DEPARTMENT OF CHEMISTRY

Estd 1864

FORMAN CHRISTIAN COLLEGE
LAHORE

SOLUTION OF QUICK CHECKS AND EXERCISES

F.Sc. CHEMISTRY PART-2 (2026-27)

Unit 17: Group 2 Elements

Answers to Quick Checks and Exercise Questions (Q2 & Q3)

Quick Check 17.1

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

i) Calcium reacting with oxygen:

$$2Ca(s) + O_2(g) \rightarrow 2CaO(s)$$

ii) Barium reacting with water:

$$Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$$

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

Group 2 metals react with dilute acids to form a salt and H_2 gas. The reactivity increases down the group. However, like Calcium the reaction of Sr and Ba with dilute H_2SO_4 stops early because the $SrSO_4$ and $BaSO_4$ formed are insoluble and coat the metal surface with a protective layer that prevents further reaction.

Compound	Solubility at 298 K (mol/100 g water)
$SrSO_4$	7.11×10^{-5}
$BaSO_4$	9.43×10^{-7}

Therefore, the reactions of Sr and Ba with H_2SO_4 are even more limited than that of Ca, an insoluble sulphate coating forms almost immediately and stops the reaction very quickly, with barium being affected the most since $BaSO_4$ is the least soluble sulphate in the group.

Extenet of reaction: Incomplete reaction due to protective metal sulphate

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

$$\text{Group 2} = ns^2$$

All Group 2 elements have two electrons in their outermost s-subshell (ns^2). By losing these two electrons, they attain a stable +2 ionic state (M^{2+}). This tendency to readily lose the two valence electrons and undergo rapid oxidation is what makes Group 2 elements reactive.

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

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

$$2Ba(s) + O_2(g) \rightarrow 2BaO(s)$$

Barium is more reactive than magnesium and burns more vigorously in air. This is because reactivity increases down Group 2 due to increasing atomic size, greater shielding effect, and decreasing ionization energy. Ba has a much lower first ionization energy (503 kJ mol^{-1}) than Mg (738 kJ mol^{-1}).

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

Melting point generally decreases going down the group after calcium (Ca 842°C > Ba 727°C), so radium is expected to have a melting point lower than that of barium (below ~727°C). Density increases down the group from calcium onward (Ca 1.54 < Ba 3.51 g/cm³), so radium is expected to have a density higher than that of barium (above 3.51 g/cm³).

Quick Check 17.2

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

- Group 1 metals are very soft and can be cut with a knife, whereas Group 2 metals are harder.
- Group 1 metals have lower densities and lower melting/boiling points, whereas Group 2 metals have higher densities and higher melting/boiling points.

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

Group 1 oxide: M_2O (e.g., Na_2O). Group 2 oxide: MO (e.g., CaO).

This is because of the electronic configuration and oxidation state of Group 1 and Group 2 elements.

	Group 1	**Group 2**
Electronic configuration	ns^1	ns^2
Oxidation state	+1	+2

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

$$SrCO_3(s) \xrightarrow{\text{heat}} SrO(s) + CO_2(g)$$

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

Mg^{2+} is smaller than Ca^{2+}, giving it a higher charge density and greater polarizing power. This allows Mg^{2+} to distort the large carbonate ion (CO_3^{2-}) to a greater extent, weakening its C–O bonds and making $MgCO_3$ easier to decompose at a lower temperature than $CaCO_3$.

Metal Carbonate	**Decomposition Temperature (°C)**
$BeCO_3$	100
$MgCO_3$	**540**
$CaCO_3$	**900**
$SrCO_3$	1150
$BaCO_3$	1360

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

$$2Mg(NO_3)_2(s) \xrightarrow{\text{heat}} 2MgO(s) + 4NO_2(g) + O_2(g)$$

$$2Ba(NO_3)_2(s) \xrightarrow{\text{heat}} 2BaO(s) + 4NO_2(g) + O_2(g)$$

Magnesium nitrate decomposes at the lower temperature. Mg^{2+}, being smaller, has a higher charge density and greater polarizing power than Ba^{2+}. Mg^{2+} polarizes the nitrate ion more thus weakening it and making decomposition easier at a lower temperature. Thermal stability of nitrates, like carbonates, increases down the group.

Quick Check 17.3

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

Mg^{2+} is a small, highly charged ion with a large (very negative) enthalpy of hydration while lattice energy of $MgSO_4$ is less due to larger size of suplate ion. which favours dissolution. Cation size increases down the group and with a larger anion like sulpate the hydration enthalpy decreases more than the lattice enthalpy. So for larger ions release comparatively little hydration energy, which is insufficient to overcome the lattice energy causing a decrease in solubility of $BaSO_4$.

Compound	Solubility at 298 K (mol/100 g water)
$MgSO_4$	1.83×10^{-1}
$BaSO_4$	9.43×10^{-7}

(b) How does lattice energy affect the solubility of Group 2 sulphates?

Lattice enthalpy decreases down the group as cation size increases (weaker electrostatic attraction between the larger cation and the sulphate anion). However, for sulphate — a large anion — the decrease in hydration enthalpy going down the group is more significant than the decrease in lattice enthalpy. This makes the overall enthalpy of solution less favourable/negative down the group, so the solubility of sulphates decreases down Group 2.

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

$Sr(OH)_2$ is more soluble than $Ca(OH)_2$, as shown below:

Compound	Solubility at 298 K (mol/100 g water)
$Ca(OH)_2$	1.5×10^{-3}
$Sr(OH)_2$	3.4×10^{-3}

Going down Group 2, both the hydration enthalpy (ΔH°hyd) and lattice enthalpy (ΔH°lattice) decrease as the cation gets larger. The decrease in lattice enthalpy is more significant than the decrease in hydration enthalpy. Since OH^- is a small anion it has high hydration enthalpy. This makes the overall enthalpy of solution (ΔH°soln) more negative/favourable, so hydroxide solubility increases down the group. This makes $Sr(OH)_2$ more soluble than $Ca(OH)_2$.

Quick Check 17.4

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

$$Mg^{2+}(l) + 2Cl^-(l) \xrightarrow{\text{Electrolysis}} Mg(l) + Cl_2(g)$$

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

$$CaCO_3(s) \xrightarrow{1000\ ^\circ C} CaO(s) + CO_2(g)$$

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

$CaCO_3$ is added to acidic soils to neutralize excess acidity and raise the soil pH, making the soil more suitable for crop growth. The chemical principle involved is acid–base neutralization (a basic metal carbonate neutralizing an acid).

Exercise Q2 — Short-Answer Questions

(a) Exactly 0.1 moles of calcium hydroxide and barium hydroxide are added to separate beakers containing 100 cm³ of water and stirred to form saturated solutions. Explain which solution has the higher pH value.

The solubility of Group 2 hydroxides increases down the group

Compound	Solubility at 298 K (mol/100 g water)
$Ca(OH)_2$	1.5×10^{-3}
$Ba(OH)_2$	1.5×10^{-2}

Going down Group 2, both the hydration enthalpy (ΔH°hyd) and lattice enthalpy (ΔH°lattice) decrease as the cation gets larger. The decrease in lattice enthalpy is more significant than the decrease in hydration enthalpy as the cation increases in size. Since OH^- is a small anion and has high hydration enthalpy. This makes the overall enthalpy of solution (ΔH°soln) more negative/favourable, so hydroxide solubility increases down the group. Hence $Ca(OH)_2$ is sparingly soluble, while $Ba(OH)_2$ is quite soluble.

Since $Ba(OH)_2$ is more soluble, more of it dissolves in the same volume of water, releasing a greater concentration of OH^- ions into solution than $Ca(OH)_2$. Therefore, the barium hydroxide solution will have the higher pH.

pH: $Ca(OH)_2$ < $Ba(OH)_2$

(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.

Solubility: $CaCr_2O_7 > SrCr_2O_7$

Dichromate ($Cr_2O_7^{2-}$) is a large anion, behaving similarly to sulphate. Following the same pattern seen for Group 2 sulphates — where solubility decreases down the group because the fall in hydration enthalpy (for large anions) outweighs the fall in lattice enthalpy — calcium dichromate would be more soluble than strontium dichromate.

(c) Write the balanced equation for the reaction of Ba with cold water.

$$Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$$

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

Be^{2+} is the smallest and most highly charged Group 2 cation, giving it the highest charge density in the group. This results in very strong electrostatic bonding — reflected in a very high lattice energy — between Be^{2+} and the oxide ion (O^{2-}), as shown below:

Metal Oxide	Lattice Energy (kJ mol^{-1})
BeO	4443
MgO	3795
CaO	3414
SrO	3217
BaO	3029

As seen above, lattice energy decreases steadily down the group as the cation gets larger and its charge density falls. BeO's very high lattice energy means the Be^{2+}–O^{2-} bond is exceptionally strong, so the oxide forms as a thin, hard, tightly adherent, and continuous layer on the metal surface. This layer effectively passivates the metal, protecting it from further reaction with oxygen or water. The larger cations of the other Group 2 members (Mg^{2+}, Ca^{2+}, etc.) have lower charge density and considerably lower lattice energy with oxide ion, so their oxide coatings are less strongly bonded and less protective, leaving these metals reactive.

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

$$2Sr(NO_3)_2(s) \rightarrow (heat) \rightarrow 2SrO(s) + 4NO_2(g) + O_2(g)$$

Products: strontium oxide, brown nitrogen dioxide gas, and oxygen gas.

(f) Why does solubility of Group 2 hydroxides increase in terms of the relative changes in ΔH°hyd and ΔH°lattice?

Going down Group 2, both the hydration enthalpy (ΔH°hyd) and lattice enthalpy (ΔH°lattice) decrease as the cation gets larger. Since OH^- is a small anion, the decrease in lattice enthalpy is more significant than the decrease in hydration enthalpy as the cation increases in size. This makes the overall enthalpy of solution (ΔH°soln) more negative/favourable, so hydroxide solubility increases down the group (e.g., $Mg(OH)_2$ is sparingly soluble, while $Ba(OH)_2$ is quite soluble).

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

$$Mg^{2+}(aq) + Ca(OH)_2(s) \rightarrow Mg(OH)_2(s) + Ca^{2+}(aq)$$

$Ca(OH)_2$, derived from limestone or oyster shell, precipitates the Mg^{2+} ions in seawater as insoluble $Mg(OH)_2$.

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

- $BaSO_4$: Used in “barium meals” for X-ray imaging of the digestive system — it is opaque to X-rays and safe because it is highly insoluble and passes through the body without being absorbed.

- $Mg(OH)_2$: Used as Milk of Magnesia to neutralize excess stomach acid, and as a mild laxative; its low solubility makes it safe to use.

Exercise Q3 — Constructed-Response Questions

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

Be has the smallest atomic radius (112 pm metallic radius) in Group 2 and the highest charge density of the group's cations. This gives beryllium the strongest metallic bonding — its small, closely-packed atoms are held together by strong electrostatic attraction between the metal cations and the delocalized electrons. This close packing and strong bonding results in a higher melting point (1287°C, the highest in the whole group) and a relatively high density (1.85 g/cm³) compared to the larger, more loosely packed Mg (650°C, 1.74 g/cm³) and Ca (842°C, 1.54 g/cm³) atoms, whose weaker metallic bonds (due to increased size) give them lower values.

(b) Compare the reactivities of Group 1 and Group 2 metals in the same period.

Group 1 (alkali) metals are more reactive than Group 2 (alkaline earth) metals in the same period. Group 1 metals have only one valence electron (ns^1) to lose to form a stable +1 ion and have lower ionization energies, making them react more readily. Group 2 metals must lose two electrons (ns^2) to form a +2 ion, which requires more energy (higher ionization energies), making them reactive, but generally less than Group 1.

(c) Explain why calcium hydroxide is used in agriculture.

Calcium hydroxide, $Ca(OH)_2$, is added to acidic soils to increase the soil pH by neutralizing excess acidity, making the soil more suitable for crop growth. Calcium is also an essential plant nutrient, crucial for cell wall development.

Unit 18: TRANSITION ELEMENTS

Quick Check 18.1

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

Co^{2+} = [Ar]$3d^7$, 3 unpaired electrons in the high-spin free-ion picture; Co^{3+} = [Ar]$3d^6$, 4 unpaired in the high-spin free-ion picture (actual complex spin depends on ligand field).

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

Transition metals use more delocalised s/d electrons in strong metallic bonding, so densities and melting points are generally much higher than Group 1.

c) The electronic configuration of Sc^{3+} ion is [Ar]$3d^0 4s^0$. Why is scandium not classified as a transition element?

Sc^{3+} is [Ar]$3d^0$; because its common ion has no incomplete d subshell, Sc is not a transition element under the stated definition.

Quick Check 18.2

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

Vanadium has a neutral outer electronic configuration of $3d^3 4s^2$. Because the energy levels of the 3d and 4s subshells are very close to each other, vanadium can successively lose or share varying numbers of these outer electrons (all valence electrons, or subsets of them). This enables it to form stable species across multiple oxidation states:

$$+2\ (V^{2+}),\ +3(V^{3+}),\ +4(VO^{2+}),\ \text{and}\ +5\ (VO^{2+})$$

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

In s block elements, the energy gap between the valence shell and inner orbitals is very large, so only the outer s-electrons participate in bonding. In contrast, for transition metals, the incoming 3d subshell and the outermost 4s subshell have very similar energies. Consequently, electrons from both subshells are close enough in energy to be readily involved in hybridization, metallic bonding, and multi-electron interactions.

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

Iron atom (Fe, Atomic Number=26): [Ar]$3d^6 4s^2$

Fe^{3+} Ion: Losing two s-electrons and one d-electron yields the electronic configuration: [Ar]$3d^5 4s^0$

d) Which properties of transition metals enable them to use as heterogeneous catalysts and homogeneous catalysts.

Multiple stable oxidation states: They can easily switch between different oxidation states (e.g. $Fe^{2+} \rightleftharpoons Fe^{3+}$) to form temporary intermediate complexes with reactant molecules.

Vacant, energetically accessible d-orbitals: Their vacant d-orbitals allow them to accept electron pairs and form coordinate (dative) bonds with reactant molecules or ligands on the catalyst surface, providing an alternative reaction pathway with a lower activation energy.

Quick Check 18.3

a) How does Lewis acid-base concept explain the transition metal complex formation?

The central transition metal ion has vacant d-orbitals to accept electron pairs (acting as a Lewis acid), while ligands have unshared electron pairs to donate (acting as Lewis bases). A coordinate covalent (dative) bond is formed.

b) Determine the overall charge of a complex ion formed from a Cr3+ metal ion with six neutral H_2O ligands and a coordination number of 6.

Calculation:
- Metal ion charge = +3
- Ligand charge = 0 (neutral H_2O)
- Overall charge = +3 + (6 * 0) = +3
- Formula/Result: $[Cr(H_2O)_6]^{3+}$

c) Predict the likely geometry for the complex ion $[MnCl_4]^{2-}$

Prediction: Tetrahedral geometry.
Reasoning: A coordination number of 4 with weak-field chloride ligands and a d5 configuration typically adopts a tetrahedral shape.

d) EDTA is described as a hexadentate ligand. Explain what "hexadentate" means.

Explanation: "Hexadentate" means the ligand possesses six donor atoms that can simultaneously coordinate and form six coordinate covalent bonds with a single central metal ion.

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

1. The availability of vacant inner d-orbitals to accept electron pairs.
2. A high charge-to-radius ratio (small ionic radius with high positive charge) providing high polarizing power.

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

Role: To donate one or more electron pairs to the central metal atom or ion.
Bond type: Coordinate covalent bond (dative covalent bond).

Quick Check 18.4

a) How does the presence of ligands affect the degeneracy of d orbitals in a complex ion?

When ligands approach a transition metal ion, their negative or partial negative charges create an electrostatic field. This removes the degeneracy (equal energy state) of the five d-orbitals, causing them to split into different energy levels depending on their spatial orientation relative to the incoming ligands.

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

Octahedral complexes (6 ligands): The d-orbitals split into two sets: a lower-energy triplet (t_2g: dxy, dyz, dxz) and a higher-energy doublet (eg: dx^2-y^2, dz^2). Tetrahedral complexes (4 ligands): The splitting pattern is inverted. The d-orbitals split into a lower-energy doublet (e) and a higher-energy triplet (t_2). The magnitude of splitting in tetrahedral complexes is also smaller (about 44% of octahedral splitting).

c) Explain the relationship between the absorbed light energy (ΔE) and the observed colour of a transition metal complex.

According to Planck's equation ($\Delta E = h\nu = hc/\lambda$), electrons absorb specific frequencies of visible light corresponding to the energy gap (ΔE) between split d-orbitals to undergo d-d transitions. The observed colour of the complex is the complementary colour of the wavelength of light that is absorbed.

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?

Since red and orange light are absorbed, you would expect the complex to appear in the complementary colour range, which is blue-green.

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

In transition metal complexes with partially filled d-orbitals, electrons can absorb energy from the visible region of the spectrum and jump from lower-energy d-orbitals to higher-energy d-orbitals (known as a d-d transition). The remaining unabsorbed wavelengths of light are transmitted or reflected, producing the characteristic visible colour of the compound.

Quick Check 18.5

a) Write the equation for the reaction when is dissolved in excess ammonia.

$Cu(OH)_2(s)$ + excess $NH_3(aq)$ forms the deep-blue tetraamminecopper(II) aqua complex, commonly written $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (with OH^-/water balance).

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

Pink $[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons$ blue $[CoCl_4]^{2-} + 6H_2O$; concentrated HCl raises $[Cl^-]$ and shifts right.

Tetrahedral complexes have a smaller crystal field splitting energy compared to octahedral complexes. The absorbed light shifts to a lower energy/longer wavelength (such as red/orange), causing the transmitted light to appear blue.

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

$[CoCl_4]^{2-}$ has coordination number 4 and tetrahedral geometry.

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.**

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

- The log10 K_{stab} value for the EDTA complex (18.8) is significantly higher than that of the monodentate chloride complex (5.6), reflecting a much larger equilibrium constant (K_{stab}).
- This extreme stability (known as the chelate effect) occurs because polydentate ligands like EDTA form multiple coordinate bonds and ring structures with a single metal ion. This multidentate binding provides a massive entropic and enthalpic advantage, making the resulting complex much harder to dissociate.

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

$$[Cu(H_2O)_6]^{2+}(aq) + NH_3(aq) \rightleftharpoons [Cu(H_2O)_5(NH_3)]^{2+}(aq) + H_2O(l)$$

Quick Check 18.7

a) Which type of geometry of complexes shows cis-trans isomerism?

Square planar (for coordination number 4, e.g., $[MA_2B_2]$) and octahedral (for coordination number 6, e.g., $[MA_4B_2]$ or $[MA_3B_3]$) geometries show cis-trans (geometrical) isomerism.

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

Bidentate or polydentate ligands (chelating ligands) that lack a plane of symmetry, such as ethylenediamine (en), are most often required for a complex to show optical isomerism.

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

Coordination number: 6 (since each bidentate "en" ligand donates 2 pairs of electrons, giving 3 x 2 = 6 coordinate bonds).
Type of ligand: Bidentate chelating ligand (ethylenediamine).

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.

Type of isomerism: Optical isomerism (enantiomerism / stereoisomerism).
Interaction with plane-polarized light: The complex exists as non-superimposable mirror images

(enantiomers). One optical isomer rotates the plane of plane-polarized light to the right (dextrorotatory, +), while the other rotates it to the exact same extent to the left (levorotatory, -).

Quick Check 18.8

a) State the principle used to determine the feasibility of a redox reaction using standard electrode potentials (E°).

• A redox reaction is feasible if the overall standard cell potential (E°_cell) calculated using the formula E°_cell = E°_cathode - E°_anode is positive.

• Practically, the species with the more positive E° value will be reduced (acting as the oxidizing agent), while the species with the more negative (or less positive) value will be oxidized (acting as the reducing agent).

b) For the reaction between MnO4- and Fe2+, the relevant reduction potentials are MnO_4^-/Mn^{2+} (E° = +1.52 V) and Fe^{3+}/Fe^{2+} (E° = +0.77 V). Identify the oxidizing agent and the reducing agent in this specific feasible reaction.

• Oxidizing Agent: MnO_4^- (since it has the higher/more positive reduction potential, it undergoes reduction).

• Reducing Agent: Fe^{2+} (since it has the lower/less positive reduction potential, it undergoes oxidation to Fe^{3+}).

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

• Standard electrode potentials (E°) depend strictly on the activities or concentrations of the active redox-participating species (ions and gases at standard conditions of 1 mol dm^{-3}).

• Water acts as the solvent and is present in large, constant excess; its concentration does not change significantly during the reaction, and pure liquids/solvents are assigned a standard activity of 1, so they are omitted from thermodynamic cell potential calculations.

QI. MULTIPLE CHOICE QUESTIONS

No.	Answer
I	B
II	D
III	A
IV	C
V	B
VI	C
VII	A
VIII	A
IX	C

Q2. Short-Answer Questions

a) Why is zinc not included in the transition metals? Although it is a d-block element and it shows electronic configuration with d orbitals.

Zinc is classified as a d-block element because its outer electrons fill the 3d subshell ([Ar] $3d^{10}$ $4s^2$), but it is not considered a transition metal because neither zinc nor its common ion (Zn^{2+}, which has a completely filled $3d^{10}$ configuration) possesses partially filled (incomplete) d-orbitals. Consequently, zinc compounds do not exhibit typical transition metal properties such as colored ions, variable oxidation states, or catalytic behavior.

b) What is the correlation between the ability of transition elements to exhibit variable oxidation states and their electron configuration?

The availability of electrons in both the 3d and 4s subshells—which have very comparable energies—allows transition metals to lose varying numbers of electrons. Once the 4s electrons are removed, electrons from the 3d subshell can also be progressively lost or shared in bonding, leading to multiple accessible oxidation states.

c) How do transition metals function as effective catalysts? Give some examples.

Transition metals and their compounds act as effective catalysts because they possess vacant d-orbitals that can temporarily bind reactant molecules and variable oxidation states that allow them to easily donate and accept electrons during a reaction mechanism.

Examples:

Nickel (Ni): Used in the hydrogenation of alkenes to alkanes (vegetable oil to margarine).

Iron (Fe): Used as a catalyst in the Haber process for ammonia synthesis.

Vanadium pentoxide (V_2O_5): Used in the Contact process for manufacturing sulfuric acid.

d) Why the complex $[Cr(en)_3]^{3+}$ is more stable than $[Cr(H_2O)_6]^{3+}$?

This is due to the chelate effect. The ligand en (ethylenediamine) is a bidentate ligand that forms five-membered ring structures with the metal ion by coordinating through two nitrogen atoms. Replacing monodentate water molecules with multidentate chelating ligands results in a large positive entropy change (delta S), making the chelate complex thermodynamically much more stable than the complex containing only monodentate ligands.

e) What is the coordination number? Give coordination number of $[Fe(CN)_6]^{4-}$.

Coordination Number: The total number of coordinate covalent bonds (or donor atoms) attached directly to the central metal ion.

Coordination Number of $[Fe(CN)_6]^{4-}$: 6 (since six monodentate cyanide ions are bound to the central iron ion).

f) Define a bidentate ligand and state how many bonds it forms to the central ion.

Definition: A ligand that possesses two donor atoms capable of simultaneously forming two coordinate covalent bonds with a single central metal ion.

Number of bonds: It forms 2 coordinate covalent bonds with the central metal ion.

g) Explain why comparing only the E° values suggests the reaction is not feasible as written.

The standard cell potential (E°cell) must be positive for a redox reaction to be thermodynamically feasible (E°cell = E°cathode - E°anode). If a direct comparison of standard reduction potentials yields a negative overall E°cell, the reaction is non-feasible in the forward direction under standard conditions.

h) Define Kstab. How it reflects the stability of coordination complexes?

Definition: Kstab (Stability constant) is the equilibrium constant for the formation of a complex ion from its constituent metal ion and ligands in an aqueous solution.

Reflection of stability: A larger Kstab value (or a higher log10 Kstab value) indicates that the equilibrium lies heavily to the right, meaning the complex has a high thermodynamic stability and strongly resists dissociation into its components.

i) How coordination number 4 has two shapes i.e., tetrahedral and square planar? Explain it.

A coordination number of 4 allows for spatial arrangements depending on the nature and electronic structure of the metal ion and its ligands:

Tetrahedral geometry: Formed when the ligands repel each other symmetrically in a 3D space, which is common for d^0, d^5, or d^{10} configurations and bulkier or weaker-field ligands (e.g., $[Cl_4]^{2-}$).

Square planar geometry: Formed typically by metal ions with a d^8 electronic configuration (such as Pt^{2+}, Pd^{2+}, and Ni^{2+}) where the strong-field ligand field forces ligands into a single flat 2D square plane at 90° angles to minimize electronic repulsion.

j) Illustrate the cis-trans isomerism shown by $[Pt(NH_3)_2Cl_2]$ complex.

This square planar complex exhibits geometrical isomerism:

Cis-isomer: The two identical chlorine atoms are adjacent to each other at a 90° angle (and the two NH_3 groups are also adjacent). This specific active compound is known as cisplatin, an effective anti-cancer drug.

Trans-isomer: The two identical chlorine atoms are positioned opposite each other at an 180° angle across the platinum metal center (with the two NH_3 groups also opposite each other).

k) Give medicinal importance of cisplatin.

Cisplatin (cis-$[Pt(NH_3)_2Cl_2]$) is widely used as a potent anti-cancer (chemotherapy) drug. It works by binding to cellular DNA, causing cross-linking that inhibits DNA replication and transcription, ultimately triggering apoptosis (cell death) in rapidly dividing cancer cells.

l) What happens when excess of ammonia solution is added to Co(II) hydroxide precipitate?

When excess aqueous ammonia is added to cobalt(II) hydroxide precipitate, a ligand exchange reaction takes place where ammonia replaces coordinated water/hydroxide molecules, dissolving the precipitate and forming a soluble amine complex (e.g., yielding a coordination complex solution).

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?

Yes, excessive dilution shifts the position of equilibrium. According to Le Chatelier's principle, diluting a solution containing a complex equilibrium shifts the equilibrium in the direction that produces a greater number of particles (dissociation). Therefore, heavy dilution can cause a stable complex to partially dissociate back into the free hydrated metal ion and free ligands.

Q3. CONSTRUCTED-RESPONSE QUESTIONS

a) Discuss the two types of stereoisomerism found in transition metal complexes. Use the examples $[Pt(NH_3)_2Cl_2]$ (square planar) and $[Ni(H_2NCH_2CH_2NH_2)_3]^{2+}$ (octahedral) to illustrate the key structural differences that give rise to geometrical and optical isomerism, respectively.

1. Geometrical (Cis-Trans) Isomerism:

Found commonly in square planar and octahedral complexes where ligands can occupy different relative spatial positions.

Example: Square planar $[Pt(NH_3)_2Cl_2]$ exhibits cis-trans isomerism. In the cis isomer, identical ligands (Cl- and Cl-) are adjacent to each other (90°). In the trans isomer, they are directly opposite each other (180°).

2. Optical Isomerism (Enantiomerism):

Found in complexes that lack a plane of symmetry, making the molecule chiral and non-superimposable on its mirror image.

Example: Octahedral $[Ni(en)_3]^{2+}$ (where en is the bidentate ligand ethylenediamine, $H_2NCH_2CH_2NH_2$) exists as two non-superimposable mirror-image forms (enantiomers) that rotate plane-polarized light in opposite directions.

b) The reaction between Cu^{2+} and I^- results in a solid precipitate of CuI and aqueous I_2.

Reduction half-equation 1: $\mathrm{Cu^{2+}_{(aq)} + I^-_{(aq)} + e^- \rightleftharpoons CuI_{(s)} \quad (E^\circ \approx +0.86\ V)}$

Oxidation half-equation (written as reduction for reference): $\mathrm{I_{2(aq)} + 2e^- \rightleftharpoons 2I^-_{(aq)} \quad (E^\circ \approx +0.54\ V)}$

Combine the relevant half-equations by choosing oxidation and reduction directions, equalising electrons, then add. For I^-/Cu^{2+}, precipitation of CuI removes Cu+ and shifts the overall equilibrium; the practical reaction is commonly represented as $2Cu^{2+} + 4I^- \rightarrow 2CuI(s) + I_2$.

(ii) EDTA is hexadentate: two amine N donors and four carboxylate O donors can coordinate to one metal ion, forming several chelate rings.

(iii) As Cu^{2+} reacts with I^-, solid cuprous iodide (CuI) precipitates out of solution, and aqueous iodine (I2) is formed. Because one of the products (CuI) is removed from the aqueous equilibrium via precipitation, Le Chatelier's principle dictates that the system responds by shifting the equilibrium to the right to consume reactants and replace the product, making the reaction go to completion.

c) Using the examples $[Co(NH_3)_6]^{3+}$ and $[Fe(CN)_6]^{4-}$, 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.

• General formula rule: Complex Ion = $[^{\text{Metal charge}}\ (\text{Ligand})_{\text{coordination number}}]^{\text{overall charge}}$

• Calculation for Example 1 ($[Co(NH_3)_6]^{3+}$):

Central metal ion: Cobalt in +3 oxidation state (Co^{3+}).

Ligand and Coordination Number: Six neutral ammonia molecules (6 x NH_3, where each NH_3 has a charge of 0).

- Overall Charge Calculation: Charge = (Charge of metal ion) + (Number of ligands x Charge of ligand) = (+3) + (6 x 0) = +3.

Final Formula: $[Co(NH_3)_6]^{3+}$

• Calculation for Example 2 ($[Fe(CN)_6]^{4-}$):

Central metal ion: Iron in +2 oxidation state (Fe^{2+}).

Ligand and Coordination Number: Six cyanide ions (6 x CN^-, where each CN^- carries a charge of -1).

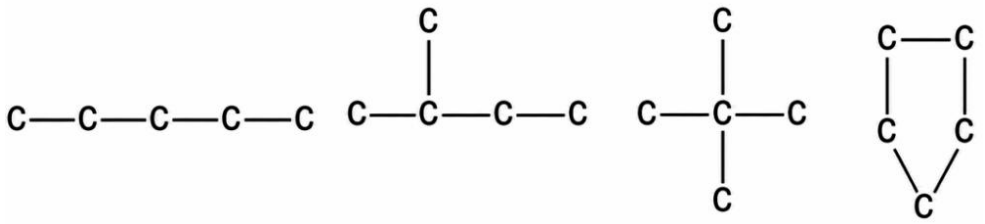
Overall Charge Calculation: Charge = (+2) + (6 x -1) = +2 - 6 = -4.

Final Formula: $[Fe(CN)_6]^{4-}$

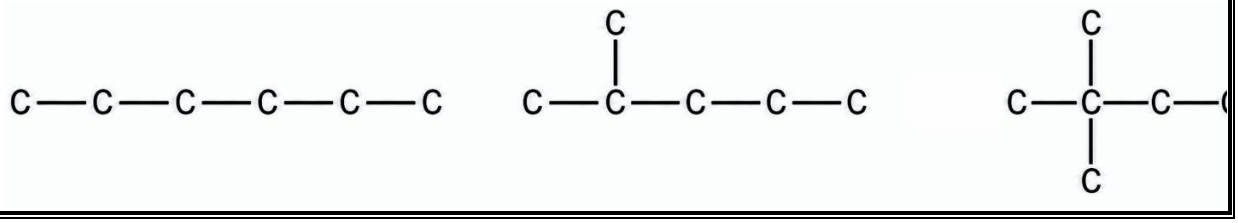
Unit 19: BASICS OF ORGANIC CHEMISTRY

Quick Check 19.1

a) **Draw the different possible structures containing five carbon atoms.**

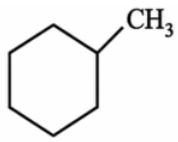
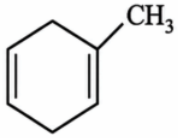
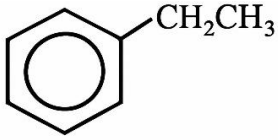
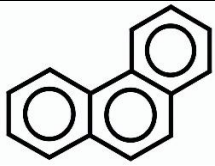
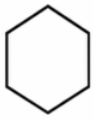
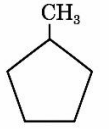


b) **Give different open chain structures containing six carbon atoms.**



Quick Check 19.2

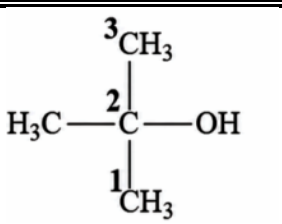
a) **Classify the following compounds as an aliphatic, alicyclic or aromatic.**

i)	**ii)**	**iii)**	**iv)**
			
Alicyclic hydrocarbon	Alicyclic hydrocarbon	Aromatic hydrocarbon	Aromatic Hydrocarbon
v)	**vi)**	**vii)**	**viii)**
$CH_3(CH_2)_2CH_3$	**$CH_3C(CH_3)_2CH_3$**		
Aliphatic Hydrocarbon	Aliphatic Hydrocarbon	Alicyclic hydrocarbon	Alicyclic hydrocarbon

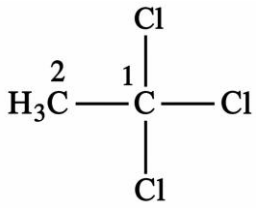
Quick Check 19.3

a) **What are the systematic names of the following?**

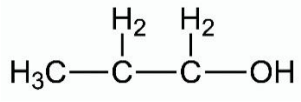
i) $(CH_3)_3COH$ **ii) CH_3CCl_3** **iii) $CH_3 – CH_2 – CH_2 – OH$**



2-methylpropan-2-ol

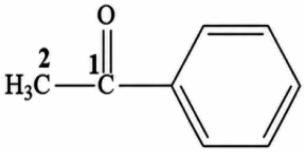


1,1,1-trichloroethane



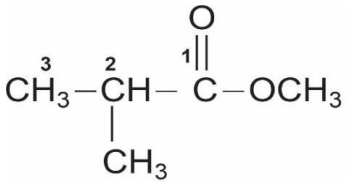
propan-1-ol

iv) $CH_3COC_6H_5$



1-phenylethan-1-one (Acetophenone)

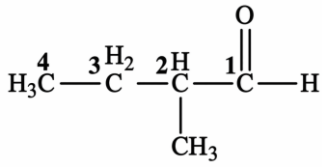
v) CH_3-C(CH_3) $COOCH_3$



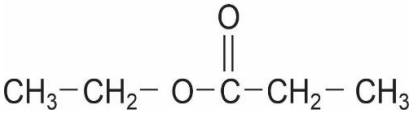
methyl-2-methylpropanoate

b) Draw the structures of the following.

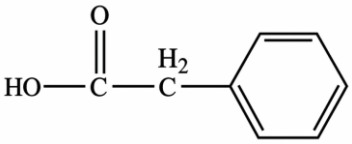
i) 2 – methylbutanal



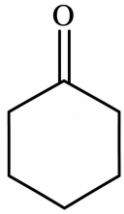
ii) ethylpropanoate



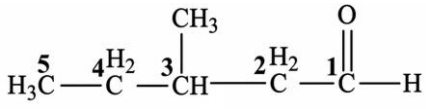
iii) phenylethanoic acid



iv) cyclohexanone



v) 3 – methylpentanal

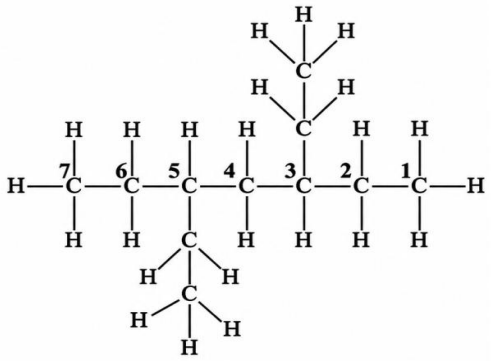


Quick Check 19.4

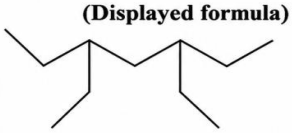
a) Draw the displayed and skeletal formulae of the following

i) 3,5- diethylheptane

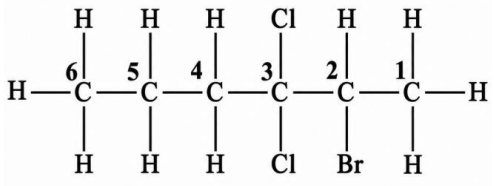
ii)) 2-bromo-3,3-dichlorohexane



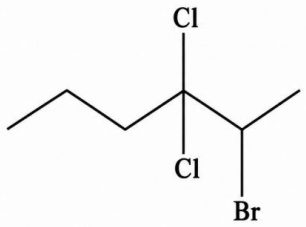
(Displayed formula)



(Skeletal formula)

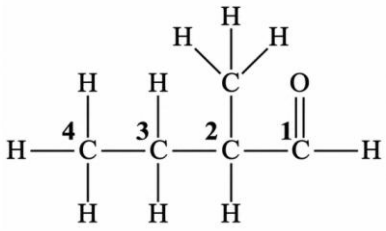


(Displayed formula)



(Skeletal formula)

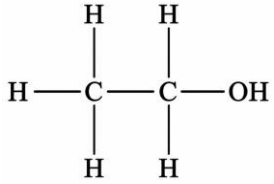
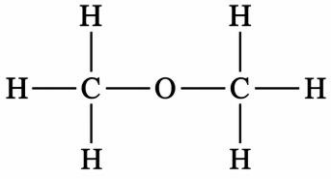
iii) 2 – methylbutanal



(Displayed formula)

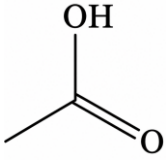
(Skeletal formula)

b) Draw the displayed and condensed structures of ethanol and methoxy methane, and explain whether they are isomers of the same molecule or not.

i) ethanol	**ii) methoxy methane**
 **(Displayed Formula)** **(Condensed formula: C_2H_6O)**	 **(Displayed Formula)** **(Condensed formula: C_2H_6O)**

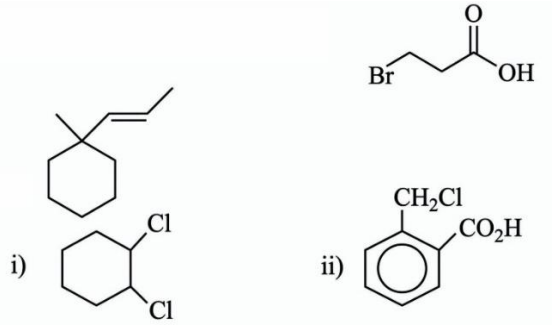
Yes, they both are functional group isomers of each other because they have same molecular formula but different structural formula (functional group).

c) Draw the skeletal formula of ethanoic acid (CH_3COOH).



Quick Check 19.5

a) Write molecular formula for the compound represented by the following bond-line structure:

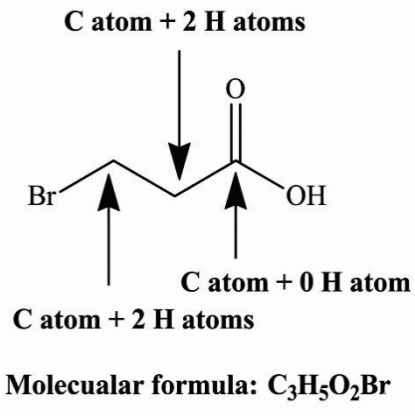


b) Draw the skeletal formula for $(CH_3)_2C=CHNH_2$

c) Write molecular formula for the compound represented by the following bond-line structure:

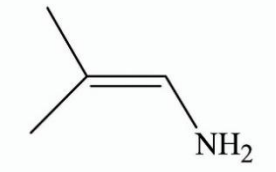
d) Give the molecular formulae of the following.

Ans (a):

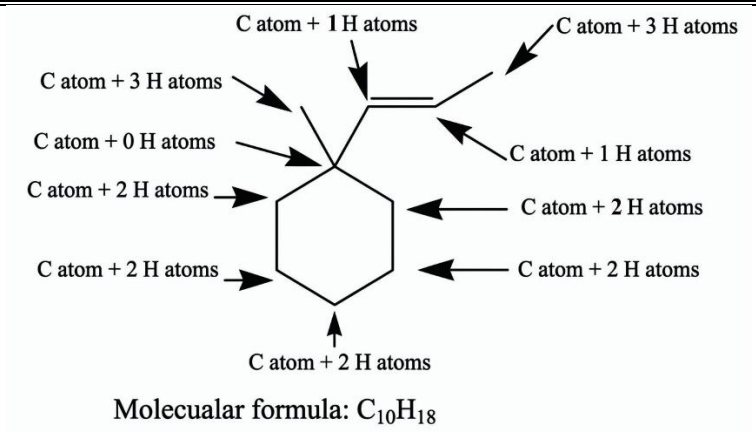


Molecualar formula: $C_3H_5O_2Br$

Ans (b):

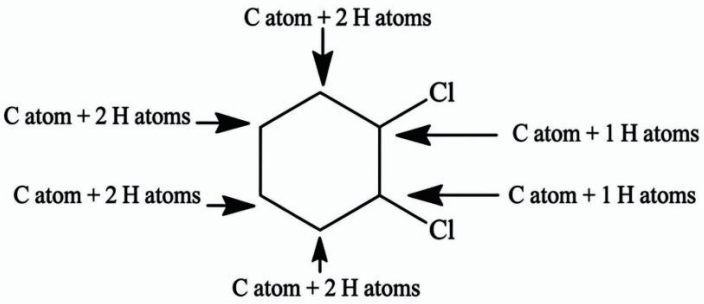


Ans (c):

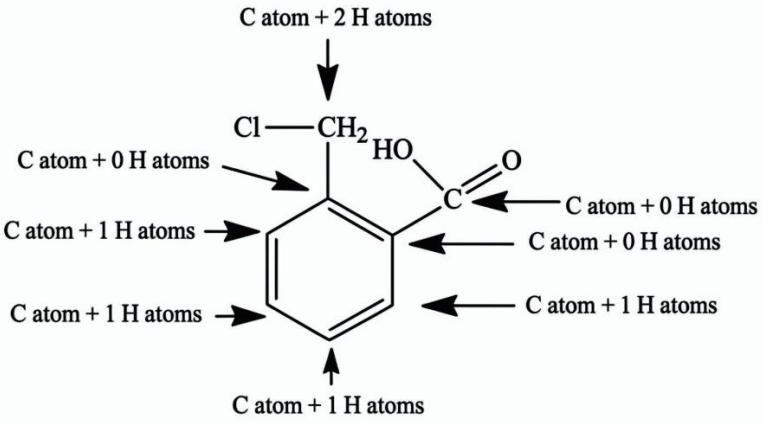


Molecualar formula: $C_{10}H_{18}$

Ans (d)



Molecualar formula: $C_6H_{10}Cl_2$



Molecualar formula: $C_8H_7O_2Cl$

Quick Check 19.6

a) Describe each of the following as electrophile, nucleophile or free radical.

i)	**NH_3**	Nucleophile (has a lone pair of electrons to donate).
ii)	**$Br^{\bullet}$**	Free Radical (contains an unpaired valence electron).
iii)	**H_2O**	Nucleophile (oxygen has lone pairs).
iv)	**$NO_2^{\oplus}$**	Electrophile (positively charged species looking for electrons).
v)	**$Cl^{\delta\oplus}$**	Electrophile (partially positive electrophilic center).

b) **Classify each of these reactions as addition, substitution, elimination or rearrangement.**

(i) $CH_3CH = CH_2 + HBr \longrightarrow CH_3CHBrCH_3$

Ans: **Addition reaction:** Because there is an addition of hydrohalogen molecule across double bond.

(ii) $CH_4 + Br_2 \longrightarrow CH_3Br + HBr$

Ans: **Substitution reaction:** It involves free radical halogenation replacing a hydrogen atom.

(iii) $CH_3CH_2CHClCH_3 \longrightarrow CH_3CH_2CH = CH_2 + HCl$

Ans: **Elimination reaction:** It involves elimination of HCl forming alkenes molecule.

c) **Classify the following reactions into one (or more) of the following six categories: Substitution, addition, hydrolysis, reduction, condensation, oxidation.**

(i) $(CH_3)_2 C = O + H_2N - NH_2 \longrightarrow (CH_3)_2 C = N - NH_2 + H_2O$

Ans: **Condensation reaction:** Because it involves joining two molecules with the removal of H_2O molecule.

(ii) $CH_3CHO + 2[H] \longrightarrow CH_3CH_2OH$

Ans: **Reduction reaction:** It involves conversion of aldehyde to primary alcohol.

Quick Check 19.7

a) **Classify the following objects as chiral or achiral.**

(a) Pencil	(b) Book	(c) Cup	(d) Spoon
Achiral	Achiral	Achiral	Achiral

b) **Glucose and fructose are two monosaccharides.**

i. **How many chiral carbon atoms are there in glucose and fructose?**

Ans: The open structure of glucose have four chiral carbons and fructose have three chiral carbons.

ii. **Calculate the possible number of optical isomers of glucose and fructose.**

Ans: We can calculate optical isomers by using formula 2^n;

Glucose: $2^n = 2^4 = 16$ optical isomers , **Fructose:** $2^n = 2^3 = 08$ optical isomers

iii. **Is there any meso form in glucose or fructose? Give reason.**

Ans: No. Neither glucose nor fructose has a meso form as they lack internal plane of symmetry because their two terminal carbon groups are structural variants (one end is an aldehyde/ketone, while the other is a primary alcohol).

EXERCISE:

MULTIPLE CHOICE QUESTIONS

Q.1 Four choices are given for each question. Select the correct choice.

I) Which of the following is organic in nature?

a) CO_2 b) CS_2 c) HCN d) CCl_4

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) $CH \equiv CH$

III) Compounds having single bonds usually undergo reactions:

a) addition b) elimination

c) substitution d) both elimination and substation

IV) The functional group present in urea (H_2N -C(=O)- 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

MCQ. NO	Choice	Explanation
I	d	CCl_4 is a halogenated derivative of methane (CH_4), directly falling under the classification of covalent organic compounds.
II	b	CH_2=CH-CH_3 (Propene is C_3H_6, which also simplifies to CH_2).
III	c	Saturated compounds like alkanes contain only strong, stable sigma-bonds and have no extra space to accept new atoms without removing existing ones.
IV	d	Urea contains two amino groups, one carbonyl group, and an amide functional group.
V	b	Carbon-2 is an asymmetric (chiral) center because it is bonded to (-H, -OH, -CH_3, -$CH_2CH_2CH_3$).
VI	b	When numbering the chain to give substituents the lowest possible locants, the carbon atom attached to the hydroxyl group (-OH) serves as the asymmetric center. It holds four distinct groups: -H, -CH_3, -OH, and the remaining branched alkyl chain.
VII	d	They can be structural (constitutional) isomers if the connectivity differs: for example, 1,1-dibromoethene (CH_2=CBr_2) versus 1,2-dibromoethene (CHBr=CHBr). They can be geometrical

		isomers if we look at 1,2-dibromoethene, which exists dynamically as either a *cis*-1,2-dibromoethene or a *trans*-1,2-dibromoethene configuration due to the restricted rotation of the double bond.
VIII	**c**	For *cis-trans* isomerism to occur, each carbon of the double bond must be attached to two completely different groups. In 2-butene (CH_3-CH=CH-CH_3), both double-bonded carbons are independently bonded to one –H and one –CH_3.
IX	**b**	Enantiomers (non-superimposable mirror images) share identical intermolecular forces and spatial layouts relative to achiral environments. They only differ in how they rotate plane-polarized light and how they interact with other chiral molecules.

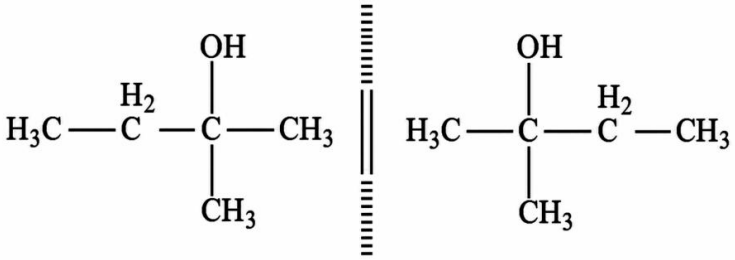
ANSWER KEY WITH EXPLANATION

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions

a) Define enantiomers. Give enantiomers of 2-methylbutan-2-ol.

Ans: Enantiomers are stereoisomers that are non-superimposable mirror images of each other. They have identical physical and chemical properties. Enantiomers of 2-methylbutan-2-ol are given below.



Both are mirror images to each other

b) Alkanes have no functional group. Justify.

Ans: Alkanes and cycloalkanes contain non-polar C-C and C-H single bonds and have no functional group which act as active site of molecule. They do not possess any atom, group of atoms, double bond, triple bonds or any charges or polarity in their structures that can act as a site for reaction.

c) Deduce the empirical and molecular formulae of the following compounds.

Ans:
a) It has molecular formula C_6H_{12} and empirical formula CH_2.
b) It has molecular formula C_5H_8 and empirical formula C_5H_8.
c) It has molecular formula C_4H_4 and 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)** propanenitrile **ii)** pentan-2-one **iii)** methyl propanoate

e) Define electrophile and nucleophile with two examples each.

Ans: **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:** BF_3, CH_3^+ , H^+ ,NO_2^+.

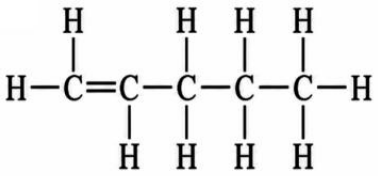
Nucleophile

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.

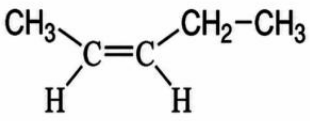
Examples: NH_3, H_2O, Br^-, OH^-,

f) Pent-2-ene shows cis-trans isomerism but pent-1-ene does not. Give reason.

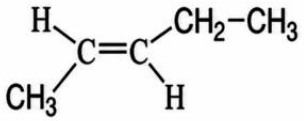
Ans:



1-Pentene



Cis-2-pentene



Trans-2-pentene

For cis-trans isomerism to exist, each carbon atom involved in the double bond must be attached to two different groups.

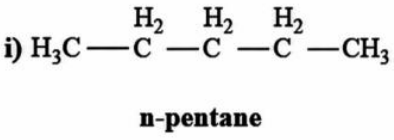
- In pent-2-ene, C_2 is bonded to -H/-CH_3 and C_3 is bonded to -H/-C_2H_5 (all distinct).
- In pent-1-ene, C_1 is bonded to two identical hydrogen atoms (-H), making restricted geometric variation impossible.

g) Define: i) Constitutional isomerism ii) Stereoisomerism

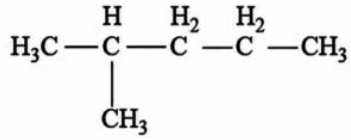
Ans: **i) Constitutional isomerism:**

When condensed groups or atoms are connected at different places in two or more molecules, it results in structural or constitutional isomerism.

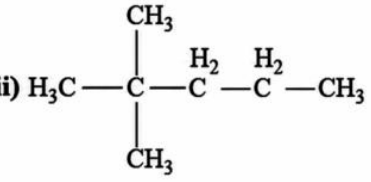
Example:



n-pentane



iso-pentane

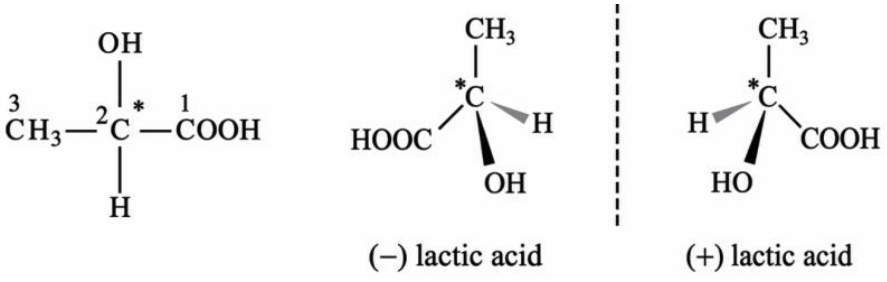


neopentane

ii) Stereoisomerism:

When the substituents or groups have different spatial arrangement in isomers, they are said to have different configuration. This type of isomerism is called stereoisomerism.

Example:



h) Define: i) racemic mixture ii) Optical activity

Ans: i) Racemic mixture:

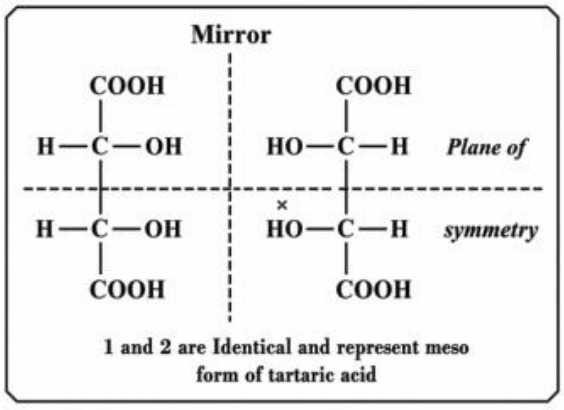
If one enantiomer is, dextrorotatory (+) and the other is levorotatory (-). When 50% dextrorotatory and 50% levorotatory enantiomers are present, they form an optically inactive mixture. Such a mixture is called a racemic mixture.

ii) Optical activity:

These are the stereoisomers which have identical physical and chemical properties except their ability to rotate the plane polarized 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.

i) Explain why meso tartaric acid is optically inactive although it has two chiral carbon atoms.

Ans: Meso tartaric acid contains an internal plane of symmetry. The optical rotation induced by one chiral half of the molecule (e.g., clockwise) is perfectly canceled out by the opposite rotation (e.g., counterclockwise) of the matching mirror-image half. This internal compensation renders the entire molecule optically inactive



CONSTRUCTED RESPONSE ANSWER QUESTIONS

Q.3 Attempt the following constructed response questions

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: Mechanism Steps

The free radical chain mechanism proceeds in three main stages: Initiation, Propagation, and Termination. To form the final product $C_6H_5CCl_3$ (benzotrichloride) from $C_6H_5CH_3$ (toluene), the propagation sequence must occur three times to replace all three hydrogen atoms of the methyl group.

I. Chain Initiation:

The reaction starts when ultraviolet (UV) light from sunlight causes the homolytic fission of a chlorine molecule into two highly reactive chlorine free radicals.

$$Cl - Cl \xrightarrow{hv\ (sunlight)} 2\dot{Cl}$$

II. Chain Propagation

This is the main part of the reaction, where the product is formed and radicals are regenerated to continue the chain. It occurs in three successive substitution cycles.

Cycle 1: Formation of Benzyl Chloride ($C_6H_5CH_2Cl$)

Step 1: A chlorine radical abstracts a hydrogen atom from the side chain (methyl group) of toluene, forming a benzyl radical and hydrogen chloride. The benzyl radical is stabilized by resonance with the benzene ring.

$$C_6H_5CH_3 + \dot{Cl} \longrightarrow C_6H_5\dot{C}H_2 + HCl$$

Step 2: The benzyl radical reacts with another molecule of chlorine to form benzyl chloride and regenerates a chlorine radical.

$$C_6H_5C\dot{H}_2 + Cl_2 \rightarrow C_6H_5CH_2\dot{C}l + \dot{Cl}$$

Cycle 2: Formation of Benzal Chloride ($C_6H_5CHCl_2$)

The regenerated chlorine radical can now attack the product of Cycle 1.

$$C_6H_5CH_2Cl + \dot{Cl} \longrightarrow C_6H_5C\dot{H}Cl + HCl$$
$$C_6H_5C\dot{H}Cl + Cl_2 \longrightarrow C_6H_5CHCl_2 + \dot{Cl}$$

Cycle 3: Formation of Benzotrichloride ($C_6H_5CCl_3$)

Finally, the chlorine radical attacks benzal chloride to replace the last hydrogen.

$$C_6H_5CHCl_2 + \dot{Cl} \longrightarrow C_6H_5C\dot{C}l_2 + HCl$$
$$C_6H_5C\dot{C}l_2 + Cl_2 \longrightarrow C_6H_5CCl_3 + \dot{Cl}$$

III. Chain Termination

The chain reaction terminates when any two free radicals combine with each other, consuming the reactive species without generating new ones. Possible termination steps include:

i) Combination of two chlorine radicals:

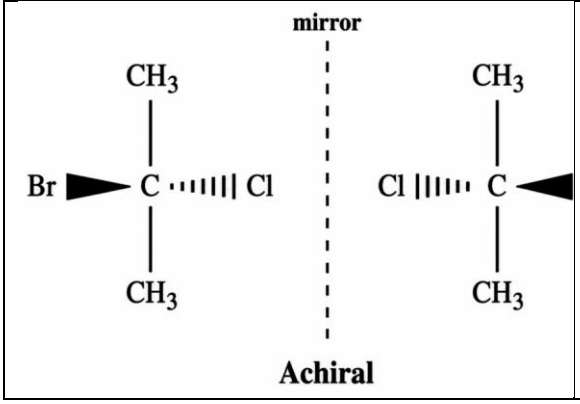
$$2\dot{Cl} \xrightarrow{hv\ (sunlight)} Cl\text{-}Cl$$

ii) Combination of a benzyl radical and a chlorine radical (forming the intermediate product):

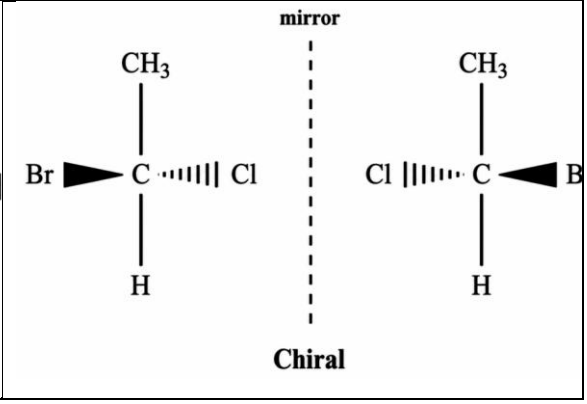
$$C_6H_5C\dot{H}_2 + \dot{Cl} \longrightarrow C_6H_5CH_2Cl$$

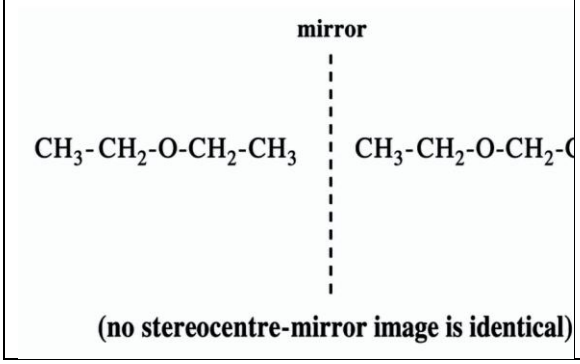
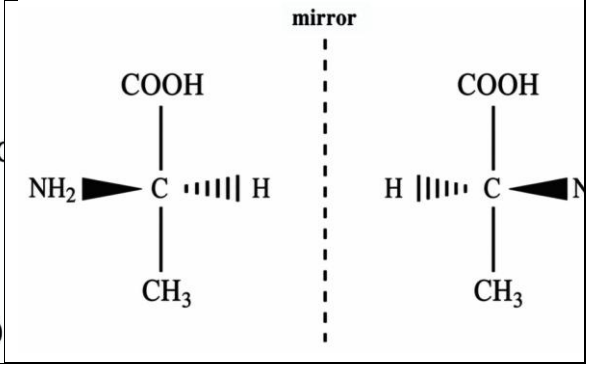
b) Draw the mirror image of each of the following compounds. Label each molecule as chiral or achiral

i) 2-bromo-2-chloropropane



ii) 1-bromo-1-chloroethane



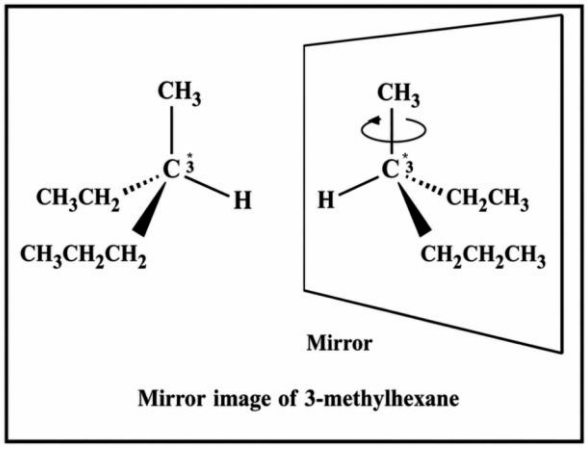
iii) ethoxyethane	iv) 2-aminopropanoic acid
	

c) **What is the alkane of lowest relative molecular mass that contains a chiral center? Give its systematic name and molecular formula. Also draw mirror image of this compound.**

Ans: 3-Methylhexane (C_7H_{16}) is alkane with relative lower molecular mass and has chiral center. Its carbon number three is a chiral carbon because it is connected to four different functional groups.
(-CH_2CH_3, -CH_3,- $CH_2CH_2CH_3$, -H).

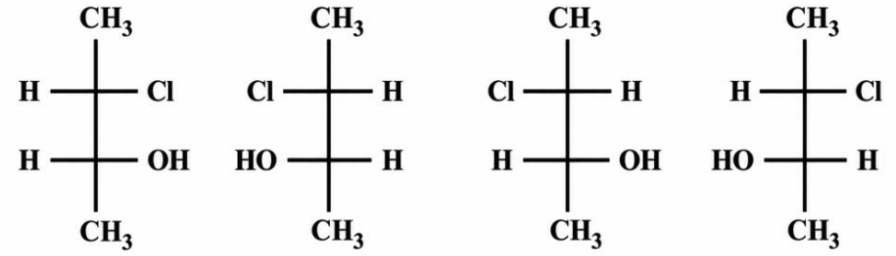
Systematic (IUPAC) Name:
3-methylhexane

Molecular Formula:
C_7H_{16}



Mirror image of 3-methylhexane

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.**



(1) **(2)** **(3)** **(4)**

3-chlorobutan-2-ol does not have a meso form because its two chiral carbons are attached to different groups (– OH and – Cl), so the molecule has no internal plane of symmetry.

DESCRIPTIVE ANSWER QUESTIONS

Q.4 Explain the difference between homolytic and heterolytic fissions of a covalent bond.

Ans: 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 general types of organic reactions.

A. Breaking of Covalent Bonds

There are three ways in which covalent bonds can break:

i. Homolytic Fission (Homolysis)

Homolytic fission occurs when the breaking bond is nonpolar.

Example: In this type of fission, the two shared electrons in the bond are distributed equally between the two atoms.

- The dot (.) beside each atom indicates the unpaired electron that the atom has gained from the shared pair in the bond.

"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.

ii. Heterolytic Fission (Heterolysis)

In this type of fission, the two shared electrons in the bond are distributed unequally between the two atoms.

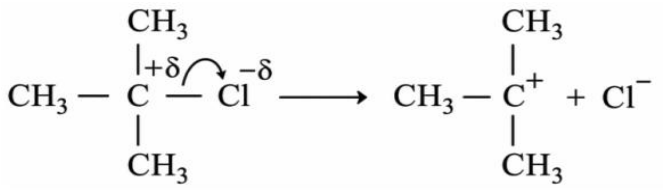
- One of the atoms keeps both electrons, and it acquires a negative charge.
- The other atom is deficient in one electron and, thus, acquires a positive charge.

Heterolytic fission occurs when the breaking bond is polar.

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. **Examples:** O, N, S, P etc.



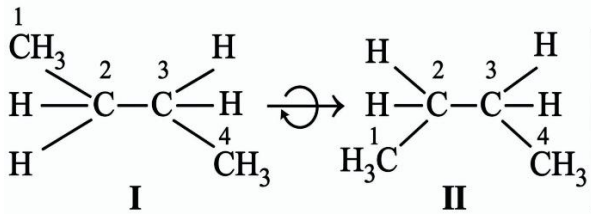
Carbanion is formed when Carbon is bonded to a heteroatom (metal) whose electronegativity is lesser than carbon e.g. Li, Mg, Cd etc.

Q.5 Discuss cis-trans isomerism. Explain with two examples.

Ans: *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.*

Example: 1 (Butane)

First of all we consider free rotation about C-C single bond in butane.



In butane, forms **I** or **II** are called conformational isomers because they are interconvertible 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: 2 (Butene)

- Now, 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 Carbon to Carbon double bond (C=C) 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 ρ 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 Carbon to Carbon double bond (C=C) is therefore restricted. This restriction of rotation about the C-C double bond is responsible for the cis-trans isomerism **(Figure 19.6)**.

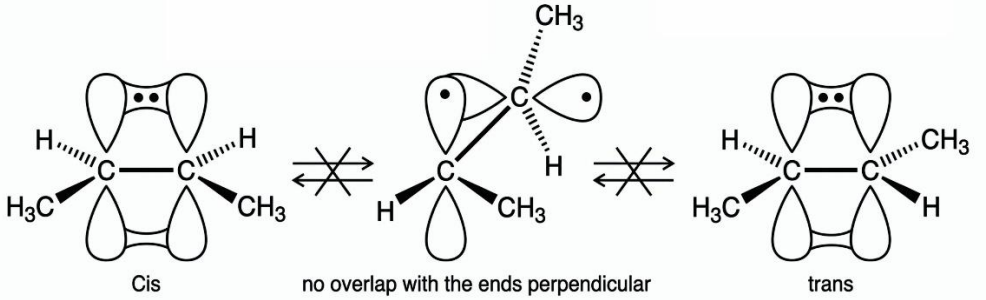
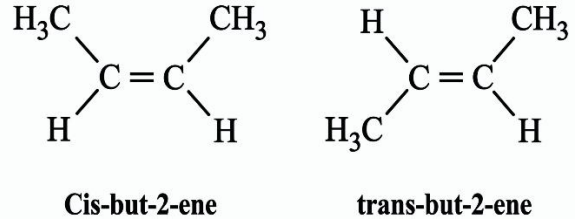


Figure 19.6 The two isomers of but-2-ene cannot interconvert by rotation about the C-C double bond without breaking the π bond

- 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:

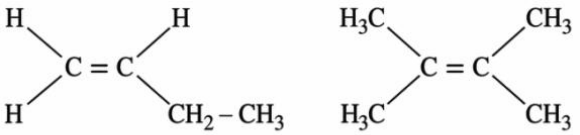
The cis isomer is one in which two similar groups are on the same side of the double bond.

Trans isomer:

The trans isomer is that in which two similar groups are on the opposite side of the double bond.

Important point:

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

Each of the above two compounds does not show cis-trans isomerism.

Condition for cis-trans isomer:

"Thus for an open chain compound the necessary and sufficient condition to show cis-trans isomerism is that,

i) It should have double bond in its molecule.

ii) Two different groups must be attacked to each of the doubly bonded carbon atoms.

Q.6 Describe the phenomenon of optical activity. Explain with an example.

Ans: Stereoisomers are further divided into two types.

a) Optical isomers

b) cis-trans isomers

a) Optical Isomers:

These are the stereoisomers which have identical physical and chemical properties except their ability to rotate the plane polarized light.

Optical activity:

Such isomers are said to be optically active and this property of these isomers of rotating the plane of polarization is called optical activity. Optical activity of a compound is identified by using plane polarized light (PPL).

Dextrorotatory and Levorotatory:

If the compound rotates the plane of polarized 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 (-).

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.

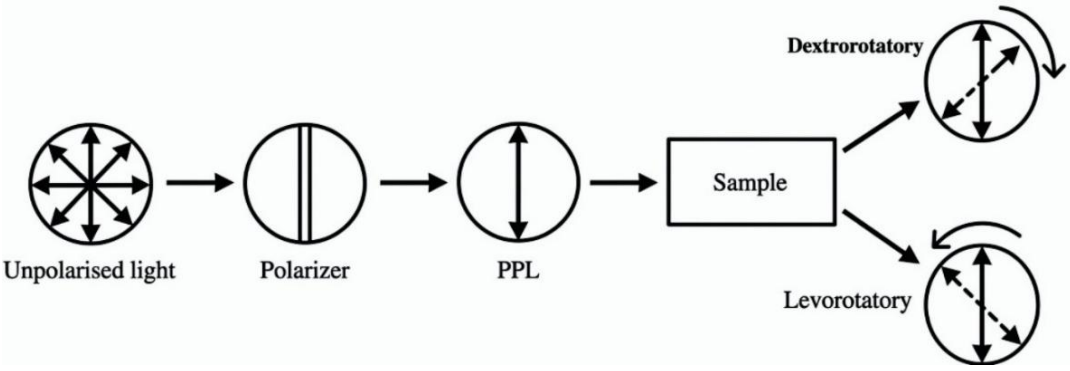


Figure 19.1 Optical rotation of PPL

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 19.5**.
- 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.

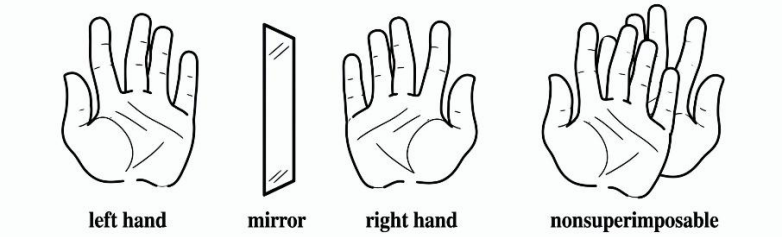


Figure 19.2 Our hands are non-superimposable on their mirror images.

Chiral carbon:

A carbon atom bearing four different atoms or group of atoms is called chiral carbon.

Asymmetric molecule:

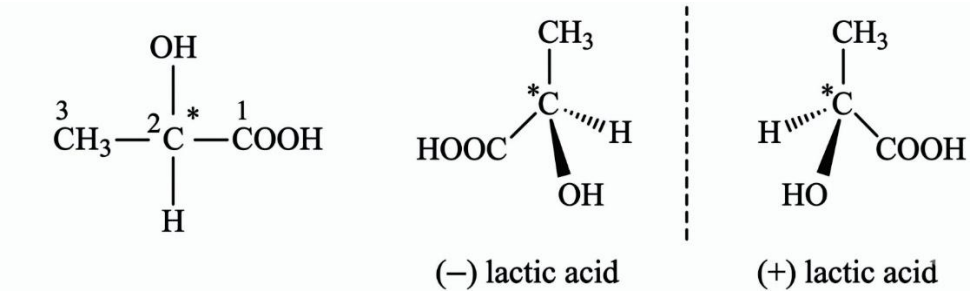
Any organic molecule which is not symmetric and it rotates the plane polarized light is a chiral or asymmetric molecule.

Important point: 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.

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 nonsuperimposable 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 polarized light in opposite directions, with the same extent.

Q.7 **What is the difference between racemic mixture and meso compound? Draw the structures of enantiomers and meso form of lactic acid.**

Ans: **Racemic mixture:**

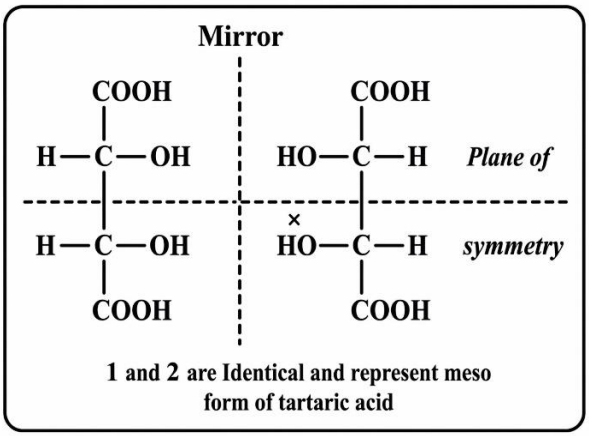
***One enantiomer is, therefore, dextrorotatory (+) and the other is levorotatory (-). When 50% dextrorotatory and 50% levorotatory enantiomers are present, they form an optically inactive mixture. Such a mixture is called a racemic mixture*.**

- 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 polarized 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.*** Tartaric acid is the classic example of this phenomenon.



UNIT 20: AROMATIC HYDROCARBONS

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: **Resonance energy α Stability of molecule**

The actual heat of hydrogenation of benzene is 152 kJ mol^{-1} lower than the theoretical value due to **delocalization of π-electrons present in benzene**. This energy is called the delocalization energy of benzene. This is the reason that benzene is **extra stab**le and resistant to addition reaction and gives preferably **electrophilic substitution reactions.**

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?**

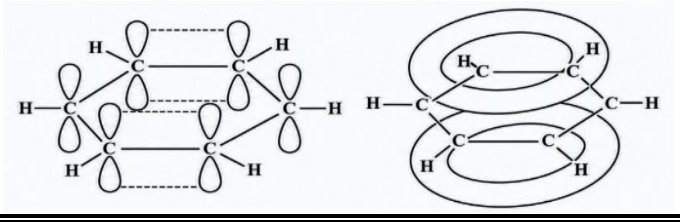
Ans: Benzene is extraordinary stable due to **planar structure** which allows its un-hybrid **p-orbitals to overlap effectively**. If benzene were not planar, effective overlap of p-orbitals would not occur and **delocalization would decrease**. Benzene would lose **aromatic stability** and become more reactive, behaving more like an alkene.

c) **Why all the bonds in the benzene ring are of equal bond length?**

Ans: Six π-electrons present in benzene are delocalized equally over all six carbon atoms. All C-C, C=C behave in between double and single and have identical bond order (1.5) as six all π-electrons are delocalized over entire ring. So all C–C bonds have identical bond order and therefore equal bond length of 139 pm.

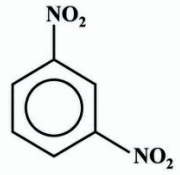
d) **How the atomic orbital concept explains the delocalization of π electrons in benzene?**

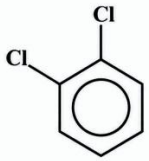
Ans: Six unhybrid '2p' orbitals, one from each carbon, are perpendicular to this sigma framework and parallel to each other. They overlap in parallel way to form a π-electron cloud above and below the plane of the benzene ring making it a conjugated molecule. Due to this overlap six electrons are shared equally among all the six carbons and is known as delocalization of π electron.



Quick Check 20.2

Give names to following arenes:

i) 

ii) 

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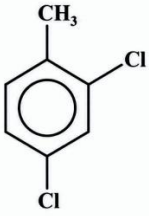
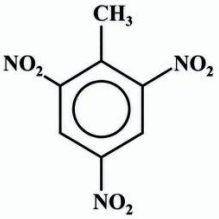
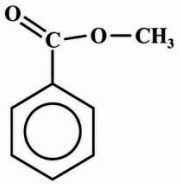
iv) 

v) 

vi) 

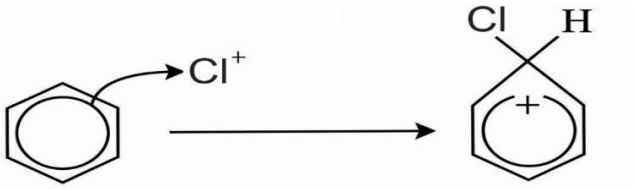
Ans: **i)** 1,3-dinitrobenzene (meta-dinitrobenzene)
ii) 1,2-dichlorobenzene(ortho-dichlorobenzene)
iii) 4-bromophenol (para-bromophenol)
iv) 2,4-dichlorotoulene(2,4-dichloro-1-methylbenzene)
v) 2,4,6-trinitrotoluene (2,4,6-trinitromethylbenzene)
vi) methyl benzoate

Quick Check 20.3

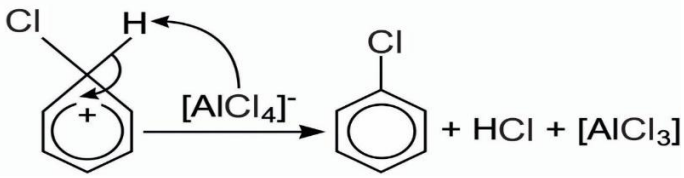
a) Write mechanism of reaction of benzene with chlorine using $AlCl_3$ as catalyst.

Ans: **Generation of electrophile:**

Attack of electrophile:



Restoration of aromaticity:



b) Although benzene is highly unsaturated yet it does not prefer to undergo addition reactions. Explain.

Ans: Addition reactions **destroy stability** of benzene by destroying its **delocalized π-electron system and aromaticity** so benzene does not undergo **addition reactions**. Moreover, the product formed as result of addition reaction would be **less stable** than benzene itself. Hence, benzene prefer substitution reaction over addition

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: The electrophile NO_2^+ ion is generated by reacting concentrated nitric acid (HNO_3) and concentrated sulphuric acid (H_2SO_4) in 1:1 at 50-55 ^{0}C.

Formation of electrophile — electrophile

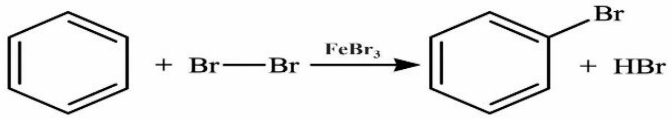
$$H_2SO_4 + HNO_3 \underset{}{\overset{50\text{-}55\,^{\circ}C}{\rightleftharpoons}} \underbrace{NO_2^+}_{\text{electrophile}} + HSO_4^- + H_2O$$

In the above reaction H_2SO_4 act as acid because it loses H^+ and HNO_3 act as base because it loses OH^- ions to form NO_2^+.

Quick Check 20.5

a) Write down reactions of benzene with bromine in the presence of $FeBr_3$.

Ans: In methylbenzene, methyl is ortho and para directing group. So, o-bromotoulene and p-bromotoulene are formed in the presence of $FeBr_3$.



b) Which of 1,1-dimethyethyllbenzene and methyl benzene is easier to form by Friedel-Craft reaction? Explain based on the stability of carbocation.

Ans: $AlCl_3$ produces carbocation (powerful electrophile) by removing the halide ion from alkyl halide molecule (R-X) in Friedel-Craft reaction. The ease of reaction depends upon stability of the carbocation.

Order of carbocation stability: Tertiary > Secondary > Primary > Methyl

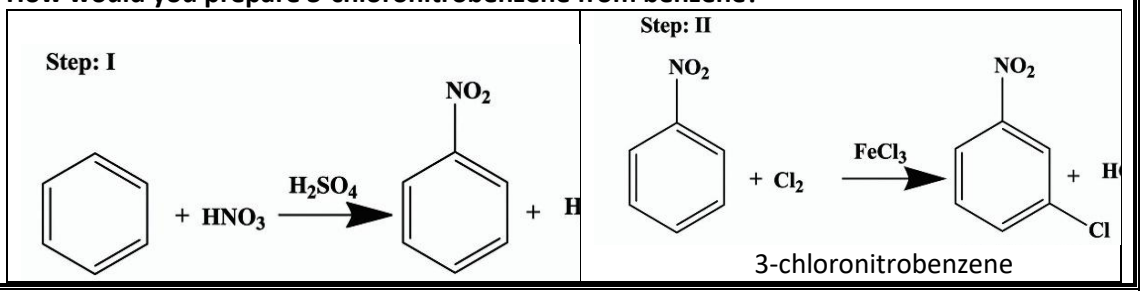
1,1-dimethylethylbenzene is formed more easily from Friedel Craft reaction than methyl benzene(toluene) because tertiary carbonation $(CH_3)_3C^+$ is **more stable than CH_3^+**. This is stability is due electron donating ability of methyl group.

Quick Check 20.6

a) Explain why phenol can be nitrated using milder conditions than for benzene.

Ans: Phenol can be easily nitrated than benzene because the -OH group present on benzene is a ring electron donating in nature. It increases the electron density on benzene ring. It activates benzene ring for electrophilic attack by donating electrons (lone pairs) present on oxygen atom of –OH group through resonance. It makes phenol more favorable for nitration than simple benzene at room temperature.

b) How would you prepare 3-chloronitrobenzene from benzene?



3-chloronitrobenzene

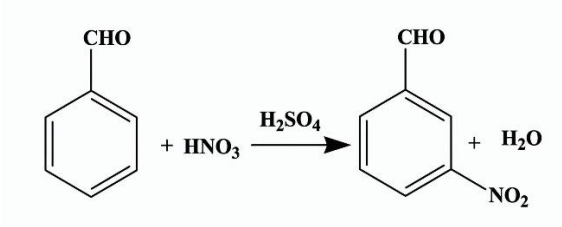
c) Which products are expected to form in majority when the following are nitrated with conc. sulphuric acid and nitic acid? Give reactions

i. benzaldehyde **ii. chlorobenzene**

iii. phenol **iv. Benzene carboxylic acid**

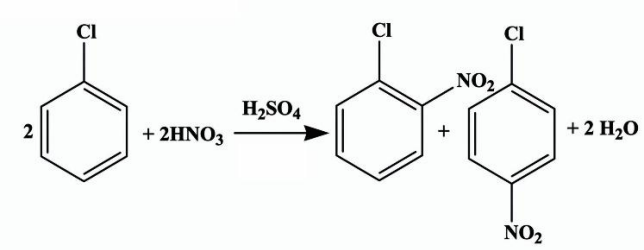
Ans: i. benzaldehyde:

m-nitrobenzaldehyde will be formed as major product because the -CHO group is meta directing group.



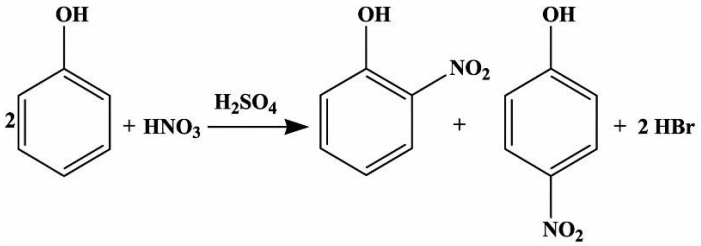
ii. Chlorobenzene:

o-chloronitrobenzene (2-nitrochlorobenzene) and p-chloronitrobenzene(4-nitrochlorobenzene) will be formed as major product because -Cl is Ortho and para directing group.



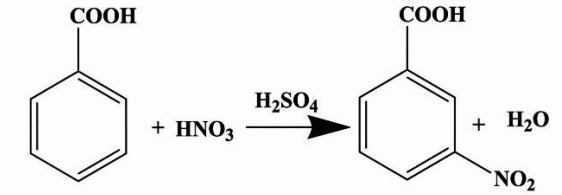
iii. Phenol:

o-nitrophenol (2-nitrophenol) and p-nitrophenol (4-nirophenol) will be formed as major product because -OH is ortho and para directing group.



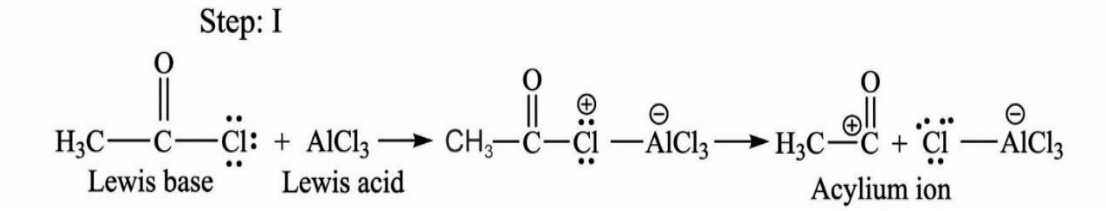
iv. Benzene carboxylic acid (Benzoic acid):

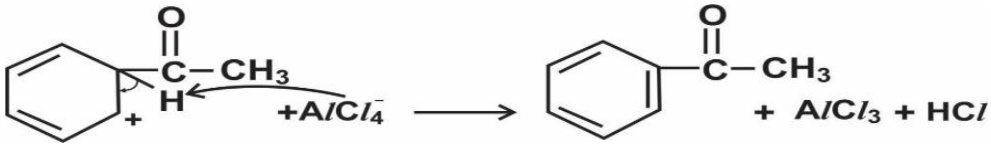
m-nitrobenzoic acid (3-nitrobenzenecarboxylic acid) will be formed as major product because the –COOH group is meta directing group.



d) Give a mechanism of the reaction between acetyl chloride and benzene.

Ans:

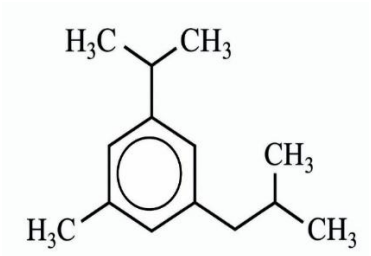




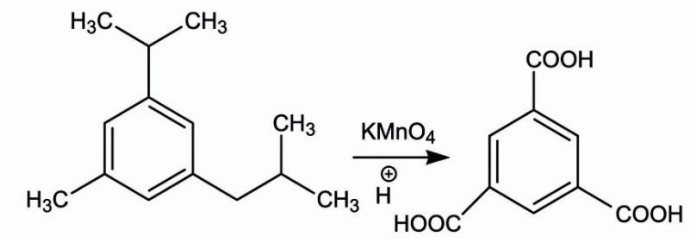
Quick Check 20.7

a) Predict the product formed when:

i. The compound given here is oxidized using acidified $KMnO_4$ or $K_2Cr_2O_7$.

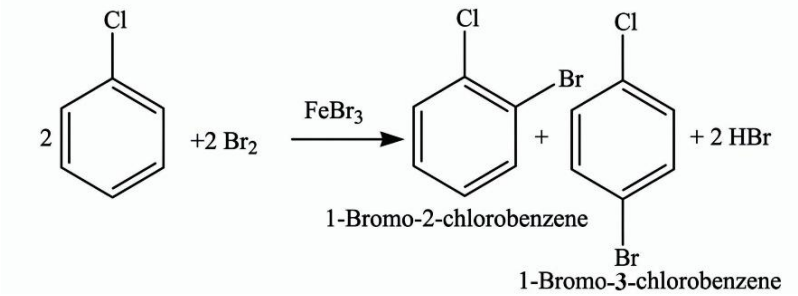


Ans: Every alkyl branch possessing at **least one benzylic hydrogen** which is completely oxidized down into a carboxylic acid group (COOH) by acidified $KMnO_4$ or $K_2Cr_2O_7$. Therefore, all three side groups are oxidized into -COOH yielding benzene-1,3,5-tricarboxylic acid.



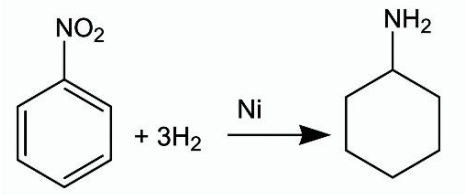
ii. Bromine is added to chlorobenzene in the presence of $AlBr_3$.

Ans: The chlorine is an ortho/para directing group. So, 1-bromo-2-chlorobenzene and p-1-bromo-3 chlorobenzene will be formed.



iii. Nitrobenzene is reduced in the presence of Ni at high temperature and pressure.

Ans: The aromatic ring will undergo catalytic hydrogenation addition to form cyclohexanamine (the nitro group reduces to an amine $–NH_2$, and the aromatic ring reduces to a cyclohexane ring).


NO2
+ 3H2
Ni
NH2

EXERCISE:

MULTIPLE CHOICE QUESTIONS

Q.1 Four choices are given for each question. Select the correct choice.

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 delocalized 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. The 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 molecules have:

a) delocalized 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 delocalized 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 EXPLANATION

MCQ. NO	Choice	Explanation
I	b	The methyl group is an ortho/para director but para directing group form major product.
II	c	Lone pair of electrons on the oxygen atom in phenol overlap with the delocalized electrons in the benzene ring (This strongly activates the ring by increasing electron density).
III	c	$AlCl_3$ is an electron pair acceptor (accepts a lone pair from the halogen to form the active electrophile.
IV	c	Protonates the nitric acid which acts as a base (Protonation followed by loss of water generates the active NO_2^+ ion).
V	d	Chloromethane to produce an electrophile ($AlCl_3$ pulls away the chlorine atom to generate the CH_3^+ carbocation).
VI	b	Electrophilic substitution (The standard mechanism for aromatic ring substitution).
VII	b	carbon-carbon bonds that are all the same length (X-ray data explicitly shows uniform carbon-carbon bond lengths of 139 pm).
VIII	a	1, 2 and 3 (All three pieces of evidence challenge the localized alternating single/double bond Kekulé model and support delocalization).
IX	c	CH_3-CO-Cl (Ethanoyl chloride provides the necessary acyl group via Friedel-Crafts acylation).

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions

Benzene reacts with chlorine in the presence of a halogen carrier, such as $AlCl_3$.

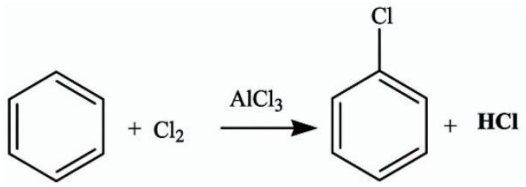
a) i) Write the equation for the reaction of benzene with chlorine.

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) Reaction:



ii) $AlCl_3$ acts as Lewis acid and polarizes the Cl-Cl bond. It accepts electron pair from one Cl atom of Cl_2 forming coordinate covalent bond and produced powerful electrophile Cl^+. It attacks delocalized π-electrons of benzene ring.

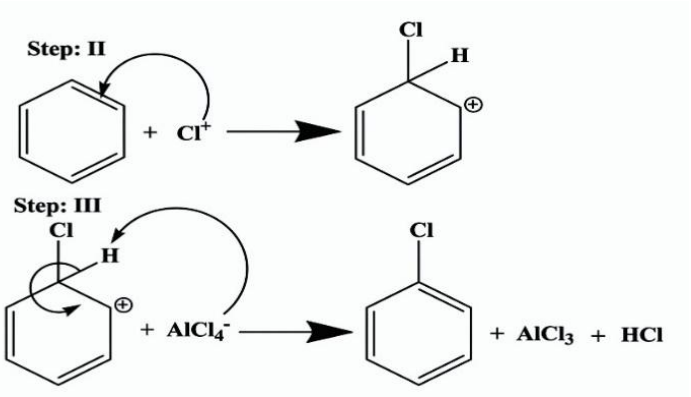
$$\overset{\delta+}{Cl} - \overset{\delta-}{Cl} + AlCl_3 \longrightarrow [AlCl_4]^- + \overset{+}{Cl}$$

iii) Mechanism of reaction:

Step 1: Generation of electrophile:

$$\overset{\delta+}{Cl} - \overset{\delta-}{Cl} + AlCl_3 \longrightarrow [AlCl_4]^- + \overset{+}{Cl}$$

Step 2: Attack of Electrophile



iv) Electrophilic Aromatic Substitution.

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b) Explain what is meant by the term delocalized π-bond electrons.

Ans: Delocalized pie electrons are the electrons that are actually shared between two or more nuclei like in benzene ring. These electrons are delocalized and formed through parallel overlapping.

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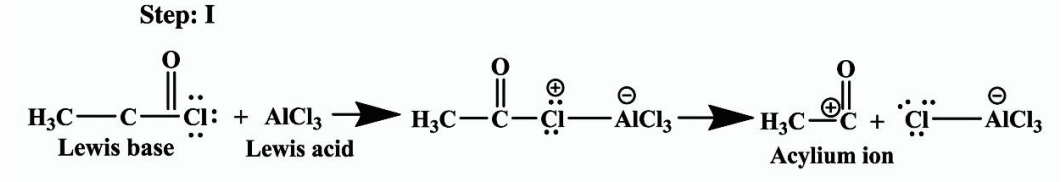
c) An acylium ion has the structure R-C=O where R is any alkyl group. In the conversion of benzene into phenylethanone, $C_6H_5COCH_3$, an acylium ion CH_3CO^+ reacts with a benzene molecule.

i) Write an equation to show the formation of this acylium ion from ethanoyl chloride and one other substance.

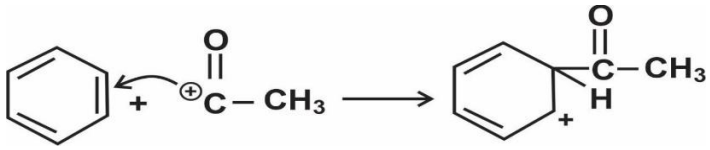
ii) Name and outline the mechanism of the reaction of this acylium ion with benzene.

Ans: i) Reaction:

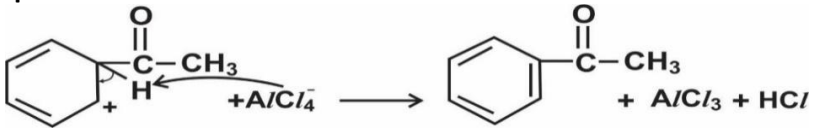


ii) Mechanism of reaction:

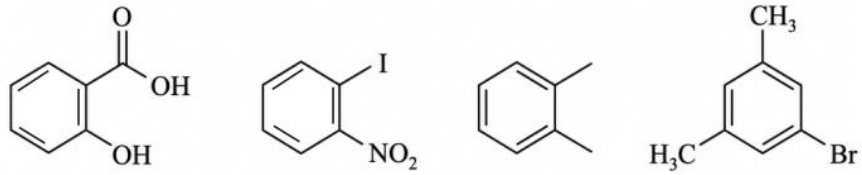
Step II:



Step III:



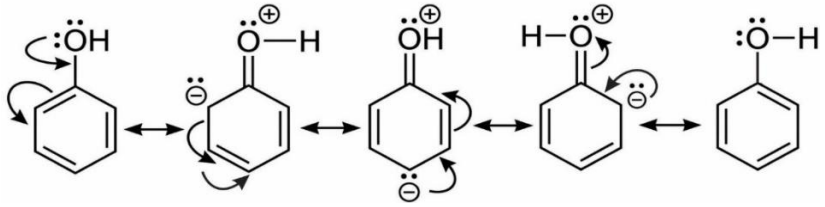
d) **Name the following molecules:**



Ans:
i) 2-hydroxybenzoic acid or o-hydroxybenzoic acid (Salicylic acid)
ii) 1-iodo-2-nitrobenzene (o-idonitrobenzene)
iii) 1,2-dimethylbenzene (o-xylene)
iv) 1-bromo-3,5-dimethylbenzene (3,5-dimethylbromobenzene)

e) **Describe, with the aid of a diagram, the bonding in phenol to show delocalization of π-electrons.**

Ans



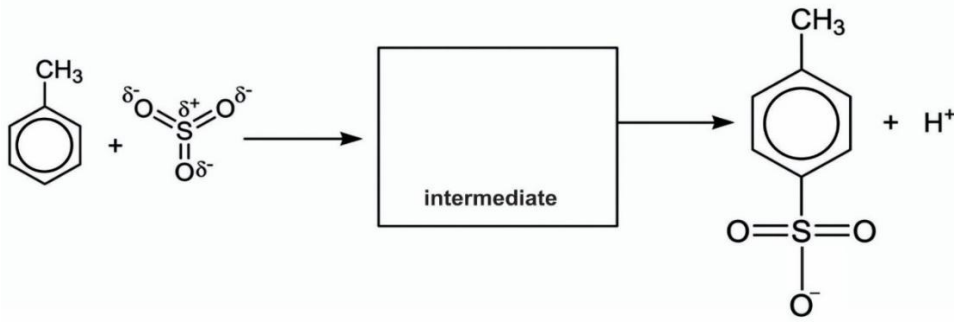
CONSTRUCTED RESPONSE ANSWER QUESTIONS

Q.3 Attempt the following constructed response questions

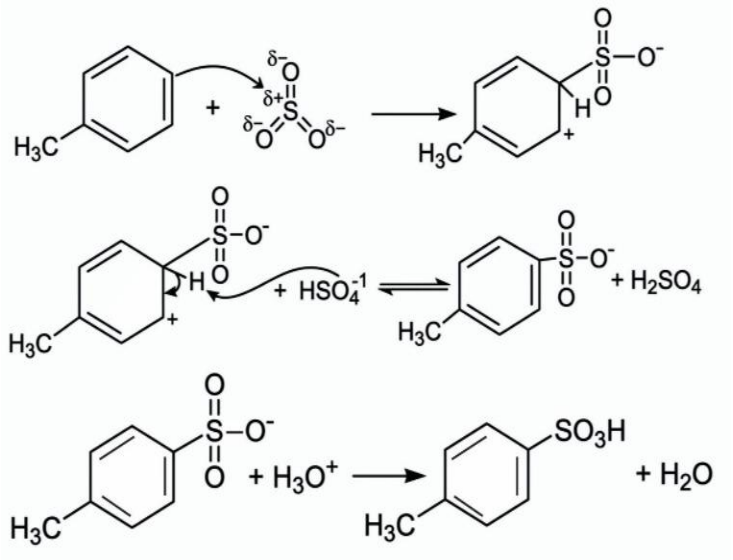
a) **The compound iodine monobromide, IBr, also reacts with benzene in an electrophilic reaction. Which compound would be the main product of this reaction, iodobenzene or bromobenzene? Explain your answer.**

Ans: The **major product will be the iodobenzene** because I is less electronegative and bond in I-Br is polar. Iodine gets +δ due to less electronegativity value and Br gets –δ charge. It produces **I^+ a powerful electrophile** needed for **electrophilic substitution** reaction of benzene which replaces H-atom of benzene to give iodobenzene.

b) **Methylbenzene reacts with sulphur trioxide, SO_3, to form D, shown below**
The electrophile in this reaction is SO_3.
Complete the mechanism for the formation of D. Show curly arrows and the structure of the intermediate.

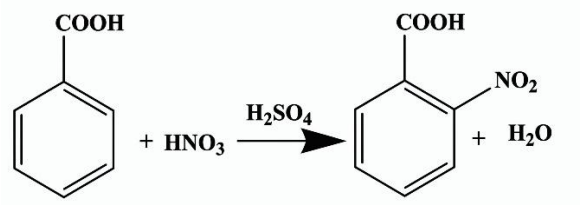


Ans: Mechanism



c) Outline the mechanism for this nitration of benzoic acid. Show how H_2SO_4 behaves as a catalyst.

Ans: i) Reaction:

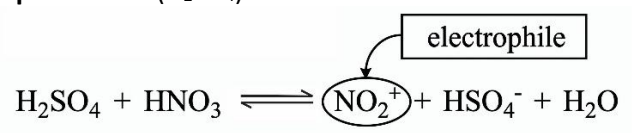


Mechanism:

The mechanism involves the following steps:

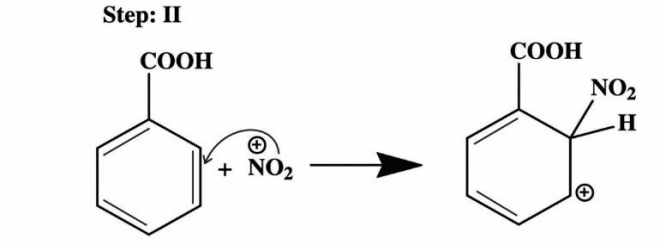
Step I: Generation of an electrophile

The electrophile **NO_2^+ ion** is generated by reacting concentrated **nitric acid** (HNO_3) and **concentrated sulphuric acid** (H_2SO_4).



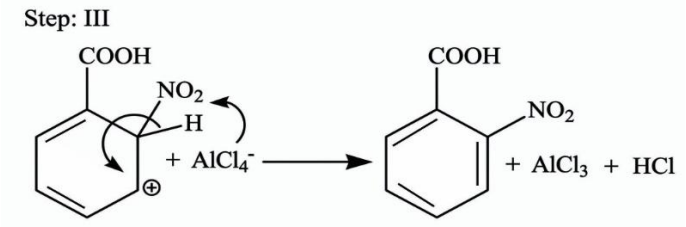
Step II: Electrophilic attack

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: Regeneration of catalyst

The C–H bond of the substituted carbon atom breaks and the electrons go back into the benzene π bonding system, restoring its aromaticity.



DESCRIPTIVE ANSWER QUESTIONS

Q.4 Explain atomic orbital model for structure of benzene.

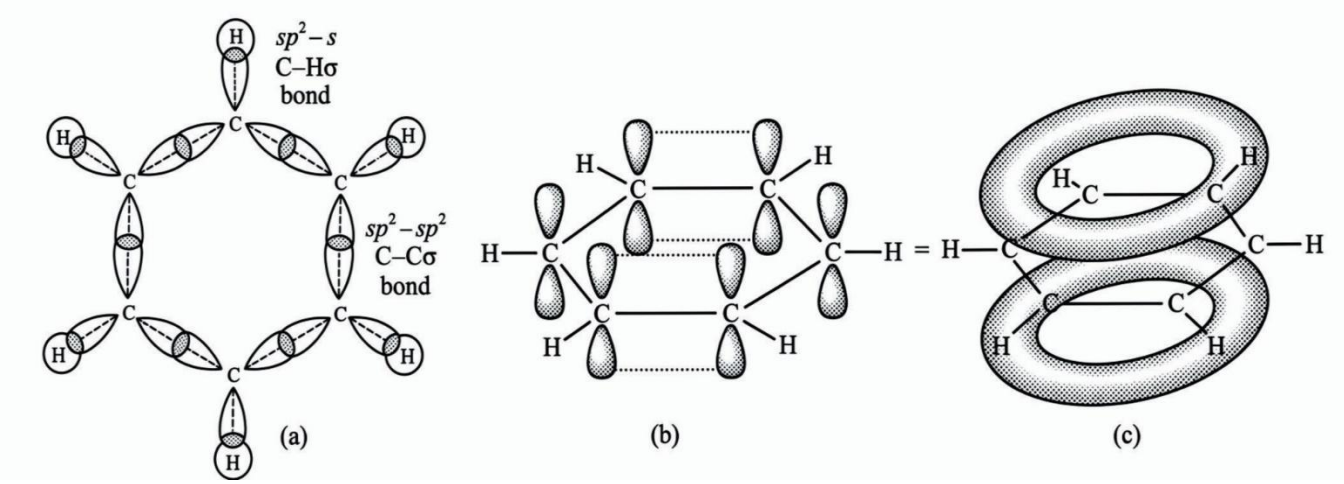
Ans: The hexagonal frame work of benzene ring can be conveniently explained by using hybridization approach.

Hybridization approach:

- According to this, each carbon atom in benzene is sp^2 hybridized.
- 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 at 120°.

Delocalization of π electron:

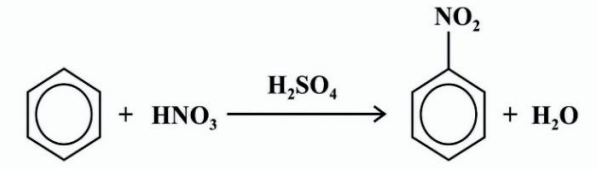
- The six unhybrid '2p' orbitals, one from each carbon, are perpendicular to this sigma framework and parallel to each other overlap sideways to form a π-electron cloud above and below the plane of the benzene ring making it a **conjugated molecule.**
- Due to this overlap six electrons are shared equally 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 (139 pm).
- Benzene is thus represented as a hexagon with a circle inscribed, where the circle represents delocalized π electrons.



Q.5 Describe the nitration of benzene. Explain its mechanism.

Ans: ***A nitro group is introduced on benzene, using mixture of conc. HNO_3 and conc. H_2SO_4 called as nitration of benzene.***

Reaction:

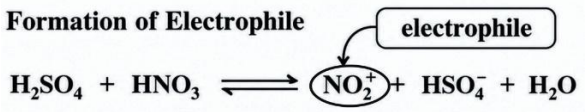


Mechanism:

The mechanism involves the following steps:

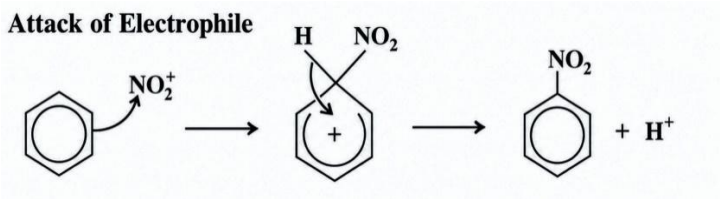
Step I: Generation of an electrophile

The electrophile **NO_2^+ ion** is generated by reacting concentrated **nitric acid** (HNO_3) and **concentrated sulphuric acid** (H_2SO_4).



Step II: Attack of an electrophile

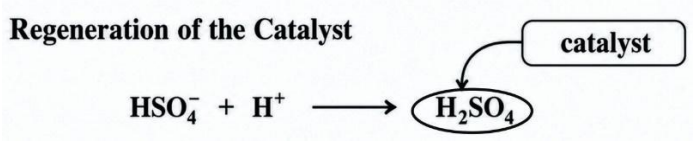
A pair of electrons from the benzene ring is donated to the NO_2^+ electrophile to form a covalent bond causing a loss in aromaticity.



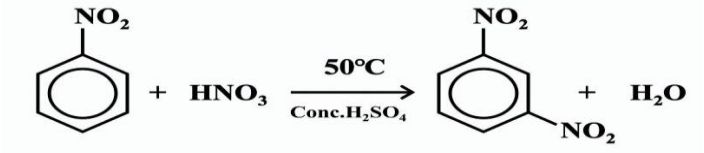
Step III: Regeneration of catalyst

The C–H bond of the substituted carbon atom breaks and the electrons go back into the benzene π bonding system, restoring its aromaticity.

Mechanism:



Concentrated sulphuric acid acts as a catalyst so is shown above the arrow rather than the reactant. At higher temperatures there is a greater chance of getting more than one nitro group substituted onto the ring. You will get a certain amount of 1,3-dinitrobenzene formed even at 50°C.

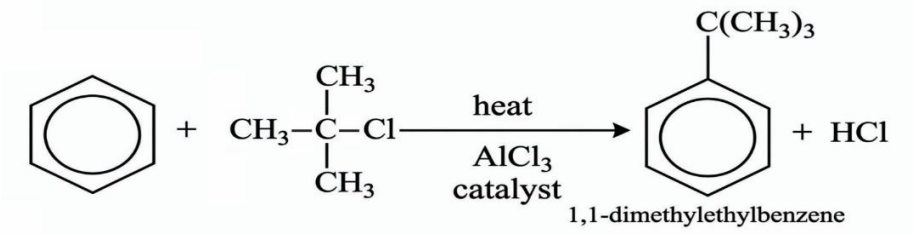


Q.6 Discuss Friedel Crafts reactions of benzene.

Ans: Friedel-Crafts Alkylation:

In the Friedel-Crafts alkylation, an alkyl group is substituted into the benzene ring.

Reaction:

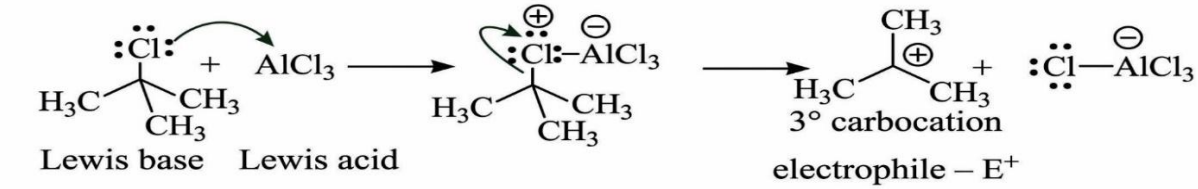


Mechanism:

The Friedel-Crafts alkylation reaction proceeds via a three-step mechanism.

Step I: Generation of carbocation (act as 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.

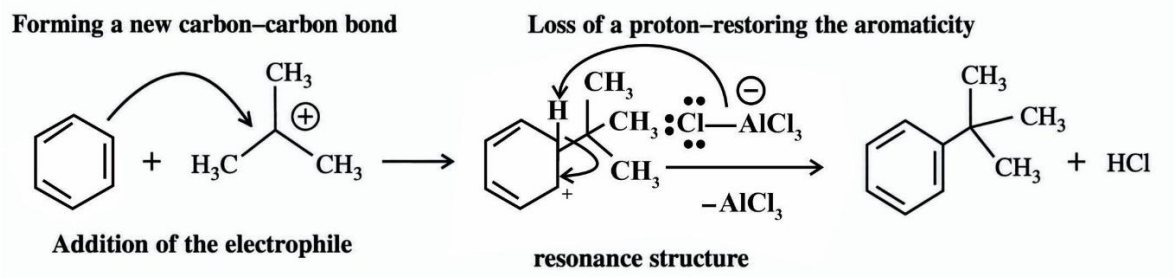


Step II: Attacking of an electrophile

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 disruption of delocalized π-electron systems.

Step III: Restoration of aromaticity

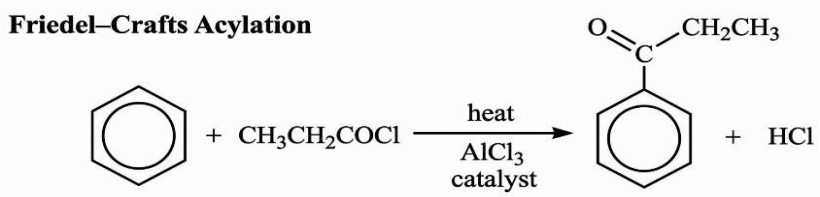
The deprotonation of the intermediate leads to the reformation of the carbon-carbon double bond, restoring aromaticity to the compound. This proton goes on to form hydrochloric acid, regenerating the AlCl catalyst.



Friedel-Crafts Acylation

In the Friedel-Crafts acylation reaction, an acyl group (R-C= O) is substituted into the benzene ring in the presence of a Lewis acid catalyst.

Reaction:

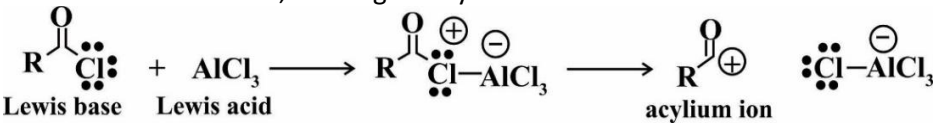


Mechanism:

Friedel-Crafts acylations proceed through a four-step mechanism.

Step I: Generation of carbocation (act as electrophile):

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.

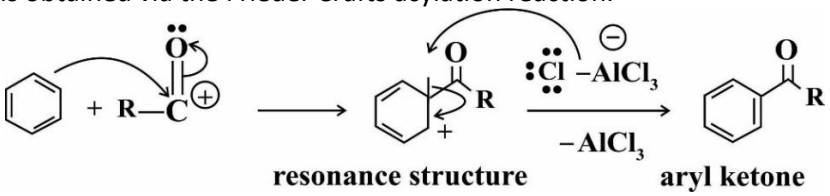


Step II: Attacking of an electrophile

An electrophilic attack of π electrons of the aromatic ring on the acylium ion (RCO^+) takes place.

Step III: Restoration of aromaticity

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.



Q.7 Write the note on orientation of electrophilic substitution reactions of benzene.

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.

20.5.1 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 as -ortho, -para director.

Examples: -SR, -R,-OH, -OR, -NR_2, -SH (Note that these are groups that have the ability to donate electrons to the benzene ring).

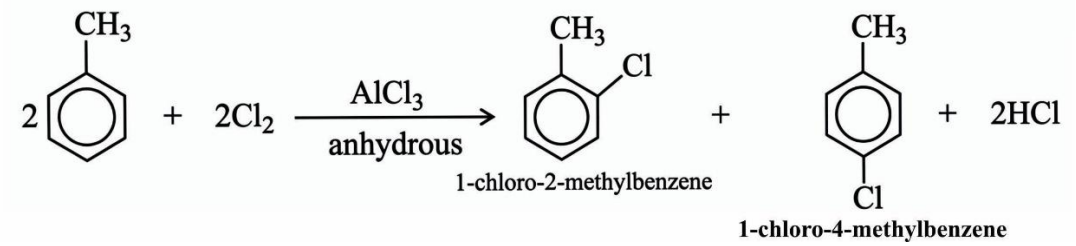
- Substituents direct the reaction to give either the "*ortho*" (1,2) or "*para*" (1,4) product, with a slight preference for "para".
- In this pattern, *ortho*- and *para*– products dominate, and the *meta*- product is an extremely minor byproduct

Exception: Halogens (-Cl,-Br,-I) which are o/p directing but they deactivate benzene ring for electrophilic attack.

Example: Chlorination of methyl benzene:

The chlorination in the methyl benzene ring takes place in the presence of **aluminum 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.



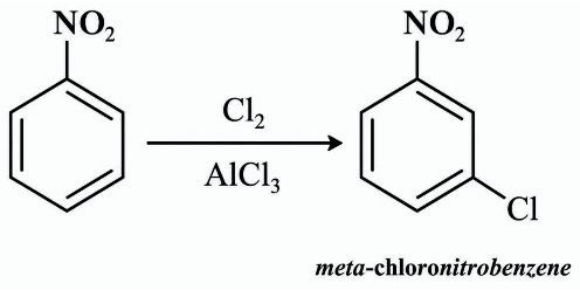
With bromine, you would get the equivalent bromine compounds. Like methyl group on benzene ring, OH group is also ring activator so incoming groups will tend to go into the 2, 4 & 6 positions on the ring.

20.5.2 Meta Directing (Deactivating) Groups:

Group that makes the ring less reactive than benzene, and directs the incoming electrophile to attack on meta position only is called as-meta director.

Examples: -CN, C=O, -NO_2, -CO_2H, -SO_3H,-CHO,-NR_3^+

- Such groups are mostly electronwithdrawing 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.



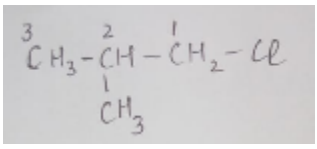
- Nitrobenzene contains a **meta directing group (-NO_2)**, its chlorination occurs at the meta position.

Unit 21: HALOGENOALKANES

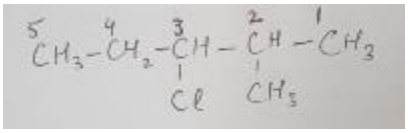
Quick Check 21.1

a) Write down the IUPAC name of the compound, $(CH_3)_2CH\text{-}CH_2\text{-}Cl$, $CH_3CH_2CH(Cl)CH(CH_3)\ CH_3$.

Ans:



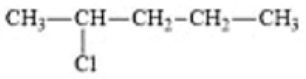
1-Chloro-2-methylpropane



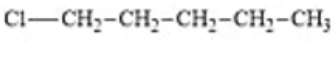
3-Chloro-2-methylpentane

b) Draw the primary, secondary and tertiary structures of the compound having molecular formula $C_5H_{11}Cl$.

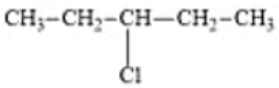
Ans:



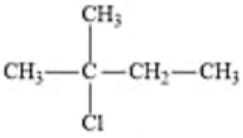
2-Chloropentane (secondary)



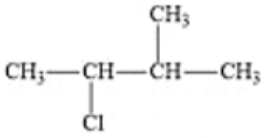
1-Chloropentane (Primary)



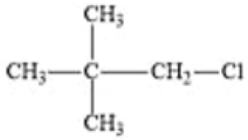
3-Chloropentane (secondary)



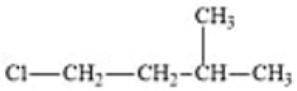
2-Chloro-2-methylbutane (Tertiary)



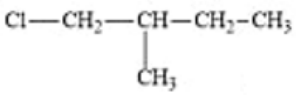
2-Chloro-3-methylbutane (secondary)



1-Chloro-2,2-dimethylpropne (Primary)



1-Chloro-3-methylbutane (Primary)



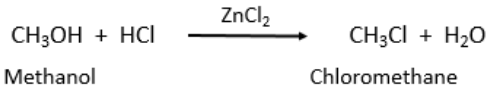
1-Chloro-2-methylbutane (Primary)

Quick Check 21.2

a) Give two methods to convert methanol into chloromethane.

Ans:

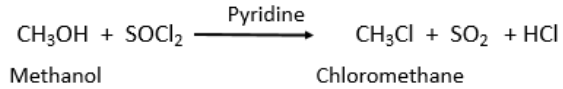
i. Alcohols may be converted to the corresponding alkyl halides by the action of halogen acid in the presence of $ZnCl_2$ which acts as a catalyst.



$CH_3OH + HCl \xrightarrow{ZnCl_2} CH_3Cl + H_2O$

Methanol — Chloromethane

ii. Alcohols also react with thionyl chloride in pyridine as a catalyst to give alkyl chlorides. This method is especially useful since the by-products (HCl and SO_2) are gases which go off leaving behind the pure product



$CH_3OH + SOCl_2 \xrightarrow{Pyridine} CH_3Cl + SO_2 + HCl$

Methanol — Chloromethane

b) Give reactions of propanol with $SOCl_2$ and PBr_3.

Ans: With $SOCl_2$

$$CH_3CH_2CH_2OH + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3CH_2CH_2Cl + SO_2 + HCl$$

Propanol — bChloropropane

With PBr_3

$$3CH_3CH_2CH_2OH + PBr_3 \longrightarrow 3CH_3CH_2CH_2Br + H_3PO_3$$

Propanol — Bromopropane

c) Can we prepare fluoromethane using methane and fluorine gas? Give reason.

Ans: No, fluoromethane cannot be prepared conveniently by reacting methane with fluorine gas. Reason is that fluorination of methane is extremely vigorous and explosive. The reaction is highly exothermic and does not stop easily at the monofluorination stage, further substitution may occur.

Quick Check 21.3

a) Why halogenoalkanes are considered as very reactive class of organic compounds?

Ans: Halogenoalkanes are considered very reactive organic compounds because of the bond polarity of C-X bond ($C^{\delta+}-X^{\delta-}$) and relatively weak nature of C-X bond.

b) Complete the following equation. CH3Br + CH3COONa →

Ans:

$$CH_3Br + CH_3COONa \rightarrow CH_3COOCH_3 + NaBr$$

c) How will you convert ethane into ethanol and ethene?

Ans:

1. Ethane → Ethanol

First, convert ethane to bromoethane by free-radical bromination:

$$CH_3CH_3 \xrightarrow{Br_2/hv} CH_3CH_2Br + HBr$$

Then hydrolyse bromoethane with aqueous KOH:

$$CH_3CH_2Br \xrightarrow{aq.\,KOH} CH_3CH_2OH + KBr$$

2. Ethane → Ethene

First, convert ethane to bromoethane by free-radical bromination:

$$CH_3CH_3 \xrightarrow{Br_2/hv} CH_3CH_2Br + HBr$$

Then heat ethylbromide with alcoholic KOH by elimination reaction.

$$CH_3CH_2Br + KOH \xrightarrow{\text{alcoholic KOH, heat}} CH_2 = CH_2 + KBr + H_2O$$

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: Since cyanide ion (CN^-) is a strong nucleophile but a weak base so it reacts with halogenoalkanes to give substitution product, a nitrile.

$$CH_3CH_2CH_2Br + KCN \xrightarrow{\text{alcohol}} CH_3CH_2CH_2CN + KBr$$

Bromopropane Propyl nitrile

Quick Check 21.4

a) What is the role of iron halide in the preparation of halogenoarene?

Ans: Role of FeX_3

- It activates the halogen molecule (X_2)
- It helps generate the electrophile X^+.
- The Cl^+ then attacks the benzene ring in an electrophilic substitution reaction.

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + HCl$$

b) Chlorobenzene does not react with NaOH under normal conditions, but chloroethane does; explain why?

Ans: Chlorobenzene does not react with NaOH under normal conditions, whereas chloroethane does, because of the difference in C-Cl bond.

In Chlorobenzene, the chlorine atom is directly attached to an sp2-hybridised carbon of the benzene ring. The lone pair on Cl interacts with the benzene ring giving C-Cl bond partial double-bond character, so C-Cl bond is shorter and stronger than that in Chloroethane.

c) Can chlorobenzene undergo elimination? Explain why or why not?

Ans: No, Chlorobenzene does not undergo elimination reaction.

The reason is that in Chlorobenzene, the chlorine atom is directly attached to an sp2-hybridised carbon of the benzene ring. The lone pair on Cl interacts with the benzene ring giving C-Cl bond partial double-bond character. Also, elimination would require removing H and Cl from adjacent carbon atoms to form a new double bond, but the benzene ring already has a stable aromatic π-electron system.

Q1. MULTIPLE CHOICE QUESTIONS

1 Encircle The Correct Answer.

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 > Chloride

c) Iodide > Bromide > Chloride > Fluoride ✓ d) Bromide > Iodide > Chloride > Fluoride

III) S_N 2 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 1 ✓

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, the most rapid ppt. 3 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 ✓

b) The concentration of the base

c) The concentrations of substrate as well as base

d) Neither the concentration of substrate nor the bas

Q2 . SHORT ANSWER QUESTIONS

a) Why halogenoalkanes are known to be very reactive compounds?

Ans: Halogenoalkanes are considered very reactive organic compounds because of the bond polarity of C-X bond ($C^{\delta+}-X^{\delta-}$) and relatively weak nature of C-X bond.

b) Why fluoroalkanes rarely undergo nucleophilic substitution reactions?

Ans: Due to the highest electronegativity and very small size of fluorine atom, the C-F bond is very strong; so fluoroalkanes rarely undergo nucleophilic substitution reactions.

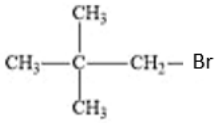
c) Why primary halogenoalkanes undergo substitution reactions by S_N2 mechanism?

Ans: Among the monohalogenoalkanes, primary monohalogenoalkanes always 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.

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

Structure:

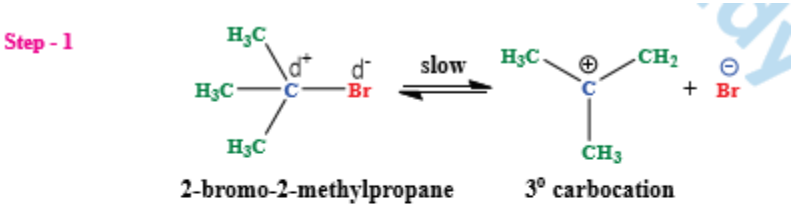


For an elimination reaction, a β-hydrogen must be present on the carbon adjacent to the carbon bearing Br. The β-carbon in this structure has no hydrogen atoms. Therefore, removal of HBr is impossible, so elimination cannot occur.

No β-H → No elimination reaction

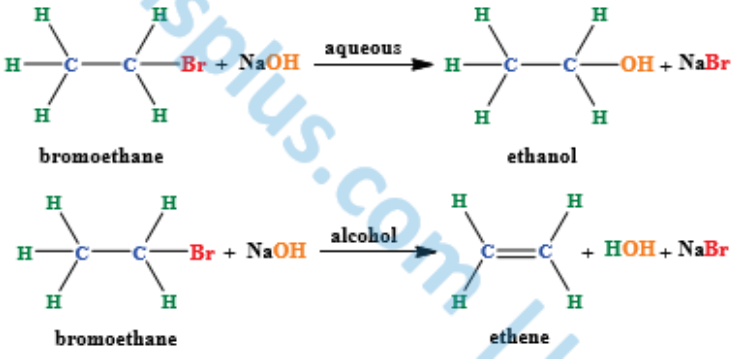
e) Why tertiary halogenoalkanes undergo elimination reaction by E1 mechanism?

Ans: Tertiary halogenoalkanes undergo elimination mainly by the E1 mechanism because they can form a stable tertiary carbocation**.**



f) Hydroxide ion is a good base as well as a good nucleophile. Justify.

Ans: Hydroxide ion is both a good nucleophile and a good base. So, when it attacks as a nucleophile, it replaces the halogen atom of the halogenoalkane to form a substitution product, alcohol. As a base, it removes both the βhydrogen atom and the halogen atom to give an elimination product, an alkene.



g) What is the role of iron chloride ($FeCl_3$) during the chlorination of benzene?

Ans: **Role of $FeCl_3$**

- It activates the halogen molecule (Cl_2)
- It helps generate the electrophile Cl^+.
- The Cl^+ then attacks the benzene ring in an electrophilic substitution reaction.

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + HCl$$

h) Which among haloalkanes or haloarenes, is more reactive towards nucleophile?

Ans: Haloalkanes are more reactive towards nucleophiles than haloarenes, because:
In haloalkanes, the C–X bond is a normal single bond and can be readily broken during nucleophilic substitution. In haloarenes, the halogen is attached directly to an sp^2-hybridised carbon of the benzene ring. Due to resonance, the C–X bond in haloarenes has partial double-bond character, making it shorter and stronger. Therefore, nucleophilic substitution is much more difficult in haloarenes.

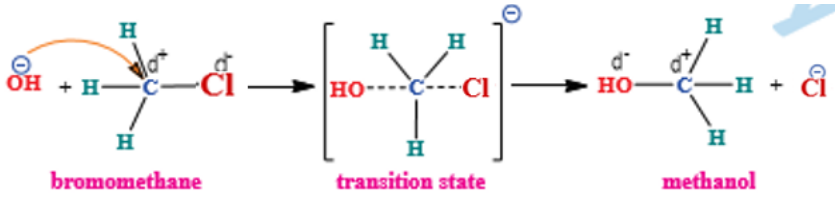
Reactivity: Haloalkanes>Haloarenes

Q3. CONSTRUCTED RESPONSE QUESTIONS

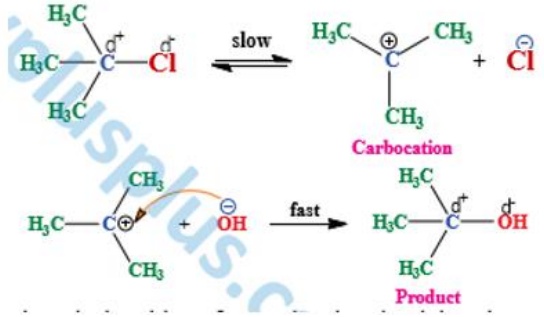
a) Predict the mechanism which the chloroalkane will adopt while giving nucleophilic substitution reactions.

Ans:

i) If it is a primary chloroalkane, it will follow S_N2 mechanism.



ii) If it is a tertiary chloroalkane, it will follow S_N1 mechanism.



b) Why nucleophilic substitution and elimination reactions of haloalkanes proceed together under similar conditions?

Ans: Nucleophilic substitution and elimination reactions of haloalkanes can occur under similar conditions because both reactions involve the same haloalkane and a nucleophile/base.
For example, when a haloalkane reacts with OH^-:

1. Substitution

OH^- attacks the carbon attached to the halogen and replaces the halide:

$$R{-}X + OH^- \rightarrow R{-}OH + X^-$$

2. Elimination

OH^- can instead remove a β-hydrogen, while the halide leaves, forming an alkene:

$$R{-}CH_2{-}CH_2{-}X + OH^- \rightarrow R{-}CH{=}CH_2 + H_2O + X^-$$

Thus, OH^- can act both as a nucleophile and as a base, so substitution and elimination can compete under the same conditions.

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 shows this behaviour because of the resonance effect of chlorine and the nature of the benzene ring.

1. Nucleophilic substitution is difficult: In chlorobenzene, chlorine is directly attached to an **sp^2-hybridised carbon**. The lone pair of chlorine participates in resonance with the benzene ring:

$C_6H_5–Cl \leftrightarrow$ resonance structures

This gives the C–Cl bond partial double-bond character, making it shorter and stronger. Hence, breaking the C–Cl bond during nucleophilic substitution is difficult.

2. Electrophilic substitution is easier: Chlorine has a **lone pair** that can donate electron density to the benzene ring by resonance (**+R effect**). This increases electron density particularly at the **ortho and para positions**. Therefore, chlorobenzene can undergo **electrophilic substitution**, mainly at the **ortho and para positions**.

d) Differentiate between E2 and E1 reactions. Draw a table for your response.

Ans:

Feature	E1 Reaction	E2 Reaction
Full form	Elimination unimolecular	Elimination bimolecular
Number of steps	**Two steps**	**One step**
Rate-determining step	Formation of carbocation	Removal of β-H and leaving of halide occur simultaneously
Rate law	Rate = k[RX]	Rate = k[RX][Base]
Molecularity	Unimolecular	Bimolecular
Carbocation formation	**Carbocation is formed**	**No carbocation is formed**
Favoured by	Mainly **tertiary halogenoalkanes**	Mainly **primary and secondary halogenoalkanes** with a strong base
Base required	Usually weak base can be sufficient	Usually requires a **strong base**
Steric hindrance	Favoured by highly substituted substrates	Strong steric hindrance can affect the reaction
Mechanism	$RX \rightarrow R^+ + X^-$, then base removes β-H	Base removes β-H as X^- leaves simultaneously
Example	Tertiary haloalkane → alkene	Primary haloalkane + alcoholic KOH → alkene

e) Why does CH_3-CH_2-I give a precipitate with aqueous silver nitrate earlier than CH_3-CH_2-Cl?

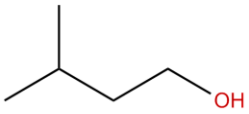
Ans: The strength of the bonds shows that iodo compounds (with the weakest bonds) would be the most reactive halogenoalkanes, while fluoro compounds will be the least reactive i.e., the order of reactivity of halogenoalkanes should be: R – I > R – Br > R – Cl > R –F , so CH_3-CH_2-I give a precipitate with aqueous silver nitrate earlier than CH_3-CH_2-Cl.

Unit 22: HYDROXY COMPOUNDS

Quick Check 22.1

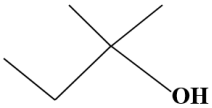
Which ones of these are 1 , 2 and 3 alcohols?

a)



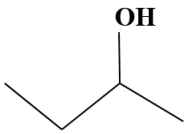
1°

b)



3°

c)

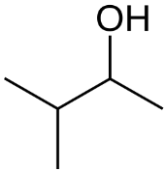


2°

d)

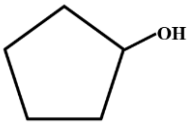
1°

e)



2°

f)



2°

Quick Check 22.2

a) Compare the relative acidic strength of methanol and ethanol.

Ans: Methanol is slightly more acidic than ethanol.

$CH_3OH > C_2H_5OH$

Acidity depends on how stable the conjugate base is after losing H^+:

Methanol → CH_3O^- (methoxide)

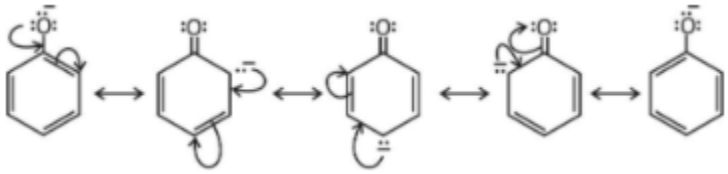
Ethanol → $C_2H_5O^-$ (ethoxide)

The ethyl group ($-C_2H_5$) has a stronger (electron-releasing) effect than the methyl group ($-CH_3$). It pushes electron density toward the oxygen, making the ethoxide ion less stable.

Therefore, ethanol is less willing to lose H^+.

b) Showing the electron delocalization explain why the phenoxide (PhO^-) is more stable than the ethoxide ion ($C_2H_5O^-$).

Ans: The key difference is that the negative charge in phenoxide can be delocalized into the benzene ring, whereas in ethoxide it remains localized on oxygen.



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.**

Ans:

i. Predict in which beaker the hydrogen gas will be evolved earlier and more rapidly.

Phenol will react with sodium earlier and more rapidly than ethanol.

The reactions are:

$$2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2 \uparrow$$

$$2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2 \uparrow$$

Phenol is more acidic than ethanol because its conjugate base, the phenoxide ion ($C_6H_5O^-$), is stabilized by resonance. The ethoxide ion ($C_2H_5O^-$) does not have this resonance stabilization.

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?

Phenolphthalein is colorless in acidic/neutral solution but turns pink in alkaline solution.
When sodium reacts with phenol or ethanol, it produces their sodium salts, which make the solution alkaline:

$$C_6H_5OH + Na \rightarrow C_6H_5ONa + \frac{1}{2}H_2$$

$$C_2H_5OH + Na \rightarrow C_2H_5ONa + \frac{1}{2}H_2$$

So the visual change will be: Colorless → pink
The phenol beaker will show the change faster, because sodium reacts more rapidly with the more acidic phenol, producing the alkaline sodium phenoxide more quickly.

Quick Check 22.3

a) How will you prepare propanol from propene? Give reaction.

Ans: Propanol can be prepared from propene by hydration (addition of water) in the presence of an acid catalyst such as H_3PO_4.

$$CH_3CH = CH_2 + H_2O \xrightarrow{H_3PO_4} CH_3CH(OH)CH_3$$

b) Suggest a suitable ester for the preparation of methanol. Provide the reaction equation.

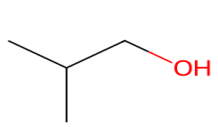
Ans: A suitable ester for preparing methanol is methyl ethanoate (methyl acetate), CH3COOCH3.
On hydrolysis, it gives methanol and ethanoic acid:

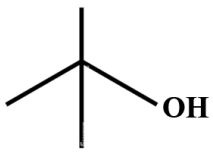
$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

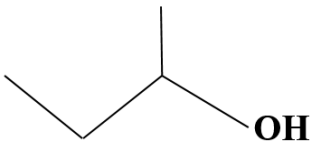
Quick Check 22.4

a) **Three alcohols A, B and C are structural isomers of $C_4H_{10}O$. Each alcohol is refluxed with acidified dichromate (VI), H^+/CrO_7^{2-} .**

A) **B)** **C)**







i) Write the systematic name for alcohol C.

Ans: 2-Butanol

ii) Write the equation for the complete combustion of alcohol A.

Ans:

$$2(CH_3)_2CHCH_2OH + 12O_2 \rightarrow 8CO_2 + 10H_2O$$

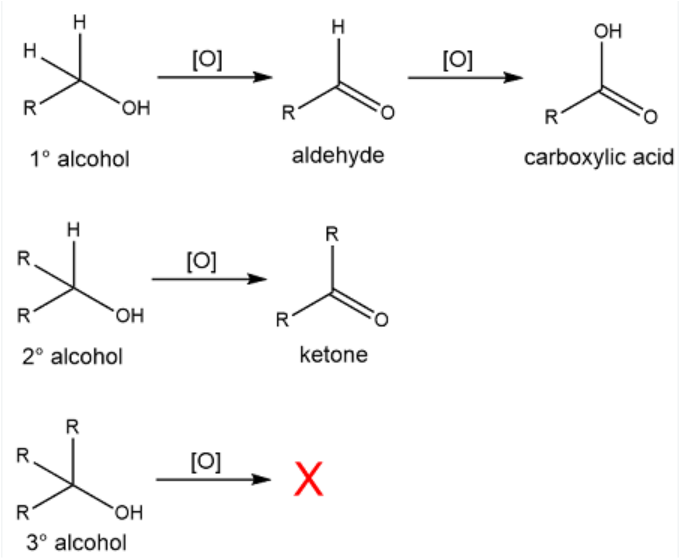
b) **Acidified potassium manganite (VII), $KMnO_4$, is a purple oxidizing agent. What colour change would you observe when alcohols are oxidized with manganate ions (MnO_4^{2-}).**

Ans: When an alcohol is oxidized by acidified potassium manganate(VII), $KMnO_4$, the purple manganite (VII) ions (MnO_4^-) are reduced to Mn^{2+}, which is colourless**.**
Therefore, the observed colour change is:

Purple → Colourless

c) **Draw the structures for the organic products of the oxidation of the given alcohols. If there is no reaction, write 'NONE'.**

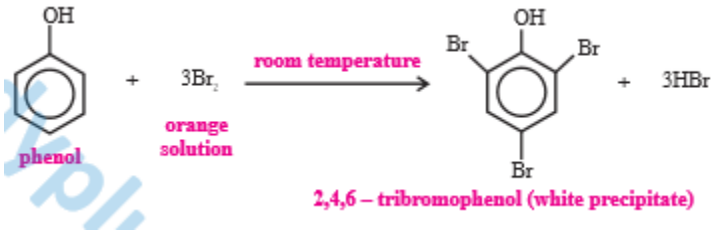
Ans:



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: The orange/brown colour of bromine water disappears, and a white precipitate is formed.



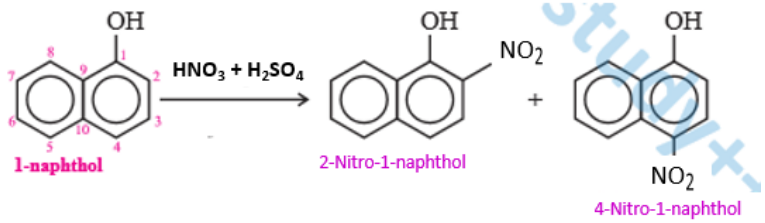
b) Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why?

Ans: 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.

c) Write the reaction equation for nitration of 1-naphthol.

Ans:



Q1. MULTIPLE CHOICE QUESTIONS

1 Encircle The Correct Answer.

I. Which compound can be oxidized to form $(CH_3)\ CH_2COCH_3$?

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 sulfuric 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?

$CH_3\ CH_3 \rightarrow CH_3\ CH_2\ Cl \rightarrow CH_3\ CH_3\ OH \rightarrow CH_2 = CH_2 \rightarrow CH_3CH_2\ Br$

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-l-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 color 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?

$CH_3\ CH_2\ CH\ OH\ CH_3 \rightarrow CH_3\ CH_2\ CH\ Br\ CH_3$

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 prpan-1-ol and propan-2-ol.

a) Br_2 and NaOH b) I_2 and NaOH

c) Acidified $K_2Cr_2O_7$✓ d) NaOH $_{(aq)}$

Q2. SHORT ANSWER QUESTIONS

a) Four alcohols are given below:

i. butan-2-ol **ii. 2-methylpentan-3-ol**

iii. 2-methylpropan-2-ol **iv. propan-1-ol**

i. Which alcohol is an example of a tertiary alcohol?

Ans: 2-Methylpropan-2-ol

ii. Which alcohol is an example of an alcohol that can be oxidized to carboxylic acid?

Ans: Propan-1-ol

iii. Which alcohols are examples of an alcohol that can be oxidised to a ketone?

Ans: Butan-2-ol

iv. Which alcohol cannot change color of acidified potassium dichromate?

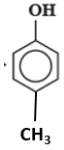
Ans: 2-methylpropan-2-ol

b) 4-methylaniline reacts with $HNO_{3(aq)}$ 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.

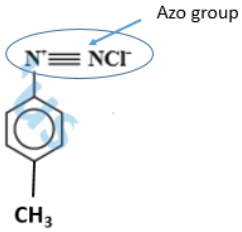
Ans:

P Q



ii) Circle the azo group on your structure.

Ans:



iii) Give the IUPAC name of Q.

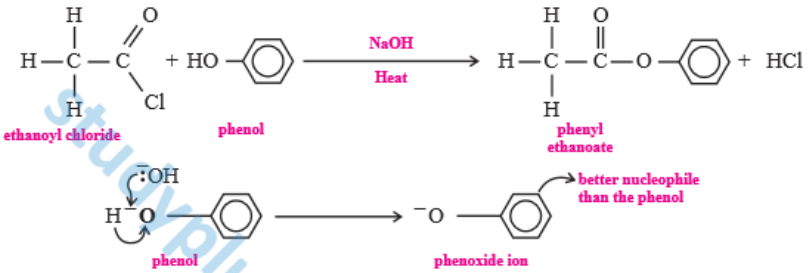
Ans: 4-Methylphenol

c) How phenol reacts with:

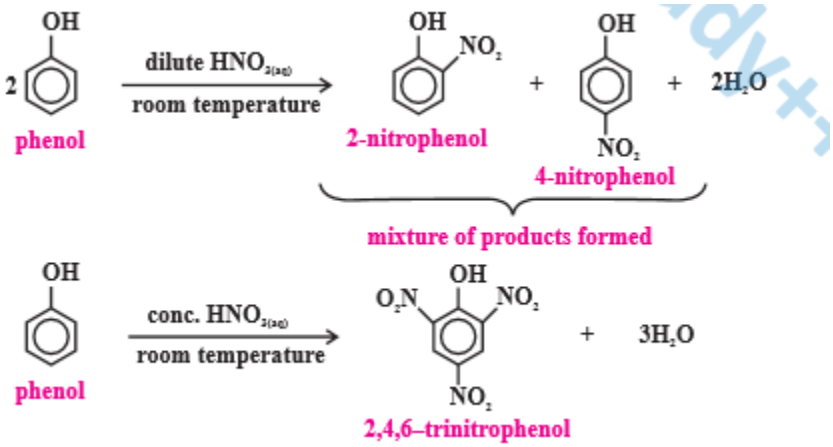
i) CH_3COCl **ii) dil. HNO_3/25°C**

Ans:

i) CH_3COCl



ii) dil. HNO_3/25°C



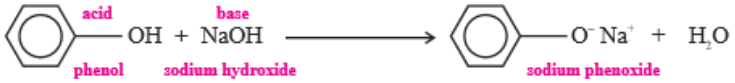
d) What is difference between the reactions of phenol with:

i) NaOH **ii) Na metal**

Ans:

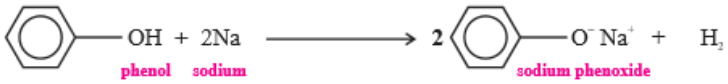
i. Reaction with bases

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

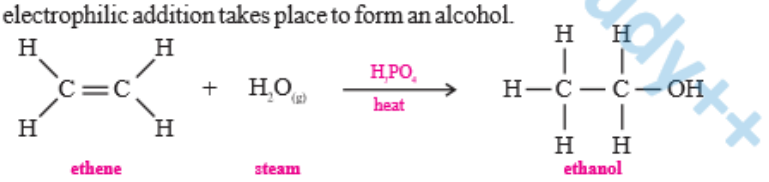
Molten phenols react vigorously with reactive metals such as sodium (Na). This is also an acid-base reaction. Now, a soluble salt is formed and hydrogen gas is given off.



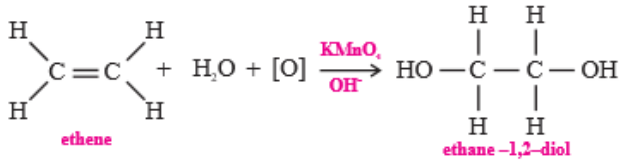
e) How alcohols can be prepared from alkene? Give two examples.

Ans:

I) 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.

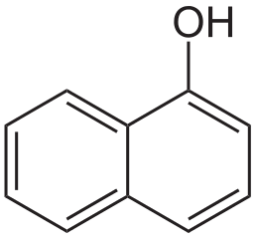


ii. Alcohols are obtained by the oxidation of alkenes with cold, dilute $KMnO_4$, a mild oxidising agent.



f) Why 1-naphthol does not give substitution at position 9 and 10?

Ans: Positions 9 and 10 are the fusion (bridgehead) carbons of the naphthalene ring. They are bonded to three carbon atoms and are part of the ring junction:



g) How will you convert propanal to propan-1-ol?

Ans:

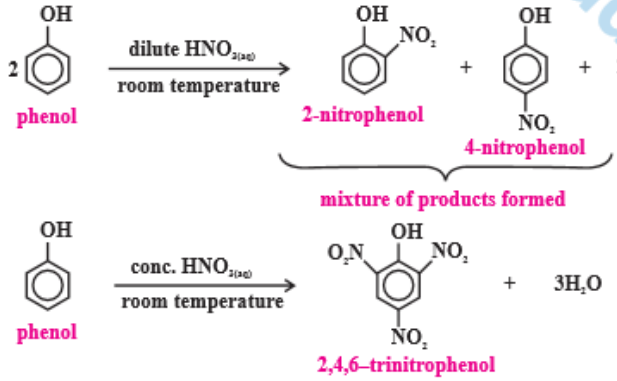
Q3. CONSTRUCTED RESPONSE QUESTIONS

a) Why nitration of phenol is easier than benzene. Which product is formed when phenol is nitrated with conc. HNO at room temperature?

Ans:

i. Nitration

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.

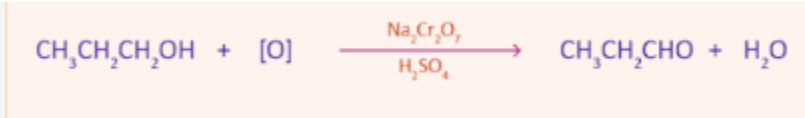


b) Sodium hydroxide reacts with phenol but not with ethanol. Give reason.

Ans: Sodium hydroxide reacts with phenol but not with ethanol because phenol is sufficiently acidic to donate H^+, whereas ethanol is too weakly acidic.

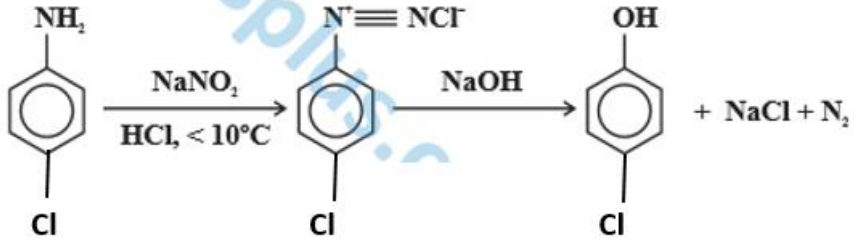
c) How propanol can be converted into propanal?

Ans:



d) Convert 4-chloroaniline into 4-chlorophenol.

Ans:



DESCRIPTIVE QUESTIONS

Q4. Explain the acidity of phenol

Q5. Describe any four methods for the preparation of phenol.

Q6. Describe the oxidation reactions of alcohols.

Q7. Explain nitration and bromination of phenol.

UNIT 23:
Carbonyl Compounds and Carboxylic Acids

Quick Check 23.1

a) Draw the structures of the following according to IUPAC system

i) 2-methylbutanal

$CH_3–CH_2–CH(CH_3)–CHO$

ii) Pentan-3-one

$CH_3–CH_2–CO–CH_2–CH_3$

iii) 3-methylpentanal

$CH_3–CH_2–CH(CH_3)–CH_2–CHO$

iv) 4-methylpentan-3-one

$CH_3–CH_2–CO–CH(CH_3)–CH_3$

b) Name the following compounds (IUPAC system).

i) –CHO

Benzaldehyde

ii) $(CH_3)_3C–CHO$

2-methylpropanal

iii) $(CH_3CH_2CH_2)_2C=O$

Heptan-4-one

c) Rank the following compounds in order of increasing reactivity towards nucleophilic attack.

i) $(CH_3)_3C–CO–CH_3$ ii) $(CH_3)_3C–CO–C(CH_3)_3$ iii) $(CH_3)_2CO$

$(CH_3)_3C–CO–C(CH_3)_3 < (CH_3)_3C–CO–CH_3 < (CH_3)_2CO$

Increasing alkyl substitution around the carbonyl carbon increases steric hindrance and increases electron donation toward the carbonyl group. Both effects make nucleophilic attack less favorably. Therefore, di-tert-butyl ketone is least reactive, tert-butyl methyl Ketone is intermediate, and acetone is most reactive.

Quick Check 23.2

a) If compound A has molecular formula C_3H_6O and 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 and B)

Compound A is propan-2-one (acetone), CH_3COCH_3.

Compound B is propan-2-ol (isopropanol), $CH_3CHOHCH_3$.

Reason: $NaBH_4$ reduces a ketone to the corresponding secondary alcohol. Both acetone and propan-2-ol give the iodoform test, producing yellow iodoform (CHI_3).

b) Why does methanol not give the iodoform test while ethanol does?

Ethanol (CH_3CH_2OH) is oxidized to ethanal (CH_3CHO), which can give the iodoform test. Methanol (CH_3OH) is oxidized to methanal (HCHO), which does not contain the required methyl carbonyl arrangement. Therefore, ethanol gives the yellow iodoform precipitate, whereas methanol does not.

c) Tests to distinguish between the following pairs

i) CH_3CH_2CHO and CH_3COCH_3

Tollens' test. Propanal gives a silver mirror because it is an aldehyde, whereas propanone gives no silver mirror.

ii) $CH_3CH_2COCH_2CH_3$ and $CH_3CH_2CH_2COCH_3$

Iodoform test. Pentan-3-one does not contain a $CH_3CO–$ group and gives no yellow precipitate in Iodoform test. Pentan-2-one contains the $CH_3CO–$ group and gives yellow iodoform.

iii) $CH_2=CH–CH_2OH$ and CH_3CH_2CHO

Tollens' test. Propanal gives a silver mirror, while allyl alcohol does not.

Quick Check 23.3

a) Write the equation for the oxidation of propanol with acidified $K_2Cr_2O_7$?

$CH_3CH_2CH_2OH + 2[O] \xrightarrow{(K_2Cr_2O_7 / H_2SO_4, \text{ heat})} CH_3CH_2COOH + H_2O$

b) What products do you expect from following? Give the chemical equations.

i) Hydrolysis of CH_3CH_2CN

$CH_3CH_2CN + 2H_2O \xrightarrow{(\text{dil. HCl, heat})} CH_3CH_2COOH + NH_4Cl$

Product: Propanoic acid

ii) Oxidation of ethylbenzene

$C_6H_5CH_2CH_3 + 6[O] \xrightarrow{(KMnO_4, \text{ heat})} C_6H_5COOH + CO_2 + 2H_2O$

Products: Benzoic acid and carbon dioxide

iii) Hydrolysis of ethyl ethanoate

$CH_3COOCH_2CH_3 + H_2O \xrightarrow{(\text{dil. acid, heat})} CH_3COOH + CH_3CH_2OH$

Products: Ethanoic acid and ethanol

Quick Check 23.4

a) Methanoic acid is stronger than ethanoic acid. Give reason.

Methanoic acid is stronger than ethanoic acid because the methyl group ($-CH_3$) in ethanoic acid has a **+I effect**, which destabilizes the carboxylate ion and decreases acidity. Methanoic acid has no 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) $CH_3CHClCOOH$

$CH_3CCl_2COOH > CH_3CHClCOOH > CH_3CH_2COOH$

c) Explain why ethanoic acid is stronger than ethanol.

Ethanoic acid is stronger than ethanol because its conjugate base, the **ethanoate ion**, is stabilized by delocalization of the negative charge around the $-COOH$ group. This makes ethanoic acid more likely to release H^+.

Quick Check 23.5

a) Why do phenols not react directly with carboxylic acids to form phenyl esters?

Phenols do not react directly with carboxylic acids to form phenyl esters because the reaction is not favorable. Phenyl esters are prepared by reacting phenol with an acyl chloride.

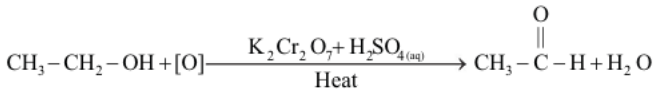
b) Phenyl ethanoate is the ester responsible for the fragrance of peach and strawberries. It can be prepared from ethanoyl chloride and phenol. Write down a chemical reaction for the preparation of this ester.
$CH_3COCl + C_6H_5OH \rightarrow CH_3COOC_6H_5 + HCl$
Ethanoyl chloride + Phenol → Phenyl ethanoate + HCl

c) Predict the products of the following reactions, write the chemical equations.
i) Chlorobenzene and ethanol
No reaction occurs under ordinary conditions.
$C_6H_5Cl + C_2H_5OH \rightarrow$ No reaction
ii) Propanoyl chloride and phenol
$CH_3CH_2COCl + C_6H_5OH \rightarrow CH_3CH_2COOC_6H_5 + HCl$
Propanoyl chloride + Phenol → Phenyl propanoate + HCl

Q2. Short-Answer Questions

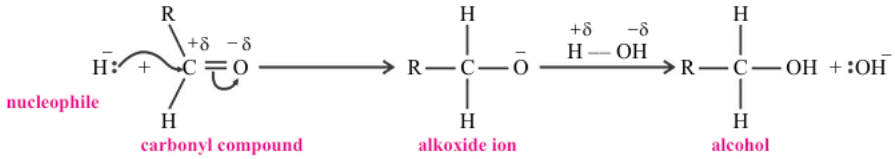
Q1. How is ethanol converted to acetic acid?

Ethanol is oxidized to ethanal by acidified $K_2Cr_2O_7$ or acidified $KMnO_4$. Ethanal is further oxidized to ethanoic acid (acetic acid).



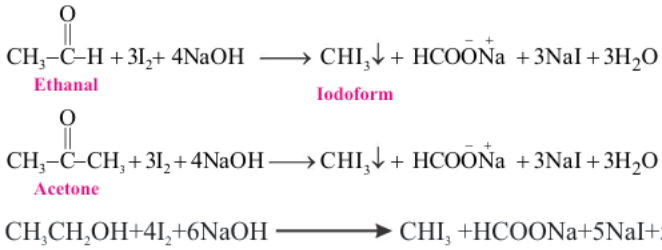
Q2. Give the mechanism for the reductions of ethanal with $NaBH_4$.

A hydride ion (H^-) from $NaBH_4$ acts as a nucleophile and attacks the partially positive carbon atom of the carbonyl group. The C=O π bond breaks and the electrons move towards oxygen, forming an alkoxide ion. The alkoxide ion then accepts H^+ from water to form ethanol.



Q3. What is iodoform reaction?

The iodoform reaction is a reaction in which compounds containing the CH_3CO- group (methyl ketones) or $CH_3CH(OH)-$ group react with iodine (I_2) in the presence of sodium hydroxide (NaOH) to form iodoform (CHI_3), a yellow crystalline precipitate. The appearance of a yellow precipitate of iodoform confirms the presence of the CH_3CO- group. Ethanal, methyl ketones, and ethanol give a positive iodoform test, while methanol does not.



$$CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

Q4. Methanoic acid can be oxidized but other carboxylic acids cannot. Why?

Methanoic acid can be oxidized by both weak and strong oxidizing agents because it contains an aldehydic portion (−CHO) in its structure. This aldehydic portion makes methanoic acid a strong reducing agent and allows it to be readily oxidized. It is the only monocarboxylic acid that gives a positive Tollens' test and Fehling's test. Other carboxylic acids do not show these reactions.

Q5. Explain the influence of chlorine substitution on the acidity of carboxylic acids

Chlorine is an electron withdrawing group (−I effect). It stabilizes the carboxylate ion by dispersing its negative charge and hence increases the acidity of carboxylic acids. The greater the number of chlorine atoms, the stronger the acid.

For example:

$ClCH_2COOH$, pKa = 2.86
$Cl_2CHCOOH$, pKa = 1.26
Cl_3CCOOH, pKa = 0.64

Thus, chloroacetic acid is stronger than ethanoic acid, while dichloroethanoic acid and trichloroacetic acid are even stronger.

Q6. Give the reaction of acyl chloride with phenol.

When phenol is heated with an acyl chloride in the presence of a base, an ester is produced. The base deprotonates phenol to form a phenoxide ion, which attacks the carbonyl carbon of the acyl chloride.

$CH_3COCl + C_6H_5OH \rightarrow CH_3COOC_6H_5 + HCl$

Ethanoyl chloride + Phenol → Phenyl ethanoate + HCl

Q7. Explain why carboxylic acid is more acidic than ethanol

Carboxylic acids are more acidic than ethanol because the conjugate base of carboxylic acid is more stable. In the carboxylate ion, the negative charge is delocalized around the –COOH group, which stabilizes the ion. Therefore, carboxylic acids release H^+ more readily than ethanol, hence more acidic.

Q8. Give reaction of methanal with the Tollen's reagent.

Methanal reacts with Tollens' reagent on gentle warming and reduces silver ions to metallic silver, forming a silver mirror.

$HCHO + 2[Ag(NH_3)_2]OH \rightarrow HCOONH_4 + 2Ag + 3NH_3 + H_2O$

The formation of a silver mirror confirms the presence of an aldehyde.

Q9. 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

i) 2-Methylhexanal
$CH_3CH_2CH_2CH_2CH(CH_3)\ CHO$

ii) 2-Methyl-3-pentanone
$CH_3CH(CH_3)\ COCH_2CH_3$

iii) 3-Hydroxypentanal
$CH_3CH_2CH(OH)CH_2CHO$

iv) 4-Nitro-2-pentanone
$CH_3COCH_2CH(NO_2)\ CH_3$

v) 2-Chlorobutanol
$CH_3CH_2CH(Cl)CH_2OH$

Q3. Constructed-Response Questions

a) Write the equation for the reaction of CH_3CH_2CHO with $LiAlH_4$ (dry ether).
Propanal is reduced to propanol by $LiAlH_4$ in dry ether, followed by hydrolysis.
$CH_3CH_2CHO \xrightarrow{LiAlH_4,\ \text{dry ether}} CH_3CH_2CH_2OH$

b) An alcohol, $C_4H_{10}O$, undergoes oxidation to form butanoic acid, $C_4H_8O_2$. Give a chemical equation along with conditions.
The alcohol must be butan-1-ol, a primary alcohol. On strong oxidation, it gives butanoic acid.
$CH_3CH_2CH_2CH_2OH + 2[O] \rightarrow CH_3CH_2CH_2COOH + H_2O$
Conditions: acidified $K_2Cr_2O_7$ (or another suitable strong oxidizing agent), heat under reflux.

c) Write the structures of all the isomeric alcohols with formula $C_4H_{10}O$. Give their systematic names. Which ones form butanoic acid? Explain why others do not.
1. $CH_3CH_2CH_2CH_2OH$ — butan-1-ol
2. $CH_3CH(OH)CH_2CH_3$ — butan-2-ol
3. $(CH_3)_2CHCH_2OH$ — 2-methylpropan-1-ol
4. $(CH_3)_3COH$ — 2-methylpropan-2-ol
Only butan-1-ol forms butanoic acid because it is a primary alcohol with the required straight-chain carbon skeleton. Butan-2-ol is a secondary alcohol and is oxidized to a ketone rather than a carboxylic acid. 2-Methylpropan-1-ol is primary but gives 2-methylpropanoic acid, not butanoic acid. 2-Methylpropan-2-ol is tertiary and does not undergo ordinary oxidation to a carboxylic acid.

d) Propanoic acid can be reduced to propan-1-ol by $LiAlH_4$. Give a balanced chemical equation. Can $NaBH_4$ be used? If not, give a reason.
Balanced equation:
$CH_3CH_2COOH + 4[H] \xrightarrow{LiAlH_4,\ \text{then } H_2O} CH_3CH_2CH_2OH + H_2O$
$NaBH_4$ is not normally used for this reduction because it is a milder reducing agent and does not readily reduce carboxylic acids to primary alcohols under ordinary conditions. $LiAlH_4$ is sufficiently strong to reduce the carboxylic acid group.

Multiple Choice Questions

I. **b) Secondary alcohol**

II. **c) Pentan-3-one**

III. **b) Ester**

IV. **c) CO_2**

V. **a) Primary**

VI. **b) sp^2**

VII. **b) CH_3COCl**

VIII. **b) Electron withdrawing due to −I**

IX. **c) Carbon dioxide and water**

X. **c) Addition-elimination**

UNIT 24: Organic Nitrogen Compounds

Multiple Choice Questions

I. **b) Metamers**

II. **b) R_2NH**

III. **d) Diethyl amine**

IV. **c) Carboxylic acid**

V. **b) 2,4,6-Tribromophenylamine**

VI. **c) Azo compound**

VII. **a) R–N=N–R**

VIII. **a) Nitrogen**

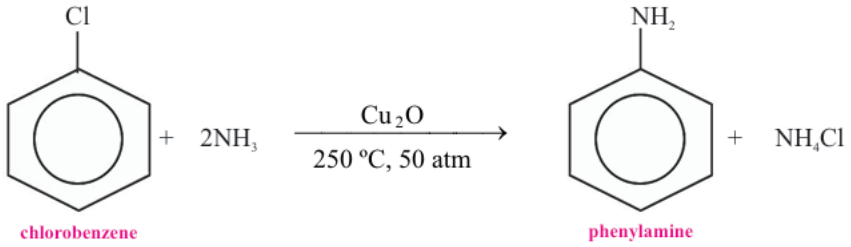
IX. **c) Zwitterion**

X. **a) Primary**

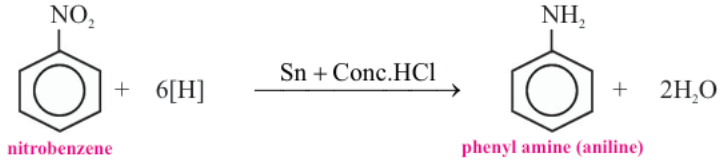
Q.2. Short-Answer Questions

Q1. Give two preparations of phenyl amine.

Phenylamine is prepared by the ammonolysis of chlorobenzene with ammonia in the presence of Cu_2O at 250°C and 50 atm pressure.

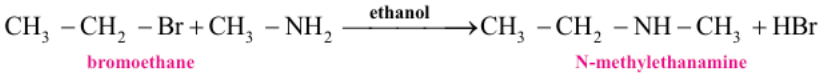


Phenylamine is prepared by the reduction of nitrobenzene with Sn and concentrated HCl.

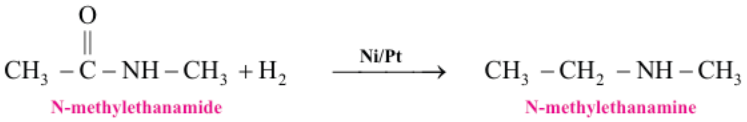


Q2. Give two preparations of secondary amines.

Secondary amines can be prepared by the alkylation of primary amines. When a halogenoalkane reacts with a primary amine in the presence of ethanol under pressure secondary amine is formed.



Secondary amines are also prepared by the reduction of N-substituted amides



Q3. What is the chromophore in azo dyes? What is its function in dyes?

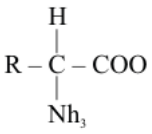
The azo group (−N=N−) in azo dyes is called the chromophore. It is responsible for the intense color of the dyes, ranging from yellow and orange to red, blue and green, depending upon the other groups attached to the benzene rings.

Q4. Why amides are less basic than ammonia?

Amides are less basic than ammonia because the lone pair of electrons on nitrogen participates in resonance with the carbonyl group. This delocalization reduces the availability of the lone pair on nitrogen to accept H^+, thereby decreasing the basicity of amides.

Q5. What is zwitterion?

A zwitterion is a dipolar ion of an α-amino acid having both a positive and a negative charge within the same molecule. It is formed when a proton transfers from the carboxyl group to the amino group. It is also called an internal salt.



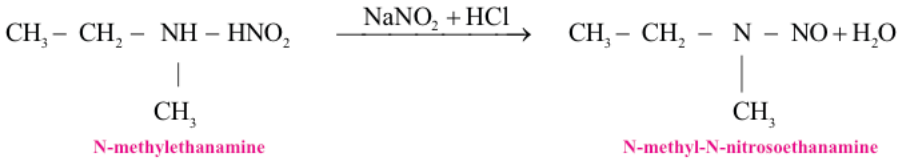
Zwitter ionic structure

Q6. Differentiate between primary, secondary & tertiary amines by a chemical test.

Primary, secondary and tertiary amines can be distinguished by their reaction with **nitrous acid (HNO_2)**.

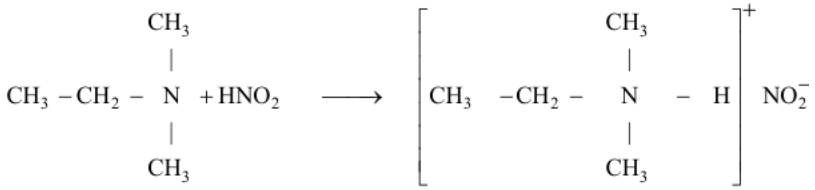
- **Primary amines:** React with HNO_2 to produce **nitrogen gas (N_2)**, seen as bubbles. The process is called **diazotization**.

- **Secondary amines:** React with HNO_2 to produce **N-nitrosoamines**, which are **yellow oily liquids**.



N-methylethanamine — N-methyl-N-nitrosoethanamine

- **Tertiary amines:** React with HNO_2 to form **soluble nitrite salts**. There is **no visible sign of reaction**.



N,N-dimethylethanamine — N,N -dimethylethanammonium nitrite (soluble)

Q7. Write names & structures of four isomeric amines having the molecular formula C_3H_9N.

1. Propan-1-amine $CH_3–CH_2–CH_2–NH_2$
2. Propan-2-amine $CH_3–CH(NH_2)–CH_3$
3. Ethyl methylamine $CH_3–CH_2–NH–CH_3$
4. Trimethylamine $(CH_3)_3N$

Q8. How will you synthesize ethanal from ethanenitrile?

Ethanenitrile is partially reduced to an imine salt, which hydrolysis gives ethanal. This reaction converts the −CN group of ethanenitrile into the −CHO group of ethanal.

CH_3CN — $(SnCl_2 / HCl) \rightarrow CH_3CH{=}NH{\cdot}HCl$ —$(H_2O)\rightarrow CH_3CHO$

Q9. Define peptide bond. How many peptide bonds are there in a tripeptide?

A peptide bond is the amide bond formed between the −COOH group of one amino acid and the $-NH_2$ group of another amino acid, with elimination of a water molecule.

A tripeptide is formed by the condensation of three amino acids. Therefore, it contains 2 peptide bonds.

Q10. Give all the dipeptides that could possibly be synthesized from glycine (Gly), alanine (Ala)

If glycine (Gly) and alanine (Ala**)** are used to form dipeptides, there are **four possible dipeptides**, because the order of amino acids matters:

1. Gly–Gly (Glycylglycine)
   $H_2N–CH_2–CO–NH–CH_2–COOH$
2. Gly–Ala (Glycylalanine)
   $H_2N–CH_2–CO–NH–CH(CH_3)–COOH$

3. Ala–Gly (Alanylglycine)
   $H_2N–CH(CH_3)–CO–NH–CH_2–COOH$

4. Ala–Ala (Alanylalanine)
   $H_2N–CH(CH_3)–CO–NH–CH(CH_3)–COOH$

Q11. Arrange cyclohexanamine, benzenamine, benzamide, and ethanamide in increasing order of their basic strength. Justify the order as well.

Benzamide < Ethanamide < Benzenamine < Cyclohexanamine

Benzamide ($C_6H_5CONH_2$) – The lone pair on nitrogen is strongly delocalized into the carbonyl group and is also influenced by the phenyl group, making it the weakest base.

Ethanamide (CH_3CONH_2) – Its nitrogen lone pair is also delocalized into the carbonyl group, so it is a very weak base, but the electron-releasing CH_3 group makes it somewhat more basic than benzamide.

Benzenamine (aniline, $C_6H_5NH_2$) – The nitrogen lone pair is delocalized into the benzene ring, reducing its availability for accepting a proton. Therefore, it is less basic than aliphatic amines.

Cyclohexanamine ($C_6H_{11}NH_2$) – The nitrogen lone pair is localized and readily available for protonation. The alkyl group has an electron-releasing (+I) effect, making it the strongest base among these compounds.

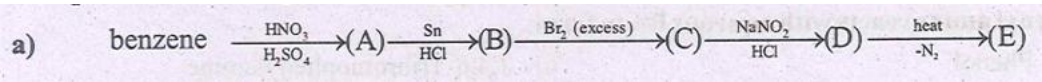
Q12. Give the chemical equation for the reaction between cyclohexanamine and excess of bromomethane.

The reaction of cyclohexanamine with excess bromomethane (CH_3Br) proceeds through successive alkylation and ultimately forms a quaternary ammonium salt.

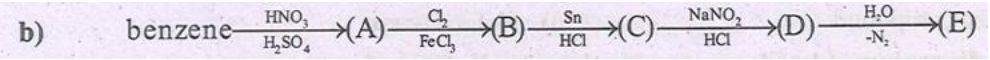
$C_6H_{11}NH_2 + 3CH_3Br \rightarrow [C_6H_{11}N(CH_3)_3]^+Br^- + 2HBr$

Q.3. Constructive-Response Questions

Complete the following reaction sequence by giving the structures of the compounds.



A = nitrobenzene $C_6H_5–NO_2$
B = Phenyl amine $C_6H_5–NH_2$
C = 2,4,6-tribromo phenyl amine 2,4,6-$Br_3C_6H_2–NH_2$
D = 2,4,6-tribromo phenyl diazonium chloride 2,4,6-$Br_3C_6H_2–N_2^+Cl^-$
E =2,4,6-tribromo phenol 2,4,6-$Br_3C_6H_2–OH$



A = nitrobenzene $C_6H_5–NO_2$

B = Meta chloronitrobenzene m-$ClC_6H_4–NO_2$
C = Meta chlorophenyl amine m-$ClC_6H_4–NH_2$
D = Meta chlorophenyl diazonium chloride m-$ClC_6H_4–N_2^+Cl^-$
E = Meta chlorophenol m-$ClC_6H_4–OH$

c) Keeping in view the above (a,b) scheme, devise a reaction sequence to prepare 4-hydroxybenzoic acid from benzene.

Benzene —$CH_3Cl/AlCl_3$→ Toluene
Toluene —conc. HNO_3/H_2SO_4→ p-Nitrotoluene (isolate the para isomer)
p-Nitrotoluene —$KMnO_4$, heat; then H^+→ p-Nitrobenzoic acid
p-Nitrobenzoic acid —Sn/HCl→ p-Aminobenzoic acid
p-Aminobenzoic acid —$NaNO_2$/HCl, 0–5 °C→ p-Carboxybenzenediazonium chloride
p-Carboxybenzenediazonium chloride —H_2O, heat; $-N_2$→ 4-Hydroxybenzoic acid
Overall structural sequence:
$C_6H_6 \rightarrow C_6H_5CH_3 \rightarrow p\text{-}NO_2C_6H_4CH_3 \rightarrow p\text{-}NO_2C_6H_4COOH \rightarrow p\text{-}NH_2C_6H_4COOH \rightarrow p\text{-}HO–C_6H_4–COOH$

d) Draw the electrophoretic separation of alanine (pI=6.02), lysine (pI=9.74) and glutamic acid (pI=3.22) at pH 9.7.

Given pI values: Glutamic acid = 3.22, Alanine = 6.02, Lysine = 9.74.
Principle: If pH > pI, the amino acid has a net negative charge and migrates toward the anode (+). If pH < pI, it has a net positive charge and migrates toward the cathode (−).
At pH 9.7:
• Glutamic acid (pI 3.22): strongly negative → moves toward the anode.
• Alanine (pI 6.02): negative → moves toward the anode.
• Lysine (pI 9.74): pH ≈ pI → approximately neutral, so it remains close to the origin.
Expected separation:

```
Cathode (−)        Origin              Anode (+)
                Lysine    Alanine    Glutamic acid
                |----------------------→----------→
```

Thus, glutamic acid travels farthest toward the anode, alanine travels a shorter distance toward the anode, and lysine remains near the origin.

Quick Check 24.1

a) Give IUPAC names of the following compounds

i) $CH_3–CH(CH_3)–CH_2–CH_2–CH_2–NH_2$

4-Methylpentan-1-amine

ii) $CH_3–CH_2–CH(NH_2)–CH_3$

Butan-2-amine

iii) $CH_3–CH_2–CH_2–CH_2–NH–CH_2–CH_3$

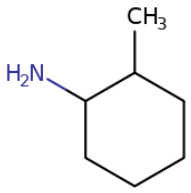
N-Ethylbutan-1-amine

b) Draw structures corresponding to each amine

i) 2,4-Dimethylhexan-3-amine
$CH_3–CH(CH_3)–CH(NH_2)–CH(CH_3)–CH_2–CH_3$

ii) N-Methylpentan-1-amine
$CH_3–NH–CH_2–CH_2–CH_2–CH_2–CH_3$

iii) 2-Methylcyclohexan-1-amine



iv) N,N-Dimethyl ethanamine
$CH_3–CH_2–N(CH_3)_2$

Quick Check 24.2

a) The feel-good factor in chocolate has been identified as 2-phenyl ethanamine $C_6H_5–CH_2–CH_2–NH_2$. Suggest a synthesis of this compound from chloromethylbenzene $C_6H_5–CH_2–Cl$.

Synthesis of 2-phenylethanamine from choro methylbenzene

$C_6H_5–CH_2–Cl + KCN \rightarrow C_6H_5–CH_2–CN + KCl$

$C_6H_5–CH_2–CN + 4[H] \rightarrow C_6H_5–CH_2–CH_2–NH_2$

Reducing agent: $LiAlH_4$ followed by hydrolysis (or catalytic hydrogenation, H_2/Ni).

b) Provide the reactions of a nitrile and an amide to yield each of the following amines.

i) $CH_3–CH(CH_3)–CH_2–NH_2$

From nitrile:

$(CH_3)_2CH–CN + 4[H] \rightarrow (CH_3)_2CH–CH_2–NH_2$

Reagent: $LiAlH_4$, followed by H_2O

From amide:

$(CH_3)_2CH–CONH_2 + 4[H] \rightarrow (CH_3)_2CH–CH_2–NH_2 + H_2O$

Reagent: $LiAlH_4$, followed by H_2O

ii) $CH_3–CH_2–CH_2–CH_2–NH_2$

From nitrile:

$CH_3–CH_2–CH_2–CN + 4[H] \rightarrow CH_3–CH_2–CH_2–CH_2–NH_2$

Reagent: $LiAlH_4$, followed by H_2O

From amide:

$CH_3–CH_2–CH_2–CONH_2 + 4[H] \rightarrow CH_3–CH_2–CH_2–CH_2–NH_2 + H_2O$

Reagent: $LiAlH_4$, followed by H_2O

Quick Check 24.3

a) Phenylamine is about a million times less basic than cyclohexylamine. Give reason.

In phenylamine, the lone pair on nitrogen is delocalized into the benzene ring by resonance. Therefore, the lone pair is less available to accept H^+, hence less basic.
In cyclohexylamine, the lone pair is not delocalized, so it is more available to accept H^+, hence more basic than phenylamine.

b) Which of ethanamine and propan-2-amine is more basic? Explain.

Propan-2-amine is more basic.
Alkyl groups have a +I electron-donating effect, which increases the electron density on nitrogen and makes its lone pair more available to accept H^+.
Propan-2-amine has two alkyl groups attached to nitrogen, whereas ethanamine has only one.
Therefore, propan-2-amine is more basic.

c) Show the reaction of propane-2-amine with HCl. Name the salt formed.

Reaction of propan-2-amine with HCl
$(CH_3)_2CHNH_2 + HCl \rightarrow (CH_3)_2CHNH_3^+Cl^-$
The salt formed is propan-2-ammonium chloride.

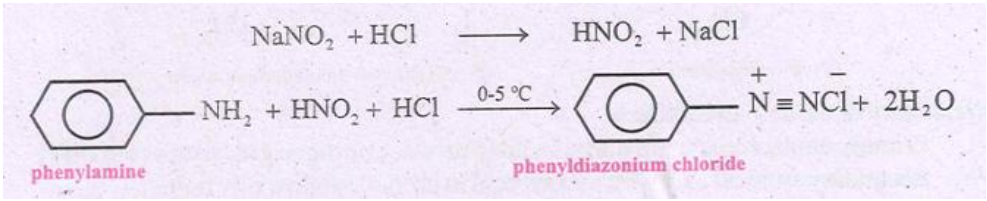
d) Which acid reacts with N, N-dimethylmethanamine (trimethyl amine) in fish when it is treated with vinegar? Write a chemical equation to show this reaction

Vinegar contains ethanoic acid (CH_3COOH).
$(CH_3)_3N + CH_3COOH \rightarrow [(CH_3)_3NH^+]CH_3COO^-$
The salt formed is trimethylammonium acetate salt.

Quick Check 24.4

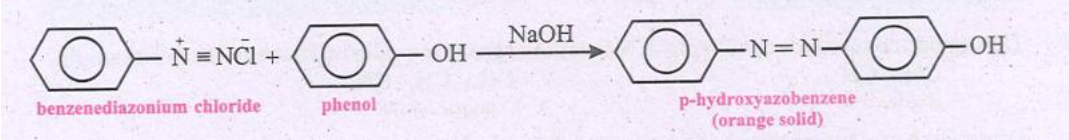
i) How will you Prepare a dye from phenylamine and 2-methylphenol

ii) Give equations stepwise along with the reaction conditions



Step I- Diazotization of phenylamine

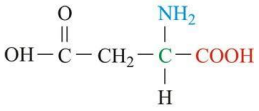
Step II- Azo coupling



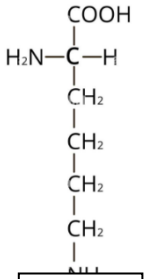
Quick Check 24.5

The R groups in the amino acids aspartic acid and lysine are (–CH_2–COOH) and (–CH_2–CH_2–CH_2–CH_2–NH_2), respectively.

a) Draw the displayed formulae of these amino acids.

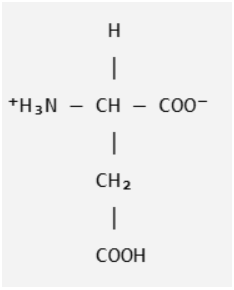


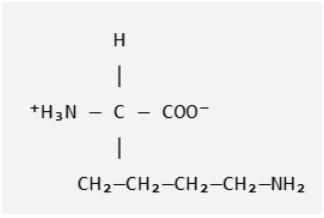
Aspartic Acid



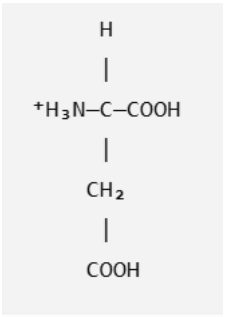
Lysine

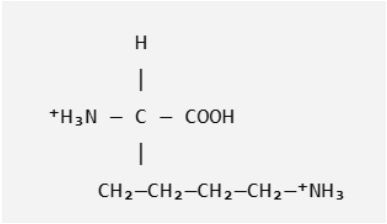
b) Draw the structures of their zwitterions.



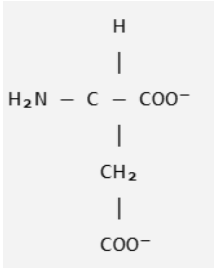


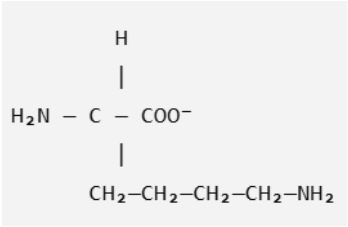
c) Draw the structures of their ions in acidic conditions





d) Draw the structures of their ions in basic conditions





e) Discuss what we mean by the isoelectric point of amino acids

The **isoelectric point (pI)** is the pH at which an amino acid has **no overall electrical charge**. At this pH, the amino acid exists predominantly as a **zwitterion** and does not move towards either electrode in an electric field.

UNIT 25: ORGANIC SYNTHESIS

25.1 Quick check

a) What are the products of oxidation and reduction of aldehydes?

The **oxidation** of aldehydes yields **carboxylic acids**, while the **reduction** of aldehydes yields **primary alcohols**.

Oxidation:

Reduction: $CH_3CHO \xrightarrow{NaBH_4} CH_3CH_2OH$

b) How will you convert an alcohol into: i) bromoalkane ii) aldehyde iii) ester

i. **bromoalkane** : $C_2H_5OH \xrightarrow{HBr} C_2H_5Br + H_2O$

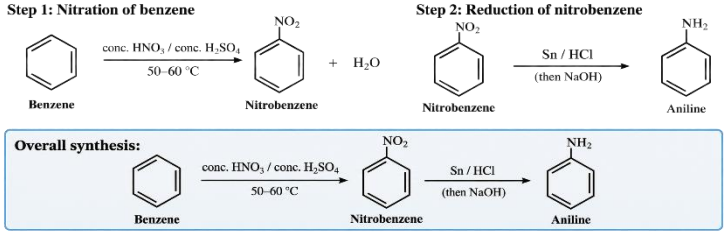
ii.- **aldehyde** $CH_3CH_2OH \xrightarrow[\text{controlled oxidation}]{K_2Cr_2O_7/H^+} CH_3CHO + H_2O$

iii. **ester** $C_2H_5OH + CH_3COOH \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} CH_3COOC_2H_5 + H_2O$

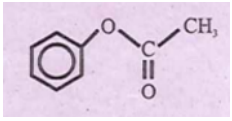
25.2 Quick check

a) Why is the nitration of benzene done during the synthesis of aniline?

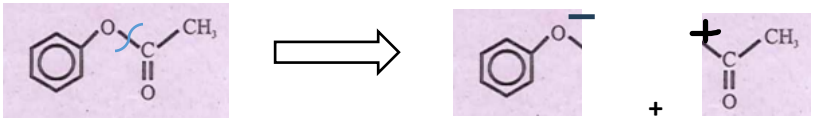
Aniline cannot be prepared conveniently by directly introducing the **–NH_2 group** into benzene. Therefore, benzene is first converted into **nitrobenzene** by nitration. The nitro group can then be easily reduced to an amino group. Thus, nitration provides an effective route for the synthesis of aniline.



b) Phenyl ethanoate is an important molecule used in the synthesis of medicines for hepatitis and various infections.

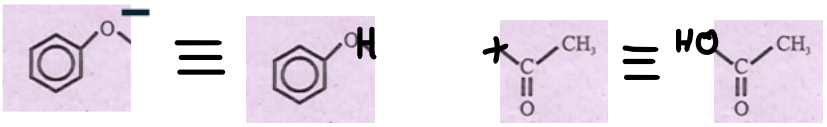


i) Draw its retrosynthesis.



Phenyl ethanoate Synthon (A) Synthon (B)

ii) Write structures of its synthetic equivalents.



Synthon(A) Phenol Synthon (B) Acetic acid

iii) Design its linear synthesis.

$$C_6H_5OH + (CH_3CO)_2O \xrightarrow{NaOH\ /\ H_2O} C_6H_5OCOCH_3 + CH_3COONa$$

Quick Check 25.3

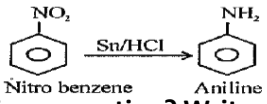
Aspirin and Paracetamol, both are synthesized starting from phenol.

i)What is the overall functional group difference in them?

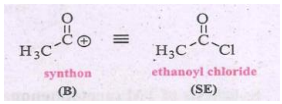
The Aspirin (acetylsalicylic acid) contain Carboxylic acid (–COOH) and Ester ($–OCOCH_3$) in it whereas the Paracetamol (acetaminophen) contain Phenolic –OH and Amide ($–NHCOCH_3$) group.

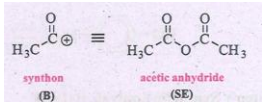
ii) Which FGI (Functional Group Interconversion) is involved when nitrobenzene is converted into aniline?

Reduction is involved when nitrobenzene is converted into aniline.



iii) Which synthon is common in their preparation? Write down its structure and mention its most common synthetic equivalent.





The common synthon is the acetyl synthon; it is involved in the acetylation step in the synthesis of both aspirin and paracetamol. Acetyl chloride and acetic anhydride are the synthetic equivalents that were formed.

Short Answer Questions –Exercise

a) Differentiate between synthesis and retrosynthesis.

Synthesis is the forward process in which a target molecule is prepared from suitable starting materials through a series of chemical reactions.

Retrosynthesis is the reverse planning process in which the target molecule is mentally broken down into simpler compounds.In retrosynthesis, bonds are disconnected to identify suitable synthons and synthetic equivalents.

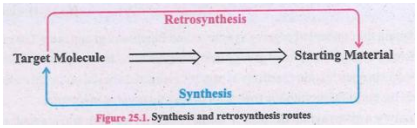


Figure 25.1. Synthesis and retrosynthesis routes

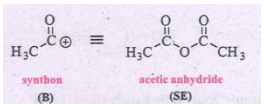
b) How is a carboxylic group converted to an amide group?

A carboxylic acid can be converted into an amide by first reacting it with ammonia to form an ammonium carboxylate salt. On heating, the salt loses water and gives the corresponding amide. For example, ethanoic acid reacts with ammonia and on heating forms ethanamide.

$CH_3COOH + NH_3 \rightarrow CH_3COO^-NH_4^+ \rightarrow$(heat) $CH_3CONH_2 + H_2O$.

c) How are synthons and synthetic equivalents related to each other?

A synthon is an idealized charged fragment obtained by disconnection of a target molecule during retrosynthetic analysis. A synthetic equivalent is the actual reagent or compound used in the laboratory to represent that synthon. So, synthons are conceptual fragments, while synthetic equivalents are real reagents used to construct the desired bond.

d) Write down the formula of a 

common reagent used for oxidation of organic compounds.

A commonly used oxidizing reagent is acidified potassium dichromate.

Its formula is $K_2Cr_2O_7$, usually used with dilute H_2SO_4 to provide the acidic medium.

For example, a primary alcohol can be oxidized to a carboxylic acid using this reagent.

$CH_3CH_2OH \xrightarrow{(K_2Cr_2O_7/H_2SO_4,\ heat)} CH_3COOH + H_2O$.

e) Show with equations how an alcohol can be converted into amines, alkenes and haloalkanes.

An alcohol can be converted into an amine by replacing the –OH group with $–NH_2$ through a suitable substitution sequence.

$C_2H_5OH \xrightarrow{(NH_3,\ heat)} C_2H_5NH_2$

It can be dehydrated with concentrated H_2SO_4 and heat to form an alkene.

$C_2H_5OH \xrightarrow{(conc.\ H_2SO_4,\ 170°C)} CH_2=CH_2 + H_2O$

It can be converted into a haloalkane by reacting it with a hydrogen halide such as HBr.

$C_2H_5OH + HBr \longrightarrow C_2H_5Br + H_2O$.

f) What is disconnection in retrosynthesis of a molecule?

Disconnection is the imaginary breaking of a selected bond in a target molecule during retrosynthetic analysis. The purpose is to divide the target into simpler fragments that can be prepared or are commercially available. The fragments formed are called synthons, and suitable real reagents are selected as their synthetic equivalents.

Thus, disconnection helps the chemist plan a practical synthetic route from simple starting materials to the target molecule.

g) Mention one useful application of FGI in organic synthesis.

Functional Group Interconversion (FGI) is used to change one functional group into another so that a required reaction can be carried out. For example, an alcohol group can be converted into a bromo group to make the molecule suitable for nucleophilic substitution.

Reaction: $C_2H_5OH \rightarrow$(HBr) $C_2H_5Br + H_2O$.

Therefore, FGI provides a useful way to modify a molecule without changing its carbon skeleton.

h) Give one method for the reduction of a nitro group ($–NO_2$) to an amino group ($–NH_2$).

A nitro group can be reduced to an amino group using tin and hydrochloric acid.

The reaction is followed by treatment with a base to liberate the free amine from the amine hydrochloride salt. For example, nitrobenzene is reduced to aniline.

Reaction: $C_6H_5NO_2$ (Sn/HCl) $C_6H_5NH_3Cl$ →(NaOH) $C_6H_5NH_2$.

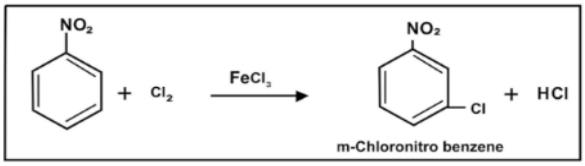
i) How is a carboxylic group converted to an alcohol?

A carboxylic acid is reduced to a primary alcohol using reducing agent like lithium aluminium hydride, $LiAlH_4$. The reaction is carried out in dry ether, followed by hydrolysis or aqueous work-up. For example, ethanoic acid gives ethanol on reduction.

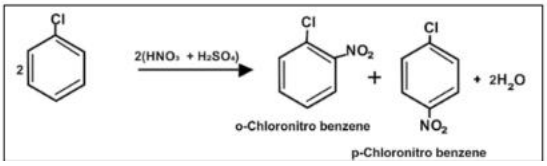
Reaction: CH_3COOH ($LiAlH_4$, dry ether,H_2O) CH_3CH_2OH.

j) Design synthesis of 3-chloronitrobenzene and 2-chloronitrobenzene starting from benzene in two steps.

For 3-chloronitrobenzene, benzene is first nitrated to nitrobenzene; the $–NO_2$ group is meta-directing, so subsequent chlorination gives the meta product.



For 2- chloronitrobenzene, benzene is first chlorinated to chlorobenzene; the –Cl group is ortho/para-directing, and nitration gives the ortho product along with the para isomer.



UNIT 26: POLYMERS

Quick Check 26.1

a) The repeating unit of nylon 6,10 is shown below. Draw the structures of its monomers from this structure. –NH$(CH_2)_6$NHCO$(CH_2)_6$CO-

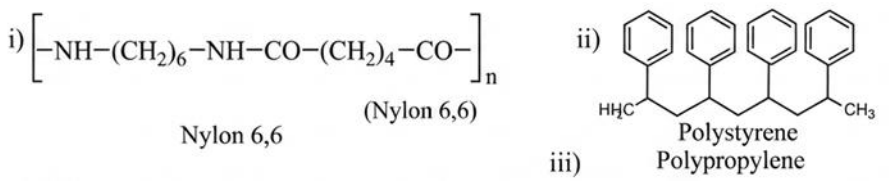
Nylon monomers are obtained by cutting each -CO-NH- bond. For nylon 6,10 the monomers are hexane-1,6-diamine $H_2N(CH_2)_6NH_2$ and decanedioic acid $HOOC(CH_2)_8COOH$ (or the diacyl chloride).

b) Monomers of nylon-6,4 are given below. Draw the structure of the repeating unit of the D polymer formed from these monomers. $H_2N(CH_2)_6NH_2$
$HOOC(CH_2)_2COOH$

Nylon 6,4 from $H_2N(CH_2)_6NH_2$ + $HOOC(CH_2)_2COOH$ has repeat unit [-NH$(CH_2)_6$NHCO$(CH_2)_2$CO-]n.

Quick Check 26.2

a) a) Identify the type of polymerization and monomers forming the following polymer sections.



i) [-NH-$(CH_2)_6$-NH-CO-$(CH_2)_4$-CO-]n (Nylon 6,6)

Type: Condensation Polymerisation (Polyamidation)

Monomers: Hexamethylenediamine (H_2N-$(CH_2)_6$-NH_2) and Adipic acid (HOOC-$(CH_2)_4$-COOH)

ii) Polystyrene Section

Type: Addition Polymerisation

Monomer: Styrene (Phenylethene, $C_6H_5CH=CH_2$)

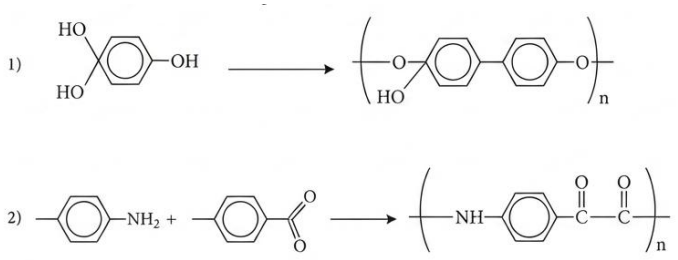
iii) Polypropylene Section

Type: Addition Polymerisation

Monomer: Propene (CH_3-$CH=CH_2$)

b) 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) Polyester formation:

i) Repeat unit: [-O-C_6H_4-O-CO-C_6H_4-CO-]

ii) Linkage: Ester linkage (-COO-)

iii) Attractive force: Dipole-dipole interactions and London dispersion forces.

2) Polyamide formation:

i) Repeat unit: [-NH-C_6H_4-NH-CO-C_6H_4-CO-]

ii) Linkage: Amide linkage (-CONH-)

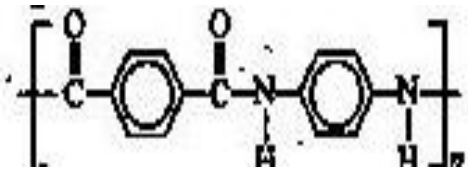
iii) Attractive force: Hydrogen bonding (intermolecular)

QI. MULTIPLE CHOICE QUESTIONS

No.	Answer
I	b
II	b
III	c
IV	b
V	a
VI	d
VII	b
VIII	c
IX	c
X	b

Q2. SHORT-ANSWER QUESTIONS

(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.

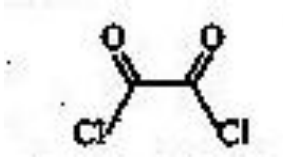
iii) Name the monomers from which it is formed.

i) Characteristic linkage: Amide linkage (Polyamide)
Type of polymerization: Condensation polymerization (step-growth polymerization)

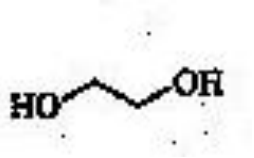
ii) Two functional groups that react to form it: Carboxylic acid (or acyl chloride) group and Amino group.

iii) Monomers: Terephthalic acid (or terephthaloyl chloride) and 1,4-diaminobenzene (p-phenylenediamine).

(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.



ethanedioyl chloride



ethane-1,2-diol

Explanation: It is classified as a condensation reaction because two molecules combine to form a larger molecule with the simultaneous elimination of a small byproduct molecule.

Small molecule eliminated: Hydrogen chloride (HCl).

(c) For the following monomers:

i) the type of the polymer formed.

ii) Draw the repeat unit and a section of the expected polymer.

iii) Name this polymer systematically.

i) Type of polymer formed: Polyester (condensation polymer).

ii) Repeat unit: [-O-CH_2-CH_2-O-CO-CO-]n

iii) Systematic name of the polymer: Poly(ethylene oxalate) or poly(ethylene ethanedioate).

(d) For Nylon 1,6-hexanediamine and hexanedioic acid:

i) Name the linkage.

ii) Name the small molecule eliminated.

iii) Draw the repeating unit.

Nylon 6,6 is a polyamide from hexane-1,6-diamine and hexanedioic acid.

i) Linkage: Amide linkage.

ii) Small molecule eliminated: Water (H_2O).

iii) Repeat unit [-$NH(CH_2)_6NHCO(CH_2)_4CO$-]n

(e) For poly(chloroethene) (PVC)

i) Name the monomer.

ii) Why can the monomer undergo addition polymerization?

PVC is formed from chloroethene, CH_2=CHCl, by addition polymerization. Repeat unit: [-CH_2-CHCl-]n.

(f) State two properties of nylon that make it suitable for ropes and fishing nets.

Nylon is strong, abrasion-resistant, tough and relatively elastic; uses include fibres, ropes, textiles, tyre cord and engineering components.

(g) Give two industrial applications of PVC and Nylon, each.

Nylon: Nylon is used for the manufacturing pf mechanical parts of automotive industry like gears, bearings, bushings, engine covers, and fuel lines due .to its strength, low friction, and heat resistance.

PVC: Pipes and fittings for water supply, drainage, and sewage systems due to its corrosion resistance and durability.

(h) Draw the repeating unit of the polymer made from propane-I,3-diol and benzene-1,4-

dicarboxylic acid.

The reaction between propane-1,3-diol and benzene-1,4-dicarboxylic acid (terephthalic acid) is a condensation polymerization that forms a polyester.

The repeating unit can be represented as:

[- O - CH_2 - CH_2 - CH_2 - O - CO - C_6H_4 - CO -]

(i) State three distinct environmental problems caused by the disposal of non-degradable

polymers.

They stay in the environment for a very long time. This means they accumulate in landfills, oceans, and natural landscapes. This leads to persistent pollution.

They take up huge 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.

(j) Name two different polymers in artificial organs and state the specific application

for each.

Artificial Blood Vessels (Grafts): Poly(tetrafluoroethene) (PTFE) and Poly(ethylene terephthalate) (PET)

Artificial Heart Valves: Specialized Polyurethanes and Silicone

Q3. CONSTRUCTED-RESPONSE QUESTIONS

a) Describe the chemical role of plasticisers in polyvinyl chloride (PVC) and explain how this modification influences the polymer's industrial applications.

Plasticisers are chemicals added to PVC to make it soft, flexible, and easier to process. They work by coming between the polymer chains and reducing the strong forces between them. This allows the chains to move more easily.

As a result, PVC can be used for many products such as flexible pipes, electrical cables, flooring, artificial leather, and packaging. Without plasticisers, PVC is relatively hard and rigid.

b) Explain why polyalkenes, like polyethene, pose a greater environmental challenge than polyesters and polyamides. Identify the chemical process that allows the latter to degrade.

Polyethene and similar plastics create a greater environmental problem because they have strong carbon–carbon (C–C) bonds that are difficult for microorganisms to break down. Therefore, they can remain in the environment for many years.

Polyesters and polyamides are comparatively easier to degrade because their polymer chains contain ester or amide bonds, respectively. These bonds can be broken by hydrolysis, in which water reacts with the bonds and breaks the polymer chain into smaller molecules.

UNIT 27:

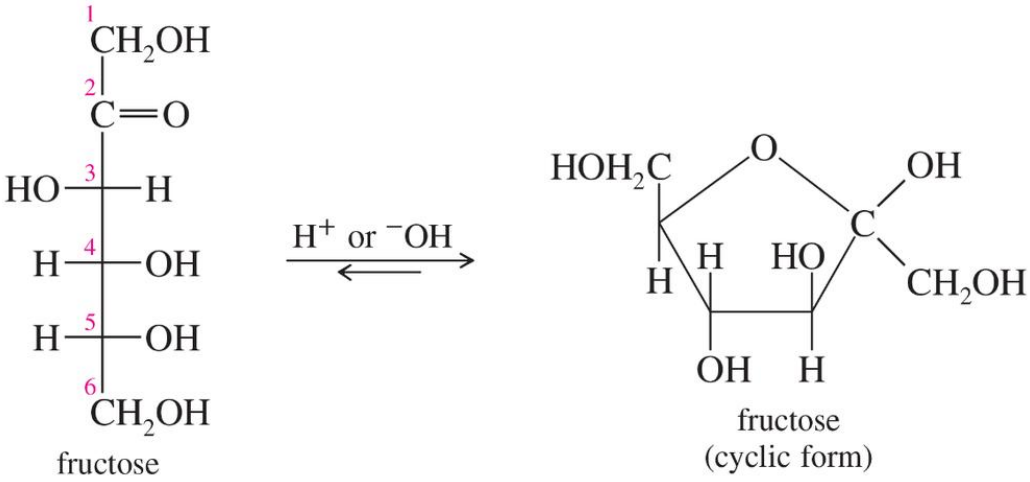
BIOCHEMISTRY

Solved Quick Check & Exercise

Quick Check 27.1:

a) The linear structure of fructose is given here.

i. Show the conversion of this structure into the cyclic structure.



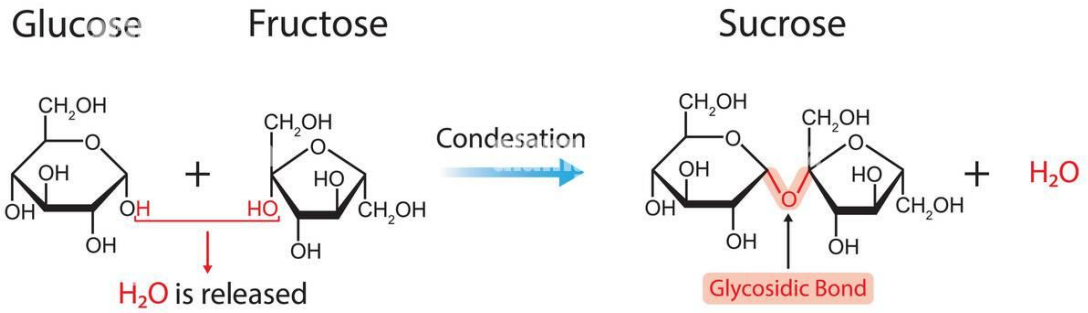
ii. Predict whether fructose is soluble in water or not. Explain your reasoning.

Fructose is very soluble in water. It dissolves easily because it has many polar hydroxyl (-OH) groups. These groups form strong hydrogen bonds with water molecules.

iii. Predict the physical state of fructose in its pure form by analyzing its Structure.

Fructose in its pure form is a solid at room temperature, specifically existing as a white, odorless, crystalline powder or solid granule with a sweet taste.

b) What is glycosidic linkage? Show how it is formed between fructose and glucose.



c) Briefly describe any two functions of carbohydrates and how these functions are related to their molecular Structures

Function:

- Polysaccharides like cellulose build rigid cell walls in plants, while chitin forms tough outer skeletons in insects and fungi.
- Monosaccharides like glucose are broken down during cellular respiration to release usable chemical energy (ATP) for daily cellular work. The small, compact ring structure of simple sugars contains numerous polar hydroxyl (-OH) groups, making them water-soluble and easy to transport and rapidly split apart through enzymatic pathways.

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.

The high stability and resistance to denaturation in keratin are primarily driven by **disulphide bonds** (cysteine bridges) rather than hydrogen bonds. Disulphide covalent bonds lock the protein chains tightly together, while hydrogen bonds break easily with heat or water.

b) How can two peptides with identical type and number of amino acids differ in, their primary structure?

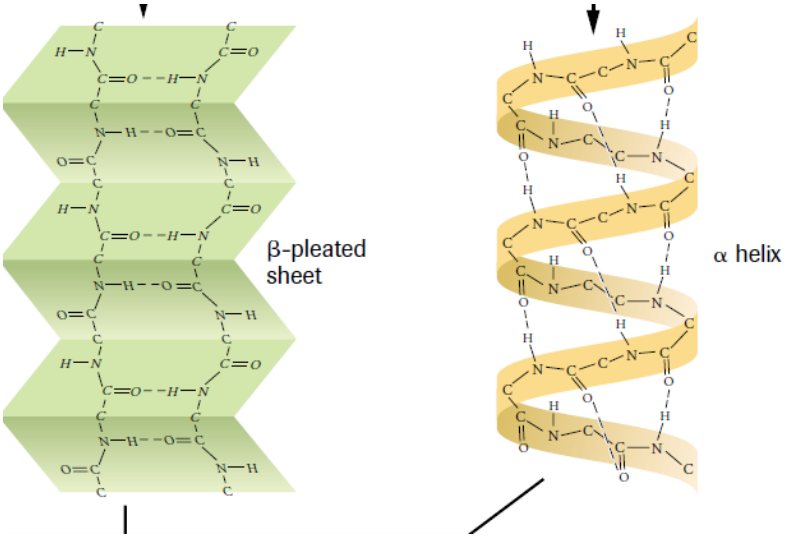
Two peptides with the exact same type and number of amino acids can differ in their primary structure because their amino acid **sequence (the linear order in which they are arranged)** is different.

- **Peptide A sequence:** Serine – Glycine – Alanine (Ser-Gly-Ala)
- **Peptide B sequence:** Alanine – Serine – Glycine (Ala-Ser-Gly)

Both peptides contain one serine, one glycine, and one alanine. They share the same amino acid types and numbers. However, they have a different primary structure because the order of the amino acids is not the same.

c) What are the two most common types of secondary protein structures in our body?

The two most common types of secondary protein structures in our body are the alpha-helix and the beta-sheet. Both forms are stable shapes held together by hydrogen bonds along the protein backbone.



d) Why does a denatured protein no longer function properly?

A denatured protein loses its function because its specific three-dimensional shape unravels. A protein's job depends entirely on its unique shape, which allows it to match and bind with other molecules. When heat or harsh chemicals break the weak bonds holding this shape together, the protein deforms and can no longer do its work.

e) The white of egg solidifies on heating. Explain why it happens.

The white of an egg turns solid when heated because heat breaks the weak bonds in the liquid egg proteins. These long protein chains unfold and tangle together. They form a firm, 3D network that traps water and changes the clear liquid into a solid white gel.

Quick Check 27.3

a) How do enzymes differ from inorganic catalysts?

Enzymes are complex, organic protein molecules produced by living cells that act as biological catalysts. In contrast, inorganic catalysts are typically simple metal ions, minerals, or small molecules that promote chemical reactions outside of living systems. While both speed up reactions by lowering activation energy, they differ significantly in structure, specificity, and how they function

b) What is the effect of decreasing and increasing: temperature on the enzyme activity?

Effect of decreasing temperature:

because molecules move slower and collide less. The reaction rate goes down. Warming it back up restores function.

Effect of increasing temperature:

Increasing temperature speeds up activity at first, but high heat changes the enzyme shape and permanently stops it. Extreme heat breaks the enzyme structure (denaturation).

c) Differentiate between competitive and non-competitive inhibitors.

Competitive Inhibitor:

Reversible inhibitors are also termed as competitive inhibitors as they are the molecules 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 dehydrogenase succinate. The propandioate ion (malonate) can inhibit this enzyme due to its resemblance with the substrate butanedioate.

$-OOC — CH_2 — CH_2 — COO^-$ succinate ion

$-OOC — CH_2 — COO—$ malonate ion

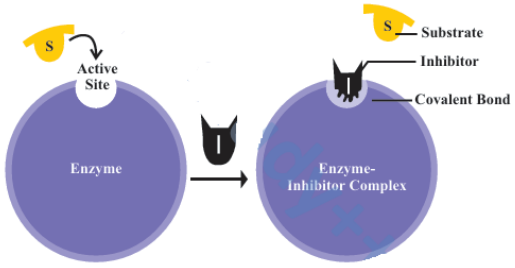


Figure Action of reversible inhibitor

Non-competitive inhibitors (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 an irreversible inhibitor, such as poisons, antibiotics, anti-metabolites and some drugs, is attached, loses enzymatic activity permanently (Figure 27.9). Substrate Noncompetitive inhibitor Enzyme. Action of non-competitive inhibitor Penicilin is an irreversible inhibitor that blocks the enzyme trans-peptidase. This enzyme acts for the synthesis of the bacterial cell wall. Thus insulin kills bacteria by disrupting the cell wall enzyme.

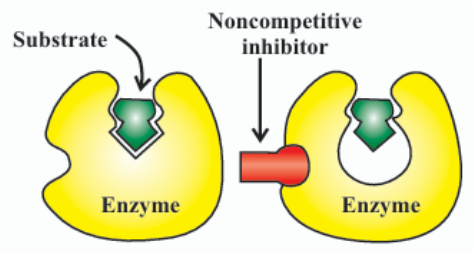
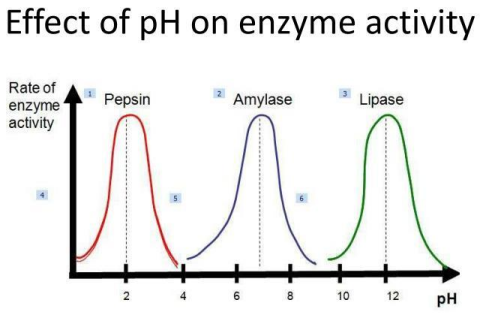


Figure Action of non-competitive inhibitor

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?

If the pH is disturbed from the optimum values, it can deactivate the enzyme action. The enzymatic reactions in the human body and other organisms occur best at a pH around the neutral value ~7

Changing the pH breaks the ionic and hydrogen bonds in an enzyme. This alters the shape of the active site. The substrate can no longer fit into the site. The enzyme loses its function.



Quick Check 27.4

a) Why lipids are not soluble in water?
Lipids do not dissolve in water because they are non-polar molecules with long carbon-hydrogen chains, while water is a polar molecule held together by strong hydrogen bonds.

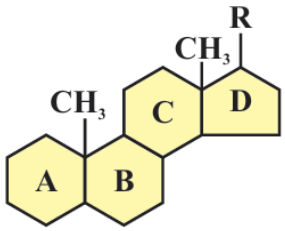
b) What are three major functions of lipids in the human body?

- 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 oxidized 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 lemon the bloodstream.
- Fats provide insulation to the body from water. hea.t. and electricity due to their non-polar nature

c) What type/s of lipid do/does not contain fatty acids? Give examples.
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.

Steroids:

Steroid 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. 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 units. $CH_2=C(CH_3)-CH=CH_2$

d) Vegetable oil and vegetable ghee both are triglycerides. What is the major structural difference between the two?

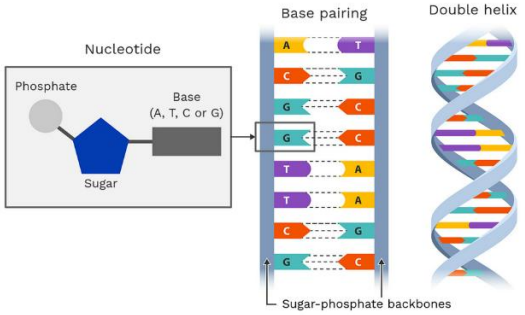
Vegetable Oil	Vegetable Ghee
Definition	
Vegetable oil is liquid at room temperature because it contains unsaturated fatty acids with one or more double bonds	Vegetable ghee is solid because it is hydrogenated, meaning double bonds are removed to make saturated fatty acids that pack closely together
Physical State	
Liquid state at room temperature	Solid or semi-solid state at room temperature
Fatty Acids	
Contains **unsaturated fatty acids**.	Contains **saturated fatty acids**
Bonds	
Carbon chains are **straight** with **single & double bonds** only.	Carbon chains are **straight** with **single bonds** only.
Melting Points	
Oils have lower melting points	Fats have greater melting points
Process	
-	Produced by adding hydrogen to oils (**hydrogenation**).

Quick Check 27.5

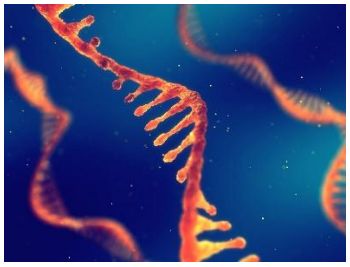
a) Compare the stability provided by the sugar-phosphate backbone versus the inter-chain base pairing, In your answer, refer to the specific types of bonds and the number of bonds formed between:
Adenine (A) and Thymine (T)
Guanine (G) and Cytosine (C)

he sugar-phosphate backbone provides structural stability through strong **covalent phosphodiester bonds** that hold the DNA strand together. Inter-chain base pairing provides

stability through weaker **hydrogen bonds** between nitrogenous bases: **two hydrogen bonds** form between Adenine (A) and Thymine (T), and **three hydrogen bonds** form between Guanine (G) and Cytosine (C).



b) How the DNA and RNA chemically different? What are the similarities between these two?

DNA	RNA
Stands For	
Deoxyribonucleic acid	Ribonucleic acid
Components	
• Deoxyribose Sugar • Phosphate group • Nitrogenous Bases	• Ribose Sugar • Phosphate Group • Nitrogenous Bases
Nitrogenous Bases	
Adenine (A) Guanine (G) Cytosine (C) Thymine (T)	Adenine (A) Guanine (G) Cytosine (C) Uracil (U)
Stranded	
Double Stranded	Usually Single stranded
Types	
	mRNA rRNA tRNA
Figure	
	

Similarities:

- **Building blocks:** Both are made of **nucleotides**.

- **Backbone:** Both have a **sugar-phosphate** chain.
- **Shared bases:** Both contain **adenine, guanine, and cytosine**.
- **Function:** Both help make **proteins** and store code.

c) Nearly every cell in the human body contains the exact same 23 pairs of chromosomes, yet a red blood cell produces hemoglobin while a skin cell produces keratin. Explain why.

Nearly every cell has the same DNA, but cells use gene expression to turn specific genes on or off. Transcription factors and chemical signals read only the exact instructions needed for that cell type. This process makes red blood cells build hemoglobin and skin cells build keratin.

Exercise

Q1: MULTIPLE CHOICE QUESTIONS

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) Thymine	**d) Uracil**
VI. Waxes are the esters of:	
a) Glycerol	b) Sterol
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 Bonds	d) Disulfide bonds
IX. The backbone of nucleic acid structure is constructed by:	
a) Peptide bonds	b) Glycosidic bonds
c) Phosphodiester bridges	d) All
X. Which element prevents the development of tooth decay?	
a) Fluorine	b) Calcium

c) Phosphorus	d) Sodium

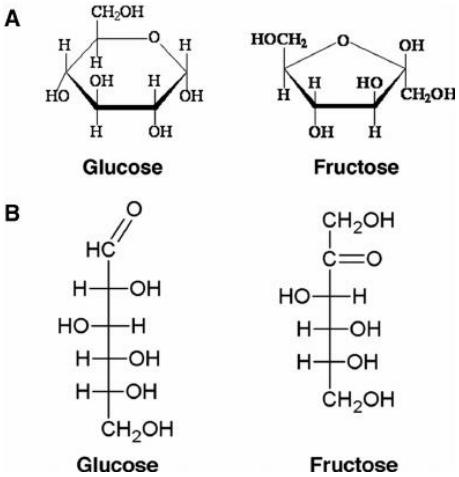
Q2: SHORT-ANSWER QUESTIONS:

a) What role does glycogen play in the human body?

Glycogen is a polymer of glucose that is stored in the liver and muscles of animals. It is also called the "animal starch". Glycogen acts as the primary short-term energy storage molecule in the human body. It stores extra glucose in the liver and skeletal muscles. When the body needs energy quickly, it breaks glycogen back down into glucose.

b) Point out the main structural difference. between the compounds in each of the following pairs:

i) Glucose and fructose



ii) Competitive and non-competitive inhibition

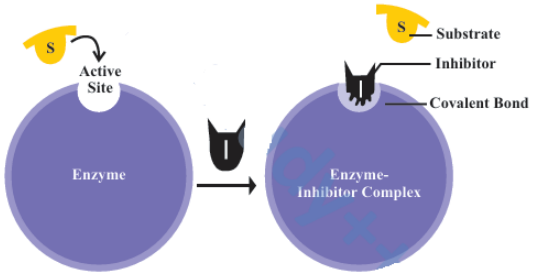


Figure Action of reversible inhibitor

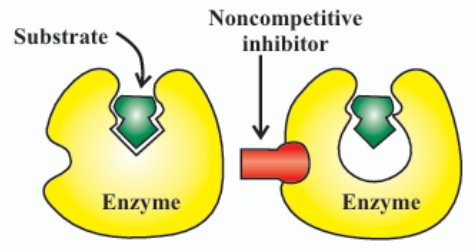


Figure Action of non-competitive inhibitor

iii) Cellulose and starch

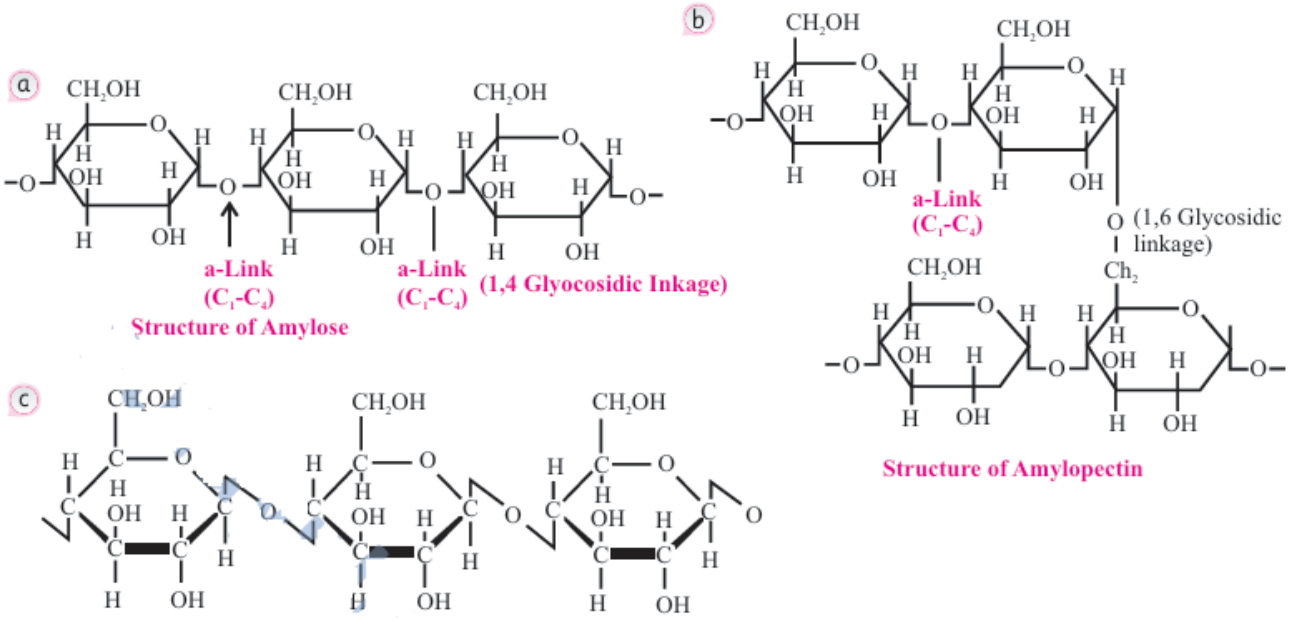


Figure Structure of a) amylose, b) amylopectin in starch, and c) cellulose

iv) Glycolipids and lipoproteins

Glycolipids is a complex (compound) lipids made of a lipid combined with a carbohydrate

Lipoprotein is a complex (compound) lipids made of a lipid combined with a protein

c) Which class of biomolecule contains each of the following linkages? Describe the function of each linkage.

i) Glycosidic

The glycosidic linkage is found in **carbohydrates** (sugars). Its main function is to join single sugar units together to build larger molecules like starch, glycogen, and cellulose, which store energy or provide structural support.

ii) Peptide

A **peptide linkage** (peptide bond) is found in **proteins** (polypeptides). It joins the carboxyl group of one amino acid to the amino group of another. Its main function is to link amino acids together to form a stable polymer chain that folds into a functional protein structure.

iii) Ester

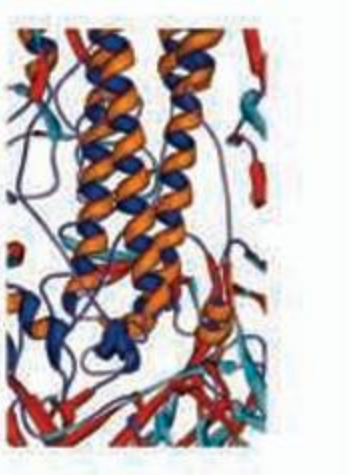
Ester linkages are found in **lipids** (specifically fats, oils, and waxes), where they join fatty acids to glycerol through a dehydration reaction. Their primary biological function is energy storage and forming structural barriers like cell membranes.

iv) Phosphodiester

The phosphodiester linkage is found in the class of biomolecules known as nucleic acids (DNA and RNA). It connects individual nucleotide monomers together.

d) How the tertiary structure of proteins is formed?

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 disulfide bridges. These interactions cause the chain to twist and bend into a specific shape, often forming globular proteins. This three-dimensional 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.



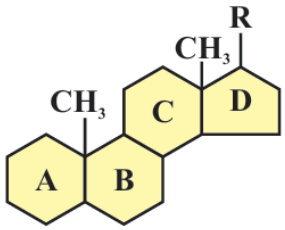
Tertiary structure
is the coiling or folding
of the primary structure

e) In what way fats and oils are different?

Vegetable Oil	Vegetable Ghee
Definition	
Vegetable oil is liquid at room temperature because it contains unsaturated fatty acids with one or more double bonds	Vegetable ghee is solid because it is hydrogenated, meaning double bonds are removed to make saturated fatty acids that pack closely together
Physical State	
Liquid state at room temperature	Solid or semi-solid state at room temperature
Fatty Acids	
Contains **unsaturated fatty acids**.	Contains **saturated fatty acids**
Bonds	
Carbon chains are **straight** with **single & double bonds** only.	Carbon chains are **straight** with **single bonds** only.
Melting Points	
Oils have lower melting points	Fats have greater melting points
Process	
-	Produced by adding hydrogen to oils (**hydrogenation**).

f) Describe the structure of steroids_ Write a note on the functions of cholesterol.

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. 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.



Cholesterol is a soft, waxy fat found in your body and in all animal foods. Despite its bad reputation, your body needs it to live. It helps build cell walls, makes key hormones, creates vitamin D, and helps digest food.

g) Describe the mechanism of enzyme action.

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 in 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. 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)

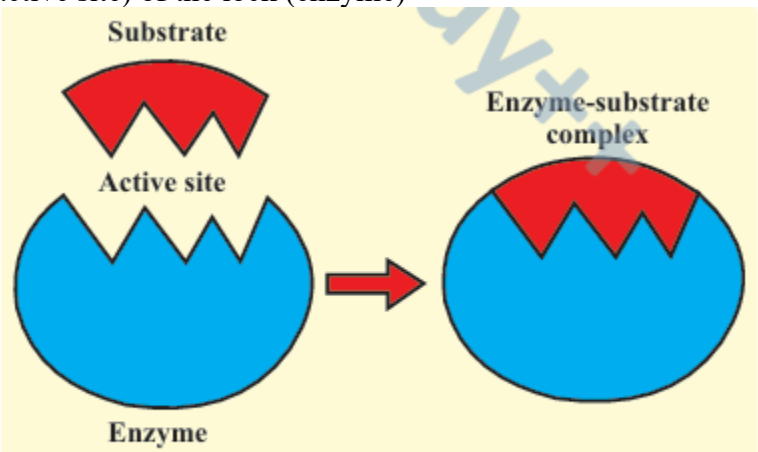


Figure 27.7 Formation of enzyme-substrate complex

h) Why does an enzyme catalyze a reaction of only a specific substrate?

An enzyme works with only one specific substrate because its active site has a unique shape and chemical charge that matches only that specific molecule. This precise fit allows the enzyme and substrate to lock together and speed up the chemical reaction

i) Name different RNAs and discuss their function.

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.

j) What are some sources of potassium, iron, calcium, magnesium and zinc in our diet?

Source of Potassium:

Salt, meat, sea food, fruit juices, vegetables, lentil

Source of Iron:

Liver, meat, egg yolks, nuts, enriched or whole grains, beans, peas and lentils.

Source of Calcium:

Milk and other dairy products, greens, broccoli, D and salmon, sardines, beans,peas and lentils.

Source of Magnesium:

Seeds, nuts, whole grains, dark green vegetables, and beans

Source of Zinc:

Meat, seafood, whole grains.

k) What is the role of iron in the body?

Hemoglobin synthesis found in red blood and myoglobin in muscle cells. Needed to carry oxygen.

l) How enzyme inhibitors are important in our body and medicine?

Enzyme inhibitors are molecules that **reduce or stop the activity of enzymes**. They are extremely important both inside our body and in modern medicine.

Importance in the Human Body

Regulation of Body Processes

- Enzyme inhibitors **regulate these reactions** by slowing or stopping enzyme activity.
- Enzyme inhibitors help maintain this balance by controlling enzyme speed.
- Some inhibitors prevent harmful or unnecessary reactions to ensures normal functioning of biological systems.

Importance in the medicine:

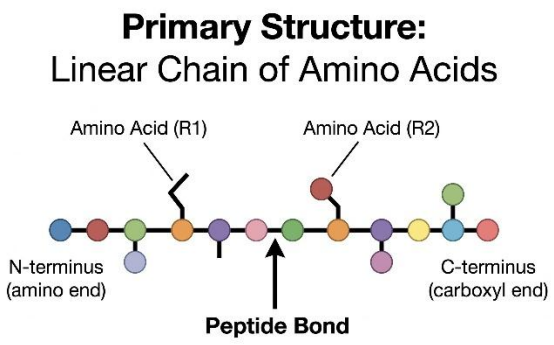
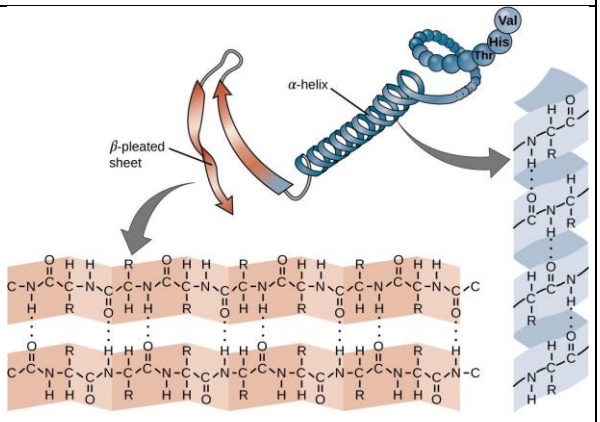
Treatment of Diseases

Medicines act by inhibiting specific enzymes involved in diseases.

For example:

- Aspirin reduces pain by inhibiting enzymes
- Penicillin stops bacterial growth by blocking enzymes

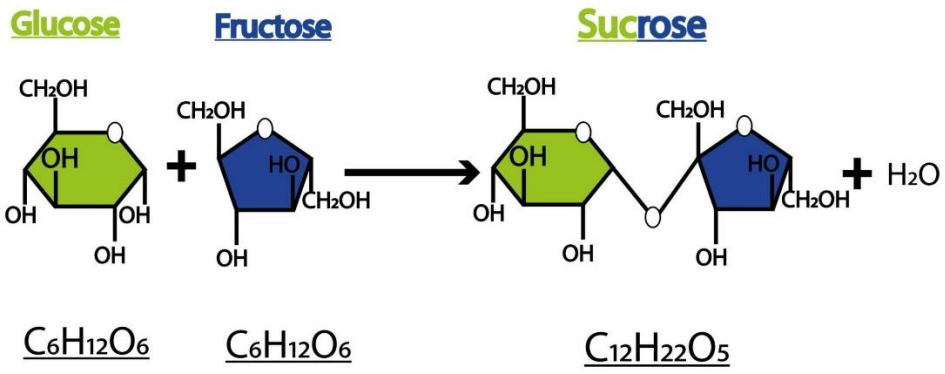
m) Differentiate between the primary and secondary' structure of proteins.

Primary Protein	Secondary Protein
Definition	
It is the **simple linear sequence of amino acids** in a protein chain.	It is the **folding of the polypeptide chain** into specific shapes.
Bonds	
Amino acids are linked by **peptide bonds**.	Stabilized by **hydrogen bonds** between peptide groups.
Function	
It determines the **identity and basic nature** of the protein. Even a small change in sequence can affect protein function.	Provides **structural stability** to proteins.
Forms	
Linear	Common forms: • **α-helix (alpha helix)** • **β-pleated sheet (beta sheet)**
Figure	
	

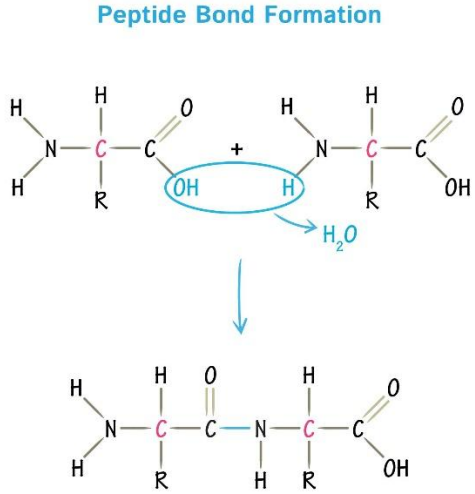
Q3. CONSTRUCTED-RESPONSE QUESTIONS

a) How condensation of sugars and condensation of amino acid are same?

Condensation of sugars and amino acids is similar because in both cases **two small molecules join together by removing water (H_2O)**. When sugars combine, they form a **glycosidic bond**, and when amino acids combine, they form a **peptide bond**. In both reactions, a larger biological molecule is produced (carbohydrates or proteins), and the basic mechanism is the same **loss of water and formation of a new covalent bond**.

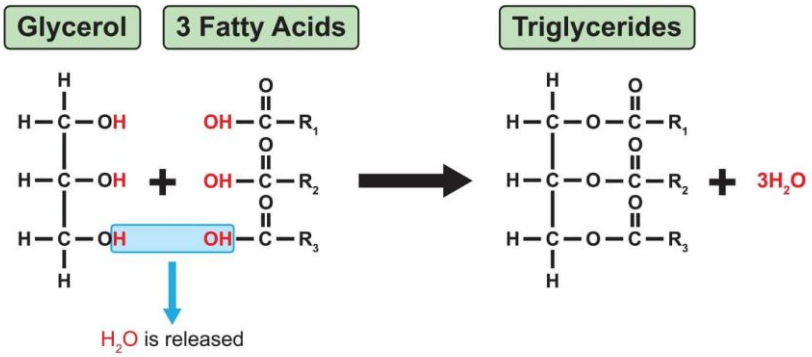


Similarly;



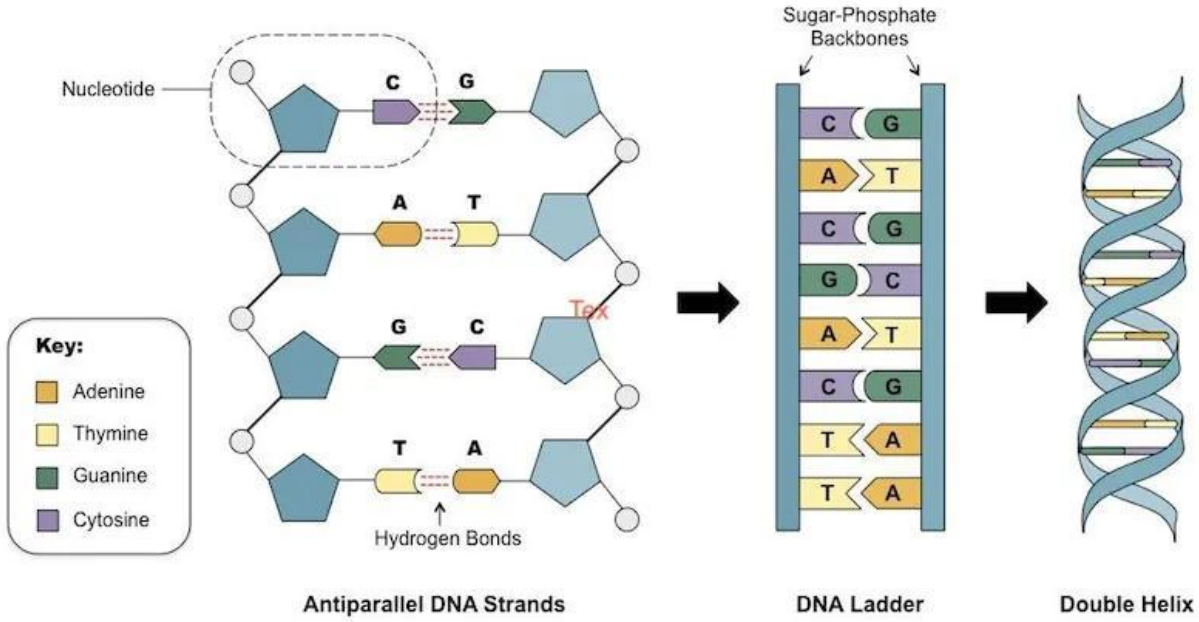
b) Why is cholesterol included in the lipid family?
Cholesterol is included in the lipid family because lipids are **hydrophobic (insoluble in water)** and soluble in organic solvents, and cholesterol behaves in the same way. Although it does not have fatty acid chains like typical fats, it has a **large non-polar hydrocarbon structure**, which gives it lipid-like characteristics.

c) Why fats and oils are also called triacylglycerides?
ats and oils are called **triacylglycerides (or triglycerides)** because their structure consists of **one glycerol molecule bonded to three fatty acid molecules**. Each fatty acid attaches to glycerol through an **ester linkage**, and **three molecules of water are removed**.



d) How hydrogen bonding is important in the double helix of DNA?
Hydrogen bonding is crucial in maintaining the structure and function of the DNA double helix. DNA consists of two antiparallel strands held together by hydrogen bonds between complementary nitrogenous bases.

Adenine (A) pairs with Thymine (T) through 2 hydrogen bonds
Guanine (G) pairs with Cytosine (C) through 3 hydrogen bonds



e) If the sequence T-A-C-C-G-A located on one strand what sequence is seen opposite to it on the other strand?

Opposite (complementary) strand will be:
A – T – G – G – C – T

T ≡ A
A = T

C ≡ G
C ≡ G
G ≡ C
A = T

CHROMATOGRAPHY

Solved Quick Check & Exercise

Quick Check 28.1:

a) **A mixture contains butanone and pentane. How can they be separated by using thin layer chromatography using aluminum oxide as stationary phase and benzene as solvent?**

To separate a mixture of butanone and pentane using thin layer chromatography (TLC), you exploit the difference in their **polarities** and their resulting **adsorption affinities** for the stationary and mobile phases.

Principles of Separation

- **Stationary Phase:** Aluminum oxide (alumina) is a **polar** solid adsorbent.
- **Mobile Phase:** Benzene is a relatively **non-polar** organic solvent.
- **Pentane** is a straight-chain alkane and is completely **non-polar**. It will have very little affinity for the polar alumina and will dissolve well in the benzene solvent, causing it to travel rapidly up the plate near the solvent front (high (R_f value).
- **Butanone** is a ketone containing a polar carbonyl group (C=O). It will interact more strongly via dipole-adsorption forces with the polar aluminum oxide surface, causing it to move slower up the plate (lower R_f value)

b) **A mixture of two substances X and Y is analyzed by thin-layer chromatography. The R, value of, substance X is larger than that of the substance Y. Suggest why the substance X has a larger R_f value.**

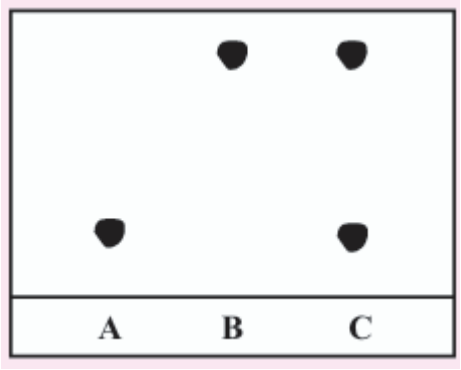
Substance X has a larger (R_f) value because it is less polar than substance Y and interacts less with the polar stationary phase.

Higher Solubility in Mobile Phase: Substance X dissolves better in the moving liquid (solvent) than substance Y.

Weaker Adsorption: Substance X sticks less to the solid stationary phase (like silica or alumina).

Greater Travel Distance: Because it binds less to the plate, substance X travels farther up the plate with the solvent, which gives it a larger (R_f) value.

c) **A separate thin layer chromatography experiment was done using the hair dyes A, B and C. The Chromatogram obtained is shown here. State three conclusions about the hair dyes A, B and C which can be deduced from the chromatogram**



Based on the provided thin-layer chromatography (TLC) chromatogram, here are **three conclusions** that can be deduced:

- **Dyes A and B are pure substances:** Both lanes A and B show only a **single spot**, meaning they each consist of only one component.
- **Dye C is a mixture:** Lane C separates into **two distinct spots**, showing that it contains at least two different substances.
- **Dye C contains both Dye A and Dye B:** The two spots in lane C have traveled the **exact same distance** (R_f value) as the individual spots from dyes A and B, confirming they are components of the mixture

Quick Check 28.2

a) **An impure sample of lactic acid, contains butanone as the only contamination. The mixture is analysed using gas chromatography. Butanone is found to have a longer retention time than lacti c i) Suggest suitable Substances that could be used as the mobile and stationary phases.**

Mobile Phase:
Nitrogen (N_2) or **Helium (He)** inert carrier gas
Stationary Phase:
Non-polar, high boiling liquid hydrocarbon (e.g., long-chain hydrocarbon)
The stationary phase is **non-polar**. Substances that **interact more strongly** with it move slowly.
Since **butanone has longer retention time**, it must interact **more strongly with the non-polar stationary phase**

ii) Describe how the percentage composition of the mixture can be determined from the gas chromatogram.

Method to determine % composition

- **Identify each peak** in the chromatogram (each substance has a different retention time).
- **Measure the area under each peak**.
- Calculate percentage using:
  The area of peak can be calculated by the following formula.
  Area of a peak = ½ x base x height
  % of component A= Area of peak of A / Total area of all peaks ×100

Exercise

Q1: MULTIPLE CHOICE QUESTIONS

▪ **Why must the solvent level be below the spot of the dye?**
a) To increase the temperature b) **To prevent the dye from dissolving directly into the solvent** c) To speed up chromatography d) To increase adsorption
▪ **Why do some components of a 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
▪ **A substance has a very low R, value. What does this indicate?**
a) It is insoluble in the solvent b) It is highly soluble in the solvent c**) It is strongly sticks to the water inside paper** d) It has a high density
▪ **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
▪ **A polar compound in TLC will usually:**
a) Travel farther up the plate **b) Stay near the baseline** c) Evaporate quickly d) Dissolve completely
▪ **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
▪ **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 vapourised sample through the column** d) To detect the substance
▪ **Why must the stationary phase in GC have a high boiling point?**
a) Evaporate quickly b) To increase pressure c) **To remain in liquid form during the process** d) To react with gases
▪ **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
▪ **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**

Q2: SHORT-ANSWER QUESTIONS:

a) What is the principle of paper chromatography?
Paper chromatography operates on the principle of partition chromatography, where components of a mixture are separated based on their differential partitioning between a stationary phase (water molecules trapped within the paper fibers) and a mobile phase (a developing solvent). As the mobile phase moves up the paper via capillary action, it carries the sample mixture with it. The individual components distribute themselves dynamically between the two phases according to their relative solubility. Substances with a higher affinity for the mobile phase travel faster and farther, while those with a higher affinity for the stationary phase move slower, resulting in distinct, separated bands on the paper.

b) Why is pencil used instead of ink in chromatography the baseline?
A pencil is used to draw the baseline in chromatography because its **graphite lead is insoluble** in the solvent, preventing it from dissolving or moving during the test

c) State two advantages of TLC over paper chromatography.
- An advantage of TLC is that it is faster than paper chromatography
- More than one samples can be on spotted at different places on the same glass slide.

d) Why do polar substances move slowly in TLC?
polar substances have greater attraction for polar solid stationary phase and are adsorbed more strongly. Therefore, they travel more slowly up the stationary phase.

e) Why is TLC not suitable for large-scale separation?
Thin Layer Chromatography (TLC) is not suitable for large-scale separations mainly because it has a very **limited sample capacity** and can only hold a tiny amount of material on the flat plate

f) What is the function of injector port in GC?

The primary function of the injector port (or inlet) in gas chromatography (GC) is to introduce a precise liquid or gas sample into the heated system, vaporize it, and mix it with the carrier gas so it can be swept onto the separation column.

g) Why must samples be volatile in GC?

Samples must be volatile in gas chromatography (GC) because the mobile phase is a gas, requiring the analytes to vaporize completely so they can move through the column and reach the detector.

h) State two limitations of gas chromatography.

i. GC works only for volatile (easily vaporized) substances.

ii. Samples must be thermally stable. Compounds that decompose at high temperatures cannot

be used.

i) What information does a chromatogram provide?

A chromatogram provides a visual graph of separated chemical components, showing individual peaks, retention times, and peak sizes that help identify and measure substances in a mixture.

j) What is adsorption? Give one example.

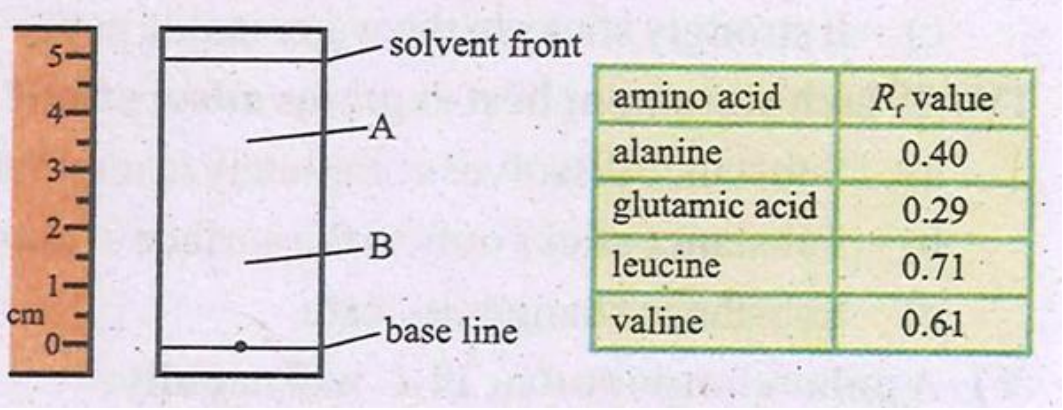
Adsorption is the process where atoms, ions, or molecules from a gas, liquid, or dissolved solid adhere to the outer surface of a material (adsorbent) rather than entering into its interior. It is a surface phenomenon and is important in chromatography because different substances are adsorbed on the stationary phase to different extents, leading to their separation.

Example:

In thin layer chromatography (TLC), when a mixture is applied on a plate coated with aluminium oxide (Al_2O_3), the components are adsorbed on its surface to different extents, resulting in separation.

Q3. CONSTRUCTED-RESPONSE QUESTIONS

a) A mixture of amino acids is analyzed using thin layer chromatography. The chromatogram obtained is shown. The table shows some R, 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.

Answer:

Deduce the Amino Acid for Spot A and Spot B

To identify the amino acids, we first need to calculate the Retardation Factor (R_f) for each spot using the formula:

$$R_f = \frac{\text{Distance traveled by the spot}}{\text{Distance traveled by the solvent front}}$$

Total Distance (Solvent Front): Aligned at **5.0 cm** on the ruler.

1. **Spot A Distance:** The mark is located at **3.55 cm**.

$$R_f \text{ for A} = \frac{3.55 \text{ cm}}{5.0 \text{ cm}} = 0.71$$

2. **Spot B Distance:** The mark is located at **1.45 cm**.

$$R_f \text{ for B} = \frac{1.45 \text{ cm}}{5.0 \text{ cm}} = 0.29$$

Matching this with the table, **Spot B is Glutamic Acid** ($R_f = 0.29$)

Spot A = Leucine

Spot B = Glutamic Acid

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.

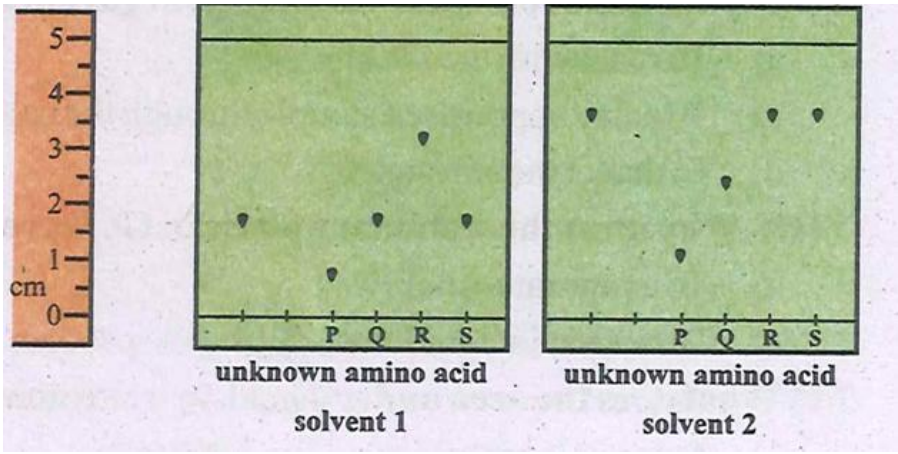
Prediction: The (R_f) values of the amino acids will **increase**.

- **Reasoning:**
    - In Thin Layer Chromatography (TLC), the stationary phase (silica) is highly polar, while amino acids themselves are also polar molecules.
    - A more polar solvent will have a higher affinity for the polar amino acids, increasing their solubility in the mobile phase.
    - The more polar solvent also competes better with the stationary phase for binding sites.
    - Consequently, the amino acids will spend more time moving with the mobile phase and travel a greater relative distance up the plate.

b) Gas chromatography involves a stationary phase and a mobile phase. Name a suitable substance that could be used for each phase.

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).
Mobile phase: is an inert gas (carrier gas), such as helium or nitrogen.

c) An unknown amino acid is analyzed 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.



To identify an unknown substance using chromatography, its spots must match the position (and thus the (R_f) value) of a known reference substance across different solvent systems.

1. **In Solvent 1:**
   - The unknown amino acid travels a distance of approximately **1.7 cm**.
   - This matches the distance traveled by reference amino acids **Q** and **S**. Therefore, the unknown could be either Q or S based on this solvent alone.
2. **In Solvent 2:**
   - The unknown amino acid travels a distance of approximately **3.6 cm**.
   - This matches the distance traveled by reference amino acids **R** and **S**. Therefore, the unknown could be either R or S based on this solvent alone.

Conclusion

By comparing both results, **amino acid S** is the only reference sample that matches the unknown in **both** solvent systems.

UNIT # 29

SPECTROSCOPY-1

Quick Check 29.1

a. Calculate IHD for each of the following;

(i) C_6H_6

Ans. Compared to C_6H_{14}, it has 8 hydrogen atoms lesser. So it's IHD is 4

ii) C_6H_{12}

Ans. Compared to C_6H_{14}, it has 2 hydrogen atoms lesser. So it's IHD is 1

(iii) C_6H_4

Ans. Compared to C_6H_{14}, it has 10 hydrogen atoms lesser. So it's IHD is 5

b) Propose the structures of the above compounds given in (a)

The IHD tells us the total number of rings + π bonds.

(i) C_6H_6, IHD = 4

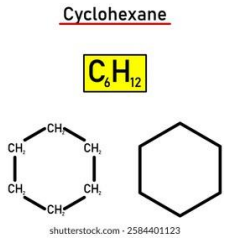
Ans. A suitable structure is benzene:

benzene: C_6H_6

It contains 3 double bonds + 1 ring = 4 IHD.

(ii) C_6H_{12}, IHD = 1

A suitable structure is cyclohexane:



It contains 1 ring and no double bond = 1 IHD.

Another possible structure is an alkene such as hex-1-ene, which has one double bond.

(iii) C_6H_4, IHD = 5

One possible structure is:

$$CH_2 = C = C = C = C = CH_2$$

This contains 5 double bonds, giving IHD = 5.

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. i) Compared to Saturated compound $C_{30}H_{62}$, it has 10 hydrogen atoms lesser so its IHD is 5

(ii) Is it saturated or unsaturated?

But hopane has only 52 hydrogen atoms, so it has 5 degrees of unsaturation.

Quick Check 29.2

a. Which type of electronic transitions require least energy in UV/Vis. spectroscopy? Explain. ib) c) i) * ii) ππ* iii) n -σ* iv) n → π*

Ans. The correct answer is:

iv) $n \rightarrow \pi^*$

The approximate energy order is:

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

The $n \rightarrow \pi^*$transition requires the least energy because the energy gap between the non-bonding $n$orbital and antibonding π^*orbital is relatively small.

b. **Arrange the following in an increasing order of λ_{max}.** (See structures from the textbook.

Ans. The compounds contain different conjugated systems. Greater conjugation and alkyl substitution generally shift absorption toward a longer wavelength.

Therefore:

$$\boxed{\text{iii} < \text{ii} < \text{i}}$$

c. Will $CH_3CHOHCH$, show a significant absorption in the UV-Vis region? Explain.

Ans. No, it will not show a significant absorption in the normal UV-Vis region.

$CH_3CHOHCH_3$(2-propanol) is a saturated alcohol and contains only σ bonds and non-bonding electrons. It has no π bond or conjugated chromophore.

Quick Check 29.3

a) Which one of the infra-red spectra is that of pentanone and which one is of pentan-2-o1? (See spectra from text book)

Ans. Spectrum A → Pentanone

Shows a strong, sharp absorption around 1700 cm^{-1}, characteristic of the C=O (carbonyl) group in a ketone. No broad O–H absorption.

Spectrum B → Pentan-2-ol

Shows a broad absorption around 3200–3600 cm^{-1}, characteristic of the O–H group in an alcohol. No strong C=O peak around 1700 cm^{-1}.

b) Compounds T and U are isomers with the molecular formula $C_3H_6O_2$. Suggest their structures based on the spectra shown below: (See spectra from text book)

Ans. The molecular formula is $C_3H_6O_2$. The two IR spectra can be identified from their characteristic absorption bands.

Compound T Spectrum shows:

- A very broad O–H absorption from about 2500–3300 cm^{-1}, characteristic of a carboxylic acid.
- A strong C=O absorption near 1700 cm^{-1}.

Therefore, T is a carboxylic acid (Propanoic acid)

$$\boxed{CH_3CH_2COOH}$$

Spectrum of U shows:

- A strong C=O absorption near 1700–1750 cm^{-1}.
- No broad O–H absorption.
- Strong C–O absorptions in the fingerprint region.

Therefore, U is an ester ,Methyl ethanoate (methyl acetate)

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 fragment ions C_4H_{10} :

$$\boxed{CH_3^+,\ C_2H_5^+,\ C_3H_7^+,\ C_4H_9^+}$$

Corresponding m/e values:

- **CH_3^+ → 15**
- **$C_2H_5^+$ → 29**
- **$C_3H_7^+$ → 43**
- **$C_4H_9^+$ → 57**

ii) Possible fragment ions C_5H_{12}**:**

$$\boxed{CH_3^+,\ C_2H_5^+,\ C_3H_7^+,\ C_4H_9^+,\ C_5H_{11}^+}$$

Corresponding m/e values:

$$\boxed{15, 29, 43, 57, 71}$$

iii) Possible fragment ions C_7H_{16}**:**

$$\boxed{CH_3^+, C_2H_5^+, C_3H_7^+, C_4H_9^+, C_5H_{11}^+, C_6H_{13}^+, C_7H_{15}^+}$$

Corresponding m/e values:

$$\boxed{15, 29, 43, 57, 71, 85, 99}$$

SOLUTION OF EXERCISE:

Q.1: MULTIPLE CHOICE QUESTIONS

Question number	Correct choice
1	a
II	b
III	c
IV	d
V	d
VI	c
VII	b
VIII	d
IX	c

Q.2 SHORT ANSWERS QUESTIONS

a. Bromobutane $CH_3CH_2CH_2CH_2Br$ can be reacted with hot aqueous sodium hydroxide prepare butan-1-ol. $CH_3CH_2CH_2CH_2Br + OH \rightarrow CH_3CH_2CH_2CH_2OH + Br^-$

butan-1-ol can be analyzed 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.

Fragment ion with m/e = 17

Butan-1-ol is $CH_3CH_2CH_2CH_2OH$. A common fragment with mass 17 is the hydroxyl ion:

$$\boxed{OH^+}$$

Mass:

$$16\,(O) + 1\,(H) = \boxed{17}$$

So, m/e = 17 → OH^+.

ii. Two other expected fragment ions

Two possible fragments are:

1. CH_2OH^+

$$12 + (3 \times 1) + 16 = \boxed{31}$$

Therefore, m/e = 31.

2. **$C_2H_5^+$**

$$(\mathbf{2 \times 12}) + (\mathbf{5 \times 1}) = \boxed{\mathbf{29}}$$

Therefore, m/e = 29.

Final answers

Fragment ion	Formula	m/e
Hydroxyl ion	OH^+	17

Fragment ion	Formula	m/e
Hydroxymethyl ion	CH_2OH^+	31
Ethyl ion	$C_2H_5^+$	29

Note: In mass spectrometry, the fragment ions are positively charged; the original equation should therefore show OH^- for the nucleophile in the NaOH reaction, not OH^+.

b. Identify the functional groups responsible for the peaks X and Y. (See Spectrum from book)

Ans.

b) Functional groups responsible for X and Y

- X: C–H stretching of alkyl group, around 2850–3000 cm^{-1}.
- Y: C=O (carbonyl) stretching, around 1650–1750 cm^{-1}.

c) Distinguishing A and B by IR spectroscopy

- A (cyclopentanone): Shows a strong C=O peak near 1715 cm^{-1}.
- B (cyclopentenol): Shows a broad O–H peak around 3200–3600 cm^{-1} and a C=C peak near 1640 cm^{-1}.
- Thus, the presence of C=O in A and O–H in B distinguishes them.

d) IHD and UV spectroscopy

i. IHD

- **But-1-ene, C_4H_8:**

$$IHD = 1$$

- **But-1,3-diene, C_4H_6:**

$$IHD = 2$$

ii. UV absorption

- **But-1,3-diene** has a **longer λmax** than but-1-ene because its two C=C bonds are **conjugated**.
- Conjugation lowers the energy gap, causing absorption at a **longer wavelength**.

e) Fragments of C_7H_{16} in mass spectrometry

Possible major alkyl fragments:

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**
$C_7H_{16}^+$ (M^+)	**100**

Constructed Response Questions

Solution of Q3(a) Identification of compound X

Given: C = 88.89%, H = 11.1%.

For 100 g:

$$\frac{88.89}{12} = 7.41,\ \frac{11.1}{1} = 11.1$$

Ratio:

$$C : H = 2 : 3$$

Empirical formula = **C_2H_3**

Empirical mass:

$$(2 \times 12) + 3 = 27$$

Molecular mass = 54:

$$\frac{54}{27} = 2$$

Therefore, molecular formula:

$$\boxed{C_4H_6}$$

It reacts with **2 moles H_2**, indicating **two C=C bonds**.

Therefore, a possible structure is:

$$\boxed{CH_2 = CH - CH = CH_2}$$

Compound X = buta-1,3-diene (1,3-butadiene).

Solution of Q3(b) UV-visible spectroscopy

- **Compound (i):** Contains a **conjugated diene** in the side chain.
- **Compound (ii):** Contains the same conjugated diene plus an **additional isolated C=C bond** in the ring.
- The conjugated system gives absorption at a **longer λmax** than isolated double bonds.

Thus, compare their **λmax and absorption intensity**; the compound with the more extensive effective conjugation absorbs at the **longer wavelength**.

UNIT 30: NMR SPECTROSCOPY

Solved Quick Checks 30.1–30.7

Quick Check 30.1

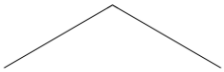
a) Explain why the 12 protons in TMS produce only a single peak.

Answer: TMS, $Si(CH_3)_4$, is highly symmetrical. All four CH_3 groups are equivalent, so all 12 protons have exactly the same chemical environment. They therefore resonate at one chemical shift (defined as $\delta = 0.00$ ppm) and give one sharp singlet.

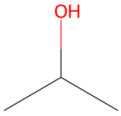
Structure: Tetramethylsilane, $Si(CH_3)_4$

b) Identify the number of proton environments and predict the expected chemical shift for each environment.

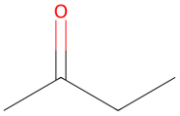
1,2-dichloroethane, $ClCH_2CH_2Cl$



Propane, $CH_3CH_2CH_3$



Propan-2-ol, $(CH_3)_2CHOH$



Butan-2-one, $CH_3COCH_2CH_3$

Molecule	No. of ^1H environments	Protons in each environment	Approx. δ / ppm
i) 1,2-dichloroethane	1	All CH_2 protons equivalent	3.5–3.8
ii) Propane	2	Terminal CH_3; central CH_2	0.9–1.1; 1.2–1.6
iii) Propan-2-ol	3	Equivalent CH_3; CH–OH; O–H	1.0–1.3; 3.7–4.2; ~1–5 (variable)
iv) Butan-2-one	3	CO–CH_3; CO–CH_2; terminal CH_3	2.0–2.2; 2.3–2.6; 0.9–1.1

c) What proton environment does a signal at δ 7.5 ppm likely represent?

Answer: An aromatic (aryl) proton, such as a proton attached directly to a benzene ring. Aromatic H atoms commonly appear around δ 6.5–8.5 ppm.

Quick Check 30.2

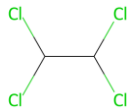
a) What does the number of signals in a ^1H NMR spectrum represent?

Answer: The number of signals equals the number of chemically non-equivalent proton environments in the molecule (allowing for symmetry).

b) Predict the number of peaks in the ^{1}H NMR spectra of the following molecules.

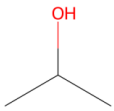
Molecule	Structure/symmetry idea	Expected ^{1}H signals
i) "1,1,2,2-dichloroethane"*	Interpreted as $CHCl_2$–$CHCl_2$; the two CH protons are equivalent by symmetry	1
ii) Butane	Two equivalent terminal CH_3 groups and two equivalent internal CH_2 groups	2
iii) Propan-2-ol	Equivalent CH_3 groups, one CH, one OH	3
iv) Pentan-3-one	Symmetric: equivalent CH_3 groups and equivalent CH_2 groups	2
v) Benzene	All six ring protons equivalent	1

"1,1,2,2-dichloroethane" is not a valid IUPAC names. The likely intended compound is 1,1,2,2-tetrachloroethane.

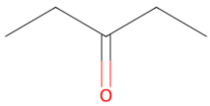


1,1,2,2-tetrachloroethane, $CHCl_2CHCl_2$

Butane, $CH_3CH_2CH_2CH_3$



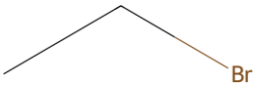
Propan-2-ol, $(CH_3)_2CHOH$



Pentan-3-one, $CH_3CH_2COCH_2CH_3$

Benzene, C_6H_6

c) Predict the number of peaks and their chemical shifts for bromoethane, CH_3–CH_2–Br.

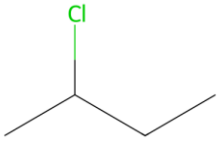


Structure: Bromoethane, CH_3CH_2Br

Proton set	Integration	Approx. δ / ppm	Typical splitting
CH_3–	3 H	1.5–1.8	Triplet
–CH_2Br	2 H	3.3–3.6	Quartet

Conclusion: Therefore, bromoethane gives 2 main ^{1}H NMR signals.

d) How many signals are observed in the ^{1}H NMR spectrum of 2-chlorobutane? Draw the structure and identify the H atoms with different chemical shifts.



Structure: 2-Chlorobutane, $CH_3CH(Cl)CH_2CH_3$

Answer: At the introductory level, 4 proton environments are counted: CH_3(a)–CH(b)(Cl)–CH_2(c)–CH_3(d). Thus four main signals are expected.

Environment	Protons	Approx. δ / ppm
a: CH_3 next to CHCl	3 H	~1.3–1.7
b: CH–Cl	1 H	~3.7–4.2
c: CH_2	2 H	~1.4–2.0

d: terminal CH_3	3 H	~0.9–1.1

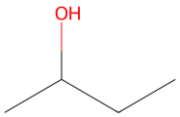
e) Arrange the different protons in $CH_3CH_2CH(CH_3)OH$ in increasing order of peak areas.

Answer: Peak area is proportional to the number of H atoms in each environment. Therefore: OH (1 H) = CH (1 H) < CH_2 (2 H) < CH_3 (3 H) = CH_3 (3 H).

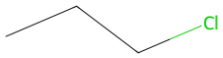
Note: The OH integral is nominally 1 H but can be less reliable because exchangeable protons may broaden or exchange.

Quick Check 30.3

a) Calculate the number of sub-peaks for each signal in the high-resolution spectra of the following compounds.



Butan-2-ol, $CH_3CH(OH)CH_2CH_3$



1-Chloropropane, $CH_3CH_2CH_2Cl$

Propanone, CH_3COCH_3

2,2-Dimethylpropane, $C(CH_3)_4$

Methanol, CH_3OH

2-Methylpropan-2-ol, $(CH_3)_3COH$

Compound	**Signal**	**Adjacent H counted**	**Sub-peaks / pattern n+1 Rule**
i) Butan-2-ol	CH_3–CH(OH)	1	2 — doublet
	CH(OH)	3 + 2 = 5	6 — sextet
	CH_2	1 + 3 = 4	5 — quintet
	terminal CH_3	2	3 — triplet
	OH	exchangeable	1 — broad singlet
ii) 1-Chloropropane	CH_3	2	3 — triplet
	middle CH_2	3 + 2 = 5	6 — sextet
	CH_2Cl	2	3 — triplet
iii) Propanone	both CH_3 groups (all 6 H equivalent)	0	1 — singlet
iv) 2,2-Dimethylpropane	all four CH_3 groups (12 H equivalent)	0	1 — singlet
v) Methanol	CH_3	no adjacent C–H	1 — singlet
	OH	exchangeable	1 — broad singlet

vi) 2-Methylpropan-2-ol	9 equivalent CH_3 H	0	1 — singlet
	OH	exchangeable	1 — broad singlet

Note: In real spectra, couplings to two non-equivalent neighboring sets can produce more complex multiplets. The table follows the simplified "total adjacent H + 1" treatment used for this type of short question.

Quick Check 30.4

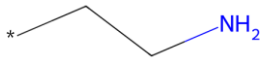
a) Why do O–H or N–H peaks disappear after a D_2O shake in NMR spectroscopy?

Answer: O–H and N–H protons are labile and rapidly exchange with deuterium from D_2O, forming O–D or N–D bonds. Deuterium (^2H) is not detected in a normal ^1H NMR spectrum, so the original O–H or N–H signal disappears.

Example: R–OH + D_2O ⇌ R–OD + HOD

Similarly, R–NH_2 exchanges H for D and its N–H signal is lost.

b) State the expected peak area and splitting pattern for (–$CH_2CH_2NH_2$).

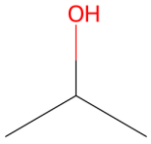


Structure: Aminoethyl fragment, –$CH_2CH_2NH_2$

Proton set	Expected area	Typical splitting
–CH_2– next to –CH_2NH_2	2 H	Triplet from the adjacent CH_2
–CH_2NH_2	2 H	Triplet from the adjacent CH_2
–NH_2	2 H	Usually a broad singlet

Quick Check 30.5

For $(CH_3)_2CHOH$ (propan-2-ol), predict: (a) number of peaks, (b) type of proton and chemical shift, (c) relative peak areas, and (d) splitting pattern.



Structure: Propan-2-ol, $(CH_3)_2CHOH$

Answer: There are 3 proton environments: the two equivalent CH_3 groups (6 H total), the methine CH (1 H), and the OH proton (1 H).

Proton type	Approx. δ / ppm	Relative area	Splitting

Two equivalent CH_3 groups	~1.0–1.3	6	Doublet (split by 1 neighboring CH)
CH attached to OH	~3.7–4.2	1	Septet/heptet (split by 6 equivalent CH_3 H)
OH	~1–5, variable	1	Broad singlet

Peak-area ratio: Relative integral ratio = 6 : 1 : 1.

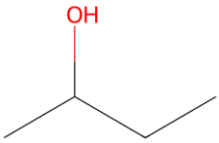
Quick Check 30.6

a) How many signals are expected in the ^{13}C NMR spectrum of butane? Justify your answer.

Structure: Butane, $CH_3CH_2CH_2CH_3$

Answer: 2 signals. By symmetry, the two terminal CH_3 carbons are equivalent to each other, and the two internal CH_2 carbons are equivalent to each other. Thus butane has only two distinct carbon environments.

b) Predict the ^{13}C NMR spectrum of butan-2-ol.

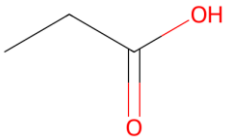


Structure: Butan-2-ol, $CH_3CH(OH)CH_2CH_3$

Answer: Butan-2-ol has no carbon symmetry, so all four carbon atoms are in different environments and 4 ^{13}C signals are expected.

Carbon environment	Approx. δ / ppm
C attached directly to OH (CHOH)	~65–70
CH_2	~30–40
CH_3 attached to CHOH	~20–25
Terminal CH_3	~10–15

c) Predict the chemical shifts of the carbon atoms in propanoic acid.

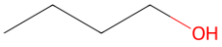


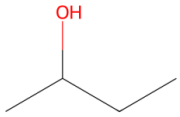
Structure: Propanoic acid, CH_3CH_2COOH

Carbon	Environment	Approx. δ / ppm
C-1	Carboxylic acid carbonyl, COOH	~175–185
C-2	CH_2 α to carbonyl	~25–35
C-3	Terminal CH_3	~8–15

Quick Check 30.7

Draw the structures of butan-1-ol and butan-2-ol.

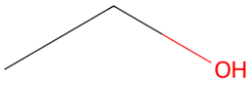




Butan-1-ol, $CH_3CH_2CH_2CH_2OH$ Butan-2-ol, $CH_3CH(OH)CH_2CH_3$

Answer: Butan-1-ol: $CH_3CH_2CH_2CH_2OH$. Butan-2-ol: $CH_3CH(OH)CH_2CH_3$.

i) Using the spectrum given in Figure 30.8, explain why this spectrum does not match either butan-1-ol or butan-2-ol.



Structure: Ethanol, CH_3CH_2OH

Answer: Figure 30.8 is the high-resolution ^1H NMR spectrum of ethanol: it has three main proton environments (about δ 1.2, 2.6 and 3.7 ppm). In contrast, both butan-1-ol and butan-2-ol have five main proton environments in the usual introductory treatment. Their integrations and splitting patterns must also account for four carbon atoms, not only the CH_3–CH_2–OH pattern of ethanol. Therefore a three-signal ethanol-type spectrum cannot match either butanol isomer.

Note: The Figure 30.8 spectrum itself was not included in the uploaded images; the chapter context identifies Figure 30.8 as ethanol. If your printed Figure 30.8 differs, compare its number of signals/integrals with the five environments listed below.

ii) Which peaks (chemical shifts) would you expect in the spectra of butan-1-ol and butan-2-ol?

Butan-1-ol proton environment	**Approx. δ / ppm**
Terminal CH_3–	~0.9–1.0
CH_2 farthest from OH	~1.2–1.4
CH_2 β to OH	~1.4–1.7
CH_2–OH	~3.4–3.8
OH	~1–5, variable/broad
Butan-2-ol proton environment	**Approx. δ / ppm**
Terminal CH_3–CH_2	~0.9–1.0
CH_3–CH(OH)	~1.0–1.3
CH_2	~1.3–1.8
CH–OH	~3.7–4.2
OH	~1–5, variable/broad

Multiple Choice Questions - Solved with Reasons

Answer Key

Question	Correct option	Answer
I	c)	Nuclear spin
II	c)	Parts per million (ppm)
III	d)	Avoid solvent signal interference
IV	d)	Relative number of protons
V	d)	Rapid chemical exchange
VI	c)	Adjacent carbon atoms
VII	b)	Functional group / chemical environment
VIII	b)	Chemically non-equivalent carbons
IX	b)	2 peaks
X	c)	Triplet

I. NMR relies on the magnetic properties of nuclei known as:

a) Chemical shift
b) Nuclear density
c) Nuclear spin
d) Signal intensity

Correct answer: c) Nuclear spin

Reason: Certain nuclei possess spin angular momentum and therefore behave like tiny magnets in an external magnetic field. NMR spectroscopy is based on transitions between nuclear spin energy levels, so nuclear spin is the fundamental magnetic property involved.

II. Chemical shift (δ) in ^{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)

Correct answer: c) Parts per million (ppm)

Reason: Chemical shift is a dimensionless relative scale referenced to tetramethylsilane (TMS), which is assigned $\delta = 0.00$ ppm. Using ppm makes chemical-shift values largely independent of the operating frequency of the NMR instrument.

III. Deuterated solvents (for example, $CDCl_3$) 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

Correct answer: d) Avoid solvent signal interference

Reason: A normal proton-containing solvent would produce a very large ^{1}H NMR peak that could obscure the sample signals. Replacing most solvent ^{1}H atoms with deuterium (^{2}H) greatly reduces this interference because deuterium is not detected in a routine ^{1}H NMR spectrum. TMS, not the deuterated solvent, is the usual chemical-shift reference.

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

Correct answer: d) Relative number of protons

Reason: The integrated area under a ^{1}H NMR signal is proportional to the number of equivalent protons producing that signal. Integration therefore gives the relative proton ratio, such as 3H:2H:1H. It does not directly give the number of neighboring protons; that information comes from splitting.

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

Correct answer: d) Rapid chemical exchange

Reason: O-H and N-H protons are exchangeable and often move rapidly between molecules through proton exchange. This rapid exchange averages out spin-spin coupling, so these signals commonly appear as broad singlets and usually do not show normal n + 1 splitting.

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

Correct answer: c) Adjacent carbon atoms

Reason: For simple first-order ^{1}H NMR spectra, a set of protons is split by n equivalent neighboring protons, usually on an adjacent carbon atom, into n + 1 sub-peaks. For example, two neighboring equivalent protons split a signal into three lines (a triplet).

VII. The chemical shift (δ) of a ^{13}C peak identifies the:

a) Number of adjacent carbons
b) Functional group environment (C-C, C-O, etc.)
c) Molecule's symmetry
d) Number of protons

Correct answer: b) Functional group / chemical environment

Reason: A carbon atom's ^{13}C chemical shift depends on its electronic environment. Bonding to electronegative atoms, participation in C=C bonds, aromatic rings, and carbonyl groups changes shielding and therefore moves the carbon signal into characteristic chemical-shift regions.

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) ^{13}C atoms

Correct answer: b) Chemically non-equivalent carbons

Reason: Each chemically distinct carbon environment normally produces one ^{13}C NMR signal. Symmetry can make two or more carbon atoms equivalent, so the number of signals may be smaller than the total number of carbon atoms in the molecule.

IX. How many ^{13}C peaks does propane ($CH_3CH_2CH_3$) show?

a) 1 b) 2

c) 3 d) 4

Correct answer: b) 2

CH_3(a) - CH_2(b) - CH_3(a) → two carbon environments: a and b

Reason: Propane is symmetrical. The two terminal CH_3 carbons are chemically equivalent and give one signal, while the central CH_2 carbon is in a different environment and gives a second signal. Therefore, propane gives 2 distinct ^{13}C NMR peaks.

X. What is the splitting pattern for a proton signal with 2 neighboring equivalent protons (n = 2)?

a) Singlet b) Doublet

c) Triplet d) Quartet

Correct answer: c) Triplet

Reason: According to the n + 1 rule, the number of lines is n + 1. With n = 2 neighboring equivalent protons, the signal is split into 2 + 1 = 3 lines, so the pattern is a triplet.

Q2. SHORT-ANSWER QUESTIONS

a) State two reasons why TMS is a standard for ^1H NMR.

Answer: Tetramethylsilane, $Si(CH_3)_4$, is used as the reference standard because:

- All 12 protons are chemically equivalent, so TMS gives one sharp, intense signal.
- Its protons are highly shielded, so the signal occurs at the extreme upfield position and is assigned $\delta = 0.00$ ppm; it therefore rarely overlaps with ordinary organic proton signals.

Also acceptable: TMS is chemically inert, soluble in common organic solvents, and volatile/easy to remove.

b) Why does deuterium (D) not appear in a ^1H NMR spectrum?

Answer: Deuterium is ^2H, not ^1H. A ^1H NMR spectrometer is tuned to the resonance frequency of protons (^1H), so deuterium resonates at a different frequency and is not detected in the ordinary ^1H NMR spectrum.

c) A compound ($C_4H_{10}O$) has a ^1H NMR peak area ratio of 1:3:6. How many protons does each signal represent?

Answer: The molecular formula contains 10 hydrogens. The integration ratio is 1 + 3 + 6 = 10 parts, so each part corresponds to one proton.

Peak areas 1 : 3 : 6 → 1 H : 3 H : 6 H

d) What is the purpose of the D_2O shake test in ^1H NMR?

Answer: The D_2O shake test is used to identify exchangeable O-H and N-H protons. These protons exchange with deuterium from D_2O, forming O-D or N-D bonds. Because deuterium is not observed in a normal ^1H NMR spectrum, the O-H or N-H peak disappears after shaking with D_2O.

e) List the key features used to interpret a ^1H NMR spectrum.

Answer: The main features are:

- Number of signals/peaks - gives the number of different proton environments.
- Chemical shift (δ, ppm) - indicates the electronic/functional-group environment of each proton set.
- Integration or peak area - gives the relative number of protons in each environment.
- Splitting pattern (multiplicity) - gives information about neighboring non-equivalent protons, commonly using the n + 1 rule.
- Coupling constant (J), when required - helps identify which split signals are coupled to one another.

f) State two differences between ^{1}H NMR and ^{13}C NMR spectroscopies.

Feature	^{1}H NMR	^{13}C NMR
What the signals represent	Chemically non-equivalent proton environments	Chemically non-equivalent carbon environments
Integration	Peak areas are normally proportional to relative proton numbers	Routine proton-decoupled ^{13}C peak intensities are generally not used for counting carbons
Splitting	Spin-spin splitting is commonly observed and is useful	Routine broadband proton-decoupled ^{13}C spectra usually show singlets

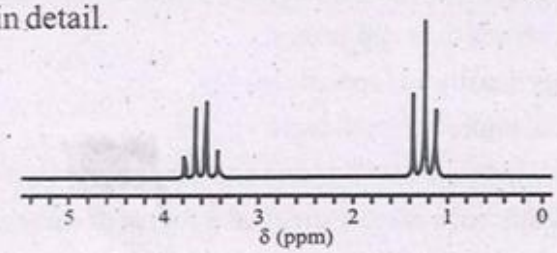
Q3. CONSTRUCTED-RESPONSE QUESTIONS

Q3. CONSTRUCTED–RESPONSE QUESTIONS

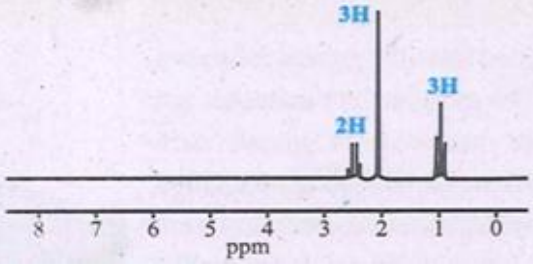
a) A $-CH_2-$ group is lying between a $-CH_3$ and a $-CH<$ group. What is the splitting pattern for the $-CH_2-$ signal? Show your calculation.

b) Predict the ^{1}H NMR spectrum of butanoic acid.

c) An organic compound has a molecular formula, chloroethane (C_2H_5Cl). The ^{1}H NMR of the compound is given below. Deduce the structure of the compound by using its spectrum. Explain your working in detail.



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 ^{1}H NMR of the compound is shown below. Deduce the structure of the compound and justify your answer.



a) A $-CH_2-$ group is lying between a $-CH_3$ and a $-CH_2-$ group. What is the splitting pattern for the central $-CH_2-$ signal? Show your calculation.

Answer: Using the simple school-level n + 1 rule, the central CH_2 has 3 neighboring protons on one side and 2 neighboring protons on the other side.

n = 3 + 2 = 5 ⇒ n + 1 = 6 ⇒ SEXTET

Note: In a high-resolution real spectrum, the two neighboring sets can have different coupling constants, so the signal may appear as a more complex multiplet. For the simple n + 1 treatment expected here, the answer is a sextet.

b) Predict the ^{1}H NMR spectrum of butanoic acid.

Structure: CH_3-CH_2-CH_2-COOH

Butanoic acid has four different proton environments, so four ^{1}H NMR signals are expected.

Proton set	Integration	Approx. δ / ppm	Splitting	Reason
CH_3-CH_2-	3 H	0.9-1.1	Triplet	Split by the adjacent CH_2 (2 H): n + 1 = 3
-CH_2-CH_2-COOH (middle CH_2)	2 H	1.4-1.8	Multiplet; often approximated as sextet	Coupled to 3 H on one side and 2 H on the other
-CH_2-COOH	2 H	2.2-2.5	Triplet	Split by the adjacent CH_2 (2 H)
-COOH	1 H	10-12 (often about 11-12)	Broad singlet	Exchangeable acid proton; normally does not show useful splitting

Relative integration: 3 : 2 : 2 : 1

c) Chloroethane (C_2H_5Cl) has the ^{1}H NMR spectrum shown. Deduce the structure and explain your working.

Deduced structure: CH_3-CH_2-Cl (chloroethane)

Explanation:

- There are two proton environments, so the spectrum should contain two main signals.
- The CH_2 bonded directly to chlorine is deshielded by electronegative Cl and appears downfield at about δ 3.4-3.7 ppm. It integrates to 2 H and is split by the neighboring CH_3 (3 H) into a quartet.
- The CH_3 group appears further upfield at about δ 1.1-1.5 ppm. It integrates to 3 H and is split by the neighboring CH_2 (2 H) into a triplet.
- The integration ratio 2:3 and the quartet-triplet pair are exactly what is expected for an ethyl group, CH_3CH_2-, with the CH_2 attached to chlorine.

Assignment	Approx. δ / ppm	Integration	Multiplicity
CH_2Cl	3.4-3.7	2 H	Quartet
CH_3	1.1-1.5	3 H	Triplet

d) A compound has molecular formula C_4H_8O, gives a positive 2,4-DNP test but a negative Fehling's test, and has the shown ^1H NMR spectrum. Deduce its structure and justify your answer.

Answer: A positive 2,4-DNP test shows that the compound contains a carbonyl group (aldehyde or ketone). A negative Fehling's test indicates that it is not an aliphatic aldehyde; therefore, the carbonyl compound is a ketone.

Deduced structure: CH_3-CO-CH_2-CH_3 (butan-2-one)

NMR justification:

- A 3 H signal at about δ 2.0-2.2 ppm corresponds to CH_3-CO-. There are no hydrogens on the adjacent carbonyl carbon, so this methyl signal is a singlet.
- A 2 H signal at about δ 2.3-2.6 ppm corresponds to -CO-CH_2-. It is split by the neighboring terminal CH_3 (3 H) into a quartet.
- A 3 H signal at about δ 0.9-1.1 ppm corresponds to the terminal -CH_3. It is split by the neighboring CH_2 (2 H) into as triplet.
- The integrations 3 H : 2 H : 3 H account for all 8 hydrogens in C_4H_8O and match butan-2-one.

Proton set	**Approx. δ / ppm**	**Integration**	**Multiplicity**
CH_3CO-	2.0-2.2	3 H	Singlet
-$COCH_2$-	2.3-2.6	2 H	Quartet
-CH_2CH_3	0.9-1.1	3 H	Triplet

Final structures

Q3(c)	CH_3-CH_2-Cl (chloroethane)
Q3(d)	CH_3-CO-CH_2-CH_3 (butan-2-one)

UNIT 31: MATERIALS AND ENERGY

Quick Check 31.1

a) Why ceramics are used as insulators on power lines?

Ceramics such as porcelain have strong bonds with no free mobile electrons or ions available to carry charge, giving them very high electrical resistance. It can combine with their high mechanical strength, hardness, and resistance to weathering, this makes them ideal for insulating power lines.

b) Why is silicon preferred for use in microchips and solar panels?

Silicon is a semiconductor, so its conductivity can be precisely controlled (e.g., through doping) to switch between conducting and insulating states as needed in circuits. It is also highly abundant, inexpensive, light, heat and voltage sensitive, and efficiently converts sunlight into electricity, making it ideal for both microchips and solar panels.

c) What do reinforcement agents provide in composite materials?

The matrix holds the reinforcement together and gives the composite its shape, the reinforcement is what bears the load and gives the composite its strength and rigidity.

Quick Check 31.2

a) Name two types of hazards caused by toxic materials.

i) Health hazards: Carcinogens, mutagens, or hormone-disrupting chemicals that damage the body upon exposure.

ii) Environmental hazards: Heavy metals leaching into soil and groundwater, harming aquatic life and ecosystems.

b) Which recycling methods would you use for: i) empty metal food cans, ii) empty beverage glass bottles, iii) shopping bags and toys?

i) Metal food cans: Thermal and chemical refining (metallurgy).

ii) Glass bottles: Cullet preparation and melting.

iii) Shopping bags and toys (plastics): Mechanical recycling (sorting, cleaning, melting, and reforming the plastic.

c) Name the types of hazards posed by: i) poly(ethene), ii) Hg metal, iii) water/glass bottles, iv) hospital waste.

i) Poly(ethene): Environmental hazard.

ii) Mercury (Hg) metal: Health hazard

iii) Glass bottles: Physical hazard.

iv) Hospital waste: Biological hazard.

d) How does recycling help conserve natural resources?

Recycling reduces the need to mine or extract fresh raw materials (ores, oil, timber) from the earth, thereby preserving limited natural resources. It also saves energy compared to producing materials from raw ore (e.g., recycling aluminium uses about 95% less energy than extracting it from ore) and reduces the amount of solid waste sent to landfills.

Quick Check 31.3

a) If fossil fuels are non-renewable resources, why are they still heavily used worldwide?

Fossil fuels have high energy density, are relatively cheap to extract and use given existing infrastructure, and provide a reliable, concentrated, and easily transportable source of energy. Renewable alternatives are still being scaled up and, in many regions, are not yet able to fully replace fossil fuels for all needs (e.g., transportation, industry).

b) Can XRD be used to find the structures of liquids?

No. X-ray crystallography relies on the regular, repeating (ordered) arrangement of atoms in a crystalline solid to produce a distinct diffraction pattern. Liquids lack this fixed, long-range ordered structure, so they do not produce a clear diffraction pattern and XRD cannot be used to determine their structure.

Quick Check 31.4

a) Why is catalytic cracking more commonly used in modern petroleum refineries?

Catalytic cracking uses a catalyst (e.g., zeolites or silica-alumina) that lowers the activation energy of the reaction. This allows cracking to occur at lower temperatures and pressures than

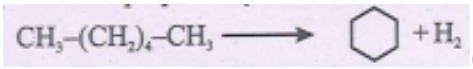
thermal cracking, saving energy and giving better control over the final product distribution, making it more efficient and economical for modern refineries.

b) If more alkenes such as ethene and propene are desired from higher hydrocarbons (diesel or kerosene), which cracking method should be preferred and why?

Thermal cracking should be preferred, because it operates at very high temperatures (450–750°C) without a catalyst and normally generates a higher percentage of alkenes, which are the key raw materials needed for the plastics and synthetic rubber industry.

c) During reforming, give one example of a straight-chain hydrocarbon.

Cyclic compounds are prepared by the conversion of straight-chain hydrocarbons e.g.



(hexane to cyclohexane)

d) Hexane is converted into benzene and hydrogen through reforming. Explain why hydrogen can be considered a valuable by-product.

The dehydrogenation aromatization of cyclohexane to benzene releases hydrogen gas (H_2) as a by-product. This hydrogen is not waste and it can be captured and reused as a clean fuel or as a valuable feedstock in other industrial chemical processes.

Quick Check 31.5

a) Why are batteries included in many solar energy systems?

Batteries store the electricity generated by the solar panels during sunny periods so that it can be used at night or on cloudy days when panels are not generating power. They also help stabilize voltage and protecting the system and ensuring a steady power supply.

b) The energy density of ethanol (24 MJ/L) is much lower than petrol (34.2 MJ/L). If ethanol were used in a combustion engine, what advantage/disadvantage would be observed?

This would be a disadvantage in terms of range and refueling frequency. Since, ethanol stores less energy per liter than petrol, a vehicle using ethanol would need to carry more fuel by volume (a larger fuel tank) to travel the same distance. It would need to be refueled more often, without any change to the engine's basic structure needed for this specific effect.

c) Identify the missing components in the reaction: $^{235}U + n \rightarrow \_\_\_ + \_\_\_ + 3n + energy$

The missing products are Barium-141 (^{141}Ba) and Krypton-92 (^{92}Kr):

$$^{235}U + {}^{1}n \rightarrow {}^{141}Ba + {}^{92}Kr + 3n + energy.$$

d) Why do nuclear reactions release much more energy than chemical reactions?

Nuclear reactions involve changes within the atomic nucleus itself (splitting or combining nuclei), which convert a small amount of mass directly into a very large amount of energy according to Einstein's mass-energy relationship ($E = mc^2$). Chemical reactions, in contrast, only involve the rearrangement of electrons in chemical bonds, which involves far smaller energy changes, so nuclear reactions release vastly more energy per reaction than chemical ones.

Exercise Q:2 (Short-Answer Questions)

a) What is a chain reaction in nuclear fission?

A chain reaction occurs when the neutrons released during the fission of one heavy nucleus (e.g., uranium-235) go on to strike and split other nuclei, releasing more neutrons and energy. These new neutrons can trigger further fission events, so the process becomes self-sustaining and continues to release energy repeatedly.

b) State the economic challenge associated with reprocessing waste materials.

Reprocessing waste (sorting, cleaning, melting, and other treatment methods) requires a large amount of energy and labour, making it expensive. This is often uneconomical, especially since raw materials are frequently available elsewhere at a lower cost.

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.

Zinc atoms are a different size from copper atoms, so when zinc is mixed into the copper lattice, it distorts the regular, orderly microstructure of the metal. This distortion disrupts the smooth slip planes along which atomic layers would normally slide over one another, making it harder for the layers to move. As a result, brass is harder and stronger than pure copper.

d) Define energy density and give one example.

Energy density is the amount of energy that can be stored per unit volume of a fuel, typically expressed in megajoules per litre (MJ/L).

For example, diesel has an energy density of about 37 MJ/L, higher than gasoline's ~34.2 MJ/L.

e) Name two specific semiconductors mentioned in the text and their modern applications.

i) Gallium arsenide (GaAs): Used in wireless communication devices, such as 5G internet devices.

ii) Gallium nitride (GaN): It is also mentioned, used in electric cars for fast charging.

f) State two applications of X-ray crystallography in science or industry.

1) Science: Determining the three-dimensional structure of biomolecules, such as the double helix structure of DNA, proteins, and enzymes.

2) Industry: Analyzing how a drug molecule binds to its target during pharmaceutical drug development, and analyzing minerals, synthetic crystals, and nanomaterials in materials science.

g) State two advantages and one disadvantage of nuclear fission.

Advantages:

i) It produces a very high amount of energy from a very small quantity of fuel.

ii) It does not release greenhouse gases such as CO_2 during electricity generation.

Disadvantage:

i) It produces radioactive waste that must be carefully handled and stored over a very long duration, and carries the risk of serious nuclear accidents (e.g., Chernobyl, Fukushima).

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 CO is a more efficient reducing agent in a large-scale furnace than solid carbon.

Carbon monoxide is a gas, so unlike solid carbon, CO can mix thoroughly and diffuse rapidly throughout the furnace, giving it much greater and more uniform contact with the solid iron oxide particles. This allows CO to reduce the ore more quickly, evenly, and completely across the large volume of a furnace than solid carbon could.

Exercise Q:3 (Constructed-Response Questions)

a) Explain environmental problems caused by fossil fuels.

Burning fossil fuels releases carbon dioxide (CO_2), a greenhouse gas that traps heat in the atmosphere, contributing to global warming and climate change. Combustion also releases sulfur oxides (SO_x) and nitrogen oxides (NO_x), which react with water vapour in the atmosphere to form sulfuric and nitric acids, causing acid rain that damages soil, crops, and aquatic ecosystems.

b) Based on the chemical equations, explain why roasting sulphide ores poses a greater environmental challenge compared to the calcination of carbonate ores.

Roasting: $2ZnS + 3O2 \rightarrow 2ZnO + 2SO_2$

Roasting a sulphide ore releases sulphur dioxide (SO_2) gas, which is toxic, causes respiratory problems, and reacts with water and oxygen in the atmosphere to form sulfuric acid, a major cause of acid rain.

Calcination: $ZnCO_3 \rightarrow ZnO + CO_2$

Calcination of a carbonate ore, by contrast, releases carbon dioxide (CO_2). While CO_2 is a greenhouse gas, it is not directly toxic or acidifying in the same immediate way as SO_2.

Therefore, roasting sulphide ores poses a greater environmental challenge due to the release of harmful, acid-rain-forming SO_2 gas.

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?

Even small amounts of impurities significantly increase the electrical resistance of copper and reduce its conductivity. For applications like electrical wiring, copper needs to be about 99.99% pure to conduct electricity efficiently and safely. The refining step (thermal, chemical, or electrochemical) removes these remaining impurities to achieve the very high purity required, which the initial 98%-pure sample from reduction alone cannot provide.

d) Explain why chemical recycling (depolymerization) is often superior to mechanical recycling.

Chemical recycling (depolymerization) is often superior to mechanical recycling because it breaks polymers into their original monomers, which can be purified and reused to produce new plastics with properties similar to virgin materials. In contrast, mechanical recycling only melts and reshapes plastics, causing degradation of polymer chains after repeated recycling.

Chemical recycling can also process mixed or contaminated plastic waste more effectively, resulting in higher-quality products and reducing environmental pollution.

e) Gold is often found in its free state, while sodium is only found in the combined state. Use the concept of the reactivity series to justify why the extraction process for sodium is significantly more energy-intensive than for gold.

Reactivity series: K > Na > Ca > Mg > Al > Zn > Fe > Pb > Cu > Ag > Au

Gold is very low in the reactivity series, so it occurs naturally in its free state and requires little energy to extract. Sodium is highly reactive and exists only in compounds, so a large amount of energy is needed to extract it by electrolysis.

UNIT 32: Medicine, Agriculture and Industry

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?

Drug B is considered safer. A higher therapeutic index ($TI = TD_{50}/ED_{50}$) means there is a much larger gap between the dose that is effective and the dose that becomes toxic, giving a greater margin of safety and more flexibility in dosing.

b) How do antacids (e.g., magnesium hydroxide, $Mg(OH)_2$) chemically regulate stomach pH? Write a simple neutralization equation to illustrate this.

Antacids are weak bases that chemically neutralize the excess hydrochloric acid (HCl) in the stomach, raising the pH and relieving symptoms such as heartburn.

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

c) Identify the core ring system in penicillin that is essential for its antibacterial activity.

The four-membered beta-lactam ring is the core ring system essential for penicillin's antibacterial activity. It is the reactive site that attacks and disables the bacterial enzymes responsible for cell wall synthesis.

d) Why do many antiviral drugs cause significant side effects for the host patient?

Viruses are not independent organisms; they replicate by hijacking and using the host cell's own DNA/RNA machinery. Because viral replication is so closely tied to normal human cellular processes, it is difficult to design a drug that blocks the virus without also disrupting or damaging the healthy host cells that share those same processes, leading to significant side effects.

Quick Check 32.2

a) State two major agricultural benefits of using fungicides, linking to crop health or yield.

1) Fungicides protect crops from fungal diseases by targeting the fungal cell membrane (disrupting ergosterol synthesis), preventing the fungus from destroying plant tissue, which preserves plant.

2) By preventing fungal damage and disease, fungicides reduce crop losses and help maintain or increase crop yield, contributing to food security.

b) Write the balanced chemical equation for the 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.

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

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.

Drought tolerance (e.g., varieties that survive with less water) and heat tolerance (e.g., heat-tolerant wheat).

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.

i) Textile industry: Relies on caustic soda (NaOH) for mercerizing cotton, along with synthetic dyes and hydrogen peroxide for bleaching.

ii) Construction/cement industry: Relies on limestone (calcium carbonate, $CaCO_3$) as the key raw material for making cement.

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.

Fractional distillation separates crude oil based on differences in boiling points among its hydrocarbon components. Larger hydrocarbon molecules have stronger intermolecular (van der Waals) forces between them, so they require more energy (higher temperatures) to vaporize and therefore have higher boiling points. They condense lower down in the fractionating column. Smaller hydrocarbons have weaker intermolecular forces, lower boiling points, and rise further up the column before condensing, allowing the mixture to be separated into fractions.

c) Many cosmetics and perfumes have esters as ingredients. Name the two types of reactants needed to synthesize an ester and the catalyst typically used.

Esters are synthesized from a carboxylic acid and an alcohol, typically using a strong acid catalyst such as concentrated sulfuric acid (H_2SO_4).

d) Explain the chemical reason why highly oxidizing chemicals (like concentrated HNO_3) must be stored separately from flammable organic chemicals (like ethanol).

Strong oxidizing agents such as concentrated nitric acid can readily supply oxygen to, or directly oxidize, flammable organic substances like ethanol. If they come into contact, this can trigger a vigorous, highly exothermic reaction that may ignite the flammable material or even cause a fire or explosion. Storing them separately prevents accidental contact and reduces the risk of such dangerous reactions.

Exercise Q:2 (Short-Answer Questions)

a) Write the significance of Therapeutic Window and how it differs from Therapeutic Index.

The Therapeutic Window shows doctors the actual range of drug concentrations in the plasma (between the Minimum Effective Concentration and Minimum Toxic Concentration) that are both effective and safe, helping determine the correct dosing range for a patient.

The Therapeutic Index, by contrast, is a single quantitative ratio (TD_{50}/ED_{50}) that compares the toxic dose to the effective dose, giving an overall numeric measure of a drug's relative safety that can be used to compare different drugs, rather than describing a specific concentration range.

b) How does the structure of penicillin allow it to inhibit an enzyme?

Penicillin's four-membered beta-lactam ring is highly strained and reactive. This ring can bind to and react with the active site of the bacterial enzyme (transpeptidase) responsible for building the bacterial cell wall, permanently blocking/inhibiting the enzyme's function. Without a functioning enzyme, the bacteria cannot properly construct their cell walls and die.

c) What is the primary mechanism of action for opiate drugs, such as morphine, in providing analgesia (pain relief)?

Opiates bind to specific opioid receptors in the brain and spinal cord (central nervous system), mimicking the body's natural painkillers (endorphins), using a key-and-lock mechanism. Binding closes calcium channels and opens potassium channels in the neuron, hyperpolarising it, which

makes it much harder for the cell to transmit pain signals to the brain, thereby reducing the sensation of pain.

d) Why is it significantly more challenging to develop safe and effective antiviral drugs compared to antibacterial drugs (antibiotics)?

Bacteria are independent, living organisms with their own distinct cellular structures (such as cell walls and unique enzymes) that drugs like penicillin can target without harming human cells. Viruses, however, are not independent and they live inside host cells and hijack the host's own DNA/RNA machinery to replicate. This makes it very difficult to design a drug that disrupts the virus's life cycle without also damaging the healthy human cells.

e) What is the concept of pesticide resistance in a target pest population?

Pesticide resistance develops when, after repeated exposure to a pesticide, a small number of pests in a population survive due to natural genetic variation. These resistant pests reproduce and pass their resistance traits on to their offspring, so over time an increasing proportion of the pest population becomes resistant, and the pesticide becomes less effective at controlling them, often forcing the use of more toxic pesticides.

f) Define soil salinization. How can it be caused by irrigation practices in regions experiencing higher temperatures and reduced precipitation?

Soil salinization is the build-up of soluble salts in the soil to levels high enough to harm plant growth and reduce soil fertility. In regions with higher temperatures and reduced rainfall, farmers rely more heavily on irrigation, and the higher temperatures cause increased evaporation of the irrigation water from the soil surface. Because there is not enough rainfall to flush the salts left behind deeper into the ground or away, these salts accumulate at the surface over time, leading to salinization and damaging crop growth.

g) How does the chemical industry contribute to both energy production from fossil fuels and the development of renewable energy technologies?

For fossil fuels, the chemical industry processes crude oil and natural gas through refining, fractional distillation, cracking, and reforming to produce usable fuels (petrol, diesel, kerosene) and petrochemical feedstock. For renewable energy, the chemical industry produces the specialized materials needed for renewable technologies, such as high-purity silicon

semiconductors for solar panels, as well as other materials and chemicals used in batteries and energy storage systems.

h) Name the industrial process used to produce caustic soda (NaOH) and chlorine (Cl_2) from rock salt (NaCl).

The Chlor-Alkali process, an industrial electrolysis method that breaks down sodium chloride (brine) to produce chlorine gas, sodium hydroxide (caustic soda), and hydrogen gas.

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.

1) Plastics (e.g., poly(ethene)/polyethylene, derived from ethene), used to make bags, bottles, and packaging.

2) Synthetic rubber (e.g., styrene-butadiene rubber, derived from butadiene), used to make tires and footwear.

j) Distinguish between a corrosive hazard and a toxic hazard, giving one example of a chemical for each.

A corrosive hazard involves a chemical that directly destroys or damages living tissue or materials on contact through a chemical reaction. For example, concentrated sulfuric acid (H_2SO_4), which causes severe burns on skin contact.

A toxic hazard involves a substance that causes harm or poisoning after it enters the body (through ingestion, inhalation, or absorption), even without necessarily damaging tissue on direct contact. For example, mercury (Hg), which is a neurotoxin that damages the nervous system once absorbed into the body.

Exercise Q:3 (Constructed-Response Questions)

a) Drug A has an ED50 of 20 mg/dm³ and a TD50 of 80 mg/dm³. Drug B has an MEC of 5 mg/dm³ and an MTC of 50 mg/dm³. 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.

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.

Drug A has TI: ED_{50} = 20mg, TD_{50} = 80mg.

So, TI = TD_{50}/ED_{50} = 80/40 = 4.

(II) Define Therapeutic Window (TW) and identify which drug (B or C) has the wider therapeutic window. Justify your answer.

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 less to be ineffective and also not too high to be dangerous.

Drug B: MEC = 5 mg /dm^3, MTC = 50 mg/dm^3. TW = 50 – 5 = 45

Drug C: MEC = 10 mg /dm^3, MTC = 15 mg /dm^3 TW = 15.- 10 = 5

Drug B has wider therapeutic wndow because 50 - 5 = 45

(III) Compare the relative safety of Drug A and Drug C.

Drug C has very narrow window 15 - 10 = 5. So, Drug A is relatively safer because small overdose is less likely to be toxic.

b) (i) Contrast synthetic and organic fertilizers based on their origin.

Synthetic fertilizers are man-made, produced through industrial chemical processes, such as the Haber-Bosch process used to manufacture ammonia (NH_3) for nitrogen fertilizers.

Organic fertilizers, in contrast, come from natural sources, such as compost or animal manure, rather than being manufactured chemically.

(ii) Identify the three primary macronutrients (N, P, K) and describe the specific biological function of each in a plant.

The three primary macronutrients are nitrogen, phosphorus and potassium (N, P, K):

Nitrogen (N): It is the main component of amino acids, proteins, chlorophyll needed for leave growth.

Phosphorus (P): It is main part of ATP and DNA needed for energy transfer and root development.

Potassium (K): It activates sixty plus enzymes and regulates water balance and stomata opening.

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.

Natural gas (methane, CH_4) is used as a source of hydrogen (H_2), while nitrogen (N_2) is obtained from the air. In the Haber-Bosch process, hydrogen and nitrogen gases are combined (using an iron catalyst) to synthesize ammonia (NH_3). This ammonia is the crucial intermediate compound. The ammonia produced is then converted/reacted further to produce urea (NH_2CONH_2), which is used directly as a nitrogen-rich fertilizer.

UNIT : 33 WATER

QUICK CHECK 33.1

i)Explain how the polarity of water facilitates the transport of agricultural pollutants like pesticides into the water cycle.

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-}). 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).

ii)Differentiate between Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) as indicators of water quality.

Biochemical Oxygen Demand (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. Whereas **Chemical Oxygen Demand (COD) is** the amount of oxygen required to chemically oxidise organic and inorganic substances in water, using **oxidizing 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.

QUICK CHECK 33.2

a) Classify these as point or non-point sources.

i. Outfall pipes used to release treated sewage into a bay or river:

Point-source pollution is the contamination that enters a water body from a single, discrete, and identifiable location or point. Because 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. An example is a factory discharging lead or mercury salts directly into a river via a specific wastewater pipe. Another example is a storage tank at a chemical plant leaking its contents into the soil and finally into the groundwater.

ii. Acid rain caused by nitrogen oxides from distant industries or power stations:

Non-point-source pollution, because the pollutants originate from dispersed sources and are transported over a wide area through atmospheric processes and rainfall.

Non-point source pollution, also 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. It results in a mixture of various pollutants at lower concentrations across a much wider area. Some examples of non-point pollution sources are: Rain washing excess ammonium nitrate (NH,NO,), fertilizers, and pesticides from thousands of hectares of farmland into a river system.

Stormwater moving over impermeable surfaces (roads and car parks), collecting leaked engine oils (hydrocarbons), zinc from tires, and road salts.

b) Give two major differences between point and non-point pollution.

	Point Source (NPS) Pollution	**Non-Point Source (NPS) Pollution**
1	Pollution comes from a single, identifiable location.	Pollution comes from many dispersed locations.
2	Pollutants usually enter water at a concentrated point	Pollutants are generally present at lower concentrations over a wider area.

QUICK CHECK 33.3

i)Name the sources of heavy metals.
Heavy metals can enter water systems through industrial discharge, mining operations, and improper waste disposal. Sources of some heavy metals are: **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,Hg]), which is more dangerous. The major sources of **lead** are leaded petrol (which is now banned worldwide); old plumbing (lead pipes), lead-acid batteries, and paints. Lead ions (Pb") often enter water systems through the corrosion of pipes. **Metal plating, plastic stabilisers, 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.

ii)How oil spill is hazardous to the marine life?
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 pollution also damages coastal habitats such as mangroves (a shrub), coral reefs, and beaches.

iii)Pesticides like DDT are "non-polar and insoluble in water" yet they "pollute water and cause severe human health issues. Explain.
Pesticides such as DDT is hazardous material that pollute water and cause severe human health issues. 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. DDT is 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.

QUICK CHECK 33.4

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. Name two.

The rural area will contribute to both organic and inorganic pollutants. For example:

I. Organic matter from cattle waste
II. Fertilizers/pesticides from agricultural activities

ii. Which metals are most likely to pollute the water near the industrial area?

The most likely heavy metals are:

i. Lead (Pb)
ii. Cadmium (Cd)
iii. Mercury (Hg)

These may come from paint and battery industries.

iii. Which regions will contaminate the water with chemicals that lead to eutrophication?

The rural agricultural areas and the residential area are likely to contribute nutrients responsible for eutrophication.

- In agricultural areas, they use fertilizers containing nitrogen and phosphorus
- In residential area, sewage and detergents may lead to eutrophication.

iv. Name four contaminants that will pollute the water near the residential area.

Four possible contaminants are:

1. Sewage
2. Detergents
3. Plastics/solid waste
4. Domestic chemicals and oils

QUICK CHECK 33.5

Methylmercury ([CH,Hg]') is "highly fat-soluble," allowing it to cross biological membranes and the bloodbrain barrier.Contrast the chemical structure of the methylmercury cation ([CH,Hg]") with the inorganic mercury ion (Hg").

Methylmercury cationconsists of a methyl group ($–CH_3$) covalently bonded to mercury, giving the positively charged species **CH_3Hg^+.** Inorganic mercury ion is a simple metal ion with a +2 charge and has no organic group attached. Hg2+

2. Why does the methyl group increase solubility in lipid bilayers?

The $–CH_3$ group is non-polar (hydrophobic). Its presence reduces the strongly ionic character of mercury and gives methylmercury greater lipophilic (fat-loving) character than inorganic Hg^{2+}. Therefore, Hg^{2+} is highly charged and interacts strongly with water, so it is mainly water-soluble and has difficulty passing through the non-polar interior of lipid membranes. CH_3Hg^+ has an attached organic methyl group, which increases its lipid solubility. Consequently, methylmercury can more readily cross biological membranes, including the blood-brain barrier, and accumulate in living tissues.

3. What would happen to biomagnification if methylmercury were highly water-soluble but had low fat solubility?

Biomagnification would be greatly reduced. If methylmercury were highly water-soluble and had low fat solubility:

- It would remain mainly in the water phase rather than accumulating in fatty tissues.
- Aquatic organisms would be less likely to retain large amounts of it in their bodies.
- Its concentration would increase less strongly at successive trophic levels.
- Therefore, biomagnification through the aquatic food chain would be much lower.

> High fat solubility → greater bioaccumulation → greater biomagnification.
> Low fat solubility → less bioaccumulation → reduced biomagnification.

4.How can water pollution contribute to global warming?

Water pollution can contribute to global warming mainly through the decomposition of organic pollutants and waste.

1. Organic waste enters water through sewage, agricultural runoff and industrial discharge.
2. Microorganisms decompose this organic matter.
3. In oxygen-deficient water, anaerobic decomposition can produce methane (CH_4).
4. Methane is a powerful greenhouse gas and contributes to global warming.
5. Decomposition can also produce carbon dioxide (CO_2), another greenhouse gas.
6. Eutrophication caused by excess nutrients can lead to algal blooms and oxygen depletion, promoting anaerobic decomposition and methane production.

Q2. Exercise Short-Answer Questions

a) Differentiate between Point Source and Non-Point Source pollution in terms of concentration.

Point-source pollution enters a water body at a single identifiable location, so pollutants are usually present in high concentrations near the discharge point.
Non-point-source pollution comes from many dispersed sources and generally contains pollutants at lower concentrations spread over a wider area.

b) Using an example, explain how an underground storage tank can become a point source of pollution.

An underground storage tank may contain fuel, chemicals, or other hazardous substances. If the tank develops a crack or leak, these substances can escape into the surrounding soil. The pollutants may then move downward and contaminate groundwater. Since the pollution originates from one specific and identifiable tank, it is classified as a point source of pollution. For example, a leaking underground fuel tank can release hydrocarbons into groundwater.

c) Identify two types of chemical pollutants commonly found in urban stormwater runoff.

Urban stormwater runoff can collect various pollutants from roads, parking areas and other urban surfaces. Two important chemical pollutants are hydrocarbons or oil and heavy metals such as zinc. Oil and hydrocarbons may come from vehicles and leaking fuel. Heavy metals can originate from vehicle components, road surfaces and other urban materials. These pollutants are carried into rivers, lakes and other water bodies during rainfall.

d) Differentiate between the solubility of pesticides like DDT and inorganic nutrients like nitrates.
DDT is a relatively non-polar organic compound and has very low solubility in water. However, it is highly soluble in fats and lipids, allowing it to accumulate in the tissues of organisms. In contrast, nitrates (NO_3^-) are ionic substances and are highly soluble in water. Therefore, nitrates can easily move through surface runoff and groundwater. This difference affects their transport and accumulation in the environment.

e) Why are microplastics considered a growing environmental crisis differently from organic solid waste?
Microplastics are extremely small plastic particles that are persistent in the environment. Unlike many organic wastes, they do not readily undergo biological decomposition. They can remain in water for long periods and can be consumed by aquatic organisms. Microplastics can consequently enter the food chain and accumulate in living organisms. Organic solid waste, on the other hand, can generally be decomposed more readily by microorganisms.

f) How does an oil spill physically disrupt the chemical balance of a marine ecosystem?
An oil spill produces a layer of oil on the **surface of water**. This layer interferes with the normal exchange of oxygen between the atmosphere and water. As a result, the amount of dissolved oxygen available to aquatic organisms may decrease. Oil can also coat the bodies and respiratory surfaces of marine organisms, interfering with their normal functions. Therefore, an oil spill can disturb the physical and chemical conditions necessary for aquatic life.

g) Why are synthetic organic pollutants such as PCBs and pesticides considered persistent?
Synthetic organic pollutants such as PCBs and certain pesticides are considered persistent because they are resistant to natural chemical and biological degradation. They can remain in soil, water and living organisms for long periods. Many of these compounds are also fat-soluble, allowing them to accumulate in the tissues of organisms. They can then pass from one organism to another through the food chain. This may result in bioaccumulation and biomagnification.

h) How does decomposition of organic matter in polluted water contribute to global warming?
Polluted water may contain large amounts of organic matter from sewage, agricultural waste and other sources. Microorganisms decompose this organic matter and consume dissolved oxygen. Under oxygen-poor or anaerobic conditions, decomposition can produce methane (CH_4). Methane is a potent greenhouse gas that contributes to the greenhouse effect. Therefore, pollution of water with organic matter can indirectly contribute to global warming.

i) Name four methods used for water conservation.
Four important methods of water conservation are:

1. **Rainwater harvesting**: this helps in collecting and storing rainwater for later use.
2. **Constructing small dams** for storing water and reducing water loss through runoff.
3. **Recharge wells** allow water to enter the ground and replenish groundwater.
4. **Community awareness and water-saving practices** This method is of prime importance; it encourages people to reduce unnecessary water consumption.

These methods help conserve available water resources and improve their sustainable use.

j) What is the role of industrial discharge in water pollution?
Industrial discharge is an important source of water pollution because industries may release different chemicals and waste into water bodies. These wastes may include heavy metals, toxic chemicals, organic compounds and other pollutants. Industries such as oil refineries, chemical plants, automobile industries, fertilizer industries and tanneries can contribute to this pollution. Industrial pollutants may reduce water quality and harm aquatic organisms. Therefore, proper treatment of industrial wastewater is essential before its discharge.

k) Both reverse osmosis (RO) and ion exchange methods are used to obtain high-purity water. Differentiate between the processes.
Reverse osmosis (RO) is a membrane-based purification process. Water is forced under pressure through a semi-permeable membrane. The membrane allows water molecules to pass while retaining many dissolved salts, ions and other impurities. Ion exchange, however, uses special ion-exchange resins to remove dissolved ions from water. The unwanted ions are exchanged with ions attached to the resin. Thus, RO mainly uses a membrane and pressure, whereas ion exchange uses chemical exchange of ions.

l) What impurities do these methods target?
Reverse osmosis (RO) targets a wide range of dissolved impurities, including dissolved salts, ions and other contaminants present in water. It is particularly useful for reducing the concentration of dissolved substances. Ion exchange mainly targets dissolved ions such as calcium (Ca^{2+}) and magnesium (Mg^{2+}). These ions are exchanged with ions present on the resin. Therefore, both methods can produce high-purity water, but they remove impurities through different mechanisms.

Q3. Constructed-Response Questions
a) Explain the relationship between acid rain and the presence of toxic heavy metals in aquatic environments.
Acid rain forms mainly due to the dissolution of sulphur dioxide (SO_2) and nitrogen oxides (NO_x) in atmospheric water. It increases the concentration of hydronium ions (H_3O^+) and lowers the pH of water.
The increased acidity can mobilise toxic heavy-metal compounds, such as aluminium compounds, making these metals more soluble and available in aquatic environments. This increases their potential toxicity to aquatic organisms.

b) Analyze the environmental impact of agricultural runoff as a Non-Point Source of pollution. Reference specific chemicals.
Agricultural runoff is a major example of Non-Point Source pollution because rainfall can wash pollutants from large areas of farmland into rivers and lakes.
Runoff may contain ammonium nitrate (NH_4NO_3), fertilizers and pesticides. Nitrogen and phosphorus compounds can cause eutrophication, leading to algal blooms and depletion of dissolved oxygen. Pesticides can harm aquatic organisms and may undergo bioaccumulation. Therefore, agricultural runoff can affect water quality, biodiversity and aquatic ecosystems.

c) Evaluate the role of agricultural runoff in contributing to different types of water pollution.

Agricultural runoff contributes to several types of water pollution:

- **Chemical pollution:** pesticides, herbicides and fertilizers enter water.
- **Nutrient pollution:** nitrogen and phosphorus cause eutrophication.
- **Sediment pollution:** soil erosion carries sediments into rivers and streams.
- **Organic pollution:** animal waste and other organic matter increase the organic load.

Thus, agricultural runoff is an important contributor to both surface-water and groundwater pollution.

d) Evaluate the benefits and long-term chemical risks involved in the use of chlorine as a disinfectant.

Benefits:

- Chlorine is effective in killing many pathogenic microorganisms.
- It makes water safer for drinking.
- It is commonly used because it provides effective disinfection.

Long-term risks:

- Excessive chlorine can alter water chemistry.
- Chlorination may lead to the formation of chemical by-products when chlorine reacts with organic substances in water.
- Therefore, chlorine must be used at controlled concentrations.