). It is an important measure in cases where weight is critical such as aviation or spacecraft mobile applications. A high-specific energy fuel will give significant amounts of energy, without contributing much mass. For example, hydrogen gas has extremely high specific energy (120 MJ/kg) that makes it potentially useful in aerospace applications, although its energy density is low.

**Interesting Information**

Compressed Natural Gas (CNG) used in the transportation sector in Pakistan is very economical. It has, however, lower energy density, which means that vehicles need to carry more storage volume to carry enough fuel when compared to petrol. That is why CNG is suitable as a means of local commuting, and it is not perfect as a long traveling means.

**Note:** CNG accounts for less than 2% of total fuel consumption in the road transport sector.

## NUCLEAR ENERGY - FISSION AND FUSION

While studying fossil fuels and their harmful effects on the environment, it is also important to learn about nuclear energy.

**Q.18 Discuss the role of nuclear energy, fusion and especially fission as source of energy.**

**Ans.** Nuclear energy is a potential and promising source of power that can help meet the world's growing energy needs.

➢ **Nuclear Energy:**

Nuclear energy is the energy that is released by nuclei of an atom, either when heavy nuclei are split (fission) or when light nuclei are combined (fusion). These reactions liberate extremely high quantities of energy as compared to chemical reactions.

➢ **Nuclear Fission:**

Fission is the process in which a heavy atomic nucleus like uranium-235 or plutonium-239 is split into two lighter atomic nuclei with energy production, generation of neutrons and radiations. Neutrons produced can also lead to additional fission in a chain reaction.

The nuclear reaction between uranium-235 and a neutron is as follows.

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3n + \text{energy}$$

CamScanner

Nuclear power plants extensively use nuclear fission to produce electricity. It has a very high energy production using small quantities as input; however, it has serious drawbacks, too. It produces radioactive waste which should be handled with care over a long duration.

➢ **Precaution:**

There is also the danger of nuclear accidents, the consequences of which have been observed in history, such as the Chernobyl catastrophe (1986) and the Fukushima accident (2011). These accidents seriously affected the environment and human health negatively.

## SOLAR ENERGY AND PHOTOVOLTAIC CELLS

**Q.19 With the help of a labelled diagram, explain the working of a solar PV system. What are advantages of solar energy?**

**Ans. Solar Energy and Photovoltaic Cells:**

Solar PV (photovoltaic) system is a clean energy system where the solar panels that are typically composed of silicon semiconducting materials convert the energy of sunlight into electricity via photovoltaic effect. The exposure of the solar panel to the sunlight activates electrons in the material that produces the direct current (DC) electricity.

**Did You Know?**

There was a great earthquake and tsunami in Japan, which triggered reactor accidents at Fukushima in (2011). More than 150,000 citizens were evacuated as a result of radioactive leaks, and the world became concerned about the safety of nuclear plants in disaster-prone regions.

➢ **Role of Inverter:**

This DC electricity is then converted into alternating current (AC) by an inverter and can be used to power homes, schools, offices and in industries. The system also has batteries to store electricity to use at night or cloudy days, and also assist in stabilizing voltage and discharging surge current. Other elements like electrical accessories, wires, appliances, and mounting structures make the entire solar energy system effective and safe.

**Did You Know?**

Surge current is a sudden rise in current in a circuit due to external factors, such as, lightning, sudden electricity fluctuation. It is harmful for solar panels and storage batteries.

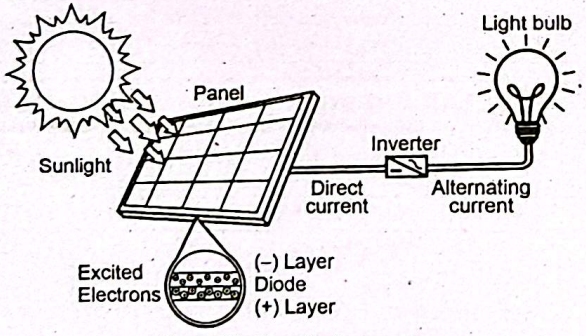



**Figure: Working of solar panels**

➢ **Advantages of Solar Energy:**

Solar energy has many key advantages over the traditional sources of energy:

- It is an environmentally friendly and renewable energy source.
- It contributes to the fight against climate change and environmental pollution.
- Solar panels are also cost-effective in the long run, since they have limited maintenance requirements once installed.

**Suggestion:** Energy shortages, high fuel prices, and climate problems show that we need to switch to renewable energy sources like solar, hydro, and wind energy.



### QUICK CHECK 31.5

**a) Why are batteries included in many solar energy systems?**

**Ans. Batteries are included because:**

- Solar panels generate electricity only when sunlight is available.
- Batteries store excess electrical energy produced during the day.
- The stored energy can be used at night or during cloudy weather.

Therefore, batteries store solar energy for use when sunlight is unavailable.

**b) The energy density of ethanol is much lower (24 MJ/L) than petrol (34.2 MJ/L). If ethanol were used in a combustion engine, what advantage/disadvantage would be observed? Keep in mind the engine structure.**

**Ans.** The main disadvantage is reduced driving range for the same tank volume. Because ethanol contains only about 24 MJ $L^{-1}$ compared with petrol at 34.2 MJ $L^{-1}$, the engine must burn a larger volume of ethanol to deliver the same energy, so a larger fuel tank or more frequent refueling is required. An engine/fuel system designed for ethanol must also supply the higher volumetric fuel flow.

**c) Identify the missing component in the reaction:**

$$^{235}_{92}U + n \longrightarrow _____ + _____ + 3n + \text{Energy}$$

**Ans.** $^{235}_{92}U + {}^{1}_{0}n \longrightarrow _____ + _____ + 3n + \text{energy}$

A common fission reaction of uranium-235 is

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3{}^{1}_{0}n + \text{energy}$$

Hence, the missing components are:

$\boxed{^{141}_{56}Ba}$ and $\boxed{^{92}_{36}Kr}$

**d) Why do nuclear reactions release much more energy than chemical reactions?**

**Ans.**

- Chemical reactions involve changes in **electron arrangements and chemical bonds.**
- Nuclear reactions involve changes in the **atomic nucleus.**
- A small amount of mass is converted into energy according to Einstein's equation:

$$E = mc^2$$

Because the speed of light (c) is extremely large, even a tiny loss of mass produces a huge amount of energy. Therefore, nuclear reactions release much more energy because mass is converted directly into energy.

### BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **X-ray crystallography is mainly used to determine the:**
   (A) Boiling point of compounds (B) Three-dimensional arrangement of atoms in crystals
   (C) Density of liquids (D) pH of solutions
2. **X-rays are suitable for crystal analysis because they have:**
   (A) Long wavelength (B) High frequency only (C) Very short wavelength (D) Low energy
3. **When X-rays strike a crystal, they undergo:**
   (A) Reflection (B) Refraction (C) Diffraction (D) Polarization
4. **The pattern produced after diffraction of X-rays is called a:**
   (A) Absorption spectrum (B) Diffraction pattern (C) Line spectrum (D) Chromatogram
5. **X-ray crystallography helps determine:**
   (A) Atomic positions and bond angles (B) Molecular mass only
   (C) Melting point (D) Colour of compounds
6. **The double-helix structure of DNA was determined using:**
   (A) IR spectroscopy (B) UV spectroscopy (C) X-ray crystallography (D) Mass spectrometry
7. **X-ray crystallography is widely used in:**
   (A) Drug development (B) Cooking oils (C) Soap manufacturing only (D) Fertilizer storage
8. **Which of the following is not a fossil fuel?**
   (A) Coal (B) Natural gas (C) Petroleum (D) Solar energy
9. **Petroleum is also known as:**
   (A) Coke (B) Crude oil (C) LPG (D) Coal tar
10. **Methane is mainly used in the manufacture of:**
    (A) Ammonia and methanol (B) PVC (C) Glass (D) Cement

CamScanner

11. Coal is an important raw material for obtaining:
(A) Benzene, toluene and xylene (B) Ethanol
(C) Acetone (D) Formaldehyde
12. Burning fossil fuels mainly increases the atmospheric concentration of:
(A) Oxygen (B) Nitrogen (C) Carbon dioxide (D) Helium
13. The major environmental effect of fossil fuel combustion is:
(A) Ozone formation (B) Global warming (C) Soil formation (D) Neutralization
14. Fractional distillation separates crude oil based on differences in:
(A) Density (B) Solubility (C) Boiling point (D) Colour
15. Crude oil is heated until it becomes:
(A) Frozen (B) Vapour (C) Solid (D) Plasma
16. In the fractionating column, heavier hydrocarbons condense:
(A) Near the top (B) Near the bottom (C) Outside the column (D) In the condenser only
17. Petrochemicals are mainly obtained from:
(A) Wood (B) Crude oil and natural gas (C) Coal only (D) Limestone
18. Poly(ethene) is prepared from:
(A) Methane (B) Ethene (C) Ethyne (D) Propane
19. Poly(propene) is produced from:
(A) Propene (B) Benzene (C) Methanol (D) Ethanol
20. Styrene is used to manufacture:
(A) Nylon (B) Polystyrene (C) PVC (D) Bakelite
21. TNT is produced from:
(A) Benzene (B) Toluene (C) Xylene (D) Ethene
22. Polyester fibres are produced from:
(A) Ethene (B) Propene (C) Xylene (D) Butadiene
23. Synthetic rubber is mainly produced from:
(A) Methane (B) Butadiene (C) Ethanol (D) Propane
24. Cracking is the process of converting:
(A) Small hydrocarbons into larger hydrocarbons (B) Large hydrocarbons into smaller hydrocarbons
(C) Alkenes into alkanes (D) Alcohols into acids
25. Thermal cracking requires:
(A) Low temperature (B) High temperature and high pressure
(C) Room temperature (D) Low pressure only
26. Catalytic cracking commonly uses:
(A) Platinum (B) Zeolites (C) Iron (D) Nickel
27. Catalytic cracking is preferred because it:
(A) Requires higher temperatures (B) Saves energy
(C) Produces only methane (D) Stops alkene formation
28. Reforming mainly converts straight-chain hydrocarbons into:
(A) Alcohols (B) Branched or aromatic hydrocarbons
(C) Carboxylic acids (D) Esters
29. Reforming improves fuel quality by increasing its:
(A) Density (B) Octane number (C) Viscosity (D) Vapour pressure
30. Energy density is expressed in:
(A) MJ/kg (B) MJ/L (C) kJ/mol (D) J/g
31. Specific energy is expressed in:
(A) MJ/L (B) MJ/kg (C) kJ/L (D) mol/L
32. Hydrogen has a very high:
(A) Energy density (B) Specific energy (C) Density (D) Viscosity
33. Nuclear energy is released by:
(A) Chemical reactions (B) Nuclear reactions (C) Combustion only (D) Oxidation only
34. Nuclear fission involves:
(A) Combining light nuclei (B) Splitting heavy nuclei (C) Burning uranium (D) Ionizing gases
35. Uranium-235 undergoes fission after absorbing a:
(A) Proton (B) Electron (C) Neutron (D) Alpha particle
36. Solar photovoltaic panels are commonly made from:
(A) Copper (B) Silicon (C) Aluminium (D) Zinc
37. In a solar power system, the inverter converts:
(A) AC into DC (B) DC into AC (C) Heat into electricity (D) Light into heat



## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

BLOCK # 01

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. B | 4. B | 5. C | 6. B | 7. C | 8. C | 9. C | 10. A | 11. B | 12. B | 13. B | 14. B | 15. B |
| 16. B | 17. B | 18. C | 19. B | 20. C | 21. B | 22. B | 23. B | 24. A | 25. B | 26. B | 27. A | 28. A | 29. B | 30. B |
| 31. B | 32. B | 33. B | 34. A | 35. A | 36. D | | | | | | | | | |

BLOCK # 02

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. C | 4. B | 5. A | 6. C | 7. A | 8. D | 9. B | 10. A | 11. A | 12. C | 13. B | 14. C | 15. B |
| 16. B | 17. B | 18. B | 19. A | 20. B | 21. B | 22. C | 23. B | 24. B | 25. B | 26. B | 27. B | 28. B | 29. B | 30. B |
| 31. B | 32. B | 33. B | 34. B | 35. C | 36. B | 37. B | | | | | | | | |

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. A mining engineer discovers a new deposit of a metal that occurs primarily as a carbonate. Which sequence is most efficient for the extraction of metals?
a) Mining, Concentration, Roasting, Reduction with Carbon
b) Mining, Concentration, Calcination, Reduction
c) Mining, Concentration, Electrolysis
d) Mining, Roasting, Refining

II. The extraction of aluminium from its oxide is done by electrolysis and not by reduction with carbon because:
a) Carbon forms alloys b) It is low melting
c) Aluminium is more reactive than carbon d) It produces huge amount of gangue

III. Which property makes ceramics suitable for furnace bricks?
a) Conductivity b) Low density c) High melting point d) Flexibility

IV. In fiberglass, the matrix mainly:
a) Provides strength b) Conducts electricity c) Holds reinforcement d) Increases weight

V. Major limitation of mechanical recycling is:
a) High energy use b) Polymer degradation c) Monomer formation d) Use of $Na_2CO_3$

VI. The mobile phone recycling is difficult because of:
a) Non-recyclable material b) Mixed materials
c) No heat sensitivity of materials d) High melting glass

VII. Chemicals from coal used in dyes are:
a) Methane series b) Benzene, toluene, xylene c) Alkenes d) $CO_2$ and $H_2$

VIII. Nuclear fission involves:
a) Combining nuclei b) Splitting nuclei c) Breaking bonds d) Molecules

### Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | b | Mining, Concentration, Calcination, Reduction | Carbonate ores are first concentrated, then converted to oxides by calcination and finally reduced to metals. |
| II. | c | Aluminium is more reactive than carbon | Aluminium cannot be reduced by carbon because it lies above carbon in the reactivity series; therefore electrolysis is used. |
| III. | c | High melting point | Ceramics can withstand very high temperatures without melting, making them ideal for furnace bricks. |
| IV. | c | Holds reinforcement | In composites such as fiberglass, the matrix binds and supports the reinforcing fibers. |
| V. | b | Polymer degradation | Repeated mechanical recycling reduces polymer quality and mechanical strength. |
| VI. | b | Mixed materials | Mobile phones contain plastics, metals, ceramics, and glass that are difficult to separate. |

CamScanner

| | | | |
|---|---|---|---|
| VII. | b | Benzene, toluene, xylene | Aromatic compounds obtained from coal tar are important raw materials for dye manufacture. |
| VIII. | b | Splitting nuclei | Nuclear fission is the splitting of a heavy nucleus into smaller nuclei with release of energy. |

## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) What is a chain reaction in nuclear fission?**

**Ans.** **A chain reaction** is a self-sustaining process in which neutrons released during one fission reaction cause further fission reactions in other nuclei, releasing more neutrons and energy.
**For Example:**

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow \text{Fission products} + 3n + \text{energy}$$

The emitted neutrons continue the reaction by striking other uranium nuclei.

**b) State the economic challenge associated with reprocessing waste materials.**

**Ans.** The major economic challenge is Collection, sorting, transportation, and processing of waste materials are expensive. Therefore, recycling or reprocessing may sometimes cost more than producing materials from raw resources.

**c) Keeping in view the concept of microstructure, explain why adding zinc to copper (to form Brass) results in a material that is stronger than pure copper.**

**Ans.** In pure copper, atoms are arranged in regular layers that can slide easily over one another.
When zinc is added to form brass its arrangement is changed:
Now, they have a different size than copper atoms. They distort the crystal lattice. This hinders the movement of dislocations and prevents layers from sliding easily. Brass is stronger and harder than pure copper because dislocation movement is restricted.

**d) Define energy density and give one example.**

**Ans.** **Energy density** is the amount of energy stored or released per unit mass or unit volume of a substance.

$$\text{Energy Density} = \frac{\text{Energy}}{\text{Mass or Volume}}$$

**Example:** Diesel is more energy dense (~37 MJ/L) in comparison to gasoline (~34.2 MJ/L), i.e., it contains more energy per liter.

**e) Name two specific semiconductors mentioned in the text and their modern applications.**

**Ans.**

| Semiconductor | Application |
|---|---|
| Silicon (Si) | Microchips, transistors, solar cells. |
| Germanium (Ge) | Transistors, diodes, infrared detectors. |

Similarly, Gallium arsenide (GaAs) and Gallium nitride (GaN) are also used.

**f) State two applications of X-ray crystallography in science or industry.**

**Ans.** 1. Determination of the **crystal structure of materials and minerals.**
2. Determination of the **structure of biological molecules** such as proteins and DNA.
Other acceptable answers include pharmaceutical drug design and semiconductor research.

**g) State two advantages and one disadvantage of nuclear fission.**

**Ans.** **Advantages:**
1. Produces a **very large amount of energy** from a small amount of fuel.
2. Produces **very low greenhouse gas emissions** during operation.

**Disadvantage:**
- Produces **radioactive waste** that requires safe storage and disposal for long periods.



**h) In the reduction of haematite ($Fe_2O_3$), carbon is added, but carbon monoxide (CO) is the actual species that displaces the oxygen. Explain why the gas (CO) is a more efficient reducing agent in a large-scale furnace than solid carbon (C).**

$$C + \frac{1}{2}O_2 \longrightarrow CO$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

**Ans.** **Reactions:**

$$C + \frac{1}{2}O_2 \longrightarrow CO$$

$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

Carbon monoxide is more efficient because:
- It is a **gas**, so it mixes and contacts the iron ore more effectively.
- It diffuses rapidly through the furnace.
- It provides a larger surface area for reaction than solid carbon.

Therefore, CO reduces iron oxide faster and more efficiently than solid carbon.

## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) Explain environmental problems, caused by fossil fuels.**

**Ans.** The use of fossil fuels causes several environmental problems:
1. **Global Warming:** Burning fossil fuels releases large amounts of carbon dioxide ($CO_2$), a greenhouse gas that traps heat in the atmosphere and causes global warming.
$$C + O_2 \longrightarrow CO_2$$
2. **Acid Rain:** Sulfur impurities in fossil fuels produce sulfur dioxide ($SO_2$) during combustion. It reacts with water vapour to form acids, leading to acid rain.
$$SO_2 + H_2O \longrightarrow H_2SO_3$$
3. **Air Pollution:** Incomplete combustion produces carbon monoxide and particulate matter, which cause respiratory diseases and smog.
4. **Environmental Damage:** Oil spills and mining activities damage ecosystems and wildlife habitats.

**b) Based on the chemical equations provided, explain why roasting sulphide ores poses a greater environmental challenge compared to the calcination of carbonate ores.**

**Ans.** **Roasting of Sulphide Ores:** $2ZnS + 3O_2 \longrightarrow 2ZnO + 2SO_2$
This process releases **sulfur dioxide ($SO_2$)**, which causes acid rain, respiratory problems and air pollution
**Calcination of carbonate ores:** $CaCO_3 \longrightarrow CaO + CO_2$
Calcination mainly releases **carbon dioxide ($CO_2$)**, which contributes to global warming but does not directly cause acid rain. Therefore, roasting sulphide ores is environmentally more harmful because it releases $SO_2$.

**c) If a sample of copper is 98% pure after reduction, why is the final "refining" step still considered crucial for the manufacturing of electrical wiring?**

**Ans.** Electrical wiring requires extremely high electrical conductivity.
**Even small amounts of impurities:**
• Increase electrical resistance. • Reduce conductivity. • Cause energy losses due to heating.
Therefore, copper used for electrical wiring is refined to approximately: 99.99% purity

**d) Explain, why chemical recycling (depolymerisation) is often superior to mechanical recycling?**

**Ans.** **Advantages of chemical recycling:**
1. Produces **pure monomers** that can be reused to make high-quality polymers.
2. Polymer properties are not degraded after recycling.
3. Mixed or contaminated plastics can often be processed more effectively.
4. Allows repeated recycling without significant loss of quality.

**Limitation of Mechanical Recycling:**
**Repeated melting causes:** • Polymer degradation • Reduced strength • Lower quality products

CamScanner

Therefore, chemical recycling produces higher quality recycled materials than mechanical recycling.

**e) Gold is often found in its free state, while sodium is only found in the combined states. Use the concept of the reactivity series to justify why the extraction process for sodium is significantly more energy-intensive than for gold.**

**Ans.** Gold lies near the bottom of the reactivity series and is very unreactive.
Therefore:
- Gold often occurs naturally in its elemental state.
- Very little processing is required for extraction.

Sodium lies near the top of the reactivity series and is highly reactive.
Therefore:
- Sodium exists only as compounds such as sodium chloride ($NaCl$).
- Carbon cannot reduce sodium compounds.
- Sodium must be extracted by **electrolysis of molten sodium chloride**, which requires large amounts of electrical energy.

$$2NaCl_{(l)} \longrightarrow 2Na_{(l)} + Cl_{2(g)}$$

Hence, Sodium extraction is much more energy intensive because of its high reactivity and the need for electrolysis, whereas gold occurs naturally in the free state.

## DESCRIPTIVE QUESTIONS DQs

**Q.4 Explain composite materials by describing and differentiating the roles of the matrix and the reinforcement in them.**

**Ans.** See Question No. 08

**Q.5 Explain how X-rays interact with crystals to produce diffraction patterns and how these patterns help determine atomic positions?**

**Ans.** See Question No. 11

**Q.6 Describe the main steps involved in the extraction of metals from their ores.**

**Ans.** See Question No. 07

**Q.7 Explain the importance and challenges to the process of recycling.**

**Ans.** See Question No. 10

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 What is materials science?**

**Ans.** Materials science is the study of the structure, properties and applications of materials. It helps scientists design materials with desired characteristics for industrial and technological applications.

**Q.2 Why are different materials selected for different applications?**

**Ans.** Different materials possess different physical and chemical properties such as strength, hardness, conductivity and corrosion resistance. Therefore, materials are selected according to the requirements of the intended application.

**Q.3 What is meant by extraction of metals?**

**Ans.** Extraction of metals is the process of obtaining pure metals from their ores using suitable chemical methods. The method used depends upon the reactivity of the metal and the nature of its ore.

**Q.4 Define alloy with an example.**

**Ans.** An alloy is a mixture of two or more elements in which at least one component is a metal. Alloys are prepared to improve properties such as hardness, strength and corrosion resistance.
**Example:** Brass is an alloy of copper and zinc.



**Q.5 Why are alloys preferred over pure metals?**

**Ans.** Alloys generally possess improved mechanical properties such as greater hardness, higher strength and better resistance to corrosion than pure metals. Therefore, they are more suitable for industrial applications.

**Q.6 Explain the role of catalysts in chemical reactions.**

**Ans.** Catalysts increase the rate of reaction by providing an alternative pathway with lower activation energy. They remain chemically unchanged and can be reused after the reaction.

**Q.7 What is meant by activation energy?**

**Ans.** Activation energy is the minimum energy required for reactant particles to undergo a successful collision and form products. Catalysts reduce this energy requirement and speed up reactions.

**Q.8 Why is recycling important?**

**Ans.** Recycling conserves natural resources, reduces energy consumption and minimizes environmental pollution. It also decreases the amount of waste sent to landfills.

**Q.9 Why is lead considered a toxic material?**

**Ans.** Lead can accumulate in body tissues and damage the nervous system, kidneys and brain. Long-term exposure may cause serious health problems, especially in children.

**Q.10 What is X-ray crystallography?**

**Ans.** X-ray crystallography is a technique used to determine the arrangement of atoms in crystalline solids by studying the diffraction of X-rays. It is widely used to determine the structures of minerals, proteins and complex molecules.

**Q.11 Differentiate between petrochemicals and petroleum.**

**Ans.** Petroleum is a naturally occurring mixture of hydrocarbons obtained from crude oil deposits, whereas petrochemicals are useful chemicals produced from petroleum and natural gas. Petrochemicals are used to manufacture plastics, detergents, fertilizers and synthetic fibers.

**Q.12 What are the major raw materials of the petrochemical industry?**

**Ans.** The petrochemical industry mainly uses crude oil and natural gas as raw materials. These are processed to produce hydrocarbons such as ethene, propene and benzene, which are further converted into valuable products.

**Q.13 Explain fractional distillation of petroleum.**

**Ans.** Fractional distillation is the process of separating crude oil into different fractions based on differences in boiling points. The crude oil is heated and vapors condense at different levels of the fractionating column according to their boiling points.

**Q.14 Why do different fractions condense at different heights in the fractionating column?**

**Ans.** The temperature decreases from the bottom to the top of the column. Fractions having higher boiling points condense near the bottom, while fractions with lower boiling points rise higher before condensing.

**Q.15 State the major fractions obtained from crude oil.**

**Ans.** The major fractions obtained from crude oil include refinery gas, petrol, naphtha, kerosene, diesel oil, fuel oil, lubricating oil and bitumen. Each fraction contains hydrocarbons with similar boiling ranges.

**Q.16 State two uses of petrol and diesel.**

**Ans.** Petrol is mainly used as fuel for cars and motorcycles, whereas diesel is used in buses, trucks and heavy machinery. Both serve as important transportation fuels.

**Q.17 What are petrochemicals? Give examples.**

**Ans.** Petrochemicals are chemicals produced from petroleum and natural gas. Important examples include ethene, propene, benzene, methanol and ethylene glycol.
These compounds are used as raw materials in many industries.

CamScanner

**Q.18 State the applications of petrochemicals.**

**Ans.** Petrochemicals are used in the manufacture of plastics, synthetic fibers, detergents, fertilizers, medicines and solvents. They play a vital role in modern industrial development.

**Q.19 Differentiate between energy density and specific energy.**

**Ans.** Energy density is the amount of energy stored per unit volume or mass of a substance, whereas specific energy is the amount of energy stored per unit mass only.
Specific energy is commonly expressed in kJ $kg^{-1}$.

**Q.20 Why are fossil fuels considered non-renewable resources?**

**Ans.** Fossil fuels require millions of years to form from the remains of plants and animals. Since their rate of consumption is much faster than their formation, they are considered non-renewable resources.

**Q.21 State two advantages and two disadvantages of fossil fuels.**

**Ans.** Fossil fuels possess high energy content and are easy to transport and store. However, their combustion releases carbon dioxide and other pollutants, contributing to global warming and environmental pollution.

**Q.22 Explain nuclear fission.**

**Ans.** Nuclear fission is the process in which a heavy nucleus such as uranium-235 splits into two smaller nuclei with the release of a large amount of energy and neutrons. This reaction is used in nuclear power plants for electricity generation.

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3{}^{1}_{0}n + \text{Energy}$$

**Q.23 Explain nuclear fusion.**

**Ans.** Nuclear fusion is the process in which two light nuclei combine to form a heavier nucleus with the release of enormous amounts of energy. Fusion reactions occur naturally in the Sun and stars.

$$^{1}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n + \text{Energy}$$

**Q.24 Differentiate between nuclear fission and nuclear fusion.**

**Ans.** In nuclear fission, a heavy nucleus splits into smaller nuclei, whereas in nuclear fusion two light nuclei combine to form a heavier nucleus. Fission is used in nuclear reactors while fusion powers the Sun and stars.

**Q.25 Why does nuclear fusion release more energy than chemical reactions?**

**Ans.** Nuclear fusion involves changes in nuclear binding energy, which are much greater than the energies involved in chemical bond breaking and formation. Therefore, fusion reactions release enormous amounts of energy.

**Q.26 Explain the working principle of solar panels.**

**Ans.** Solar panels contain photovoltaic cells that convert sunlight directly into electrical energy through the photovoltaic effect. When sunlight strikes the semiconductor material, electrons are excited and produce an electric current.

**Q.27 State two advantages of solar energy.**

**Ans.** Solar energy is renewable and environmentally friendly because it does not produce greenhouse gases during operation. It also reduces dependence on fossil fuels and lowers electricity costs in the long term.

**Q.28 Explain the term carbon footprint.**

**Ans.** Carbon footprint is the total amount of greenhouse gases, especially carbon dioxide, released directly or indirectly due to human activities such as transportation, industry and electricity generation.
It is usually expressed in tones of $CO_2$ equivalent.

**Q.29 How does energy consumption contribute to global warming?**

**Ans.** The combustion of fossil fuels releases carbon dioxide and other greenhouse gases into the atmosphere. These gases trap heat and increase the Earth's average temperature, leading to global warming.

$$C + O_2 \longrightarrow CO_2$$



**Q.30 Evaluate renewable and non-renewable energy sources.**

**Ans.** Renewable energy sources such as solar, wind and hydroelectric power are sustainable and produce less pollution, whereas non-renewable sources such as coal, oil and natural gas are limited in supply and contribute to environmental problems.
Therefore, future energy strategies should focus on increasing the use of renewable energy sources.

## SELF-ASSESSMENT

**Total Mark: 30**

**Q.1 Encircle the correct option.** **(1 × 6 = 6)**

(i) **The property that allows metals to be drawn into wires is:**
(A) Malleability (B) Ductility (C) Brittleness (D) Elasticity

(ii) **Highly reactive metals such as sodium are extracted by:**
(A) Roasting (B) Calcination (C) Electrolysis (D) Carbon reduction

(iii) **The double-helix structure of DNA was determined using:**
(A) IR spectroscopy (B) UV spectroscopy (C) X-ray crystallography (D) Mass spectrometry

(iv) **Reforming improves fuel quality by increasing its:**
(A) Density (B) Octane number (C) Viscosity (D) Vapour pressure

(v) **The extraction of aluminium from its oxide is done by electrolysis and not by reduction with carbon because:**
(A) Carbon forms alloys (B) It is low melting
(C) Aluminium is more reactive than carbon (D) It produces huge amount of gangue

(vi) **Major limitation of mechanical recycling is:**
(A) High energy use (B) Polymer degradation (C) Monomer formation (D) Use of $Na_2CO_3$

**Q.2 Write short answers of the following questions.** **(2 × 8 = 16)**

(i) Why is silicon preferred for use in microchips and solar panels?
(ii) What do reinforcement agents provide in composite materials?
(iii) Name the types of hazards posed by: i) poly(ethene) ii) water glass bottles
(iv) Can XRD be used to find the structure of liquids?
(v) During reforming, give one example of the straight chain hydrocarbon.
(vi) Why are batteries included in many solar energy systems?
(vii) State the economic challenge associated with reprocessing waste materials.
(viii) Name two specific semiconductors mentioned in the text and their modern applications.

**Q.3 Extensive Questions.** **(4 + 4 = 8)**

(a) Explain how X-rays interact with crystals to produce diffraction patterns and how these patterns help determine atomic positions?
(b) Describe the main steps involved in the extraction of metals from their ores.

CamScanner

## ENTRANCE TEST MCQs

1. **Gallium nitride is used in electric vehicles for:**
   (A) Fuel combustion (B) Paper de-inking (C) Copper refining (D) Fast charging & power electronics
2. **Separating materials from modern products is difficult because:**
   (A) Only water-soluble materials (B) No polymers
   (C) Mixed and bonded materials (D) Only single pure elements
3. **A famous application of X-ray crystallography was determining the:**
   (A) Discovery of sodium metal (B) Composition of crude oil
   (C) DNA double helix (D) Boiling point of water
4. **In XRD, structural information arises from:**
   (A) Electrolysis of the sample (B) Random light absorption
   (C) X-ray diffraction from ordered atomic planes (D) Combustion of the crystal
5. **If maximum alkene production is desired from heavy oil, the preferred method is often:**
   (A) Fractional distillation only (B) Calcination
   (C) Electro refining (D) Thermal cracking
6. **Why does a catalyst save energy in a refinery?**
   (A) It makes fuel heavier (B) It stops all collisions
   (C) The same rate is achieved at lower temperature (D) It increases activation energy
7. **Catalyst poisoning reduces activity by:**
   (A) Blocking active sites (B) Lowering product mass (C) Increasing surface area (D) Creating more active sites
8. **The scatter plot shows which fuel with the highest specific energy?**
   (A) Diesel (B) Gasoline (C) All equal (D) Hydrogen
9. **Which energy source has low direct greenhouse-gas emissions but raises concerns about radioactive waste?**
   (A) Petroleum (B) Natural gas (C) Nuclear fission (D) Coal
10. **Which material class best suits an extreme-heat, electrically insulating furnace lining?**
    (A) Natural gas (B) Ceramic (C) Copper (D) Low-carbon polymer
11. **A lightweight aircraft frame requiring strength and corrosion resistance is best matched with:**
    (A) Duralumin or a fibre composite (B) Pure lead
    (C) Bitumen (D) Paper

**Answers Key**

| 1. D | 2. C | 3. C | 4. C | 5. D | 6. C | 7. A | 8. D | 9. C | 10. B | 11. A |
|---|---|---|---|---|---|---|---|---|---|---|



32 CHAPTER

# MEDICINE, AGRICULTURE AND INDUSTRY

## Student Learning Outcomes (SLOs)

[C-12-E-50 to C-12-E-65]

**Part I-MEDICINE**

- Recognize the concept of therapeutic index and therapeutic window in relation to drug administration.
- Describe the pH regulation of stomach and its relation to the concept of non- specific reactions and active metabolites.
- Explain the mechanism of action and uses of aspirin and penicillin and explain the chemical structure of the same.
- Describe the mechanism of action of opiates and the concept of opioid receptors in the brain.
- Recognize the challenges in treating viral infections with drugs and the concept of antiviral medications.

**Part II-AGRICULTURE**

- Explain the chemical composition and function of different types of fertilizers, including their role in providing essential nutrients to crops and the impact of their application on soil health.
- Identify the different types of pesticides used in agriculture and describe their mode of action, including the potential benefits and risks associated with their use.
- Identify the chemical reactions that occur when acid rain falls on crops and soil and explain the effects it has on crop growth, including nutrient uptake and crop yield.
- Explain how changes in temperature, precipitation, and extreme weather events can affect crop growth and yield, including the potential for crop failures and food shortages, as well as the potential to develop new crop varieties that are more resilient to changing climate conditions.
- Explain the basics of genetic engineering and how it is used in agriculture, including the development of genetically modified crops and the potential benefits and risks associated with their use.

**Part III-INDUSTRY**

- Justify the importance and significance of industrial chemistry in various industries such as manufacturing, energy, healthcare, and environmental protection.
- Identify the raw materials and resources used in industrial chemistry, including those readily available in the context of Pakistan.
- Discuss the importance of chemical industries in the economy of Pakistan, and describe the raw materials that are available in the country for various chemical industries.
- Describe the chemical processes involved in industrial production, including addition and condensation polymerization, and the properties and materials.
- Explain the applications of industrial chemistry in industries such as petrochemical, cosmetics, cement, food production and more.
- Elaborate on the safety measures and precautions necessary in industrial chemical processes and facilities.

## MEDICINE

Medicines prepared in the pharmaceutical industry are of vital significance as regards human health. Chemistry unlocks the secrets behind how drugs truly work inside the body. A drug's safety limits and optimal dose range are two very crucial aspects of medicine. The knowledge of safety and the action of a drug ensures the safe absorption and action of a drug on the target disease. In this chapter, these aspects will be discussed in the following sections.

CamScanner

## THERAPEUTIC INDEX AND THERAPEUTIC WINDOW

**Q.1 What is Pharmacology?** S/Q

**Ans.** *Pharmacology is the science which deals with, what a drug does and the safety margins within which it operates.* Every drug may be a potential poison; the difference lies in the dose of each drug. The therapeutic index and therapeutic window are central concepts for understanding how safe and effective a medicine is. They help doctors to determine the right amount of a drug to give to a patient.

**Q.2 Write notes on: (i) Therapeutic Window (ii) Therapeutic Index** L/Q

**Ans.**

### i. Therapeutic Window

- Therapeutic window is the range of drug concentrations in the plasma that are effective without causing harmful side effects. *It is the "sweet spot" of medicine i.e., not too low to be ineffective and also not too high to be dangerous.*
- Minimum effective concentration (MEC) is the lowest concentration of the drug below which it fails to produce a clinical effect. Minimum toxic concentration (MTC) is the lowest concentration at which drug begins to cause adverse effects or "poisoning". Duration of action is the time duration in which the drug concentration remains within its therapeutic window.
- A wide therapeutic window indicates the safety limits of a drug, as there is a large gap between the dose that works and the dose that's harmful. This allows more flexibility in dosing. A narrow therapeutic window means the drug is less safe because the effective dose is very close to the toxic dose. Doctors must be extremely careful when prescribing these drugs and often need to check the patient's blood to ensure the drug level stays within the correct narrow range.
- The simultaneous use of multiple medicines, genetic factors, obesity, age, or overall health may also affect the therapeutic window of a drug. All these factors govern the metabolism and efficacy of a drug.

### ii. Therapeutic Index

- ***The therapeutic index (TI) is a quantitative measurement of a drug's safety.***
- It compares the dose that causes a toxic effect to the dose that produces a desired therapeutic effect. A higher TI means the drug is safer because there's a larger difference between the effective dose and the toxic dose. A low TI means the drug is more dangerous and requires careful monitoring to avoid toxicity.
- ***$Td_{50}$ (Toxic Dose 50) is the dose that causes a toxic effect in 50% of the people who take it.***
- For example, a drug with a TI of 10 is much safer than one with a TI of 2. $ED_{50}$ (Effective Dose 50) is defined as the dose that works for 50% of the people who take it.
- Drugs like Penicillin or Paracetamol have high TI. It means if patients accidently double their dose, this will not put a potential threat to their lives. On the other hand, drugs like Warfarin (a blood thinner) or Digoxin (heart medicine) have to be taken very carefully only in proper dosage. Otherwise, they may risk the life of the patient. Patients using low TI drugs must carry regular blood tests for therapeutic drug monitoring (TDM).

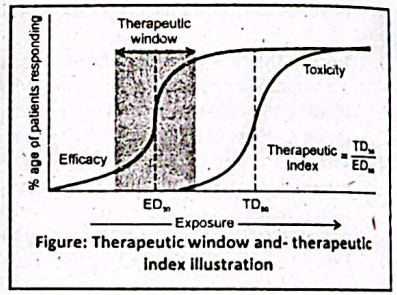


Figure: Therapeutic window and- therapeutic index illustration

**Did You Know?**
Digoxin's narrow therapeutic index means that accidental overdosing is a documented clinical risk, requiring carful blood monitoring. Its toxicity causes ventricular fibrillation (a fatal heart rhythm) and "yellow-tinted" vision (xanthopsia).



## IMPORTANCE OF pH IN STOMACH

**Q.3 Discuss the importance of pH in stomach.** S/Q

**Ans.** The stomach has a highly acidic environment with a low pH(1.5-3.5). This acidity is regulated by parietal cells, which actively pump hydrogen ions ($H^+$) into the stomach. This process is important for digesting food and killing bacteria. Although the stomach has very low pH but it protects itself via a thick layer of mucus and bicarbonate ions, which neutralize acid at the cell surface. The low pH of stomach can cause non-specific reactions, meaning it can chemically change some drugs. For example, some drugs may break down in the acidic environment before they can be absorbed into the bloodstream. This is why some medications are given in a protective coating that only dissolves in the less acidic small intestine.

## MECHANISM OF DRUG ACTION

**Q.4 Describe the structure and mechanism of action of penicillin.** Exercise Q.Q.4

**Ans.** The mechanism of action means how a drug works at a cellular level to produce therapeutic effects. Here we shall take two famous medicines i.e., aspirin and penicillin as examples. The action of aspirin in blocking cyclooxygenase (COX) enzyme's has been discussed previously. Now the mechanism of action of penicillin is being discussed.

➢ **Penicillin:**

It is a powerful antibiotic used to treat many types of bacterial infections, such as respiratory infections like, strep throat, pneumonia, scarlet fever and sinusitis. It also helps to treat skin and soft tissue infections.

**The structure of Penicillin** contains two core rings; a four membered beta-lactam ring and a five membered thiazolidine ring. Both the rings have certain side chains attached to them. The beta-lactam ring is crucial for the antibiotic's activity, as it is the site where bacterial enzymes called beta-lactamases can attack and deactivate penicillin.

The structure of penicillin looks identical to the amino acid sequence of the enzyme which strengthens the cell wall. The enzyme mistakenly takes up penicillin molecule, where the beta lactam ring opens and bind permanently to get inactivated. Bacteria continue to grow, but without the functional cell wall, and eventually burst to die. Since human cells don't have cell walls, penicillin does not harm our cells.

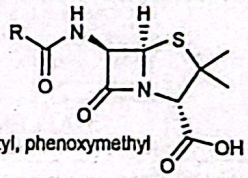


Figure: Chemical Structure of Penicillin

**Did You Know?**
In 1928, Alexander Fleming accidentally discovered penicillin when he noticed that mold growing on a contaminated petri dish had killed surrounding bacteria. The mold, later identified as Penicillium, released a substance that inhibited bacterial growth. This chance observation led to the development of the first antibiotic, revolutionising modern medicine industry.

### ➲ Opiates And Opioid Receptors

**Q.5 What are opiates and opioid receptors? Discuss the mechanism of action of opiates.** L/Q

**Ans.** Opiates are a class of drugs that come from the opium poppy plant. They are powerful pain relievers but also cause addiction. The legal drugs include the morphine, codeine, oxycodone, hydrocodone etc. The illegal category contains drugs like heroin, fentanyl etc.

➢ **Concept of Opioid Receptors:**

The human brain produces our own painkillers called endorphins. These bind with opioid receptors in our Central Nervous System (CNS). Opiates "hijack" this natural system, and become effective for pain relief but also highly addictive.

CamScanner

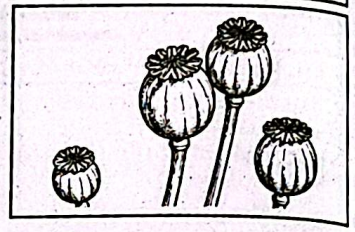
There are three types of opioid receptors. Mu(μ) receptors are located in the brain and spinal cord. These are primary target for most of the opioids like morphine. They are responsible for analgesic activity of opiates, but activation of these receptors can also cause respiratory depression and intense euphoria. Kappa (κ) receptors are involved in spinal analgesia and sedation; but they are less associated with euphoria. Delta (δ) receptors play a vital role in emotional response and mood regulation.

➢ **Mechanism of Action:**

***Opiates work by binding to special proteins in the brain and spinal cord called opioid receptors.*** It works like a key (opiate) and lock (receptor) model. When the opiate binds to the receptor, it blocks pain signals from reaching the brain, making the person feel less pain. In actual, when an opiate binds the receptor, it closes the calcium channels and opens the potassium channel. This hyperpolarizes the neuron, making it much harder for the cell to send the pain signal. It has been experimentally found that opiates start a neurochemical reaction in the reward center of brain, leading to excessive release of dopamine, which give a sense of relief and well-being.

**Keep in Mind**

Analgesic medicines give pain relief, sedatives provide calm and induce sleep, whereas, anaesthetics block all body sensations.



Opioids are used to relief acute pain like sudden and short-term pain. They are also used to manage the severe pain associated to cancer. Opioids like codeine is used in cough syrups as they suppress the cough reflex.

Opium Poppy (Papaver somniferulum) contains opiates morphine, codeine and thebaine. Other opium drugs, such as, heroin is derived from morphine and codeine, whereas, oxycodone from thebaine.

**Did You Know?**

Before it became a street drug, Heroin (diacetylmorphine) was a trademarked medicine sold by Bayer as a "non-addictive" alternative to morphine and a cough suppressant for children. Because its potency is roughly five times that of morphine, it crossed the blood-brain barrier faster, creating a "rush" that led to a global addiction epidemic.

## CHALLENGES IN TREATING VIRAL INFECTIONS

**Q.6 What challenges are faced during treatment of viral infections?** S/Q

**Ans.** Treating viral infections is fundamentally different from bacterial treatment. Bacteria are independent organisms, while viruses are parasites. Unlike bacteria, which are living organisms on their own, viruses are not truly alive. Viruses live inside our cells and use our own DNA/RNA machinery to replicate. This makes it hard to develop a drug that kills the virus without harming the healthy human cells.

***Viruses can change their genetic material very quickly. This is called mutation.***

➢ **Challenges:**

- A drug that works against a virus one year might not work the next because the virus has changed by mutation. This is why flu vaccines need to be updated every year.
- Viruses also merge with our genome and stay asleep for years. Drugs at recent times can kill only active viruses and not those which have been sleeping for years.
- Antiviral medications work by targeting specific stages of the viral life cycle. **For example,** some antivirals prevent the virus from entering our cells, while others stop the virus from making copies of its genetic material. One of the most common mechanisms of action of antiviral drugs is enzyme inhibition.
  **Example:** Protease inhibitor, does not allow the virus to produce their protein in one long strand. These inhibitors also help in the treatment of HIV and hepatitis C infections.
- Some antiviral drugs enhance the immune response to viral infections. Interferons are proteins that can boost immune system to fight against viruses.



### QUICK CHECK 32.1

**a) Drug A has a TI of 3, and Drug B has a TI of 50. Which drug is considered safer, and why?**

**Ans.** The Therapeutic Index (TI) is:

$$TI = \frac{LD_{50}}{ED_{50}}$$

where:

- $LD_{50}$ = lethal dose for 50% of the population, $ED_{50}$ = effective dose for 50% of the population

A larger TI means a wider safety margin between the effective dose and toxic dose.

- Drug A: TI = 3TI
- Drug B: TI = 50TI

Therefore, Drug B is safer because it has a much larger therapeutic index and wider safety margin.

**b) How do antacids (e.g., magnesium hydroxide, $Mg(OH)_2$) chemically regulate stomach pH? Write a simple neutralization equation to illustrate this.**

**Ans.** Antacids neutralize excess hydrochloric acid present in the stomach and reduce acidity. e.g., $Mg(OH)_2$

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O$$

Thus, Antacids increase stomach pH by neutralizing excess acid.

**c) Identify the core, strained heterocyclic ring system in penicillin that is essential for its antibacterial activity.**

**Ans.** The essential ring system in penicillin is the: β-lactam ring

It is a four-membered cyclic amide ring that is highly strained and responsible for inhibiting bacterial cell wall synthesis.

**d) Why do many antiviral drugs cause significant side effects for the host patient?**

**Ans.** Viruses reproduce inside host cells and use the host's cellular machinery for replication.

As a result:

- Antiviral drugs often affect both viral processes and normal host cell functions.
- This lack of selectivity can damage healthy cells.

Therefore, many antiviral drugs produce side effects because viruses and host cells share many biochemical pathways. **e.g.,** Liver damage, kidney damage (Nephrotoxicity), anaemia, bone marrow suppression.

### BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Pharmacology is the science that studies:**
   (A) Plant diseases (B) Drug action and safety (C) Food preservation (D) Industrial chemistry
2. **The therapeutic window is the range of drug concentrations that is:**
   (A) Toxic only (B) Effective without harmful side effects
   (C) Always ineffective (D) Equal to the lethal dose
3. **Minimum Effective Concentration (MEC) is the:**
   (A) Highest safe dose (B) Lowest dose producing a therapeutic effect
   (C) Toxic dose (D) Lethal dose
4. **Minimum Toxic Concentration (MTC) is the:**
   (A) Lowest dose causing adverse effects (B) Maximum effective dose
   (C) Average dose (D) Safe dose
5. **Duration of action refers to the time during which the drug concentration remains:**
   (A) Above the toxic level (B) Within the therapeutic window
   (C) Below MEC (D) Equal to $ED_{50}$
6. **A wide therapeutic window indicates that a drug is:**
   (A) Less effective (B) More dangerous (C) Relatively safer (D) Highly addictive
7. **Drugs having a narrow therapeutic window require:**
   (A) No monitoring (B) Careful dose monitoring (C) Double doses (D) Higher toxicity
8. **The therapeutic index (TI) is a measure of a drug's:**
   (A) Solubility (B) Safety (C) Taste (D) Colour
9. **Therapeutic index is calculated as:**
   (A) $ED_{50} / TD_{50}$ (B) $TD_{50} / ED_{50}$ (C) MEC / MTC (D) MTC / MEC
10. **$ED_{50}$ represents the dose effective for:**
    (A) 25% of people (B) 50% of people (C) 75% of people (D) 100% of people
11. **$TD_{50}$ represents the dose producing toxicity in:**
    (A) 10% of people (B) 25% of people (C) 50% of people (D) 100% of people

CamScanner

12. A higher therapeutic index means the drug is:
(A) Less safe (B) More toxic (C) Safer (D) Less effective
13. Which drug has a high therapeutic index?
(A) Warfarin (B) Digoxin (C) Paracetamol (D) None of these
14. Therapeutic Drug Monitoring (TDM) is mainly required for drugs with:
(A) High TI (B) Low TI (C) High solubility (D) High molecular mass
15. The normal pH of the stomach is approximately:
(A) 7–8 (B) 5–6 (C) 1.5–3.5 (D) 9–10
16. Hydrogen ions in the stomach are secreted by:
(A) Chief cells (B) Goblet cells (C) Parietal cells (D) Liver cells
17. The acidic environment of the stomach helps in:
(A) Photosynthesis (B) Food digestion and killing bacteria
(C) Blood clotting (D) Bone formation
18. The stomach protects itself from acid by:
(A) Calcium carbonate (B) Mucus and bicarbonate ions
(C) Sodium chloride (D) Pepsin only
19. Some medicines are enteric-coated to:
(A) Increase toxicity (B) Prevent breakdown in stomach acid
(C) Increase bitterness (D) Slow digestion
20. Penicillin is classified as a:
(A) Antiviral drug (B) Antibiotic (C) Analgesic (D) Antacid
21. Penicillin is commonly used to treat:
(A) Viral infections (B) Bacterial infections (C) Fungal infections only (D) Cancer
22. The antibacterial activity of penicillin mainly depends on its:
(A) Benzene ring (B) β-Lactam ring (C) Alcohol group (D) Ester group
23. Penicillin inhibits the formation of the bacterial:
(A) Cell membrane (B) Cell wall (C) Ribosome (D) Nucleus
24. Human cells are not damaged by penicillin because they lack:
(A) DNA (B) Cell wall (C) Cytoplasm (D) Enzymes
25. Penicillin was discovered by:
(A) Louis Pasteur (B) Robert Koch (C) Alexander Fleming (D) Edward Jenner
26. Which of the following is an opioid?
(A) Morphine (B) Aspirin (C) Ibuprofen (D) Penicillin
27. The natural pain-relieving chemicals produced by the brain are:
(A) Hormones (B) Endorphins (C) Enzymes (D) Antibodies
28. Most opioid analgesics primarily act on:
(A) κ receptors (B) δ receptors (C) μ receptors (D) Nicotinic receptors
29. Morphine reduces pain by:
(A) Destroying nerves (B) Blocking pain signals (C) Increasing blood pressure (D) Producing antibodies
30. Opiates produce euphoria mainly due to increased release of:
(A) Insulin (B) Dopamine (C) Adrenaline (D) Thyroxine
31. Codeine is commonly used as:
(A) An antibiotic (B) A cough suppressant (C) An antacid (D) A vaccine
32. Viruses differ from bacteria because viruses:
(A) Live independently (B) Replicate only inside host cells
(C) Have cell walls (D) Produce spores
33. Developing antiviral drugs is difficult because viruses:
(A) Lack DNA (B) Use host cell machinery (C) Are larger than bacteria (D) Have no proteins
34. Rapid genetic changes in viruses are called:
(A) Diffusion (B) Mutation (C) Hydrolysis (D) Polymerization
35. Flu vaccines are updated regularly because viruses:
(A) Become heavier (B) Mutate rapidly (C) Lose DNA (D) Stop reproducing
36. Protease inhibitors act by:
(A) Destroying red blood cells (B) Preventing viral protein formation
(C) Increasing stomach acid (D) Neutralizing toxins
37. Interferons help fight viruses by:
(A) Killing bacteria directly (B) Boosting the immune response
(C) Neutralizing acids (D) Destroying antibodies



38. One major challenge in treating viral infections is that viruses:
(A) Never mutate (B) Can remain dormant for years
(C) Lack proteins (D) Cannot infect humans
39. Antiviral drugs mainly target:
(A) Human DNA (B) Specific stages of the viral life cycle
(C) Blood cells only (D) Bone marrow

## AGRICULTURE

In this section, we shall explore the role of chemistry in modern agriculture. Here we shall discuss the importance and role of fertilizers, pesticides, and genetic engineering to increase the supply for growing demand of food. The section will also describe the chemical reactions of acid rain in crops and soils and explain how climate change affects crop growth.

### FERTILIZERS

**Q.7 What are fertilizers, micronutrients, macronutrients? Discuss their role of fertilizers in plant growth.** LQ

**Ans.** Fertilizers are the mineral rich superfood given to the soil which improves its fertility. They replenish (replace with the same) the depleted soil and boost healthy growth, increase crop yields, and ensure better food production.

- Fertilizers are chemicals that provide essential nutrients to plants to promote growth and increase crop yields.
- Synthetic fertilizers are man-made through chemical processes like the Haber-Bosch process for ammonia ($NH_3$).
- Organic fertilizers come from natural sources like compost or animal manure.

**Micronutrients and Macronutrients:**

Plants require seventeen essential elements, as micronutrients and macronutrients. The micronutrients include boron, iron, nickel, copper, chlorine, manganese, molybdenum and zinc. Whereas the macronutrients are carbon, hydrogen, oxygen, nitrogen, phosphorus, sulphur, potassium, calcium and magnesium. Out of these nine macronutrients nitrogen, phosphorus, and potassium are needed in such large quantities that they are termed primary macronutrients. Commercial fertilizers are labeled with an N-P-K ratio, which represents the concentrations of these three elements.

**Role of Fertilizers in Plant Growth:**

1. **Nitrogen:** Nitrogen is often the most limiting factor in crop production. It is a fundamental component of amino acids, which build proteins, and chlorophyll.
2. **Phosphorus:** It is typically supplied as superphosphates or ammonium phosphates. Phosphorus is a structural component of ATP (adenosine triphosphate) which stores and releases energy.
3. **Potassium:** Unlike nitrogen and phosphorus, potassium does not become part of the plant's physical structure. Instead, it acts as an osmoregulator. It also activates over 60 different enzymes that facilitate plant metabolism.

When applied, these chemicals are taken up by plant roots. However, in excess they can wash away into rivers and lakes, causing an overgrowth of algae, which is harmful to aquatic life. Long-term use of some synthetic fertilizers can also change the soil's pH and kill beneficial microorganisms, hurting soil health.

**Did You Know?**

Why farmers rotate crops? Growing the same crop every year removes the same nutrients from the soil. Crop rotation restores soil nutrients and reduces the need for synthetic fertilizers.

### PESTICIDES

**Q.8 What are pesticides? Discuss their role in modern food development program.** LQ

**Ans. Pesticides:**

Pesticides are chemicals used to kill or control pests like insects, weeds, or fungi. Pesticides protect crops from damage, preventing food loss and ensuring a stable food supply.

CamScanner

## ➲ Classification of Pesticides:

They are classified by their target pest into insecticides, herbicides and fungicides.

i. **Insecticides** are the chemicals which control the insects by targeting their nervous system. Many modern insecticides like organophosphates or neonicotinoids act as neurotoxins, which damage the nervous system of insects leading to paralysis and death.

ii. **Neonicotinoids** have been reported to be linked to "Colony Collapse Disorder" in honeybees, threatening global pollination. This environmental concern illustrates that while insecticides protect crops, their non-selective toxicity can harm beneficial insects such as pollinators.

iii. **Herbicides** are the chemicals which control unwanted, competitive plants called weeds. Some herbicides cause enzyme inhibition, and do not allow synthesis of essential amino acids. Some herbicides disrupt electron transport and prevent weeds from performing photosynthesis.

**Fungicides** kill the fungi by targeting their cellular integrity. They target ergosterol synthesis in fungal cell membranes, and without a stable membrane, the fungal cell leaks and dies.

**Examples:** triazoles, strobilurins, zineb etc.

## ➲ Role of Pesticides:

Pesticides are playing a central role in modern food development programs.

### ➢ Benefits:

- They help to protect plants from pests and diseases and enhance the yield of crops.
- They reduce the risk of epidemics and improve human health as well.
- They also contribute in food security and stability worldwide.

### ➢ Drawbacks:

- Pesticides can cause adverse health effects being carcinogenic and neurotoxic.
- Beneficial insects, birds and aquatic organism can also be affected by pesticides.
- Runoff water from fields can contaminate water sources and harm aquatic organisms.
- Pesticides can harm non-target species like pollinators (e.g., bees) which play a key role in pollination of many crops.
- Overtime, pests can develop immunity against certain pesticides, making them less effective. This forces us to use more toxic pesticides, which may pose further adverse environmental and health issues.

# ACID RAIN

**Q.9 What is Acid Rain? What are the causes of acid rain?** U/Q

**Ans. Acid Rain:**

- Acid rain is precipitation with an unusually low pH caused by dissolved sulphuric and nitric acids from pollution.
- **pH of Acid Rain:** Normal rain water has pH about 5.6, owing to carbonic acid. If it has a pH lower than 5.6, it potentially becomes the acid rain.

### ➢ Causes of Acid Rain:

- Acid rain is caused due to sulphur oxides ($SO_x$) and nitrogen oxides ($NO_x$) in the atmosphere. These gases, often from industrial pollution, react with water to form sulphuric acid ($H_2SO_4$) and nitric acid ($HNO_3$).

$$2SO_2 + O_2 + 2H_2O \longrightarrow 2H_2SO_4 \quad \text{(Sulphuric acid formation)}$$
$$4NO_2 + O_2 + 2H_2O \longrightarrow 4HNO_3 \quad \text{(Nitric acid formation)}$$

- When acid rain falls on soil, it causes a chemical reaction that leaches out essential nutrients, such as calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), and potassium ($K^+$) from the soil, making them unavailable to plants.

$$K^+ — Soil + H^+ \longrightarrow H^+ — Soil + K^+ \quad \text{(Potassium leaching)}$$
$$Ca^{2+} — Soil + 2H^+ \longrightarrow 2(H_2 — Soil) + Ca^{2+} \quad \text{(Calcium leaching)}$$

- Acid rain can increase the solubility of toxic metals, like aluminium ($Al^{3+}$), which can then be absorbed by the plant's roots and damage them. This reduces the ability of plant to take up nutrients, leading to slower growth and lower crop yields.

$$Al^{3+} — Soil + 3H^+ \longrightarrow 3(H — Soil) + Al^{3+} \quad \text{(Aluminium leaching)}$$



- Direct acid rain can damage the leaves, dehydrate them and makes the plant vulnerable to disease and environmental effects. Acid rain can reduce the soyabean and wheat yields by reducing nitrogen fixation and nutrition intake. Acid rain can adversely affect the soil microbial communities, and disrupt the natural nutrient cycles and decomposition of organic matter.

**Did You Know?**
Fish die in acidic lakes. This is because acid rain releases $Al^{3+}$ from soil, which clogs fish gills and reduces oxygen absorption leading to fish suffocation.

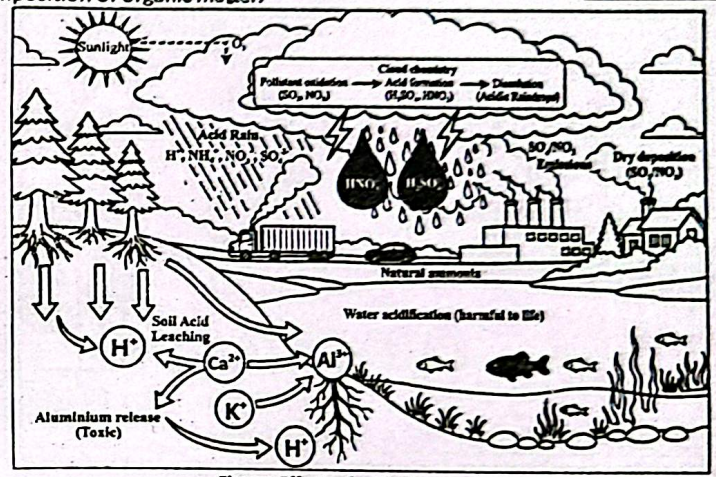



Figure: Effects of acid rain on agriculture

# EFFECT OF CLIMATE CHANGE ON CROPS

**Q.10 What is the effect of climate change on crops?** S/Q

**Ans.** Agriculture is the sector that is most sensitive to shifting climates. Changes in temperature, precipitation, and extreme weather events due to climate change directly affect agriculture. Heat stress causes dehydration, which ultimately results in poor photosynthesis and respiration. Higher temperatures can speed up a plant's metabolism, but if they get too hot, plants suffer from heat stress, reducing their growth and yield. Similarly, cold climate also damages certain crops. It is fatal to young plants, resulting in complete yield loss.

## ➲ Benefits of Normal Rain:

Normal rain helps plants by providing adequate amount of water and nutrients required for their healthy growth. However, changes in rainfall patterns can lead to drought in some areas and floods in others, both of which can cause crop failure. Unpredictable rains and cloud bursts can cause soil erosion taking the nutrient-rich top soil away.

## ➲ Potential Damages to Crops:

Events like hurricanes, heatwaves, and hailstorms can destroy crops and agricultural infrastructure, leading to food shortages. Storms can cause uprooting and branch damage. Strong winds cause water loss and can cause drought. Hails damage the leaves, fruit, stems, causing tissue damage, which result in poor photosynthesis. Severe hailing can cause total loss of yield by crop destruction. Higher UV-index and heat waves can put crops under severe heat stress, which speed up the water loss, may also result in leaf burning. To adapt these changes, scientists are developing new crop varieties that are more resistant to different climates, **for example**, by creating drought-resistant corn or heat-tolerant wheat. Some drought tolerant and flood-proof traits have also been developed. For example, "Sub 1 rice" which can survive being submerged underwater for two weeks.

CamScanner

## GENETIC ENGINEERING

**Q.11 What is Genetic Engineering? Give its main advantages and risks.** Exercise D/Q.5

**Ans.** Genetic engineering in agriculture involves changing an organism's DNA by adding, removing, or modifying specific genes. This is used to create genetically modified (GM) crops with desired traits.

i. **Identification: Selection of Useful Gene:** Scientists identify a useful gene (e.g., for pest resistance from a bacterium) with a desired trait, such as drought tolerance etc.

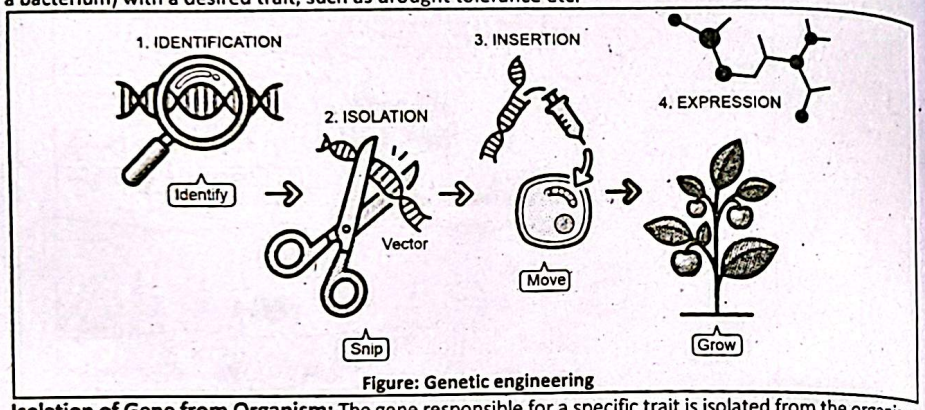



**Figure: Genetic engineering**

ii. **Isolation of Gene from Organism:** The gene responsible for a specific trait is isolated from the organism.

iii. **Insertion of Gene in target plant's genome:** The isolated gene is inserted into the target genome and DNA gun or a carrier bacterium to sew that gene into the plant's DNA.

iv. **Expression of Gene:** This new gene is then expressed by the plant cells, giving it the new trait.

**Result:** The modified plant now produces new protein that it could not produce before.

**Advantages of Genetic Engineering:** GM crops can have improved resistance to pests and diseases, tolerance to herbicides, and enhanced nutritional value. This can increase crop yields and reduce the need for certain pesticides.

➢ **Examples:**

i. **Bt-Cotton** produces its own pesticide, reducing the need for chemical sprays.

ii. Golden Rice is engineered with beta-carotene to prevent blindness in developing nations.

**Concerns:** Concerns includes:

a. The potential for GM genes to spread to wild plants (outcrossing), the development of "superweeds" where herbicide-resistant genes jump from GM crops to wild weeds via cross-pollination, making them impossible to kill.

b. It also produces resistant insects, and the long-term effects on human health and biodiversity.

### ☑ QUICK CHECK 32.2

**a) State two major agricultural benefits of using fungicides, linking to crop health or yield.**

**Ans.** Fungicides provide several agricultural benefits:

1. **Protect crops from fungal diseases**, keeping plants healthy and reducing damage.
2. **Increase crop yield and improve crop quality** by preventing losses caused by fungal infections.

Therefore, fungicides improve crop health and increase agricultural productivity.

**b) Write the balanced chemical equation for reaction that occurs when powdered limestone ($CaCO_3$) is added to a lake or field to neutralize sulphuric acid ($H_2SO_4$) from acid rain.**

**Ans.** The powdered lime stone shows neutralization reaction with $H_2SO_4$ as follows:

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O$$

This reaction removes acidity and increases the pH of the soil or lake.



**c) Identify two specific traits (e.g., heat tolerance, salt tolerance) that scientists aim to develop in new crop varieties to make them more resilient to climate change.**

**Ans.** Scientists aim to develop crops with traits such as:

1. **Heat tolerance** — enables crops to survive high temperatures.
2. **Salt tolerance** — allows crops to grow in saline soils.

## INDUSTRY

➢ **Introduction:**

Industrial chemistry is crucial for the economy and daily life. Here we will discuss its importance in sectors like manufacturing and energy and identifies key raw materials, especially those available in Pakistan. It describes essential industrial processes such as polymerization and their applications in industries like petrochemicals, cosmetics, and cement. The section concludes by emphasizing the vital safety measures required in chemical processes and facilities.

## RAW MATERIALS IN PAKISTAN

**Q.12 Explain the role of industrial chemistry in economy of Pakistan. Also account the main raw materials available in Pakistan for these industries.** Exercise D/Q.5

**Ans. Raw Material Available in Pakistan:**

Pakistan has several **raw materials** that are important for its chemical industries. The raw material of an industry determines its location and economic viability.

i. Air provides nitrogen for fertilizers and oxygen for steel manufacturing.

ii. Water is used as a solvent, a cooling agent, and a source of hydrogen.

iii. Fossil fuels like coal, oil, and natural gas provide the hydrocarbons required for the majority of organic chemicals.

Pakistan possesses a unique geological profile that **supports several chemical sub-sectors** like:

i. **Natural Gas:** It is a major source of methane ($CH_4$), used to produce fertilizers (urea) and petrochemicals. It serves as both a fuel and a source of hydrogen.

ii. **Rock Salt (Khewra Mines):** Khewra mines are one of the world's largest rock salt deposits. It is the source of sodium chloride ($NaCl$) which is a raw material for soda ash ($Na_2CO_3$), caustic soda ($NaOH$), and chlorine.

iii. **Limestone:** Limestone is highly abundant in salt range and Sindh. It is a source of calcium carbonate ($CaCO_3$) for the cement industry.

iv. **Gypsum:** It is used in the cement industry and for making plaster. It is also used as a source of calcium and sulphur and employed as a soil conditioner.

v. **Chromite:** It is found in Muslim Bagh, and is used in stainless steel and pigment production.

vi. **Crude Oil:** It is refined to produce a wide range of fuels and petrochemicals.

vii. **Sulphur:** Sulphur is used to make sulphuric acid ($H_2SO_4$), a key industrial chemical.

**Did You Know?**

Pakistan has abundant natural gas, the main raw material for making urea ($NH_2CONH_2$). Because raw material is locally available, production costs are lower making fertilizers more affordable for farmers.

## CHEMICAL INDUSTRIES AND PAKISTAN'S ECONOMY

**Q.13 Explain the role of industrial chemistry in economy of Pakistan. Also account the main raw materials available in Pakistan for these industries.** Exercise D/Q.6

**Ans. Role of Industrial Chemistry in Economy of Pakistan:**

The chemical industry is vital to Pakistan's economy. It contributes significantly to its GDP (Gross Domestic Product) and providing jobs. It supports other major sectors like agriculture (through fertilizers), construction (through cement), and textiles (through dyes and synthetic fibres).

The chemical industries use the country's locally available raw materials, such as natural gas, rock salt, limestone, and crude oil, to produce key products, which reduces reliance on imports. Pakistan is considered as an agrarian economy.

CamScanner

Pakistan's food security depends on the chemical industry. Local companies utilize natural gas to produce urea. This reduces the national import bill by billions of dollars.
Textiles has the major part i.e., over 50% of Pakistan's exports. Textile industry is a massive consumer of caustic soda for mercerizing cotton, synthetic dyes to provide colour and fastness and hydrogen peroxide for bleaching fabrics. Due to infrastructure projects and urbanization, the cement industry has become a leading exporter to neighboring regions.

## INDUSTRIAL CHEMICAL PROCESSES

**Q.14 Write a note on various industrial chemical processes. Also account for the applications of these chemical industries in Pakistan.** Exercise Q.No 7

**Ans.** Chemical manufacturing relies on two main pillars, reaction engineering and separation technology. Industrial production uses several key chemical processes. Some of them are:

1. **Polymerisation:** This is a process where small molecules called monomers link up to form large chains called polymers. Addition polymerisation and condensation polymerisation processes are used in the polymer industry. **For example** Engro polymer and chemicals is the producer of Polyvinyl Chloride (PVC) and other polymers in Pakistan. These industries use the above polymerization processes.
2. **Refining and Reforming:** In refineries, fractional distillation separates crude oil into different products based on their boiling points. The most important fractions include gasoline, diesel, kerosene etc. Reforming is the conversion of straight chain hydrocarbons to branched hydrocarbons to enhance the quality of fuel. During catalytic reforming, hydrocarbons are heated with catalyst to obtain a high-octane number gasoline. While often categorized as "Oil and Gas" the chemical cracking and reforming processes at refineries like PARCO and Attock Refinery provide essential petrochemical feedstocks for wider chemical industry in Pakistan.
3. **Haber-Bosch Process:** In Haber process ammonia ($NH_3$) gas is synthesized from nitrogen ($N_2$) and hydrogen ($H_2$) gases. Iron metal crystals are used as catalyst in this process. This process contributes the 40-50% of the nitrogen fixation being done on the earth, as 70% of ammonia is utilized directly into fertilizer manufacture. Large-scale plants like Engro Fertilizers and FFC use natural gas as a feedstock and produce ammonia, which is then converted into urea.
4. **Contact Process:** This process produces highly pure and concentrated form of $H_2SO_4$. Sulphuric acid is the most utilized chemical in the world, so it is often called the "King of Chemicals". In Pakistan, several plants run contact process e.g., Nimir Indutrial Chemicals.
5. **Solvay Process:** The famous Solvay process produces sodium carbonate ($Na_2CO_3$) from brine and limestone. Ammonia is added to brine, and carbon dioxide is passed through it to form a sodium bicarbonate ($NaHCO_3$) precipitate. Heating converts it into sodium carbonate. Ammonia is regenerated using lime from calcium carbonate decomposition. The by-product formed is calcium chloride ($CaCl_2$): Lucky Core Industries (formerly ICI) produce soda ash for the glass, detergent and paper industries.
6. **Chlor-Alkali Process:** The chlor-alkali process is an industrial electrolysis method that breaks down sodium chloride (brine) ($NaCl$) to produce three key chemical products, i.e., chlorine ($Cl_2$), sodium hydroxide ($NaOH$) or caustic soda), and hydrogen ($H_2$). It is crucial for manufacturing plastics, detergents, and water treatment products, commonly using modern membrane cell technology for high efficiency and purity. In this regard, Sitara Chemical Industries and Ittehad Chemicals are primary manufacturers, supporting the textile and water treatment sectors.

## APPLICATIONS OF INDUSTRIAL CHEMISTRY

**Q.15 What are the applications of industrial chemistry?** SQ

**Ans.** i. **Petrochemical Industry** produces plastics, synthetic rubber, and fibres from crude oil. Crude oil is cracked (broken down) into smaller molecules. These become the building blocks for lubricants, waxes, and synthetic rubbers.

ii. **Cosmetics Industry** creates ingredients for makeup, soaps, and perfumes. This industry uses surfactants (for soaps), emulsifiers (to keep creams smooth), and preservatives (to prevent bacterial growth). Chemistry ensures that these products are pH -balanced for human skin.



iii. **Cement Industry** uses limestone and clay to make a key building material. Cement manufacturing process involves heating an intimate mixture of limestone and clay to [illegible] in a rotary kiln. The resulting product is ground with gypsum to make cement.

iv. **Food Industry** creates food additives, preservatives, and food processing chemicals. Sodium benzoate is mostly used as food preservatives. Hydrogenation is done to turn edible oils into solid fats like margarine. Leavening agents like sodium bicarbonate (baking soda) is used in baking. Fortification is done by adding iodine or iodate as $KIO_3$ to salts or Vitamin A to oil.

**Did You Know?**
Why cement gets hot when you add water? Cement reacts with water in an exothermic hydration reaction, releasing heat. This is why freshly mixed cement becomes warm.

## SAFETY MEASURES AND PRECAUTIONS

**Q.16 What are important safety measures which must be followed while working in different chemical industries? Make a checklist to verify their adoption.** Exercise Q.No 8

**Ans.** Industrial chemical facilities require strict safety measures to prevent accidents and protect workers and the environment. These include:

i. Workers should use personal protective equipment (PPE) such as gloves, goggles, helmets, lab coats, and protective shoes to avoid injuries from chemicals, heat, or harmful fumes.
ii. Chemicals must be properly labeled, handled, and stored according to their properties. Flammable, toxic, or corrosive substances should be kept in suitable containers and separate storage areas to prevent leaks, spills, contamination, or dangerous reactions.
iii. Industries should have clear emergency plans to handle fires, chemical spills, gas leaks, or explosions. Emergency exits, fire extinguishers, first-aid kits, and spill control materials should be available, and workers should know how to respond during emergencies.
iv. Good ventilation systems are necessary to remove toxic gases, fumes, and dust from the workplace. Proper airflow reduces the risk of breathing harmful substances and helps maintain a safe and healthy working environment.
v. Workers must receive proper safety training on handling hazardous materials and operating equipment. Regular inspection and maintenance of machines, pipelines, and storage tanks help detect faults early and reduce the risk of industrial accidents.

### ☑ QUICK CHECK 32.3

**a) Identify two major sectors of Pakistan's economy (other than agriculture) that are heavily reliant on the chemical industry, and name one chemical product essential for each.**

**Ans.** 1. **Textile Industry:**
Pakistan's textile industry heavily depends on chemicals such as dyes and bleaching agents for coloring and processing fabrics.

2. **Pharmaceutical Industry:**
The pharmaceutical sector relies on chemical products such as:
Medicines and active pharmaceutical ingredients (APIs) for the production of drugs.
(**Note:** Other sectors include construction (cement) and fertilizer industries).

**b) Explain the physical principle of the process used to separate crude oil (in terms of intermolecular forces and boiling points) on which this separation depends.**

**Ans.** Crude oil is separated by **fractional distillation.**
The separation depends on differences in:
I) Intermolecular forces (Van der Waals forces).
II) Boiling points.
Hydrocarbons with stronger intermolecular forces have higher boiling points and weaker intermolecular forces have lower boiling points.
As the crude oil vapors rise through the fractionating column:
- High-boiling fractions condense near the bottom.
- Low-boiling fractions condense higher up in the column.

CamScanner

Thus, Fractional distillation separates crude oil because different hydrocarbons have different boiling points resulting from different intermolecular forces.

c) **Many cosmetics and perfumes have esters as ingredients. Name the two types of reactants needed to synthesize an ester and name the catalyst typically used.**

**Ans.** Esters are produced by the reaction between: 1. An alcohol 2. A carboxylic acid
The catalyst used is conc. sulfuric acid ($H_2SO_4$) which acts as both a catalyst and a dehydrating agent.
**General reaction:** $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$

d) **Explain the chemical reason why highly oxidizing chemicals (like concentrated $HNO_3$) must be stored separately from flammable organic chemicals (like ethanol).**

**Ans.** Concentrated nitric acid is a **strong oxidizing agent**, while ethanol is a **flammable reducing agent.**
If stored together, nitric acid can rapidly oxidize ethanol. The reaction releases a large amount of heat and may cause fire, explosion, or violent reactions.
Therefore, strong oxidizing agents and flammable organic compounds must be stored separately to prevent dangerous oxidation reactions and fires.

## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **Fertilizers are added to soil primarily to:**
(A) Increase soil acidity (B) Improve soil fertility (C) Kill insects (D) Reduce rainfall
2. **Synthetic fertilizers are commonly produced through the:**
(A) Solvay process (B) Contact process (C) Haber–Bosch process (D) Chlor-alkali process
3. **Organic fertilizers are obtained from:**
(A) Petroleum (B) Animal manure & compost (C) Coal (D) Natural gas
4. **Plants require a total of:**
(A) 10 essential elements (B) 12 essential elements (C) 15 essential elements (D) 17 essential elements
5. **Which of the following is a primary macronutrient?**
(A) Zinc (B) Iron (C) Nitrogen (D) Boron
6. **The N-P-K ratio on fertilizer bags represents the percentages of:**
(A) Sodium, phosphorus and potassium (B) Nitrogen, phosphorus and potassium
(C) Nitrogen, sulphur and potassium (D) Nitrogen, phosphorus and calcium
7. **Nitrogen is an essential component of:**
(A) Cellulose only (B) Amino acids and chlorophyll
(C) Lipids only (D) Starch only
8. **Phosphorus is an important component of:**
(A) ATP (B) Glucose (C) Chlorophyll (D) Cellulose
9. **Potassium mainly functions as:**
(A) A structural component (B) An osmoregulator and enzyme activator
(C) A pigment (D) A carbohydrate
10. **Excessive use of fertilizers may cause:**
(A) Improved water quality (B) Algal blooms
(C) Reduced plant growth only (D) Increased soil fertility forever
11. **Pesticides are chemicals used to control:**
(A) Only insects (B) Pests such as insects, weeds and fungi
(C) Bacteria only (D) Viruses only
12. **Chemicals used to kill insects are called:**
(A) Herbicides (B) Fungicides (C) Insecticides (D) Fertilizers
13. **Herbicides are mainly used to control:**
(A) Fungi (B) Weeds (C) Insects (D) Bacteria
14. **Fungicides act by targeting:**
(A) Chlorophyll (B) Ergosterol synthesis (C) DNA replication (D) ATP synthesis
15. **Neonicotinoids have been associated with:**
(A) Acid rain (B) Colony Collapse Disorder in honeybees
(C) Ozone depletion (D) Global warming
16. **Long-term pesticide use may result in:**
(A) Increased soil fertility (B) Pest resistance (C) Elimination of all insects (D) Increased rainfall
17. **Acid rain mainly contains:**
(A) Carbonic and hydrochloric acids (B) Sulphuric and nitric acids
(C) Acetic and formic acids (D) Hydrofluoric and phosphoric acids



18. **Rainwater with a pH below _____ is considered acid rain.**
(A) 7.0 (B) 6.5 (C) 5.6 (D) 4.0
19. **Acid rain is mainly caused by atmospheric:**
(A) $CO_2$ and $H_2$ (B) $SO_x$ and $NO_x$ (C) $O_2$ and $N_2$ (D) $NH_3$ and $CH_4$
20. **Acid rain leaches which nutrient from soil?**
(A) Potassium (B) Calcium (C) Magnesium (D) All of these
21. **Acid rain increases the availability of toxic:**
(A) Sodium ions (B) Aluminium ions (C) Chloride ions (D) Iron ions
22. **One direct effect of acid rain on plants is:**
(A) Increased photosynthesis (B) Leaf damage and dehydration
(C) Increased flowering (D) Improved nitrogen fixation
23. **Heat stress mainly reduces crop yield by affecting:**
(A) Photosynthesis (B) Digestion (C) Respiration of animals (D) Pollination only
24. **Climate change can cause:**
(A) Droughts and floods (B) Only snowfall (C) Stable weather (D) Reduced UV radiation
25. **Genetic engineering involves:**
(A) Cross-breeding only (B) Modification of DNA (C) Natural selection only (D) Cloning animals
26. **Bt cotton is genetically modified mainly for:**
(A) Salt tolerance (B) Pest resistance (C) Larger flowers (D) Faster germination
27. **Golden Rice is enriched with:**
(A) Vitamin C (B) β-Carotene (C) Vitamin D (D) Iron
28. **One concern regarding GM crops is:**
(A) Increased biodiversity (B) Development of superweeds
(C) Reduced crop yield (D) Increased soil erosion
29. **Pakistan's major source of methane for chemical industries is:**
(A) Coal (B) Natural gas (C) Limestone (D) Gypsum
30. **Khewra Mines are famous for deposits of:**
(A) Limestone (B) Rock salt (C) Chromite (D) Gypsum
31. **Limestone is the major raw material used in the:**
(A) Fertilizer industry (B) Cement industry (C) Textile industry (D) Pharmaceutical industry
32. **The Haber–Bosch process is used to manufacture:**
(A) Sulphuric acid (B) Ammonia (C) Sodium carbonate (D) Sodium hydroxide
33. **The catalyst used in the Haber process is:**
(A) Platinum (B) Iron (C) Vanadium(V) oxide (D) Nickel
34. **The Contact process is used to manufacture:**
(A) Nitric acid (B) Sulphuric acid (C) Hydrochloric acid (D) Acetic acid
35. **The Solvay process produces:**
(A) Sodium carbonate (B) Sodium chloride (C) Potassium nitrate (D) Calcium carbonate
36. **The chlor-alkali process produces:**
(A) NaOH, $Cl_2$ and $H_2$ (B) $NH_3$ and $H_2$ (C) $H_2SO_4$ and $SO_2$ (D) $CO_2$ and $O_2$
37. **Fractional distillation separates crude oil on the basis of:**
(A) Density (B) Boiling point (C) Solubility (D) Colour
38. **Which industry extensively uses surfactants and emulsifiers?**
(A) Cement industry (B) Cosmetic industry (C) Steel industry (D) Fertilizer industry
39. **Personal Protective Equipment (PPE) includes:**
(A) Gloves and goggles (B) Helmets only (C) Lab coats only (D) All of these
40. **Proper ventilation in industries primarily helps to:**
(A) Increase temperature (B) Remove toxic gases and fumes
(C) Increase humidity (D) Reduce production

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

### BLOCK # 01

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. B | 3. B | 4. A | 5. B | 6. C | 7. B | 8. B | 9. B | 10. B | 11. C | 12. C | 13. C | 14. B | 15. C |
| 16. C | 17. B | 18. B | 19. B | 20. B | 21. B | 22. B | 23. B | 24. B | 25. C | 26. A | 27. B | 28. C | 29. B | 30. B |
| 31. B | 32. B | 33. B | 34. B | 35. B | 36. B | 37. B | 38. B | 39. B | | | | | | |

### BLOCK # 02

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. B | 2. C | 3. B | 4. D | 5. C | 6. B | 7. B | 8. A | 9. B | 10. B | 11. B | 12. C | 13. B | 14. B | 15. B |
| 16. B | 17. B | 18. C | 19. B | 20. D | 21. B | 22. B | 23. A | 24. A | 25. B | 26. B | 27. B | 28. B | 29. B | 30. B |
| 31. B | 32. B | 33. B | 34. B | 35. A | 36. A | 37. B | 38. B | 39. D | 40. B | | | | | |

CamScanner

# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

I. **What does the $TD_{50}$ value in the TI formula represent?**
a) Dose effective for 100% of people. b) Lowest dose that causes harm MTC.
c) Lowest dose that works MEC d) Dose causing a toxic effect in 50% of people.

II. **What is the key structural feature for penicillin's antibiotic activity of penicillin?**
a) A carboxylic acid group b) A benzene ring
c) A thiazolidine ring d) A four-membered beta-lactam ring

III. **How do opiates like morphine reduce pain?**
a) They destroy pain signals. b) They bind to opioid receptors, blocking pain signals.
c) They come from the opium poppy. d) They build new cell walls in the brain.

IV. **Which N-P-K nutrient promotes protein synthesis and chlorophyll?**
a) Nitrogen b) Phosphorus c) Potassium d) Sulphur

V. **How does acid rain primarily damage soil?**
a) It increases soil pH. b) It leaches essential nutrients and releases toxic $Al^{3+}$.
c) It adds excess nitrogen. d) It directly destroys plant roots.

VI. **What is a primary effect of climate change on agriculture?**
a) Reduced atmospheric $CO_2$
b) Increased crop yields globally
c) Reduced yields due to heat stress and erratic rainfall
d) Fewer extreme weather events

VII. **In Pakistan, rock salt (halite) is a key raw material for producing:**
a) Fertilizers b) Caustic soda and chlorine
c) Cement d) Petrochemicals

VIII. **Ammonia gas in industry is prepared by:**
a) Contact process b) Haber-Bosch process c) Solvay process d) Refining process

IX. **Plastics, synthetic fibres, and synthetic rubber are primary products of the:**
a) Cement industry b) Petrochemical industry c) Cosmetics industry d) Food production industry

X. **What is the primary purpose of ventilation systems in a chemical facility?**
a) To control storage temperature b) To provide clear emergency exits
c) To assist in labeling chemicals d) To remove toxic fumes

### Answer Key with Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | d | Dose causing a toxic effect in 50% of people | $TD_{50}$ is the dose that produces toxic effects in 50% of the test population and is used in calculating Therapeutic Index. |
| II. | d | A four-membered beta-lactam ring | The strained β-lactam ring is essential for penicillin's antibacterial activity. |
| III. | b | They bind to opioid receptors, blocking pain signals | Morphine and related opiates act by binding to opioid receptors in the nervous system. |
| IV. | a | Nitrogen | Nitrogen is essential for amino acid synthesis, protein formation, and chlorophyll production. |
| V. | b | It leaches essential nutrients and releases toxic $Al^{3+}$ | Acid rain removes nutrients from soil and mobilizes toxic aluminium ions. |
| VI. | c | Reduced yields due to heat stress and erratic rainfall | Climate change negatively affects crop production through droughts, heat waves, and irregular rainfall patterns. |
| VII. | b | Caustic soda and chlorine | Rock salt (NaCl) is the raw material for the chlor-alkali industry producing NaOH and $Cl_2$. |



| | | | |
|---|---|---|---|
| VIII. | b | Haber-Bosch process | Industrial ammonia is manufactured by the Haber process using nitrogen and hydrogen gases. |
| IX. | b | Petrochemical industry | Plastics, fibres, and synthetic rubber are major products of petrochemicals derived from petroleum. |
| X. | d | To remove toxic fumes | Ventilation systems maintain air quality and protect workers from harmful vapors and gases |

## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) Write the significance of Therapeutic Window and how it differs from Therapeutic Index.**

Ans. **Therapeutic Window**
The **Therapeutic Window** is the range of drug concentrations between the:
- Minimum Effective Concentration (MEC), and
- Minimum Toxic Concentration (MTC).

Within this range, the drug produces the desired effect without causing toxicity.

**Difference between Therapeutic Window and Therapeutic Index:**

| Therapeutic Window | Therapeutic Index |
|---|---|
| Concentration range of safe use | Numerical ratio of safety |
| Defined by MEC and MTC | Defined by $TD_{50}$ and $ED_{50}$ |
| Used in dosage monitoring | Used to compare drug safety |

**b) How structure of penicillin allows it to inhibit an enzyme?**

Ans. Penicillin contains a highly strained **β-lactam ring.**
- The β-lactam ring resembles the natural substrate of the bacterial enzyme **transpeptidase.**
- The enzyme binds penicillin instead of its normal substrate.
- Penicillin forms a stable covalent bond with the active site of transpeptidase.
- This blocks bacterial cell wall synthesis.

As a result, bacteria cannot form a proper cell wall and eventually die.

**c) What is the primary mechanism of action for opiate drugs, such as morphine, in providing analgesia (pain relief)?**

Ans. **Morphine and other opiates:**
- Bind to **opioid receptors** in the brain and spinal cord.
- Reduce the transmission of pain signals through the nervous system.
- Alter the perception of pain by the brain.

Therefore, Opiates relieve pain by activating opioid receptors and blocking pain transmission.

**d) What is the concept of pesticide resistance in a target pest population?**

Ans. Pesticide resistance is the inherited ability of some individuals in a pest population to survive a pesticide dose that previously controlled the population. Repeated use of the same pesticide kills susceptible pests but allows resistant individuals to survive and reproduce, so resistance alleles become more common over generations and the pesticide becomes less effective.

**e) What is the concept of pesticide resistance in a target pest population, linking it to the principles of natural selection and repeated application?**

Ans. Pesticide resistance develops through **natural selection.**
1. A pest population contains some naturally resistant individuals.
2. Pesticide application kills susceptible pests.
3. Resistant individuals survive and reproduce.
4. Repeated pesticide use increases the proportion of resistant pests.

Eventually, the pesticide becomes less effective against the population.

CamScanner

**f) Define soil salinization. How it can be caused by irrigation practices in regions experiencing higher temperatures and reduced precipitation.**

**Ans. Soil Salinization**

Soil salinization is the accumulation of soluble salts in the soil to levels harmful to plant growth.

**Causes:**

- Irrigation water contains dissolved salts.
- In hot and dry climates, water evaporates rapidly.
- The water evaporates but salts remain in the soil.
- Low rainfall prevents salts from being washed away.

This leads to reduced soil fertility and crop yield. Salinization is particularly common in arid and semi-arid regions.

**g) How does the chemical industry contribute to both energy production from fossil fuels and the development of renewable energy technologies?**

**Ans. Contribution to Fossil Fuel Energy**

The chemical industry contributes through

- Petroleum refining.
- Production of fuels such as petrol, diesel, and LPG.
- Catalytic cracking and reforming processes.

**Contribution to Renewable Energy**

The chemical industry also supports renewable technologies through:

- Production of materials for **solar panels**
- Manufacturing of **lithium-ion batteries.**
- Development of **hydrogen fuel technologies.**
- Production of **biofuels.**
- Manufacturing materials for wind turbines.

Therefore, the chemical industry supports both conventional energy production and the transition to renewable energy technologies.

**h) Name the industrial process used to produce caustic soda (NaOH) and chlorine ($Cl_2$) from the rock salt (NaCl).**

**Ans.** The industrial process used is the Chlor-alkali process

In this process, concentrated sodium chloride solution (brine) is electrolyzed.

**Overall Reaction:** $2NaCl_{(aq)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + Cl_{2(g)} + H_{2(g)}$

**Products obtained,** caustic soda (NaOH), chlorine gas ($Cl_2$) and hydrogen gas ($H_2$).

**i) State two different types of products (other than fuels) that are derived from the petrochemical industry, linking them to their use in daily life.**

**Ans. 1. Plastics**

**Examples:** Polyethylene, PVC and polypropylene.

**Daily uses:** Packaging materials, bottles, water pipes, household goods.

**2. Synthetic Fibres**

**Examples:** Nylon, polyester, acrylic.

**Daily uses:** Clothing, carpets, ropes, sports equipment..

Other acceptable answers include synthetic rubber, detergents, fertilizers, medicines, and cosmetics.

**j) Distinguish between a corrosive hazard and a toxic hazard, giving one example of a chemical for each.**

**Ans.**

| Corrosive Hazard | Toxic Hazard |
|---|---|
| Causes destruction or burns to living tissue and materials upon contact. | Causes harmful effects when inhaled, swallowed, or absorbed into the body. |
| Mainly damages by chemical attack. | Mainly damages through poisoning or interference with biological processes. |
| **Example:** **Corrosive Chemical:** Concentrated sulfuric acid ($H_2SO_4$) It can cause severe skin burns and damage to materials. | **Example:** **Toxic Chemical:** Carbon monoxide (CO) It is poisonous because it binds strongly to hemoglobin and reduces oxygen transport in blood. |



## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) Drug A has an $ED_{50}$ of 20 mg $dm^{-3}$ and a $TD_{50}$ of 80 mg $dm^{-3}$. Drug B has a Minimum Effective Concentration (MEC) of 5 mg $dm^{-3}$ and a Minimum Toxic Concentration (MTC) of 50 mg $dm^{-3}$. Drug C has a therapeutic window where the effective dose is 10 mg and the toxic dose is 15 mg.**

**(i) Define Therapeutic Index (TI) and calculate the TI for Drug A.**

**(ii) Define Therapeutic Window (TW) and identify which drug (B or C) has the wider therapeutic window. Justify your answer.**

**(iii) Compare the relative safety of Drug A and Drug C.**

**Ans. (i) Definition:**

The **Therapeutic Index (TI)** is a measure of drug safety and is defined as:

$$TI = \frac{TD_{50}}{ED_{50}}$$

where:

- $TD_{50}$ = dose causing toxic effects in 50% of individuals.
- $ED_{50}$ = dose producing the desired effect in 50% of individuals.

For Drug A:

$ED_{50} = 20$ mg

$TD_{50} = 80$ mg

Therefore, $TI = \frac{80}{20} = 4$

**Ans. (ii) Definition:**

The **Therapeutic Window** is the concentration or dose range between the minimum effective level and the minimum toxic level.

$$TW = MTC - MEC$$

**Drug B**

$MEC = 5\ mgL^{-1}$

$MTC = 50\ mgL^{-1}$

$TW = MTC - MEC = 50 - 5 = 45\ mgL^{-1}$

**Drug C**

Effective does: 10 mg

Toxic dose: 15 mg

TW = Toxic dose – Effective dose = 15 – 10 = 5 mg

**Comparison:**

| Drug | Therapeutic Window |
|---|---|
| B | 45 mg $L^{-1}$ |
| C | 5 mg |

Therefore, drug B has the wider therapeutic window means a larger safety margin between effective and toxic doses.

**Ans. (iii)**

**Drug A** TI = 4TI

This means the toxic dose is four times greater than the effective dose.

**Drug C**

Effective dose: 10 mg

Toxic dose: 15 mg

$TI = \frac{15}{10} = 1.5$ mg

**Conclusion:**

Drug A is safer than Drug C because it has a larger safety margin between effective and toxic doses.

CamScanner

**b) (i) Contrast synthetic and organic fertilizers based on their origin.**
**(ii) Identify the three primary macronutrients (N, P, K) and describe the specific biological function of each in a plant.**

**Ans. (i)**

| Synthetic Fertilizers | Organic Fertilizers |
|---|---|
| Manufactured chemically in industries. | Obtained from plant or animal materials. |
| Produced from minerals or industrial chemicals. | Derived from manure, compost, and plant residues. |
| Nutrients are immediately available. | Nutrients are released slowly. |
| Examples: Urea and ammonium nitrate. | Examples: Farmyard manure and compost. |

**Ans. (ii)**

| Nutrient | Function |
|---|---|
| Nitrogen (N) | Required for protein synthesis, amino acids, and chlorophyll production. |
| Phosphorus (P) | Essential for ATP production, root growth, and seed formation. |
| Potassium (K) | Regulates enzyme activity, water balance, and disease resistance. |

**c) Describe the chemical pathway from Natural Gas ($CH_4$) to urea fertilizer. Your answer must identify the crucial intermediate compound that is synthesized from $CH_4$ and air.**

**Ans.** The manufacture of urea involves several stages.

**Step 1: Production of Hydrogen from Methane**

Natural gas reacts with steam:

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

This process is called **steam reforming**.

**Step 2: Production of Nitrogen From Air**

Air contains approximately: 78%

Nitrogen is separated from air.

**Step 3: Manufacture of Ammonia**

Hydrogen reacts with nitrogen in the Haber process:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

**Step 4: Manufacture of Urea**

Ammonia reacts with carbon dioxide:

$$2NH_3 + CO_2 \longrightarrow NH_2CONH_2 + H_2O$$

Producing urea:

$$NH_2CONH_2$$

**Crucial Intermediate Compound**

The important intermediate produced from methane and air is: Ammonia ($NH_3$)

Thus, methane is ultimately converted into urea fertilizer through the intermediate formation of ammonia using the Haber process.

## DESCRIPTIVE QUESTIONS DQs

**Q.4 Describe the structure and mechanism of action of penicillin.**

**Ans.** See Question No. 04

**Q.5 What is Genetic Engineering? Give its main benefits and risks.**

**Ans.** See Question No. 11

**Q.6 Explain the role of industrial chemistry in economy of Pakistan. Also account the main raw materials available in Pakistan for these industries.**

**Ans.** See Question No. 12, 13



**Q.7 Write a note on various industrial chemical processes. Also account for the applications of these chemical industries in Pakistan.**

**Ans.** See Question No. 14

**Q.8 What are important safety measures which must be followed while working in different chemical industries? Make a checklist to verify their adoption.**

**Ans.** See Question No. 16

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 Define therapeutic index.**

**Ans.** Therapeutic index is the ratio between the toxic dose and the effective dose of a drug. It provides information about the safety margin of a medicine.

$$\text{Therapeutic Index} = \frac{\text{Toxic Dose}}{\text{Effective Dose}}$$

A larger therapeutic index indicates a safer drug.

**Q.2 What is meant by therapeutic window?**

**Ans.** The therapeutic window is the range of drug concentration that produces the desired therapeutic effect without causing toxic effects. Drugs should be administered within this range for safe treatment.

**Q.3 Explain the role of hydrochloric acid in the stomach.**

**Ans.** Hydrochloric acid maintains the acidic environment of the stomach with a pH of about 1–3. It activates digestive enzymes such as pepsin and helps destroy harmful microorganisms entering with food.

**Q.4 What is aspirin and what are its uses?**

**Ans.** Aspirin or acetylsalicylic acid is an analgesic and anti-inflammatory drug. It is commonly used to relieve pain, reduce fever and decrease inflammation. **Structure:** $C_9H_8O_4$

**Q.5 Explain the mechanism of action of aspirin.**

**Ans.** Aspirin inhibits the enzyme cyclooxygenase ($CO_X$), which is responsible for the production of prostaglandins that cause pain and inflammation. As a result, pain and swelling are reduced.

**Q.6 What is penicillin?**

**Ans.** Penicillin is an antibiotic produced by the fungus *Penicillium*. It is used to treat bacterial infections by preventing the formation of bacterial cell walls.

**Q.7 What are opiates?**

**Ans.** Opiates are drugs that act on opioid receptors in the brain and nervous system to relieve pain. Examples include morphine and codeine.

**Q.8 What are opioid receptors?**

**Ans.** Opioid receptors are specialized proteins present in the brain and nervous system that bind opiate drugs. Their activation reduces pain signals reaching the brain.

**Q.9 Why are antiviral drugs difficult to develop?**

**Ans.** Viruses reproduce inside host cells and use the host's cellular machinery for replication. Therefore, antiviral drugs must destroy viruses without damaging normal body cells, making their development difficult.

**Q.10 Explain the role of nitrogen fertilizers in crop growth.**

**Ans.** Nitrogen fertilizers promote the growth of leaves and stems by increasing chlorophyll and protein synthesis in plants. They improve vegetative growth and increase crop yield.
**Examples** include ammonium nitrate and urea.

**Q.11 Explain the role of phosphorus fertilizers in plants.**

**Ans.** Phosphorus fertilizers promote root development, seed formation and flowering in plants. They also help in energy transfer through ATP and improve crop maturity.

CamScanner

Examples include superphosphate and ammonium phosphate.

**Q.12 Explain the role of potassium fertilizers in agriculture.**

**Ans.** Potassium fertilizers improve disease resistance, fruit quality and water regulation in plants. They also strengthen stems and increase the ability of crops to tolerate environmental stress.
**Example:** Potassium sulfate ($K_2SO_4$).

**Q.13 What are pesticides? Give examples.**

**Ans.** Pesticides are chemicals used to protect crops from insects, weeds, fungi and other harmful organisms. Their use increases agricultural productivity and crop quality.
**Examples** include DDT, glyphosate and malathion.

**Q.14 Differentiate between insecticides, herbicides and fungicides.**

**Ans.** Insecticides kill harmful insects, herbicides destroy weeds and fungicides control fungal diseases in plants. Each type of pesticide targets a specific agricultural problem.

**Q.15 Explain the harmful effects of acid rain on agriculture.**

**Ans.** Acid rain lowers the pH of soil and decreases the availability of essential nutrients required by plants. It can damage crops, reduce yield and affect plant growth.

**Q.16 How does climate change affect agriculture?**

**Ans.** Changes in temperature, rainfall patterns and extreme weather events can reduce crop productivity and increase the chances of crop failure. Climate change may also lead to food shortages in many regions.

**Q.17 Why are drought-resistant crop varieties important?**

**Ans.** Drought-resistant crops can survive under low water conditions and maintain crop production during periods of water scarcity. They help improve food security in areas affected by climate change.

**Q.18 What is genetic engineering?**

**Ans.** Genetic engineering is the process of altering the genetic material of an organism to introduce desirable characteristics. It involves the transfer or modification of specific genes.

**Q.19 What are genetically modified (GM) crops?**

**Ans.** Genetically modified crops are plants whose genetic material has been altered to improve desirable traits such as disease resistance, higher yield and drought tolerance.
**Examples** include Bt cotton and Golden Rice.

**Q.20 State two advantages of genetically modified crops.**

**Ans.** GM crops can provide higher yields and increased resistance to pests and diseases. They may also reduce the use of pesticides and improve nutritional value.

**Q.21 State two concerns associated with genetically modified crops.**

**Ans.** Possible concerns include environmental effects, loss of biodiversity and uncertainty regarding long-term health impacts. Therefore, careful monitoring and regulation are required.

**Q.22 Discuss the importance of chemical industries in Pakistan. What are the major raw materials used in chemical industries in Pakistan?**

**Ans.** Chemical industries contribute significantly to Pakistan's economy by producing fertilizers, cement, pharmaceuticals and petrochemicals. They also create employment opportunities and support industrial growth. Major raw materials include crude oil, natural gas, limestone, rock salt, sulfur and phosphate rocks. These materials are used in fertilizer, cement and petrochemical industries.

**Q.23 Explain the role of polymerization in industry.**

**Ans.** Polymerization is used in industry to manufacture plastics, synthetic fibers and rubber products. Addition polymerization produces PVC and polythene, whereas condensation polymerization produces nylon and Terylene.



## SELF-ASSESSMENT

Total Mark: 30

**Q.1 Encircle the correct option.** (1 × 6 = 6)

(i) **A wide therapeutic window indicates that a drug is:**
(A) Less effective (B) More dangerous (C) Relatively safer (D) Highly addictive

(ii) **Hydrogen ions in the stomach are secreted by:**
(A) Chief cells (B) Goblet cells (C) Parietal cells (D) Liver cells

(iii) **Acid rain leaches which nutrient from soil?**
(A) Potassium (B) Calcium (C) Magnesium (D) All of these

(iv) **Limestone is the major raw material used in the:**
(A) Fertilizer industry (B) Cement industry (C) Textile industry (D) Pharmaceutical industry

(v) **How does acid rain primarily damage soil?**
(A) It increases soil pH. (B) It leaches essential nutrients and releases toxic $Al^{3+}$.
(C) It adds excess nitrogen. (D) It directly destroys plant roots.

(vi) **Plastics, synthetic fibres, and synthetic rubber are primary products of the:**
(A) Cement industry (B) Petrochemical industry (C) Cosmetics industry (D) Food production industry

**Q.2 Write short answers of the following questions.** (2 × 8 = 16)

(i) Drug A has a TI of 3, and Drug B has a TI of 50. Which drug is considered safer, and why?
(ii) Why do many antiviral drugs cause significant side effects for the host patient?
(iii) State two major agricultural benefits of using fungicides, linking to crop health or yield.
(iv) Explain the physical principle of the process used to separate crude oil (in terms of intermolecular forces and boiling points) on which this separation depends.
(v) How structure of penicillin allows it to inhibit an enzyme?
(vi) Define soil salinization. How it can be caused by irrigation practices in regions experiencing higher temperatures and reduced precipitation.
(vii) Distinguish between a corrosive hazard and a toxic hazard, giving one example of a chemical for each.
(viii) Contrast synthetic and organic fertilizers based on their origin.

**Q.3 Extensive Questions.** (4 + 4 = 8)

(a) What is Genetic Engineering? Give its main benefits and risks.
(b) Write a note on various industrial chemical processes. Also account for the applications of these chemical industries in Pakistan.

CamScanner

## ENTRANCE TEST MCQs

1. **The displayed molecule containing an acetyl ester and carboxylic acid is:**
   A. Urea B. Aspirin C. Penicillin D. Codeine
2. **Opening potassium channels during opioid action causes the neuron to:**
   A. Synthesize chlorophyll B. Hyperpolarize
   C. Depolarize continuously D. Become a bacterial cell
3. **The N-P-K graphic assigns chlorophyll and protein formation mainly to:**
   A. Calcium B. Nitrogen C. Phosphorus D. Potassium
4. **In the genetic-engineering flowchart, the step immediately after gene isolation is:**
   A. Application of pesticide B. Acid-rain neutralization
   C. Insertion into a vector or gene-delivery system D. Selection of mature crop only
5. **Locating an industry near limestone deposits mainly reduces:**
   A. Bulk raw-material transport cost B. Therapeutic index
   C. Viral mutation rate D. Pesticide resistance
6. **The polymerization diagram shows poly(ethene) as an example of:**
   A. Addition polymerization B. Condensation polymerization
   C. Electrolysis D. Neutralization
7. **In the genetic-engineering flowchart, expression of the inserted gene causes the plant to:**
   A. Lose all DNA B. Become a fertilizer
   C. Stop cell division permanently D. Produce a new protein and trait
8. **Why does $V_2O_5$ not change the equilibrium constant in the Contact process?**
   A. Is the limiting reagent B. Lowers forward and reverse activation energies equally
   C. Changes reaction enthalpy D. Adds oxygen atoms permanently
9. **The most balanced strategy for industrial development is to:**
   A. Ignore worker training B. Use local feedstocks with safety and pollution controls
   C. Maximize output with no waste controls D. Import all raw materials despite local supply

**Answers Key**

| 1. B | 2. B | 3. B | 4. C | 5. A | 6. A | 7. D | 8. B | 9. B |
|---|---|---|---|---|---|---|---|---|



33 CHAPTER

# WATER

### Student Learning Outcomes (SLOs)

[C-12-C-01 to C-12-C-08]

- Explain the chemical properties of water and how they relate to water quality and pollution.
- Identify different types of water pollution, (some examples include point source and nonpoint source pollution).
- Identify common water pollutants (some examples include oil, pesticides, and heavy metals).
- Identify and explain the sources and effects of water pollution on human health and the environment.
- Evaluate the impact of human activities on water resources, such as agriculture and industrial processes.
- Identify and explain water treatment methods and technologies, such as filtration and purification.
- Explain conservation and management strategies for protecting and preserving water resources.
- Explain the laws and regulations related to water pollution and conservation.

**Q.1 Why water is vital for life?** S/Q

**Ans.** There is no life without water. Water is the foundation of life. Water keeps humans alive and healthy through hydration and hygiene, and removes toxic materials from the body. It allows plants to perform photosynthesis and supports agriculture by enabling crop growth. Animals rely on it to regulate body functions, and countless microorganisms depend on it for survival. Human development, agriculture, and food security all revolve around a steady supply of water. In nature, water shapes the land, maintains a balance in the climate, and recharges underground reservoirs. Ecosystems like rivers, lakes, wetlands, and oceans rely on water to support diverse plant and animal life. It is very important for energy production, transportation, urban development, and scientific research. Water scarcity threatens the environment, communities, and economies.

## PROPERTIES AND QUALITY OF WATER

**Q.2 Discuss the peculiar features of water that emerge from its structure.** U/Q

**Ans.** The chemical and physical properties of water are central to studying the nature and extent of pollution in the water bodies. The water molecule ($H_2O$) is a permanent dipole. This polarity gives water unique properties essential for life and the environment. Some peculiar features of water that emerge from its structure are discussed here.

### 1. Thermal Stability

The polarity of the water molecule results in the formation of hydrogen bonds among water molecules. Hydrogen bonding gives water a high specific heat capacity and high heat of vaporisation. This means that large bodies of water are thermally stable, resisting rapid temperature changes.

### 2. Unique Solvent Abilities of Water

Water is the universal solvent. Polarity also makes water a good solvent for a wide range of ionic substances, such as metallic ions, nitrates ($NO_3^-$) and phosphates ($PO_4^{3-}$), by surrounding the ions. Furthermore, the ability of water to dissolve polar organic compounds means that many pesticides and herbicides easily enter the water cycle, where they can persist and undergo bioaccumulation (collection in living bodies).

### 3. Amphoteric Nature

The ability of water to act as both an acid and a base i.e., amphoteric nature is also important for water quality. The self-ionization of water ($K_w = 1.0 \times 10^{-14}$ at 25°C) provides the baseline for the pH scale. Water is amphiprotic. It can both donate and accept a proton. Most of the aquatic life is highly sensitive to pH fluctuations.

CamScanner

**Example:** Pollution in the form of acid rain, caused by the dissolution of sulphur dioxide ($SO_2$) and nitrogen oxides ($NO_x$), increases the concentration of hydronium ions ($H_3O^+$). This acidity can mobilise toxic heavy metal compounds, such as aluminium hydroxide and lead salts, from sediments into the water column by increasing their solubility through protonation or by displacing them from mineral surfaces.

**Q.3 Explain the difference between DO, BOD and COD; How they relate to the water pollution?** Exercise D/Q 7

## 4. Oxygen in Water

The oxygen gas plays a crucial role in water. It is an indicator of water quality and the level of pollution. Oxygen in water can be interpreted based on its different roles.

- **Dissolved oxygen (DO):** DO is a key indicator of water quality and aquatic ecosystem health. It refers to the amount of oxygen available in water for aquatic organisms to breathe. High DO levels generally indicate clean, unpolluted water, while low levels may suggest pollution or excessive organic matter decomposition.
- **Biochemical Oxygen Demand (BOD):** BOD is the amount of oxygen required by microorganisms to break down organic matter in water over a specific period, usually five days at 20°C. It is a key indicator of the level of organic pollution in water. High BOD values indicate a large amount of organic matter, suggesting heavy pollution, which can deplete dissolved oxygen and harm aquatic life.
- **Chemical Oxygen Demand (COD):** COD is the amount of oxygen required to chemically oxidise organic and inorganic substances in water, using oxidising agents ($KMnO_4$, $K_2Cr_2O_7$, etc.). High COD values indicate a high concentration of oxidisable chemical pollutants, suggesting poor water quality and potential contamination from industrial or domestic waste. COD is useful for assessing the total pollution load in water.

The following table outlines the typical ranges for these parameters across different types of water sources.

**Table: Typical ranges of DO, BOD, and COD in water**

| Water Type | DO (Dissolved Oxygen) mg/L | BOD (Biochemical Oxygen Demand) mg/L | COD (Chemical Oxygen Demand) mg/L |
|---|---|---|---|
| Very Pure Water | 7-10 | < 1 | < 2 |
| Drinking Water | > 6 | <2 | < 5 |
| Moderately Polluted | 4-6 | 2-8 | 10-20 |
| Treated Sewage | 2-4 | 10-30 | 30-100 |
| Raw Sewage | < 1 | 100-400 | 200-1000 |
| Industrial Waste | 0-2 | 500-5000+ | 1000-20,000+ |

## 5. Redox Potential

The redox potential of water is a measure of the oxidising and reducing nature of a water body. In well-oxygenated water, chemical species exist in their most oxidised forms, such as $SO_4^{2-}$ and $CO_2$. In polluted or stagnant water, the oxygen is depleted, so the environment becomes reducing. It leads to the formation of toxic substances like hydrogen sulphide ($H_2S$) and ammonia ($NH_3$). Understanding these chemical equilibria and the molecular behaviour of $H_2O$ allows us to predict how specific contaminants will migrate, transform, and ultimately impact the global water supply.

### ☑ QUICK CHECK 33.1

**I. Explain how the polarity of water facilitates the transport of agricultural pollutants like pesticides into the water cycle.**

**Ans.** Water is a **polar solvent**, meaning it can dissolve many ionic and polar substances.
Many agricultural chemicals such as fertilizers and some pesticides contain –OH, –NH etc. (polar functional groups) soluble in water. Rainwater and irrigation water dissolve these pollutants. The dissolved pollutants are carried by surface runoff into rivers, lakes, and reservoirs. They can also move through the soil by leaching and contaminate groundwater.
Thus, the **polarity of water** allows it to act as an effective transport medium for pollutants in the water cycle. Water's polarity enables agricultural pollutants to dissolve and spread through surface and groundwater systems.



**II. Differentiate between Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) as indicators of water quality.**

**Ans.**

| Biological Oxygen Demand (BOD) | Chemical Oxygen Demand (COD) |
|---|---|
| BOD is the amount of oxygen required by microorganisms to break down organic matter in water over a specific period, usually five days at 20°C. | COD is the amount of oxygen required to chemically oxidize both biodegradable and non-biodegradable pollutants. |
| It indicates the level of biodegradable pollution in water. | It indicates the total amount of oxidizable pollutants present. |
| It is determined using microbial activity over several days (typically 5 days). | It is determined by chemical oxidation methods and is much faster. |
| BOD values are usually lower than COD values. | Values of COD usually higher than BOD values because more substances are oxidized. |

## SOURCES OF WATER POLLUTION

**Q.4 Discuss the sources of water pollution.** LIQ

**Ans.** The sources of pollution may either be small scale and single point or a variety of locations or points adding the same or various types of pollutants. Based on this, the sources of water pollution are divided into two types.

### 1. Point Source Pollution

Point-source pollution is the contamination that enters a water body from a single, discrete, and identifiable location or point. As the discharge is concentrated at one point, it often causes a **pollution plume**. Immediately downstream or at the site of discharge, concentrations of the pollutant (such as heavy metals or organic waste) are at their highest, leading to localized acute toxicity.

**Examples:**

I) A factory discharging lead or mercury salts directly into a river via a specific wastewater pipe.
II) A storage tank at a chemical plant leaking its contents into the soil and finally into the groundwater.

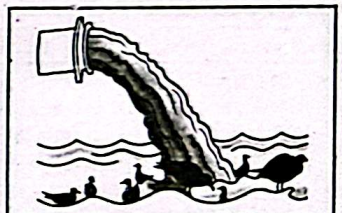


**Figure: Urban Sewage polluting water channels (point source pollution)**

### 2. Non-Point Source (NPS) Pollution

Non-point source pollution (known as diffused pollution) occurs when rainfall or snowmelt moves over and through the ground. As the water moves, it picks up and carries away natural and human-made pollutants, finally depositing them into lakes, rivers, wetlands, and coastal waters. Unlike point sources, NPS pollution is heavily dependent on weather events like heavy storms. NPS results in a mixture of various pollutants at lower concentrations across a much wider area.

➢ **Examples of Non-Point Pollution Sources:**

i. **Rain washing** excess ammonium nitrate ($NH_4NO_3$), fertilizers, and pesticides from thousands of hectares of farmland into a river system.
ii. **Storm water** moving over impermeable surfaces (roads and car parks), collecting leaked engine oils (hydrocarbons), zinc from tires, and road salts.

### ☑ QUICK CHECK 33.2

**a) Classify these as point or non-point sources of water pollution, explain your choice.**
**i) The outfall pipes used to release treated sewage into a bay or river from wastewater treatment plants.**
**ii) The "acid rain" caused by the nitrogen oxides ($NO_x$) from distant traffic or power stations dissolved in rain water.**

**Ans. (I)** Out fall pipes are point source of water pollution as the treated sewage is put into a bay or river (fixed location). The pollutants enter the water body from a single, identifiable location **the discharge pipe.** The source can be easily monitored and controlled.

CamScanner

**Examples:** Factory discharge pipes, sewage treatment plant outlets and industrial effluent pipes.

(ii) Acid rain is a non-point source pollution.

**Reason:** The $NO_x$ is released from many dispersed traffic and power-station sources, transported through the atmosphere and deposited over a wide area in rain; there is no single identifiable discharge point into the water body.

**b) Give two major differences between point and non-point pollution sources.**

**Ans.**

| Point Source Pollution | Non-point Source Pollution |
|---|---|
| • The pollutants enter the water body from a single, identifiable location the discharge pipe. | • The pollution originates from many scattered sources i.e., from diffuse sources outer a large area such as vehicles and power plants. |
| • The source can be easily monitored and controlled as small area is affected. | • The pollutants are transported through the atmosphere and deposited over large areas by rainfall. |
| **Examples:** | • There is no single discharge point. |
| • Factory discharge pipes. | **Examples:** |
| • Sewage treatment plant outlets. | • Agricultural runoff, urban runoff and atmospheric deposition (acid rain) |
| • Industrial effluent pipes. | |

## COMMON WATER POLLUTANTS

### 1. Microbiological Pollutants

**Q.5 What are microbiological pollutants?** SQ

**Ans.** Microbiological pollution is the contamination of water by harmful microorganisms, such as bacteria, viruses, protozoa, and parasites which can pose serious health risks to humans and animals. This type of pollution typically results from the discharge of untreated or inadequately treated sewage, animal waste, hospital waste, and runoff from agricultural lands into water bodies.

- **Common pathogens** found in microbiologically polluted water include Escherichia coli, Salmonella, and Giardia.
- **Microorganisms** in water, such as bacteria, viruses, and protozoa are the **major cause of water-borne diseases.** Common water-borne diseases include cholera, typhoid, dysentery, and hepatitis A.

### 2. Chemical Pollutants (Heavy Metals and Pesticides)

**Q.6 Describe the effects of heavy metals and pesticides on the human body.** Exercise Q.4

**Q.7 Explain the different sources of heavy metals and organic compounds.** Exercise Q.5

**Ans.**

**a) Heavy Metals**

This type of pollution often includes toxic heavy metals e.g., mercury (Hg), lead (Pb), arsenic (As), and cadmium (Cd) and agricultural chemicals such as pesticides and herbicides. Heavy metals can enter water systems through industrial discharge, mining operations, and improper waste disposal.

➢ **Sources of Heavy Metals:**

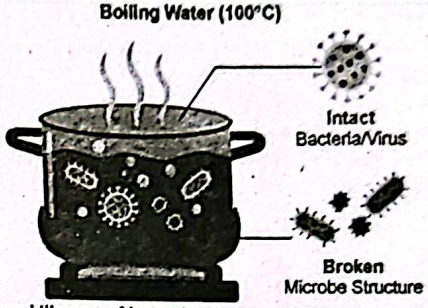
The sources of three significant heavy metals are given below:

i) **Mercury (Hg):** Mercury can enter water primarily from coal combustion, gold mining, and industrial waste from thermometer or battery manufacturing. In aquatic sediments, bacteria convert inorganic mercury into methylmercury ($[CH_3Hg]^+$), which is more dangerous.

ii) **The major sources of Lead (Pb):** A leaded petrol (which is now banned worldwide); old plumbing (lead pipes), lead-acid batteries, and paints. Lead ions ($Pb^{2+}$) often enter water systems through the corrosion of pipes.

iii) **The major sources of Cadmium:** Metal plating, plastic stabilizers, and phosphate fertilizer impurities are major sources of cadmium in water. These chemicals are usually of non-biodegradable nature and can accumulate in the food chain, posing long-term risks to aquatic life and humans, equally.



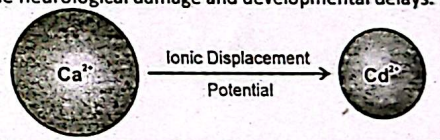



**Boiling can kill most of bacteria, viruses and protozoa to make water drinkable. But other pollutants cannot be removed by boiling only.**

➢ **Health effects of Heavy Metals:**

Heavy metals have high atomic weights and densities. Due to their non-biodegradable nature, they tend to accumulate in the tissues of living organisms, and are particularly dangerous. Some common heavy metals and their hazards are given as follows.

- **Methyl mercury** ($[CH_3Hg]^+$) is highly fat-soluble, allowing it to easily cross biological membranes and undergo bio magnification. It is a potent neurotoxin that crosses the blood brain barrier. Long term exposure leads to Minamata disease, characterized by ataxia (lack of muscle coordination), numbness in the hands and feet, and general muscle weakness.
- **Lead** interferes with the production of haemoglobin, leading to anaemia. In children, it acts as a poison that causes irreversible neurological damage and developmental delays.




**$Cd^{2+}$ ions have higher charge density so they can replace $Ca^{2+}$ ions in bones**

- Long-term ingestion of **Cadmium (Cd)** leads to "Itai-itai" disease, where cadmium replaces calcium in the bones, making them extremely brittle. It also causes severe kidney damage (nephrotoxicity).
- The limiting concentrations (mg/L) of some heavy metals are provided in Table.

**Table: WHO permissible limits of heavy metals in drinking water**

| Heavy Metal | WHO Limit (mg/L) |
|---|---|
| Arsenic (As) | 0.01 |
| Chromium (Cr) | 0.05 |
| Copper (Cu) | 2.0 |
| Lead (Pb) | 0.01 |
| Cadmium (Cd) | 0.003 |
| Mercury (Hg) | 0.006 |

**Did You Know?**



The Minamata Disaster was a severe case of industrial pollution that occurred in the 1950s in Minamata, Japan. Caused by the release of methylmercury into the water, it led to widespread mercury poisoning, affecting thousands of people with neurological damage and causing birth defects, deaths, and environmental devastation. At right is the picture of a patient inflicted by such a neurological disease.

**b) Pesticides and Herbicides**

Pesticides and Herbicides such as DDT and Glyphosate are another hazardous material that pollute water and cause severe human health issues.

**Sources of herbicides and Pesticides**

The major sources of these are agricultural runoff and domestic gardening. They are non-polar and insoluble in water but highly soluble in the fatty tissues of fish and birds. Many older pesticides like DDT are persistent organic pollutants (POPs). Pesticides are linked to hormonal disruption and developmental problems. Chemical pollution also degrades water quality, reduces biodiversity, and disrupts aquatic ecosystems.

CamScanner

### ➢ Harmful Effects of Pesticides and Herbicides on Human Health:

S/Q. Discuss their harmful effects of pesticides and herbicides.

Many pesticides act as endocrine disruptors such as natural hormones, e.g., estrogen. This can lead to the reproductive failure in wildlife (e.g., thinning of eggshells in birds) and is linked to hormonal cancers in humans. Polychlorinated biphenyls (PCBs) have been used in electrical transformers as coolants; they leak into water from hazardous waste sites. PCBs are classified as probable human carcinogens. They also suppress the immune system and cause skin conditions e.g., chloracne.

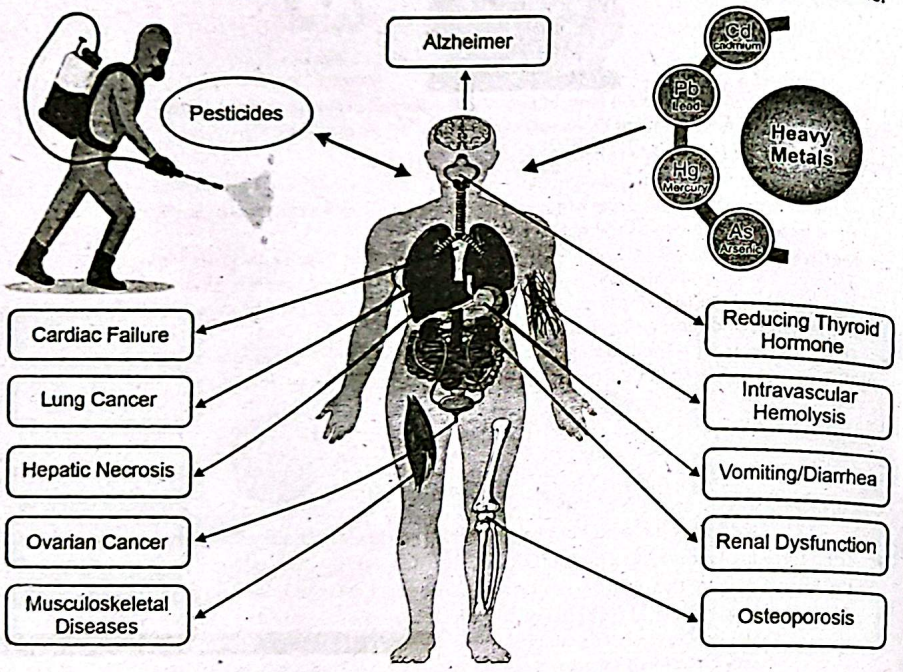



**Figure: Effects of heavy metals and pesticides on the human body**

**Q.8 What is Eutrophication?** S/Q

## 3. Eutrophication

Eutrophication also known as nutrient pollution, occurs when excessive amounts of nutrients, primarily nitrogen and phosphorus, enter into water bodies, usually from agricultural runoff, wastewater discharge, and stormwater.

- **Algal Bloom:** Although these nutrients are essential for plant growth, their excess in aquatic environments leads to the rapid growth of algae, commonly referred to as algal blooms. These blooms can block sunlight from reaching underwater plants. When they die and decompose, they consume large amounts of oxygen, creating hypoxic (low oxygen) or anoxic (oxygen free) **"dead zones"** where aquatic life cannot survive.
- **Ill Effects of Eutrophication:** Eutrophication severely disrupts aquatic ecosystems, reduces biodiversity, harms fisheries, and affects water quality for recreational and drinking purposes. High nitrate levels in drinking water are particularly dangerous for infants. It can lead to "Blue Baby Syndrome" (Methaemoglobinaemia), where nitrates reduce the blood's capacity to carry oxygen.



**Q.9 What is oil pollution?** S/Q

## 4. Oil (Oil Spilling)

Oil pollution in oceans, particularly from oil leaks and spills caused by ships, is a major environmental threat. When oil is accidentally released into the sea, it spreads rapidly across the water surface, forming a layer that blocks sunlight and reduces oxygen exchange. This severely harms marine life, including fish, birds, and mammals. Marine mammals can ingest the toxic oil while grooming, and fish may suffer from long-term health issues due to the exposure to hydrocarbons. Oil poliution also damages coastal habitats such as mangroves (a shrub), coral reefs, and beaches.



(a) (b)

**Figure: (a) Eutrophication in water bodies damages aquatic life, (b) Marine life suffers from oil pollution**

**Q.10 How plastic and solid waste cause water pollution?** S/Q

## 5. Plastic and Solid Waste

Plastic and solid waste pollution in **oceans and other water bodies** is a growing environmental crisis. Millions of tons of plastic waste including bottles, bags, fishing nets, and microplastics are dumped into rivers, lakes, and oceans every year. Unlike other organic materials, plastics do not biodegrade; instead, they break down into smaller particles that persist in the environment for very long period.

**Marine animals** often mistake **plastic for food**, leading to ingestion, choking, or internal injury, which can be fatal. Sometimes entanglement in old fishing gear and other debris in the sea bed also causes injury or death to countless sea creatures, including turtles, dolphins, and birds.

Furthermore, microplastics have entered the food chain, raising concerns about their impact on the human health. Solid waste pollution also clogs waterways, disrupts aquatic habitats, and reduces water quality.

### ☑ QUICK CHECK 33.3

**I. Name the sources of heavy metals.**

**Ans. Major Sources of Heavy Metals**

- **Mercury (Hg):** Mercury can enter water primarily from coal combustion, gold mining, and industrial waste from thermometer or battery manufacturing. In aquatic sediments, bacteria convert inorganic mercury into methylmercury ($[CH_3Hg]^+$), which is more dangerous.
- **Lead (Pb):** A leaded petrol (which is now banned worldwide); old plumbing (lead pipes), lead-acid batteries, and paints. Lead ions ($Pb^{2+}$) often enter water systems through the corrosion of pipes.
- **Cadmium (Cd):** Metal plating, plastic stabilizers, and phosphate fertilizer impurities are major sources of cadmium in water.

**II. How oil spill is hazardous to the marine life?**

**Ans.** Oil spills are harmful to marine ecosystems because:

- Oil forms a thin layer on the water surface that blocks oxygen exchange.
- It coats the feathers of birds and the fur of marine mammals, reducing insulation and buoyancy.
- It **damages fish** gills and affects respiration.
- Toxic hydrocarbons in oil can poison marine organisms.
- Oil contaminates food chains and breeding habitats.
- Oil spilage can damage coastal habitats e.g., mangrouls, coral reefs, beaches etc.

As a result, oil spills can cause death of marine organisms and severe ecosystem damage.

CamScanner

iii. **Pesticides like DDT are "non-polar and insoluble in water" yet they "pollute water and cause severe human health issues. Explain.**

**Ans.** Although DDT is non-polar and insoluble in water, it still enters water bodies through:

- Agricultural runoff carrying soil particles contaminated with DDT.
- Atmospheric transport and deposition.

**Because DDT is non-polar:**

- It dissolves readily in fats and oils instead of water.
- It accumulates in the fatty tissues of organisms (**bioaccumulation**).
- Its concentration increases at each trophic level of the food chain (**biomagnification**).

This can lead to nervous system disorders, reproductive problems, cancer risks and damage to wildlife populations.

## BLOCK # 01 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **The unique properties of water are mainly due to its:**
   (A) High density (B) Non-polar nature (C) Polarity (D) High molecular mass
2. **Water molecules are held together by:**
   (A) Ionic bonds (B) Covalent bonds (C) Hydrogen bonds (D) Metallic bonds
3. **Hydrogen bonding gives water a high:**
   (A) Electrical conductivity (B) Specific heat capacity (C) Vapour pressure (D) Density only
4. **Large water bodies resist rapid temperature changes because water has:**
   (A) Low boiling point (B) High specific heat capacity (C) Low density (D) High viscosity
5. **Water is considered an excellent solvent because of its:**
   (A) Colour (B) Polarity (C) Odour (D) Neutral taste
6. **Water readily dissolves:**
   (A) Non-polar compounds only (B) Ionic and polar substances
   (C) Metals only (D) Hydrocarbons only
7. **Water is described as amphoteric because it can act as:**
   (A) An oxidizing agent only (B) A reducing agent only (C) Both an acid and a base (D) A catalyst
8. **The ionic product of water at 25°C is:**
   (A) $1 \times 10^{-7}$ (B) $1 \times 10^{-14}$ (C) $1 \times 10^{-10}$ (D) 14
9. **Acid rain increases the concentration of:**
   (A) $OH^-$ ions (B) $H_3O^+$ ions (C) $Na^+$ ions (D) $Cl^-$ ions
10. **Acidic water increases the solubility of toxic:**
    (A) Sugars (B) Heavy metals (C) Proteins (D) Alcohols
11. **Dissolved Oxygen (DO) is an indicator of:**
    (A) Water hardness (B) Water quality (C) Salinity (D) Acidity only
12. **High dissolved oxygen generally indicates:**
    (A) Polluted water (B) Clean water (C) Acid rain (D) High BOD
13. **Biochemical Oxygen Demand (BOD) measures oxygen required by:**
    (A) Fish (B) Microorganisms (C) Plants (D) Birds
14. **BOD is commonly measured over:**
    (A) 24 hours (B) 2 days (C) 5 days (D) 10 days
15. **High BOD indicates:**
    (A) Clean water (B) Heavy organic pollution (C) Low microbial activity (D) High dissolved oxygen
16. **Chemical Oxygen Demand (COD) measures oxygen required to:**
    (A) Dissolve salts (B) Chemically oxidize pollutants
    (C) Neutralize acids (D) Produce oxygen
17. **Potassium dichromate ($K_2Cr_2O_7$) is commonly used to determine:**
    (A) DO (B) BOD (C) COD (D) pH
18. **High COD values indicate:**
    (A) Excellent water quality (B) High chemical pollution (C) Low pollution (D) Neutral water
19. **In well-oxygenated water, sulphur mainly exists as:**
    (A) $H_2S$ (B) $SO_4^{2-}$ (C) $SO_2$ (D) $S^{2-}$
20. **Oxygen-depleted water promotes formation of:**
    (A) Carbon dioxide only (B) Hydrogen sulphide (C) Oxygen gas (D) Sulphur dioxide
21. **Point source pollution originates from:**
    (A) A single identifiable source (B) Rainfall only
    (C) Forests (D) Agricultural land only



22. **A factory wastewater pipe discharging into a river is an example of:**
    (A) Non-point pollution (B) Point source pollution (C) Atmospheric pollution (D) Soil pollution
23. **Non-point source pollution is mainly associated with:**
    (A) A single discharge pipe (B) Rainfall runoff (C) Factory chimneys (D) Oil refineries only
24. **Agricultural runoff is an example of:**
    (A) Point source pollution (B) Non-point source pollution
    (C) Thermal pollution (D) Radioactive pollution
25. **Water contaminated with bacteria, viruses and protozoa contains:**
    (A) Thermal pollution (B) Microbiological pollutants (C) Heavy metals (D) Radioactive waste
26. **Cholera is primarily a:**
    (A) Genetic disease (B) Water-borne disease (C) Viral cancer (D) Respiratory disease
27. **Which microorganism commonly contaminates polluted water?**
    (A) Escherichia coli (B) Rhizobium (C) Lactobacillus (D) Yeast
28. **Heavy metals enter water mainly through:**
    (A) Photosynthesis (B) Industrial discharge and mining
    (C) Rainfall only (D) Evaporation
29. **Mercury is converted by bacteria into:**
    (A) Mercuric oxide (B) Methylmercury (C) Mercury chloride (D) Mercury sulphide
30. **Methylmercury is especially dangerous because it:**
    (A) Is highly water soluble (B) Is fat soluble (C) Evaporates quickly (D) Is biodegradable
31. **Long-term mercury poisoning causes:**
    (A) Itai-Itai disease (B) Minamata disease (C) Cholera (D) Hepatitis A
32. **Lead poisoning interferes with the production of:**
    (A) Insulin (B) Haemoglobin (C) DNA (D) Collagen
33. **Lead poisoning in children mainly causes:**
    (A) Kidney stones (B) Neurological damage (C) Blindness (D) Osteoporosis
34. **Cadmium toxicity is associated with:**
    (A) Itai-Itai disease (B) Malaria (C) Typhoid (D) Minamata disease
35. **Cadmium primarily damages the:**
    (A) Heart (B) Kidneys (C) Lungs (D) Eyes
36. **According to WHO, the permissible limit of lead in drinking water is:**
    (A) 2.0 mg/L (B) 0.5 mg/L (C) 0.01 mg/L (D) 0.1 mg/L
37. **The WHO permissible limit for cadmium is:**
    (A) 0.003 mg/L (B) 0.03 mg/L (C) 0.3 mg/L (D) 3.0 mg/L
38. **Mercury contamination is commonly associated with:**
    (A) Battery manufacturing (B) Sugar industry (C) Textile industry (D) Paper industry
39. **Which heavy metal replaces calcium in bones?**
    (A) Mercury (B) Cadmium (C) Lead (D) Copper
40. **High DO with low BOD generally indicates:**
    (A) Polluted water (B) Healthy aquatic ecosystem
    (C) Industrial waste (D) Sewage contamination

## WATER POLLUTION DUE TO HUMAN ACTIVITIES

**Q.11 Discuss water pollution due to human activities.** L/Q

**Ans.** Human activities are a major cause of water pollution across the globe. As populations grow and industries expand, more waste and pollutants are introduced into water bodies. Improper waste management and lack of environmental regulations often lead to contaminants reaching rivers, lakes, and oceans.

### i) Industrial Activities

Industrial activities are the major source of water pollution. Factories often discharge harmful chemicals, heavy metals, and toxic waste directly into rivers, lakes, and oceans. The common industries that release pollution, are oil refineries, chemical plants, automobile industry, fertilizers, tanneries, etc.

### ii) Agricultural Activities

Agricultural activities contribute significantly to water pollution through the runoff of fertilizers, pesticides, and herbicides into nearby water bodies. Poor irrigation practices can increase soil erosion, washing sediments into rivers and streams. In many areas, drainage from farmlands carries pollutants that contaminate both surface and groundwater sources.

CamScanner

### iii) Domestic and Municipal Waste

Domestic and municipal waste is one of the major sources of water pollution. In many areas, untreated or poorly treated sewage and solid waste from cities is discharged directly into rivers, lakes, or oceans, introducing harmful bacteria and viruses. Household waste such as detergents, oils, and chemicals often enter drains and eventually reach water bodies. Especially, plastics are frequently dumped in or near water channels, leading to blockages and long-term pollution.

### iv) Deforestation and Land Use for Urban Development

Deforestation and land use significantly contribute to the water pollution. When trees and vegetation are removed, the soil becomes loose and more prone to erosion, leading to increased sediment in rivers and streams. This sediment can clog waterways, harm aquatic habitats, and reduce water quality. Urban development and construction activities often introduce pollutants and debris into runoff water.

### v) Recreational Activities

Recreational activities such as boating, swimming, and camping can contribute to water pollution if not properly managed. Boats often release oil, fuel, and other chemicals into the water, harming aquatic life. Littering by visitors, including plastics, food wrappers, and other waste, can pollute lakes and rivers.

### vi) Marine Transport

Marine transport activities contribute to water pollution through the discharge of oil, fuel, and other chemicals from ships and boats. Accidental oil spills, wastewater and sewage from vessels, and ships are major causes of pollution. Routine maintenance, such as hull cleaning and painting, can also release toxic substances into the water. These practices collectively harm aquatic life and reduce water quality.

### ☑ QUICK CHECK 33.4

**a) A river passes by three regions in a country: a rural area with vast agricultural land and a lot of cattle; an industrial area with many paint and battery industries; and a large residential area of a big city:**

**i) Predict which type of pollutants will be added to the river in the rural area; organic, inorganic, or both? Name two of them.**

**ii) Which metals are most likely to pollute the water near the industrial area?**

**iii) Name the regions that will contaminate the water with chemicals that lead to Eutrophication.**

**iv) Name four contaminants that will pollute the water near the residential area.**

**Ans.**

**(i)** Both organic and inorganic pollutants will be present.

**Examples:**

**Organic Pollutants:**

- Animal manure and cattle waste.
- Pesticides and plant residues.

**Inorganic pollutants:**

- Nitrate fertilizers.
- Phosphate fertilizers.

**(ii)** Since the area contains **paint and battery industries**, the most likely heavy metal pollutants are:

- **Lead (Pb):** commonly used in batteries and paints.
- **Cadmium (Cd):** present in batteries and industrial waste.
- **Mercury (Hg):** used in some industrial processes.
- **Chromium (Cr):** used in pigments and coatings.

**(iii)** Eutrophication is caused by excess nutrients such as nitrates and phosphates.
The regions responsible are **rural agricultural area** (fertilizer runoff) and **residential area** (detergents and sewage).

**(iv)** The major contaminants near the residential area include:

1. Sewage and organic waste
2. Detergents
3. Plastics and solid waste
4. Pathogenic microorganisms (bacteria and viruses)



## EFFECT OF WATER POLLUTION ON THE ENVIRONMENT

**Q.12 Discuss the effect of water pollution on the environment.** LO

**Ans.** Pollutants can alter the physical and chemical properties of water, making it difficult for plants and animals to survive. Common environmental impacts include loss of biodiversity, habitat destruction, disruption of food chains, and decline in water quality.

### 1. Destruction of Eco Systems and Biodiversity

Water pollution, such as oil, heavy metals, and pesticides severely damages ecosystems and aquatic life by introducing harmful chemicals, plastics, and waste into rivers, lakes, and oceans. Toxic chemicals, sewage, and industrial waste can kill or harm aquatic organisms, reducing the variety of life in rivers, lakes, and oceans. It also affects birds and animals that rely on water bodies for survival.

### 2. Nutrient Overload (Eutrophication)

Nutrient overload from water pollution, especially excess nitrogen and phosphorus from fertilizers and sewage, leads to a rapid growth of algae, which block sunlight and reduce oxygen levels in the water. Eutrophication disrupts ecosystems, kills fish and other marine species, and damages water quality.

### 3. Bioaccumulation and Magnification

Bioaccumulation and biomagnification are serious adverse effects of water pollution, where toxic substances like mercury, lead, and pesticides build up in organisms over time. These toxins accumulate in the bodies of aquatic animals and become more concentrated as they move up the food chain. Top predators, including humans, often receive the highest doses.

### 4. Soil Degradation and Plant Life Damage

Water pollution significantly contributes to soil degradation and damages plant life. Contaminants like heavy metals, industrial waste, and excessive nutrients seep into the soil, altering its structure and fertility. Accumulated chemicals disrupt the soil's natural microbial activity, essential for plant health. Plants exposed to polluted water may exhibit stunted growth, leaf discoloration, and they may even die.

### 5. Methane Emission by Decaying Organic Matter

When sewage, agricultural runoff, or industrial waste enters water bodies, it boosts the growth of algae and other organisms. As these organisms die and decompose in oxygen-poor (anaerobic) conditions, methane, a potent greenhouse gas, is released. The excess methane contributes to climate change and worsens global warming.

### ☑ QUICK CHECK 33.5

**a) Methylmercury ($[CH_3Hg]^+$) is "highly fat-soluble," allowing it to cross biological membranes and the bloodbrain barrier.**

**i. Contrast the chemical structure of the methylmercury cation ($[CH_3Hg]^+$) with the inorganic mercury ion ($Hg^{2+}$). Explain why the presence of the methyl group ($-CH_3$) alters its solubility in lipid bilayers of living cells compared to the inorganic ion.**

**ii. Predict the impact on the "biomagnification" process if ($[CH_3Hg]^+$) was highly water-soluble but had low fat solubility.**

**Ans. (i) Inorganic Mercury Ion ($Hg^{2+}$)**

- It exists as a simple positively charged ion. It is highly polar and strongly attracted to water molecules. Therefore, it is **water-soluble** but has difficulty passing through the non-polar lipid membranes of cells.

**Methylmercury Ion ($[CH_3Hg]^+$)**

- It contains a **non-polar methyl group ($-CH_3$)** attached to mercury. The methyl group reduces the overall polarity of the compound. This increases its affinity for non-polar substances such as fats and cell membranes.

CamScanner

Since biological membranes consist mainly of phospholipid bilayers with hydrophobic interiors, Methylmercury dissolves readily in lipid membranes and can cross cell membranes and the blood-brain barrier. In contrast, Inorganic $Hg^{2+}$ is more water-soluble and crosses membranes less readily.

**Ans.** (ii)

Biomagnification occurs because substances accumulate in fatty tissues (**bioaccumulation**), are not easily excreted from organisms and become increasingly concentrated at higher trophic levels.

If methylmercury were highly water-soluble, and poorly fat-soluble then, it would remain dissolved in body fluids rather than accumulating in fat. Organisms would excrete it more easily through urine and other body fluids. Its concentration would not increase significantly through food chains.

Therefore, biomagnification would be greatly reduced or may not occur at all.

**b) How the water pollution can contribute to the global warming?**

**Ans.** Water pollution contributes to global warming through several mechanisms four important contributions are as under:

**1. Decomposition of Organic Waste:**

Organic pollutants in water are decomposed by microorganisms, producing greenhouse gases such as:

- Carbon dioxide ($CO_2$)
- **Methane ($CH_4$):** Methane is a particularly powerful greenhouse gas.

**2. Eutrophication:**

Excess nitrates and phosphates cause algal blooms.

When algae die and decompose the large amounts of oxygen are consumed.

Here, Anaerobic decomposition may occur. Methane and nitrous oxide ($N_2O$) are released.

**3. Wetland and Sediment Emissions:**

Polluted sediments and stagnant water bodies often produce methane under anaerobic conditions.

**4. Reduced Carbon Uptake:**

- Pollution damages aquatic plants and phytoplankton that normally absorb atmospheric carbon dioxide through photosynthesis. This reduces the natural removal of $CO_2$ from the atmosphere.
- Therefore, water pollution can increase greenhouse gas emissions and reduce carbon absorption, thereby contributing to global warming.

## WASTEWATER TREATMENT

**Q.13 Describe various technologies used in water treatment.** Exercise Q.13

**Ans.** Depending on the type and severity of pollution, such as organic matter, chemicals, or pathogens, different water treatment methods are used. These techniques are used at different levels of water treatment, i.e., primary treatment (removal of physical debris), secondary treatment (biological processing), and tertiary treatment (chemical purification).

**Technologies:** In the following steps different technologies (physical, biological, and chemical) suitable to remove various contaminants in water are being provided

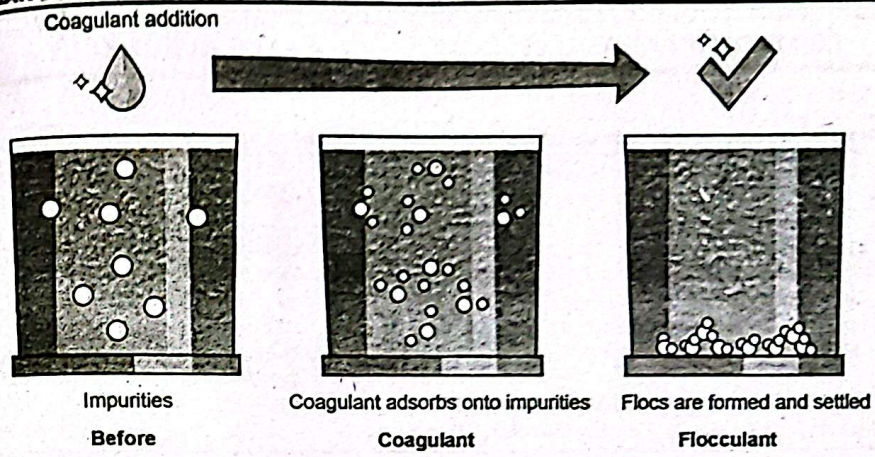
### i. Screening and Sedimentation

The initial stage of water treatment typically involves screening and sedimentation. Large insoluble particles are removed by passing water through metal screens. This is followed by sedimentation, where water is held in large tanks to allow suspended solids to settle at the bottom under the influence of gravity.

### ii. Coagulation and Flocculation

To speed up the settling of finer colloidal particles, coagulation and flocculation are employed. This process is done if required. It involves the precipitation of dissolved contaminants (e.g., heavy metals, phosphates) into insoluble forms for removal. Chemical coagulants, such as aluminium sulphate ($Al_2(SO_4)_3$), are added to the water. These chemicals cause the smaller particles to clump together into larger masses called "floc", which are then easily removed.






### iii. Filtration

Once the bulk of the solids has been removed, the water undergoes filtration. This is a mechanical process designed to remove the remaining fine suspended matter and some microorganisms. In a standard treatment plant, water passes through layers of graded sand and gravel. The sand acts as a physical barrier, trapping particles within the pores between grains. For more advanced purification, activated carbon is used.

### iv. Disinfection

Filtration alone cannot remove dissolved ions or microscopic pathogens; therefore, chemical purification is necessary. Chlorination is the most common method of disinfection. The other methods include sodium chlorate (I) ($NaOCl$); ozone ($O_3$) or sometimes with hydrogen peroxide ($H_2O_2$). When chlorine gas or sodium hypochlorite is added to water, it forms chloric (I) acid ($HOCl$), which penetrates the cell walls of bacteria and viruses, disrupting their cell functions.

### v. Reverse Osmosis (RO) and Ion Exchange Methods

For the production of high-purity water, such as that required in laboratory settings or regions with high salinity, reverse osmosis (RO) and ion exchange methods are utilized.

The RO method uses a semi-permeable membrane, which filters out dissolved salts, bacteria, and other impurities under pressure. Ion exchange is an important technology for "softening" water. Hard water contains high concentrations of $Ca^{2+}$ and $Mg^{2+}$ ions, which interfere with industrial processes and soap efficiency. In an ion-exchange column, these ions are swapped for $Na^+$ or $H^+$ ions.

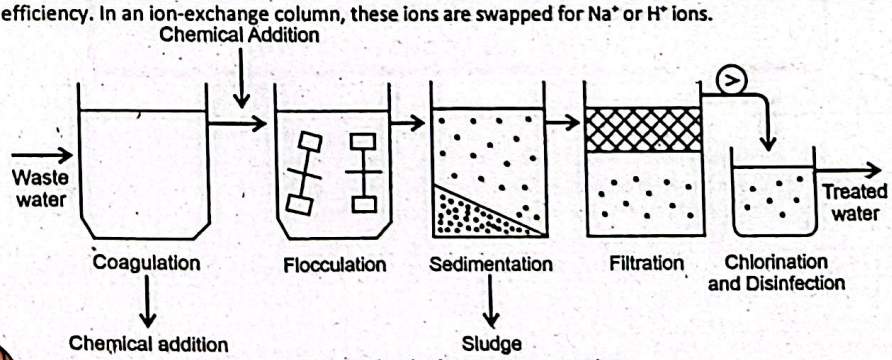



**Figure: A sketch of water treatment plant**

## PROTECTION AND CONSERVATION OF WATER RESOURCES

### ➲ Pollution Control

**Q.14 How water pollution can be controlled?** S/Q

**Ans.** It can be done by the following strategies.

- Imposing strict discharge standards for industries and municipalities to prevent harmful pollutants from entering water bodies.
- By upgrading and expanding sewage treatment plants (STPs), Installing Effluent Treatment Plants (ETPs), and adopting modern technologies, such as membrane filtration and bioreactors.
- By continuous water quality monitoring, which enables the detection of pollutants, ensuring timely responses to contamination events.
- By implementing strict penalties for polluters and offering incentives for clean practices. This approach discourages environmental violations while encouraging industries and communities to adopt sustainable, pollution-free operations.

### ➲ Efficient Use of Water (Water Conservation)

**Q.15 Conservation of water is of utmost importance discuss the strategies to conserve water.** S/Q

**Ans.** Conservation of water is of utmost importance in the current era due to water shortage faced by a large fraction of world's population. Following strategies help conserve water.

➢ **Strategies to Conserve Water:**

Following strategies help conserve water.

- Water-saving technologies in agriculture such as, drip irrigation and sprinkler irrigation in agriculture significantly reduced water wastage while improving crop yield and efficiency.
- Reusing and recycling greywater, such as household laundry, dishwashing, and bathing water for landscaping, toilet flushing, and industrial cooling helps conserve freshwater resources and reduces the burden on sewage treatment systems.
- Implementing rainwater harvesting systems in both urban and rural areas is a sustainable method to capture and store valuable water resources.
- Regular repair and maintenance of water supply infrastructure minimize leaks and water loss, ensuring efficient delivery and reduced resource wastage.
- Constructing small dams and recharge wells helps store rainwater and replenish groundwater levels, providing a reliable source of water during dry periods.
- Community engagement and awareness through public education campaigns on watersaving behaviours and involvement of local communities in water body protection.

## RULES AND REGULATIONS REGARDING WATER POLLUTION AND CONSERVATION

**Q.16 What are the rules and regulations regarding waste pollution and conservation?** S/Q

**Ans.** The Government of Punjab has made several acts and laws to address the water pollution within its jurisdiction. The Punjab Environmental Protection Agency (EPA) Punjab regularly issues relevant rules and regulations for all concerned stakeholders. Below is a comprehensive overview of the key self-explanatory rules and regulations issued by EPA Punjab (Pakistan) related to water pollution control and conservation.

**Table: Key environmental regulations and conservation measures**

| Act / Regulation | Primary Scope and Powers | Penalties for Non-Compliance |
|---|---|---|
| Punjab Environmental Protection Act, 1997 | Pollution prevention. | Fines up to Rs. 5 million, plus additional daily fines of up to Rs. 100,000. |
| Punjab Water Act, 2019 | Prohibits discharging pollutants or blocking flow. | Up to 3 months imprisonment and/or a Rs. 500,000 fine. |
| Punjab Irrigation, Drainage and Rivers Act, 2023 | Sets water usage and drainage fees, regulates discharge permits to prevent industrial/agricultural pollution. | _____ |
| Punjab Water and Sanitation Authority Act, 2025 | Establishes the Authority in major cities (Lahore, Multan, etc.) for integrated resource management and groundwater conservation. | _____ |



**Did You Know?**

The penalty for the use of hosepipes for car-washing and flood irrigation in domestic lawns or gardens is a Fine of Rs. 10,000 under the Pakistan Penal Code.

## BLOCK # 02 MULTIPLE CHOICE QUESTIONS (MCQs)

1. **DDT is classified as a:**
   (A) Fertilizer (B) Herbicide (C) Persistent organic pollutant (D) Fungicide
2. **Glyphosate is a commonly used:**
   (A) Herbicide (B) Insecticide (C) Fungicide (D) Rodenticide
3. **Agricultural runoff is the major source of:**
   (A) Radioactive waste (B) Pesticides & herbicides (C) Plastic waste only (D) Oil spills
4. **DDT is highly soluble in:**
   (A) Water (B) Fatty tissues (C) Dilute acids (D) Alcohol only
5. **PCBs were mainly used in:**
   (A) Fertilizers (B) Electrical transformers (C) Paints (D) Cement
6. **PCBs are classified as probable human:**
   (A) Antibiotics (B) Vitamins (C) Carcinogens (D) Hormones
7. **Eutrophication is mainly caused by excessive:**
   (A) Sodium chloride (B) Nitrogen & phosphorus (C) Oxygen (D) Carbon dioxide
8. **Algal blooms mainly block:**
   (A) Heat (B) Sunlight (C) Wind (D) Rainfall
9. **During decomposition of algae, dissolved oxygen:**
   (A) Increases (B) Decreases (C) Remains unchanged (D) Doubles
10. **High nitrate levels in drinking water may cause:**
    (A) Minamata disease (B) Blue Baby Syndrome (C) Itai-Itai disease (D) Cholera
11. **Oil spills primarily affect marine life by:**
    (A) Increasing dissolved oxygen (B) Blocking sunlight and oxygen exchange
    (C) Increasing photosynthesis (D) Neutralizing seawater
12. **Marine mammals are harmed because they may:**
    (A) Produce oil (B) Increase reproduction
    (C) Convert oil into oxygen (D) Ingest toxic oil while grooming
13. **Plastics in water bodies are dangerous because they:**
    (A) Biodegrade rapidly (B) Persist for centuries (C) Dissolve completely (D) Increase dissolved oxygen
14. **Marine animals often mistake plastic for:**
    (A) Water (B) Food (C) Sand (D) Salt
15. **Microplastics are a concern because they:**
    (A) Enter the food chain (B) Improve water quality (C) Increase oxygen levels (D) Neutralize pollutants
16. **Water pollution from factories mainly results from:**
    (A) Industrial activities (B) Recreation (C) Tourism (D) Forestry
17. **Agricultural water pollution mainly occurs due to runoff of:**
    (A) Sand (B) Fertilizers and pesticides (C) Oxygen (D) Carbon dioxide
18. **Domestic sewage commonly introduces:**
    (A) Bacteria and viruses (B) Pure oxygen (C) Nitrogen gas (D) Helium
19. **Deforestation increases water pollution by promoting:**
    (A) Photosynthesis (B) Soil erosion (C) Nitrogen fixation (D) Water purification
20. **Marine transport contributes to pollution mainly through:**
    (A) Oil spills (B) Oxygen release (C) Rainwater harvesting (D) Evaporation

CamScanner

21. **Water pollution reduces biodiversity by:**
(A) Improving habitats (B) Damaging ecosystems
(C) Increasing dissolved oxygen (D) Enhancing reproduction

22. **Biomagnification refers to:**
(A) Decrease of pollutants up the food chain (B) Increase of toxin concentration up the food chain
(C) Removal of pollutants (D) Neutralization of heavy metals

23. **Top predators receive the highest concentration of toxins due to:**
(A) Filtration (B) Biomagnification (C) Sedimentation (D) Distillation

24. **Excess nutrients mainly lead to:**
(A) Desertification (B) Eutrophication (C) Acid rain (D) Ozone depletion

25. **Methane released from polluted water is produced under:**
(A) Aerobic conditions (B) Anaerobic conditions (C) Vacuum conditions (D) High pressure only

26. **The first step in wastewater treatment is:**
(A) Chlorination (B) Screening (C) Reverse osmosis (D) Ion exchange

27. **Sedimentation removes suspended particles mainly by:**
(A) Filtration (B) Gravity (C) Oxidation (D) Distillation

28. **Aluminium sulphate is commonly used for:**
(A) Coagulation (B) Disinfection (C) Reverse osmosis (D) Water softening

29. **Flocculation converts fine particles into:**
(A) Vapours (B) Flocs (C) Crystals (D) Gases

30. **Activated carbon is mainly used to:**
(A) Remove fine impurities (B) Increase hardness
(C) Add chlorine (D) Increase salinity

31. **The most common disinfectant used in water treatment is:**
(A) Bromine (B) Chlorine (C) Nitrogen (D) Hydrogen

32. **Chlorination produces:**
(A) Hypochlorous acid (HOCl) (B) HCl only (C) NaOH only (D) $H_2O_2$

33. **Reverse osmosis uses a:**
(A) Metal screen (B) Semipermeable membrane (C) Cotton cloth (D) Glass filter

34. **Ion exchange is mainly used for:**
(A) Water softening (B) Oil purification (C) Oxygen production (D) Desalination only

35. **Hard water mainly contains:**
(A) $Na^+$ and $K^+$ (B) $Ca^{2+}$ and $Mg^{2+}$ (C) $Fe^{3+}$ and $Al^{3+}$ (D) $Cl^-$ and $SO_4^{2-}$

36. **Drip irrigation helps to:**
(A) Waste water (B) Conserve water (C) Increase flooding (D) Increase evaporation

37. **Greywater can be reused for:**
(A) Intravenous injection (B) Landscaping and toilet flushing
(C) Drinking without treatment (D) Food preparation

38. **Rainwater harvesting is mainly used to:**
(A) Increase pollution (B) Store water resources (C) Produce electricity (D) Remove salts

## ANSWERS KEY (TOPIC-WISE IMPORTANT MCQs)

### BLOCK # 01

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. C | 2. C | 3. B | 4. B | 5. B | 6. B | 7. C | 8. B | 9. B | 10. B | 11. B | 12. B | 13. B | 14. C | 15. B |
| 16. B | 17. C | 18. B | 19. B | 20. B | 21. A | 22. B | 23. B | 24. B | 25. B | 26. B | 27. A | 28. B | 29. B | 30. B |
| 31. B | 32. B | 33. B | 34. A | 35. B | 36. C | 37. A | 38. A | 39. B | 40. B | | | | | |

### BLOCK # 02

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1. C | 2. A | 3. B | 4. B | 5. B | 6. C | 7. B | 8. B | 9. B | 10. B | 11. B | 12. D | 13. B | 14. B | 15. A |
| 16. A | 17. B | 18. A | 19. B | 20. A | 21. B | 22. B | 23. B | 24. B | 25. B | 26. B | 27. B | 28. A | 29. B | 30. A |
| 31. B | 32. A | 33. B | 34. A | 35. B | 36. B | 37. B | 38. B | | | | | | | |



# EXERCISE

## Q 1. MULTIPLE CHOICE QUESTIONS MCQs

*Four choices are given for each questions. Select the correct choice.*

I. **Which property of water is primarily responsible for its ability to resist rapid temperature changes in large aquatic ecosystems?**
a) Amphoteric nature b) High specific heat c) The permanent dipole d) High redox potential

II. **A water sample is found to have a very high Biochemical Oxygen Demand (BOD). What does this most likely indicate about the water body?**
a) Highly oxygenated and healthy b) High concentration of nitrates and phosphates
c) High organic pollution d) A high pH

III. **The Non-Point Source (NPS) pollution is considered "weather-dependent" compared to point source pollution because:**
a) NPS pollutants are only toxic when the temperature of the water rises.
b) NPS pollution requires events like rain, storm, precipitation, etc.
c) NPS only discharge waste during specific seasons.
d) NPS cause plumes in running water.

IV. **Bacteria in aquatic sediments convert inorganic mercury into methylmercury ($[CH_3Hg]^+$). Which statement best explains why this conversion increases the ecological hazard?**
a) Methylmercury dissolves more readily in the water
b) Methylmercury is biodegradable and enters nutrient cycle
c) Methylmercury is highly fat-soluble
d) Methylmercury is a solid that clogs the gills of fish.

V. **Which condition is a direct result of Cadmium (Cd) replacing Calcium (Ca) in the skeletal system?**
a) Minamata disease b) Blue Baby Syndrome c) Itai-itai disease d) Chloracne

IV. **The primary chemical role of Aluminium Sulphate ($Al_2(SO_4)_3$) in the wastewater treatment process is:**
a) To kill pathogenic bacteria. b) To act as a semi-permeable membrane.
c) Converting colloidal particles to floc. d) To adsorb organic contaminants.

VII. **Ion exchange technology "softens" water by replacing calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) ions with:**
a) Chlorine ($Cl_2$) or ozone ($O_3$) b) Sodium ($Na^+$) or hydrogen ($H^+$) ions
c) Aluminum ($Al^{3+}$) or iron ($Fe^{3+}$) ions d) Carbonate ($CO_3^{2-}$) or phosphate ($PO_4^{3-}$) ions

### Answer Key With Explanations

| Sr.# | Option | Answer | Explanation |
|---|---|---|---|
| I. | b | High specific heat | Water absorbs or releases large amounts of heat with only small temperature changes, stabilizing aquatic ecosystems. |
| II. | c | High organic pollution | High BOD means microorganisms require large amounts of oxygen to decompose organic matter, indicating organic pollution. |
| III. | b | NPS pollution requires events like rain, storm, precipitation, etc. | Non-point pollution is strongly influenced by rainfall and surface runoff. |
| IV. | c | Methylmercury is highly fat-soluble. | Its fat solubility allows bioaccumulation and biomagnification through food chains. |
| V. | c | Itai-itai disease | Cadmium replaces calcium in bones, causing bone pain and skeletal damage known as Itai-itai disease. |
| IV. | c | Converting colloidal particles to floc | $Al_2(SO_4)_3$ acts as a coagulant; hydrolysed aluminium species neutralize colloid charges and form flocs that can settle/filter. |
| VII. | b | Sodium ($Na^+$) or hydrogen ($H^+$) ions | Ion exchange resins replace hardness-causing ions with sodium or hydrogen ions, producing soft water. |

CamScanner

## Q 2. SHORT ANSWER QUESTIONS SAQs

**a) Differentiate between Point Source and Non-Point Source pollution in terms of the "concentration" of pollutants at the site of entry.**

**Ans.**

| Point Source Pollution | Non-Point Source Pollution |
|---|---|
| Pollutants enter the water at a single location, producing a high local concentration. | Pollutants enter from many scattered locations, resulting in a lower concentration at each entry point but affecting larger areas. |
| Example: Factory discharge pipe. | Example: Agricultural runoff. |

**b) Using an example from the text, explain how an underground storage tank can become a point source of pollution.**

**Ans.** An underground storage tank containing fuel or chemicals may develop leaks due to corrosion or damage.
- The leaking chemicals enter the surrounding soil and groundwater from a **single identifiable location.**
- Since the contamination originates from one specific source, it is classified as **point source pollution.**

**Example:** Leakage of petrol from underground fuel storage tanks contaminating groundwater.

**c) Identify two types of chemical pollutants commonly found in urban storm water runoff.**

**Ans. Two common pollutants are:**
i. **Hydrocarbons and oils** (e.g., engine oils etc.) from vehicles.
ii. **Heavy metals** such as lead, zinc, and copper.
Other pollutants include detergents, and pesticides.

**d) Differentiate between the "solubility" of pesticides like DDT and inorganic nutrients like nitrates in the context of the water cycle.**

**Ans.**

| Solubility of DDT | Solubility of Nitrates |
|---|---|
| Non-polar in soluble in water, soluble in fats. | Highly soluble in water. |
| Binds to soil particles and sediments. | Easily dissolves and moves with water. |
| Result: Undergoes bioaccumulation and biomagnification. | Result: Causes eutrophication in water bodies. |

**e) Explain why microplastics are considered a "growing environmental crisis" differently than organic solid waste.**

**Ans.** Microplastics are considered a growing environmental crisis because:
- They are **non-biodegradable.**
- They persist and accumulate in the environment for long periods.
- They can be ingested by aquatic organisms.
- They enter food chains and accumulate in organisms.

Organic waste, on the other hand, is generally decomposed naturally by microorganisms i.e., organic waste is biodegradable.

**f) How an oil spill physically disrupts the chemical balance of a marine ecosystem?**

**Ans. Oil spills:**
- Form a layer on the water surface.
- Reduce oxygen transfer from air to water.
- Decrease dissolved oxygen concentration.
- Reduce light penetration, affecting photosynthesis of aquatic plants and phytoplankton.

This disturbs the chemical balance of the ecosystem.

**g) Why are synthetic organic pollutants, like PCBs and pesticides, considered "persistent" in the environment?**

**Ans. Reasons:**
Synthetic organic pollutants, like PCBs, pesticides and herbicides **(e.g., DDT and glyphosate)** are persistent because they resist chemical and biological degradation. Microorganisms cannot easily break them down. They remain in soil and water for many years. They accumulate in living organisms. Their chemical stability allows them to persist in the environment for long periods.



**h) How does the decomposition of organic matter in polluted water contribute to global warming?**

**Ans.** Microorganisms decompose organic matter and release greenhouse gases such as carbon dioxide ($CO_2$) and methane ($CH_4$). Methane is particularly important because it is a powerful greenhouse gas. Thus, decomposition increases greenhouse gas emissions and contributes to global warming.

**i) Name four methods used for water conservation.**

**Ans.**
1. Rainwater harvesting.
2. Drip irrigation.
3. Recycling and reuse of wastewater.
4. Repairing leaks and reducing wastage.

**j) What is the role of "industrial discharge" in water pollution?**

**Ans.** Industrial discharge introduces pollutants such as heavy metals, acids and alkalis, toxic organic chemicals and suspended solids. These pollutants degrade water quality and harm aquatic organisms.

**k) Both reverse osmosis (RO) and ion exchange methods are used to obtain high-purity water.**
**i) Differentiate between the processes involved in both these methods.**
**ii) What impurities do these methods target?**

**Ans. (i)**

| Reverse Osmosis (RO) | Ion Exchange |
|---|---|
| Water is forced through a semi-permeable membrane under high pressure. | Water passes through ion exchange resins. |
| Dissolved impurities are physically separated by the membrane. | Undesirable ions are chemically exchanged with harmless ions. |

**Ans. (ii)**

| Method | Target Impurities |
|---|---|
| Reverse Osmosis | It removes dissolved salts, microorganisms, organic molecules, and suspended particles. |
| Ion Exchange | It removes dissolved ions such as $Ca^{2+}$, $Mg^{2+}$, $Fe^{2+}$, and other charged species. |

## Q 3. CONSTRUCTED RESPONSE QUESTIONS CRQs

**a) Explain the relationship between acid rain and the presence of toxic heavy metals in aquatic environments.**

**Ans.** Acid rain is formed when sulfur dioxide ($SO_2$) and nitrogen oxides ($NO_x$) react with water in the atmosphere to produce sulfuric and nitric acids.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$
$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$

When acid rain enters lakes and rivers, it lowers the pH of water and sediments.
The acidic conditions dissolve heavy metals such as Aluminium ($Al^{3+}$), Lead ($Pb^{2+}$), Cadmium ($Cd^{2+}$) and Mercury ($Hg^{2+}$).
These metals are released from rocks and sediments into the water, increasing their concentration and toxicity.
Effects include damage to fish gills. Reduced reproduction in aquatic organisms and Bioaccumulation and biomagnification in food chains.
Thus, acid rain increases the mobility and toxicity of heavy metals in aquatic environments.

**b) Analyze the environmental impact of agricultural runoff as a Non-Point Source of pollution. Reference specific chemicals in your answer.**

**Ans.** Agricultural runoff is a major example of **Non-Point Source (NPS) pollution** because pollutants enter water bodies from many scattered locations rather than a single discharge point.

➢ **Fertilizers:**
Common fertilizer chemicals include: Nitrates ($NO_3^-$) and Phosphates ($PO_4^{3-}$). These nutrients enter rivers and lakes through rainfall runoff and cause:

**Eutrophication:**
- Excess nutrients stimulate algal blooms. Algae eventually die and decompose. Microorganisms consume dissolved oxygen.

CamScanner

- This increases biological oxygen demand (BOD), fish mortality and dead zones.

➢ **Pesticides:**
Examples include DDT and organophosphate pesticides.
These chemicals harm aquatic organisms, persist in the environment, undergo bioaccumulation and biomagnification.

➢ **Animal Waste:**
Livestock waste contributes organic matter and Pathogenic microorganisms. This increases BOD and promotes waterborne diseases. Therefore, agricultural runoff contributes nutrients, pesticides, and organic waste to aquatic ecosystems.

**c) Evaluate the role of agricultural runoff in contributing to different types of water pollution.**

**Ans. Agricultural runoff contributes to several forms of water pollution:**

1. **Nutrient Pollution**
   **Caused by:** Nitrate fertilizers and phosphate fertilizers.
   **Effects:** Eutrophication, Algal blooms and Oxygen depletion.
2. **Chemical Pollution**
   **Caused by:** Herbicides, pesticides and fungicides.
   **Examples:** DDT and Organophosphates.
   **Effects:** Toxicity to aquatic organisms and Bioaccumulation.
3. **Organic Pollution**
   **Caused by:** Animal manure and plant residues.
   **Effects:** Increased BOD and reduced dissolved oxygen.
4. **Microbial Pollution**
   **Caused by:** Bacteria, viruses and parasites from animal waste.
   **Effects:** Waterborne diseases and unsafe drinking water.

Thus, agricultural runoff contributes simultaneously to nutrient, chemical, organic, and microbial pollution.

**d) Evaluate the benefits and the long-term chemical risks involved in the use of chlorine as a disinfectant.**

**Ans. Benefits of Chlorination**

1. **Effective Disinfection:** Chlorine kills bacteria, viruses and protozoa. This prevents waterborne diseases such as, cholera, typhoid and dysentery.
2. **Residual Protection:** Unlike some disinfectants, chlorine remains in water for some time and provides continued protection during distribution.
3. **Low Cost:** Chlorination is inexpensive and suitable for large-scale water treatment.

**Long-Term Chemical Risks**

1. **Formation of Disinfection By-products**
   Chlorine reacts with natural organic matter to produce compounds such as: Trihalomethanes (THMs) and Haloacetic acids (HAAs). Some of these compounds may have carcinogenic effects.
2. **Toxicity to Aquatic Organisms**
   Excess chlorine discharged into water bodies can harm fish and aquatic life.
3. **Taste and Odour Problems**
   High chlorine concentrations may produce unpleasant taste and smell in drinking water.

**Conclusion:** Chlorination is highly effective for disease prevention, but excessive use can produce harmful disinfection by-products and environmental risks.

## DESCRIPTIVE QUESTIONS DQs

**Q.4 Describe the effects of heavy metals and pesticides on the human body.**

**Ans.** See Question No. 06



**Q.5 Explain the different sources of heavy metals and organic compounds.**

**Ans.** See Question No. 07

**Q.6 Describe various technologies used in water treatment.**

**Ans.** See Question No. 13

**Q.7 Explain the difference between DO, BOD and COD; How they relate to the water pollution?**

**Ans.** See Question No. Q.3

## ADDITIONAL SHORT ANSWER QUESTIONS ASAQs

**Q.1 Explain how the chemical properties of water make it an excellent solvent.**

**Ans.** Water is a polar molecule due to the difference in electronegativity between hydrogen and oxygen atoms. Its polarity allows it to dissolve many ionic and polar substances by surrounding and separating their ions or molecules. Therefore, water is known as the universal solvent.

**Q.2 Differentiate between point source and non-point source pollution.**

**Ans.** Point source pollution originates from a single identifiable source such as industrial discharge pipes, whereas non-point source pollution originates from widespread areas such as agricultural fields and urban runoff. Therefore, point source pollution is easier to monitor and control.

**Q.3 What are common water pollutants? Give examples.**

**Ans.** Common water pollutants include heavy metals, oil, pesticides, fertilizers, sewage and industrial chemicals. These pollutants degrade water quality and harm aquatic life.
**Examples** include mercury, lead, crude oil and DDT.

**Q.4 Explain the harmful effects of heavy metals in water.**

**Ans.** Heavy metals such as mercury and lead accumulate in living organisms through bioaccumulation and biomagnification. They can damage the nervous system, kidneys and other organs in humans and animals. Therefore, heavy metal contamination is a serious environmental issue.

**Q.5 Explain the environmental effects of oil pollution.**

**Ans.** Oil forms a thin layer on the water surface that reduces oxygen exchange between air and water. It damages marine ecosystems and affects fish, birds and other aquatic organisms.
Oil spills can cause long-term environmental damage.

**Q.6 How do pesticides pollute water resources?**

**Ans.** Pesticides applied to agricultural land can be carried into rivers and lakes by rainwater runoff. These chemicals may accumulate in aquatic organisms and enter the food chain.
This can affect both wildlife and human health.

**Q.7 Explain eutrophication.**

**Ans.** Eutrophication is the excessive growth of algae caused by an increase in nutrients such as nitrates and phosphates in water bodies. The decomposition of algae decreases dissolved oxygen levels and harms aquatic life.

**Q.8 Explain the impact of human activities on water resources.**

**Ans.** Agricultural runoff, industrial discharge and improper waste disposal contaminate water resources and reduce water quality. These activities also increase the risk of waterborne diseases and ecosystem damage.

**Q.9 Describe the process of water filtration.**

**Ans.** Filtration is the process of passing water through sand, gravel or other filter materials to remove suspended particles and impurities. It is an important step in water treatment plants.

**Q.10 Why is chlorination carried out during water treatment?**

**Ans.** Chlorination is used to destroy harmful bacteria, viruses and other microorganisms present in water. It helps ensure that drinking water is safe for human consumption.

CamScanner

$$Cl_2 + H_2O \longrightarrow HCl + HOCl$$

Hypochlorous acid ($HOCl$) acts as a disinfectant.

**Q.11 What is desalination?**

**Ans.** Desalination is the process of removing dissolved salts from seawater to produce fresh water suitable for drinking and irrigation. It is particularly important in regions facing water shortages.

**Q.12 Explain reverse osmosis.**

**Ans.** Reverse osmosis is a desalination technique in which water is forced through a semi-permeable membrane under high pressure. The membrane allows water molecules to pass through while retaining dissolved salts.

**Q.13 Why is water conservation important?**

**Ans.** Water conservation ensures the availability of clean water for future generations and reduces pressure on natural water resources. It also helps maintain ecological balance and sustainable development.

**Q.14 Explain the importance of drip irrigation.**

**Ans.** Drip irrigation delivers water directly to plant roots in small amounts, reducing evaporation and water wastage. It improves water-use efficiency and increases crop productivity.

**Q.15 What is rainwater harvesting?**

**Ans.** Rainwater harvesting is the collection and storage of rainwater for future use. It helps recharge groundwater supplies and reduces dependence on freshwater resources.

**Q.16 Why should industrial wastewater be treated before disposal?**

**Ans.** Industrial wastewater often contains toxic chemicals and heavy metals that can harm aquatic organisms and human health. Treatment removes harmful substances before discharge into the environment.

**Q.17 Explain the effects of water pollution on human health.**

**Ans.** Contaminated water can spread diseases such as cholera, typhoid and dysentery. Long-term exposure to pollutants may also cause serious health problems including neurological disorders and cancer.

**Q.18 Explain the effects of water pollution on aquatic ecosystems.**

**Ans.** Water pollution decreases dissolved oxygen levels and disrupts food chains, leading to the death of fish and other aquatic organisms. It also reduces biodiversity in aquatic ecosystems.

**Q.19 What are waterborne diseases? Give examples.**

**Ans.** Waterborne diseases are illnesses transmitted through contaminated water. Common examples include cholera, typhoid, dysentery and hepatitis A.

**Q.20 Explain the role of environmental laws in controlling water pollution.**

**Ans.** Environmental laws regulate industrial discharge, sewage disposal and waste management to protect water resources. These laws help maintain water quality and protect public health.

**Q.21 What is sustainable water management?**

**Ans.** Sustainable water management involves the efficient use, conservation and protection of water resources to meet present needs without compromising future generations.

**Q.22 How does agriculture contribute to water pollution?**

**Ans.** Agriculture contributes to water pollution through runoff containing fertilizers, pesticides and animal waste. These substances contaminate rivers, lakes and groundwater.

**Q.23 Explain the role of wastewater treatment plants.**

**Ans.** Wastewater treatment plants remove suspended solids, harmful chemicals and microorganisms from sewage and industrial effluents before releasing the treated water into the environment.



**Q.24 Why is clean drinking water essential for human health?**

**Ans.** Clean drinking water is necessary for hydration, digestion and normal body functions. It also prevents the spread of infectious diseases caused by contaminated water.

**Q.25 Explain bioaccumulation in relation to water pollution.**

**Ans.** Bioaccumulation is the gradual buildup of toxic substances such as mercury and pesticides in living organisms over time. These substances may reach dangerous levels in higher organisms of the food chain.

**Q.26 Explain biomagnification.**

**Ans.** Biomagnification is the increase in concentration of toxic substances at successive trophic levels of a food chain. Top predators usually contain the highest concentrations of pollutants.

**Q.27 Explain the importance of preserving freshwater resources.**

**Ans.** Freshwater resources are limited and essential for drinking, agriculture and industrial activities. Their conservation is necessary to meet the growing demands of increasing populations.

**Q.28 How can individuals help reduce water pollution?**

**Ans.** Individuals can reduce water pollution by minimizing the use of harmful chemicals, properly disposing of waste and conserving water. Community awareness also plays an important role.

## SELF-ASSESSMENT

**Total Mark: 30**

**Q.1 Encircle the correct option.** **(1 × 6 = 6)**

**(i)** **Large water bodies resist rapid temperature changes because water has:**
(A) Low boiling point (B) High specific heat capacity (C) Low density (D) High viscosity

**(ii)** **Water contaminated with bacteria, viruses and protozoa contains:**
(A) Thermal pollution (B) Microbiological pollutants (C) Heavy metals (D) Radioactive waste

**(iii)** **The WHO permissible limit for cadmium is:**
(A) 0.003 mg/L (B) 0.03 mg/L (C) 0.3 mg/L (D) 3.0 mg/L

**(iv)** **Excess nutrients mainly lead to:**
(A) Desertification (B) Eutrophication (C) Acid rain (D) Ozone depletion

**(v)** **Rainwater harvesting is mainly used to:**
(A) Increase pollution (B) Store water resources (C) Produce electricity (D) Remove salts

**(vi)** **A water sample is found to have a very high Biochemical Oxygen Demand (BOD). What does this most likely indicate about the water body?**
(A) Highly oxygenated and healthy (B) High concentration of nitrates and phosphates
(C) High organic pollution (D) A high pH

**Q.2 Write short answers of the following questions.** **(2 × 8 = 16)**

(i) How oil spill is hazardous to the marine life?
(ii) Pesticides like DDT are "non-polar and insoluble in water" yet they "pollute water and cause severe human health issues. Explain.
(iii) How the water pollution can contribute to the global warming?
(iv) Name the sources of heavy metals.
(v) Differentiate between the "solubility" of pesticides like DDT and inorganic nutrients like nitrates in the context of the water cycle.
(vi) How an oil spill physically disrupts the chemical balance of a marine ecosystem?
(vii) Name four methods used for water conservation.
(viii) What is the role of "industrial discharge" in water pollution?

**3 Extensive Questions.** **(4 + 4 = 8)**

Explain the different sources of heavy metals and organic compounds.
Explain the difference between DO, BOD and COD; How they relate to the water pollution?

CamScanner

## ENTRANCE TEST MCQs

1. **Heavy metals accumulate in organisms mainly because they are:**
   (A) Highly volatile and disappear rapidly (B) Essential nutrients at all levels
   (C) Destroyed by sunlight immediately (D) Non-biodegradable
2. **Why does a methyl group increase mercury toxicity?**
   (A) Rapidly biodegradable (B) Unable to cross membranes
   (C) More compatible with lipids and body tissues (D) More ionic and less absorbed
3. **The final ecological condition shown in the eutrophication graphic is:**
   (A) Complete nutrient removal (B) A low-oxygen dead zone
   (C) Very pure water (D) High dissolved oxygen
4. **If methylmercury were water-soluble but poorly fat-soluble, biomagnification would:**
   (A) Become a disinfection process (B) Decrease because tissue retention would be lower
   (C) Increase indefinitely (D) Remain exactly unchanged
5. **A limitation of chlorination is that organic matter can react with chlorine to form:**
   (A) Potentially harmful disinfection by-products (B) Only oxygen
   (C) Pure sodium chloride (D) No secondary products
6. **COD may be higher than BOD for the same water sample because:**
   (A) BOD includes all inorganic pollutants
   (B) COD measures only oxygen already dissolved
   (C) They must always be equal
   (D) COD oxidizes more substances than microbes can biodegrade
7. **Why can agricultural runoff cause both chemical and ecological pollution?**
   (A) Only pure water (B) Only dissolved oxygen
   (C) Only harmless calcium (D) Soluble nutrients plus persistent pesticides & sediment
8. **Which result best confirms that water treatment is effective?**
   (A) A single uncalibrated test (B) Treated water consistently meets quality standards
   (C) Clear appearance alone (D) No odour on one day
9. **A pollution plume is most characteristic of:**
   (A) Diffuse rainfall runoff (B) Rainwater harvesting
   (C) Groundwater recharge (D) A concentrated point-source discharge
10. **A watershed has storm-related pesticide pulses but no pipe source. What is the strongest inference?**
    (A) Diffuse non-point runoff from land surfaces (B) A constant point source with no weather relation
    (C) Natural deionization (D) Reverse osmosis failure

**Answers Key**

| 1. D | 2. C | 3. B | 4. B | 5. A | 6. D | 7. D | 8. B | 9. D | 10. A |
|---|---|---|---|---|---|---|---|---|---|



## Instructions for Preparation of Exam Paper of Chemistry for Class 12

### ESSENTIAL INSTRUCTIONS FOR PAPER SETTERS

*The paper of Chemistry for class will consist of eighty-five (85) marks. Timing of the paper will be three (03) hours. The paper will be made as per following details.*

**Objective:** Q.1: One multiple-choice question (MCQ) from each chapter. — 1 × 17 = 17

**Subjective: Part-I:**

Q.2: 8 short answer questions have to be answered out of 12. The detail is as follows: — 2 × 8 = 16

| Chapter | 17 | 18 | 19 | 20 | 24 | 25 |
|---|---|---|---|---|---|---|
| No. of Short Questions | 1 | 1 | 3 | 2 | 3 | 2 |

Q.3: 8 short answer questions have to be answered out of 12. The detail is as follows: — 2 × 8 = 16

| Chapter | 21 | 22 | 23 | 27 | 28 | 29 |
|---|---|---|---|---|---|---|
| No. of Short Questions | 1 | 1 | 2 | 2 | 3 | 3 |

Q.4: 8 short answer questions have to be answered out of 9. The detail is as follows: — 2 × 6 = 12

| Chapter | 26 | 30 | 31 | 32 | 33 |
|---|---|---|---|---|---|
| No. of Short Questions | 1 | 2 | 2 | 2 | 2 |

**Subjective: Part-II:**

This section well contain five detailed questions bifurcated in two-part a & b (carrying 4 & 4 marks each) and students have to attempt 3 questions. The detail is as follows: — 3 × 8 = 24

**Question No 5:**

| Chapter | 17 | 21 |
|---|---|---|
| Part | a | b |

**Question No 6:**

| Chapter | 18 | 26 |
|---|---|---|
| Part | a | b |

**Question No 7:**

| Chapter | 20 | 31 |
|---|---|---|
| Part | a | b |

**Question No 8:**

| Chapter | 22 | 32 |
|---|---|---|
| Part | a | b |

**Question No 9:**

| Chapter | 23 | 33 |
|---|---|---|
| Part | a | b |

CamScanner

# MODEL PAPER OF CHEMISTRY FOR CLASS-12

## OBJECTIVE TYPE

**Time allowed: 20 Min.** **Max. Marks: 17**

**Note:** Four possible answers A, B, C and D to each question are given. The choice which you think is correct, fill that circle with marker or ink in the answer-book. Cutting or filling two or more circles will result in zero mark in that question.

i) **Why does $Be^{2+}$ form complexes more easily than $Ba^{2+}$?**
(a) Larger size (b) Lower charge density (c) Higher charge density (d) More orbitals

ii) **In the complex ion, $[Fe(CN)_6]^{4-}$, what is the coordination number of central metal ion?**
(a) 2 (b) 4 (c) 6 (d) 8

iii) **The characteristic functional group present in urea is:**
(a) Carbonyl (b) Amino (c) Amide (d) Ester

iv) **Activating groups direct the incoming electrophile to which position(s) of benzene ring?**
(a) Ortho (b) Para (c) Meta (d) Both ortho and para

v) **Which one of the following is not a nucleophile?**
(a) $H_2O$ (b) $H_2S$ (c) $BF_3$ (d) $NH_3$

vi) **Dehydration of alcohol is an example of:**
(a) Substitution Reaction (b) Addition Reaction (c) Elimination Reaction (d) Redox Reaction

vii) **Ketones are prepared by the oxidation of:**
(a) Primary alcohols (b) Secondary alcohols (c) Tertiary alcohols (d) Phenol alcohols

viii) **When diazonium salt is heated with water, the gas evolved is:**
(a) Nitrogen (b) Ammonia (c) Nitrogen monoxide (d) Nitrogen dioxide

ix) **Which functional group is formed when a carboxylic acid reacts with an alcohol in the presence of an acid as catalyst?**
(a) Alkane (b) Alcohol (c) Aldehyde (d) Ester

x) **Which pair of monomers reacts to form a polyester?**
(a) Diamine and dicarboxylic acid (b) Diol and dicarboxylic acid
(c) Ethene and chloroethene (d) Amino-carboxylic acid

xi) **Glucose is a building block for all of the following except:**
(a) Cellulose (b) Glycogen (c) Insulin (d) Starch

xii) **A substance has a very low $R_f$ value. What does this indicate?**
(a) It is insoluble in the solvent (b) It is highly soluble in the solvent
(c) It strongly sticks to the paper (d) It has a high density

xiii) **The types of transitions possible in UV-visible region for a compound with molecular formula $C_2H_6$ are:**
(a) $n \rightarrow \pi^*$ (b) $n \rightarrow \sigma^*$ (c) $\sigma \rightarrow \sigma^*$ (d) $\pi \rightarrow \pi^*$

xiv) **NMR relies on the magnetic properties of nuclei known as:**
(a) Chemical shift (b) Nuclear density (c) Nuclear spin (d) Signal intensity

xv) **Which property makes ceramics suitable for furnace bricks?**
(a) Conductivity (b) Low density (c) High melting point (d) Flexibility

xvi) **Which N-P-K nutrient promotes protein synthesis and chlorophyll?**
(a) Nitrogen (b) Phosphorus (c) Potassium (d) Sulphur

xvii) **Which condition is a direct result of cadmium (Cd) replacing calcium (Ca) in the skeletal system?**
(a) Minamata disease (b) Blue Baby Syndrome (c) Itai-itai disease (d) Chloracne



## SUBJECTIVE TYPE

**Time allowed: 2 Hrs 40 Min** **Max. Marks: 68**

### (Part I)

**Q.2: Write short answers to any eight (08) questions:** (16)
i. Give the products of the thermal decomposition of strontium nitrate. Write chemical equation.
ii. Define a bidentate ligand and state how many bonds it forms to the central ion.
iii. Give the names and examples of two functional groups containing oxygen.
iv. Define catenation. Give its importance.
v. Alkanes have no functional group. Justify.
vi. What is a zwitterion?
vii. Describe, with the help of a diagram, the bonding in phenol to show delocalisation of pi-electrons.
viii. Explain why electrophiles, such as bromine, react much more readily with phenol than with benzene.
ix. What is the chromophore in azo dyes? What are its functions in dyes?
x. Why are amides less basic than ammonia?
xi. Differentiate between synthesis and retrosynthesis.
xii. How is a carboxylic group converted to an amide group?

**Q.3: Write short answers to any eight (08) questions:** (16)
i. Which is more reactive towards electrophiles, haloalkanes or haloarenes?
ii. Which alcohol cannot change the colour of acidified potassium dichromate?
iii. What is iodoform reaction?
iv. Give the reaction of methanal with the Tollen's reagent.
v. What is the role of iron in the body?
vi. How are enzyme inhibitors important in our body and medicine?
vii. Why is TLC not suitable for large-scale separation?
viii. What is the function of injector port in GC?
ix. State two limitations of gas chromatography.
x. Write the ranges of electromagnetic spectrum.
xi. How can the chemical composition of a substance be investigated by using spectroscopy?
xii. Show all the possible fragments of $C_7H_{16}$, and their m/e values in its mass spectrum.

**Q.4: Write short answers to any six (06) questions:** (12)
i. Name two different polymers used in artificial organs and state the specific application for each.
ii. What is the purpose of the $D_2O$ shake in $^1H$ NMR?
iii. Why do O–H and N–H peaks disappear after a $D_2O$ shake?
iv. Define energy density and give one example.
v. Name two specific semiconductors mentioned in the text and their modern applications.
vi. How does the structure of penicillin allow it to inhibit the transpeptidase enzyme?
vii. What is the concept of pesticide resistance in a target pest population?
viii. Name four methods used for water conservation.
ix. What is the role of "industrial discharge" in water pollution?

### Subjective Type (Part II)

**Note: Attempt any three questions.**

**Q.5:** (a) Explain the solubility of sulphates and hydroxides of Group 2 elements, and discuss the trend in their solubility down the group with appropriate examples. (4)
(b) Describe the $S_N1$ and $S_N2$ mechanisms of nucleophilic substitution in halogenoalkanes. (4)

**Q.6:** (a) Describe the various redox reactions that take place in transition metal complexes. (4)
(b) Define the condensation polymer. Discuss the formation of polyester. (4)

**Q.7:** (a) Discuss Friedel-Crafts reactions of benzene. (4)
(b) Explain how X-rays interact with crystals to produce diffraction patterns and how these patterns help determine atomic positions. (4)

**Q.8:** (a) Write any two reactions of phenol involving substitution on the benzene ring. (4)
(b) What are important safety measures which must be followed while working in different chemical industries? Make a checklist to verify their adoption. (4)

**Q.9:** (a) Prepare a carboxylic acid starting from ester, alcohol, alkanenitrile and methylbenzene. (4)
(b) Evaluate the benefits and the long-term chemical risks involved in the use of chlorine as a disinfectant. (4)

CamScanner