

CHSE Odisha · +2 Science

CHEMISTRY

+2 2nd Year (Class XII) · As per CHSE Syllabus 2023-24

Theory in simple language · Formula boxes
Solved problems · Exam Q&A · Practice & revision

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CHEMISTRY

+2 2nd Year (Class XII) · Theory 70 + Practical 30

Exam Pattern & How to Study

Chemistry - Unit Weightage

Class XI Unit	Marks	Class XII Unit	Marks
Some Basic Concepts of Chemistry	7	Solutions	7
Structure of Atom	9	Electrochemistry	9
Classification of Elements	6	Chemical Kinetics	7
Chemical Bonding	7	d- and f-Block Elements	7
Chemical Thermodynamics	9	Coordination Compounds	7
Equilibrium	7	Haloalkanes and Haloarenes	6
Redox Reactions	4	Alcohols, Phenols and Ethers	6
Organic Chemistry - Basic Principles	11	Aldehydes, Ketones, Carboxylic Acids	8
Hydrocarbons	10	Amines	6
		Biomolecules	7

GOLDEN RULES FOR WRITING ANSWERS

- Always write the **formula first**, then substitute values, then the answer **with units**.
- Underline or box the final answer. Examiners mark step-by-step, so even a wrong final answer earns step marks.
- For theory answers, use short points and draw a diagram wherever possible.
- Attempt questions you know best first, but keep their numbering exactly as in the paper.

XII-1. Solutions

Idea: A solution is a **homogeneous mixture** of two or more substances. The component present in larger amount is the **solvent**; the other is the **solute**. Sea water, air, brass and soda water are all solutions.

Solute	Solvent	Example
Gas	Gas	Air (O_2 in N_2)
Gas	Liquid	Soda water (CO_2 in water)
Liquid	Liquid	Ethanol in water
Solid	Liquid	Sugar / salt in water
Gas	Solid	H_2 in palladium
Liquid	Solid	Amalgam of Hg with Na
Solid	Solid	Alloys (brass, bronze) – solid solutions

CONCENTRATION TERMS

Mass % = (mass of solute/mass of solution) $\times$ 100 ppm = (mass of solute/mass of solution) $\times 10^6$

Mole fraction $x_A = n_A/(n_A + n_B)$ Molarity $M = n/V(L)$ Molality $m = n/\text{mass of solvent (kg)}$

Solubility of gases in liquids - Henry's law

At constant temperature, the solubility of a gas in a liquid is directly proportional to its partial pressure above the liquid: **$p = K_H x$** (x = mole fraction of gas). Higher $K_H \rightarrow$ lower solubility. Solubility of gases **decreases with rise in temperature** (fish need cold water).

Applications: soda bottles are sealed under high CO_2 pressure; deep-sea divers use air diluted with helium to avoid "bends" (N_2 bubbles in blood); climbers at high altitude suffer anoxia due to low O_2 pressure.

Raoult's law and vapour pressure

RAOULT'S LAW

For volatile liquids: $p_A = p_A^\circ x_A$, $p_B = p_B^\circ x_B$, $p_{\text{total}} = p_A^\circ x_A + p_B^\circ x_B$

For a non-volatile solute: relative lowering of vapour pressure $(p^\circ - p)/p^\circ = x_{\text{solute}} = n_2/(n_1 + n_2) \approx (w_2 M_1)/(w_1 M_2)$ for dilute solutions

Ideal solution	Non-ideal, positive deviation	Non-ideal, negative deviation
Obeys Raoult's law at all concentrations; $\Delta H_{\text{mix}} = 0$, $\Delta V_{\text{mix}} = 0$	$p >$ Raoult value; A-B attractions weaker; $\Delta H_{\text{mix}} > 0$	$p <$ Raoult value; A-B attractions stronger; $\Delta H_{\text{mix}} < 0$
n-hexane + n-heptane; benzene + toluene	ethanol + acetone; ethanol + water	chloroform + acetone; HNO_3 + water
—	Forms minimum-boiling azeotrope	Forms maximum-boiling azeotrope

Azeotropes are mixtures that boil at constant temperature with the same composition in liquid and vapour, so they cannot be separated by fractional distillation (e.g. 95% ethanol + water).

Colligative properties

Properties that depend only on the **number** of solute particles, not on their nature: (1) relative lowering of vapour pressure, (2) elevation of boiling point, (3) depression of freezing point, (4) osmotic pressure.

FORMULAS (w_2 , M_2 = MASS AND MOLAR MASS OF SOLUTE; w_1 = MASS OF SOLVENT IN G)

Elevation of boiling point: $\Delta T_b = K_b m \Rightarrow M_2 = (K_b \times w_2 \times 1000)/(\Delta T_b \times w_1)$

Depression of freezing point: $\Delta T_f = K_f m \Rightarrow M_2 = (K_f \times w_2 \times 1000)/(\Delta T_f \times w_1)$

Osmotic pressure: $\pi = CRT = (n_2/V)RT \Rightarrow M_2 = w_2 RT/(\pi V)$

K_b (water) = $0.52 \text{ K kg mol}^{-1}$; K_f (water) = $1.86 \text{ K kg mol}^{-1}$; $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$

With van't Hoff factor i : $\Delta T_b = iK_b m$, $\Delta T_f = iK_f m$, $\pi = iCRT$

Osmosis: flow of solvent through a semipermeable membrane from a dilute solution (or pure solvent) to a concentrated one. **Osmotic pressure** is the extra pressure needed to stop osmosis. **Isotonic** solutions have equal osmotic pressure (0.9% NaCl = normal saline is isotonic with blood). Hypertonic solution makes cells shrink; hypotonic makes them swell. **Reverse osmosis:** applying pressure greater than π pushes solvent from concentrated to dilute side — used in RO water purifiers and desalination. Osmotic pressure is the best method for finding molar masses of proteins/polymers (measured at room temperature, large values).

Abnormal molar mass and van't Hoff factor

When solute particles **dissociate** ($\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$) the number of particles increases, the colligative property is larger, and the calculated molar mass is **lower** than actual. When they **associate** (acetic acid forms dimers in benzene) the molar mass appears **higher**.

VAN'T HOFF FACTOR

i = normal molar mass / abnormal molar mass = observed colligative property / calculated colligative property

Dissociation: $i = 1 + (n - 1)\alpha$ (n = ions per formula unit) — $i > 1$

Association: $i = 1 - \alpha(1 - 1/n)$ — $i < 1$

For complete dissociation: NaCl $i = 2$, K_2SO_4 $i = 3$, $AlCl_3$ $i = 4$

Example 1. Calculate the molality of a solution of 2.5 g ethanoic acid (CH_3COOH) in 75 g benzene.

$M = 60$. $n = 2.5/60 = 0.0417$ mol. $m = 0.0417/0.075 = \mathbf{0.556 \text{ mol/kg}}$.

Example 2. Vapour pressure of water at 293 K is 17.535 mm Hg. Find the vapour pressure when 25 g glucose is dissolved in 450 g water.

$n(\text{glucose}) = 25/180 = 0.139$; $n(\text{water}) = 450/18 = 25$. $x_2 = 0.139/25.139 = 0.00553$. $p = p^\circ(1 - x_2) = 17.535 \times 0.99447 = \mathbf{17.44 \text{ mm Hg}}$.

Example 3. 18 g glucose is dissolved in 1 kg water. At what temperature will it boil? ($K_b = 0.52$)

$m = 0.1$. $\Delta T_b = 0.52 \times 0.1 = 0.052$ K. Boiling point = $373.15 + 0.052 = \mathbf{373.202 \text{ K}}$.

Example 4. 1.00 g of a non-electrolyte dissolved in 50 g benzene lowered its freezing point by 0.40 K. K_f of benzene = 5.12. Find the molar mass.

$M_2 = (5.12 \times 1.00 \times 1000)/(0.40 \times 50) = \mathbf{256 \text{ g/mol}}$.

Example 5. 200 cm^3 of an aqueous solution of a protein contains 1.26 g of it. Osmotic pressure at 300 K is 2.57×10^{-3} bar. Find the molar mass ($R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$).

$M = wRT/(\pi V) = (1.26 \times 0.083 \times 300)/(2.57 \times 10^{-3} \times 0.200) = 31.37/(5.14 \times 10^{-4}) = \mathbf{\approx 61,000 \text{ g/mol}}$.

Example 6. Find the freezing point of a solution of 0.1 mol NaCl in 1 kg water, assuming complete dissociation.

$i = 2$. $\Delta T_f = 2 \times 1.86 \times 0.1 = 0.372$ K. Freezing point = $\mathbf{-0.372 \text{ }^\circ\text{C}}$ (272.778 K).

XII-2. Electrochemistry

Idea: Electrochemistry links chemical reactions with electricity. In a **galvanic (voltaic) cell**, a redox reaction produces electricity (battery). In an **electrolytic cell**, electricity drives a non-spontaneous reaction (electroplating).

Feature	Galvanic cell	Electrolytic cell
Energy change	Chemical → electrical	Electrical → chemical
Reaction	Spontaneous ($\Delta G < 0$)	Non-spontaneous
Anode	Negative; oxidation	Positive; oxidation
Cathode	Positive; reduction	Negative; reduction
Example	Daniell cell	Electrolysis of NaCl

MEMORY AID

"An Ox, Red Cat": **Anode = Oxidation, Reduction = Cathode** — true in both types of cell.

Daniell cell

Zn rod in ZnSO_4 (anode) and Cu rod in CuSO_4 (cathode), connected by a **salt bridge** (KCl/KNO_3 in agar), which completes the circuit and keeps solutions electrically neutral.

Reaction: $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$; $E^\circ = 1.10 \text{ V}$. Cell notation: $\text{Zn} | \text{Zn}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}$.

Electrode potential and EMF

Standard electrode potential (E°): potential of an electrode at 1 M concentration, 298 K and 1 bar, measured against the **Standard Hydrogen Electrode (SHE)**, whose $E^\circ = 0.00 \text{ V}$. Arranging E° values gives the **electrochemical series**. More negative E° (Li, K, Zn) → stronger reducing agent; more positive (F_2 , Au) → stronger oxidising agent.

ELECTROCHEMISTRY FORMULAS

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ (both as reduction potentials)

Nernst equation: for $\text{M}^{n+} + n\text{e}^- \rightarrow \text{M}$: $E = E^\circ - (0.059/n) \log(1/[\text{M}^{n+}])$ at 298 K

For a cell $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$: $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.059/n) \log([\text{C}]^c[\text{D}]^d/[\text{A}]^a[\text{B}]^b)$

At equilibrium: $E^\circ_{\text{cell}} = (0.059/n) \log K_c$

$\Delta G = -nFE_{\text{cell}}$; $\Delta G^\circ = -nFE^\circ_{\text{cell}} = -2.303RT \log K$; $F = 96500 \text{ C mol}^{-1}$

Conductance $G = 1/R$ (S); κ (specific conductivity) = $G \times (l/A) = G \times \text{cell constant}$

Molar conductivity $\Lambda_m = \kappa \times 1000/M$ ($\text{S cm}^2 \text{ mol}^{-1}$)

Kohlrausch's law: $\Lambda^\circ_m = \nu_+ \lambda^\circ_+ + \nu_- \lambda^\circ_-$; degree of dissociation $\alpha = \Lambda_m/\Lambda^\circ_m$

Faraday's 1st law: $m = ZIt = (E/96500) \times I \times t$; 2nd law: $m_1/m_2 = E_1/E_2$ for the same charge

Conductance and its variation

Specific conductivity (κ) decreases on dilution (fewer ions per cm^3). **Molar conductivity (Λ_m)** increases on dilution. For **strong electrolytes** (KCl) Λ_m increases slowly and linearly with $\sqrt{C}$ (Debye-Hückel-Onsager: $\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$), so Λ°_m is found by extrapolation. For **weak electrolytes** (CH_3COOH) Λ_m rises sharply at low concentration (more ionisation), so Λ°_m cannot be found by extrapolation — it is calculated by Kohlrausch's law.

Electrolysis

Products depend on the electrolyte, electrodes and concentration. Molten NaCl → Na at cathode, Cl₂ at anode. Aqueous NaCl → H₂ at cathode (water is reduced more easily than Na⁺), Cl₂ at anode; NaOH remains in solution.

Batteries, fuel cells and corrosion

Cell	Type	Anode / Cathode	Notes
Dry cell (Leclanché)	Primary (not rechargeable)	Zn container / graphite rod with MnO ₂ + C; paste of NH ₄ Cl + ZnCl ₂	About 1.5 V; torches, clocks
Mercury cell	Primary	Zn-Hg amalgam / HgO + C	Constant 1.35 V; watches, hearing aids
Lead storage battery (accumulator)	Secondary (rechargeable)	Pb / PbO ₂ in 38% H ₂ SO ₄	Car batteries. Discharge: Pb + PbO ₂ + 2H ₂ SO ₄ → 2PbSO ₄ + 2H ₂ O
H ₂ -O ₂ fuel cell	Fuel cell	Porous carbon with catalyst; H ₂ and O ₂ bubbled in conc. NaOH	2H ₂ + O ₂ → 2H ₂ O; ~70% efficient, pollution-free; used in Apollo space missions

Corrosion (rusting of iron) is an electrochemical process. At an anodic spot: Fe → Fe²⁺ + 2e⁻. At a cathodic spot: O₂ + 4H⁺ + 4e⁻ → 2H₂O. Fe²⁺ is further oxidised to rust, Fe₂O₃·xH₂O. Moisture, CO₂, salts and acids speed it up. **Prevention:** painting, oiling, galvanising (Zn coating), tinning, alloying (stainless steel), cathodic protection with a more reactive metal (Mg/Zn sacrificial anode).

Example 1. Calculate E°_{cell} for Zn | Zn²⁺ || Ag⁺ | Ag (E°_{Zn} = -0.76 V, E°_{Ag} = +0.80 V).

$$E^{\circ}_{\text{cell}} = 0.80 - (-0.76) = \mathbf{1.56 \text{ V}}.$$

Example 2. Find the emf of Mg | Mg²⁺ (0.001 M) || Cu²⁺ (0.0001 M) | Cu (E°_{cell} = 2.71 V).

$$n = 2. E = 2.71 - (0.059/2) \log(10^{-3}/10^{-4}) = 2.71 - 0.0295 \times 1 = \mathbf{2.68 \text{ V}}.$$

Example 3. Calculate ΔG° and K for the Daniell cell (E° = 1.10 V).

$$\Delta G^{\circ} = -2 \times 96500 \times 1.10 = -212300 \text{ J} = \mathbf{-212.3 \text{ kJ}}. \log K = 2 \times 1.10/0.059 = 37.29 \\ \Rightarrow K \approx \mathbf{1.95 \times 10^{37}}.$$

Example 4. Resistance of a 0.1 M KCl solution in a cell is 100 Ω. If κ = 1.29 S m⁻¹, find the cell constant and molar conductivity.

$$\text{Cell constant} = \kappa \times R = 1.29 \times 100 = 129 \text{ m}^{-1}. \Lambda_{\text{m}} = \kappa/C = 1.29 \text{ S m}^{-1}/(100 \text{ mol m}^{-3}) = \mathbf{0.0129 \text{ S m}^2 \text{ mol}^{-1}} (= 129 \text{ S cm}^2 \text{ mol}^{-1}).$$

Example 5. Find Λ_m° for CaCl_2 if $\lambda^\circ(\text{Ca}^{2+}) = 119.0$ and $\lambda^\circ(\text{Cl}^-) = 76.3 \text{ S cm}^2 \text{ mol}^{-1}$.

$$\Lambda^\circ = 119.0 + 2(76.3) = 271.6 \text{ S cm}^2 \text{ mol}^{-1}.$$

Example 6. A current of 1.5 A is passed through CuSO_4 solution for 10 minutes. Find the mass of copper deposited ($\text{Cu} = 63.5$).

$$Q = 1.5 \times 600 = 900 \text{ C. } \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu: } 2 \times 96500 \text{ C deposit } 63.5 \text{ g. } m = 63.5 \times 900/193000 = 0.296 \text{ g.}$$

XII-3. Chemical Kinetics

Idea: Thermodynamics tells whether a reaction can happen; kinetics tells **how fast**. Rusting is slow, explosions are fast.

RATE OF REACTION

Change in concentration of reactant or product per unit time. For $\text{R} \rightarrow \text{P}$: rate = $-\Delta[\text{R}]/\Delta t = +\Delta[\text{P}]/\Delta t$ (unit $\text{mol L}^{-1} \text{ s}^{-1}$). **Average rate** is over a time interval;

instantaneous rate is at a particular moment = slope of the tangent on the concentration-time graph ($-d[\text{R}]/dt$). For $a\text{A} + b\text{B} \rightarrow c\text{C}$: rate = $-(1/a)d[\text{A}]/dt = -(1/b)d[\text{B}]/dt = (1/c)d[\text{C}]/dt$.

Factors affecting rate: concentration (more collisions), temperature (rate roughly doubles for each 10 K rise), catalyst (lowers activation energy), surface area, nature of reactants, light.

Rate law, order and molecularity

For $a\text{A} + b\text{B} \rightarrow \text{products}$, rate law: **Rate** = $k[\text{A}]^x[\text{B}]^y$. x and y are found by experiment and need not equal a and b . **k** is the rate constant (specific reaction rate) — rate when all concentrations are 1 M.

Order	Molecularity
Sum of powers in the rate law ($x + y$)	Number of molecules colliding in an elementary step
Experimental	Theoretical
Can be 0, fraction or whole number	Always a whole number (1, 2, 3), never zero
Applies to overall reaction	Applies to elementary steps

Units of k : zero order $\text{mol L}^{-1} \text{ s}^{-1}$; first order s^{-1} ; second order $\text{L mol}^{-1} \text{ s}^{-1}$. In general $(\text{mol L}^{-1})^{1-n} \text{ s}^{-1}$.

Pseudo first-order reaction: appears first order because one reactant is in large excess. Example: hydrolysis of ethyl acetate in excess water; inversion of cane sugar.

INTEGRATED RATE EQUATIONS AND HALF-LIFE

Zero order: $[R] = [R]_0 - kt$; $k = ([R]_0 - [R])/t$; $t_{1/2} = [R]_0/2k$ (depends on initial concentration).

Example: decomposition of NH_3 on hot Pt.

First order: $k = (2.303/t) \log([R]_0/[R])$; $t_{1/2} = 0.693/k$ (independent of initial concentration).

Examples: radioactive decay, decomposition of N_2O_5 .

Time for 99% completion = 2 × time for 90% completion (first order)

Arrhenius equation: $k = A e^{-E_a/RT}$; $\log(k_2/k_1) = (E_a/2.303R)[(T_2 - T_1)/(T_1 T_2)]$

Collision theory and activation energy

Molecules must **collide** to react. Only collisions with energy $\geq$ a minimum value (threshold energy) and the **proper orientation** are effective. **Activation energy (E_a)** = threshold energy – average energy of reactants; it is the "energy hill" reactants must climb (forming an activated complex). Raising the temperature increases the fraction of molecules with energy $\geq E_a$ (Maxwell-Boltzmann distribution), so the rate rises sharply. A **catalyst** provides a new path with lower E_a ; it does not change ΔG or the equilibrium constant.

Example 1. For $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, the rate of formation of NO_2 is $2.8 \times 10^{-3} \text{ M s}^{-1}$. Find the rate of disappearance of N_2O_5 .

$$-\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} \Rightarrow -\frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} \times 2.8 \times 10^{-3} = 1.4 \times 10^{-3} \text{ M s}^{-1}.$$

Example 2. Rate = $k[A][B]^2$. How does the rate change if $[B]$ is doubled? If both are doubled?

$[B]$ doubled: rate $\times 4$. Both doubled: rate $\times 2 \times 4 = \times 8$. Order = 3.

Example 3. A first-order reaction has $k = 1.15 \times 10^{-3} \text{ s}^{-1}$. How long will 5 g of reactant take to reduce to 3 g?

$$t = (2.303/1.15 \times 10^{-3}) \log(5/3) = 2002.6 \times 0.2218 = \approx 444 \text{ s}.$$

Example 4. Half-life of a first-order reaction is 60 min. Find k and the time for 87.5% completion.

$$k = 0.693/60 = 0.01155 \text{ min}^{-1}. 87.5\% \text{ complete means } 12.5\% = 1/8 \text{ left} = 3 \text{ half-lives} = 180 \text{ min}.$$

Example 5. Show that for a first-order reaction $t_{99\%} = 2 t_{90\%}$.

$$t_{99} = (2.303/k) \log(100/1) = (2.303/k) \times 2. \quad t_{90} = (2.303/k) \log(100/10) = (2.303/k) \times 1. \quad \text{Ratio} = 2.$$

Example 6. The rate constant doubles when the temperature rises from 300 K to 310 K. Find E_a .

$$\log 2 = (E_a / (2.303 \times 8.314)) \times (10 / (300 \times 310)). \quad 0.3010 = E_a \times 10 / (19.147 \times 93000) \\ \Rightarrow E_a = 0.3010 \times 19.147 \times 9300 = \approx \mathbf{53.6 \text{ kJ/mol.}}$$

Exam Q&A - Solutions, Electrochemistry, Kinetics

Q1. Why is osmotic pressure preferred for finding molar masses of proteins? [2]

It is measured at room temperature (proteins are not damaged) and gives a large, easily measured value even for very dilute solutions.

Q2. Why do we use a salt bridge? [2]

It completes the inner circuit and maintains electrical neutrality of the two half-cell solutions, preventing liquid junction potential.

Q3. Why can't Λ_m° of acetic acid be found by extrapolation? [2]

It is a weak electrolyte; Λ_m rises steeply at low concentration and the graph does not approach the axis linearly. It is found using Kohlrausch's law.

Q4. Give one example each of zero and first order reactions. [2]

Zero: decomposition of NH_3 on platinum. First: decomposition of N_2O_5 / radioactive decay.

Q5. State Kohlrausch's law and give two applications. [3]

At infinite dilution, molar conductivity of an electrolyte is the sum of the limiting molar conductivities of its cation and anion. Uses: (1) finding Λ_m° of weak electrolytes; (2) finding degree of dissociation $\alpha = \Lambda_m / \Lambda_m^\circ$ and dissociation constant.

XII-4. d- and f-Block Elements

Idea: The d-block (groups 3-12) contains the **transition metals** — iron, copper, zinc, chromium, silver, gold. The f-block contains the **lanthanoids** (Ce-Lu) and **actinoids** (Th-Lr), placed below the main table.

TRANSITION ELEMENT

An element with an incompletely filled d subshell in its atom or in any of its common ions. Zn, Cd, Hg (d^{10} in atom and ions) are therefore not typical transition elements. General configuration: $(n-1)d^{1-10} ns^{1-2}$.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3d, 4s	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$

Occurrence: mostly as oxides, sulphides and carbonates — haematite (Fe_2O_3), chalcopyrite ($CuFeS_2$), chromite ($FeCr_2O_4$) — Odisha has large chromite and iron-ore deposits.

General properties of the first transition series

Property	Trend / Reason
Metallic character	All are hard, strong metals with high melting points due to strong metallic bonding involving d electrons. Melting point peaks in the middle (Cr, V); Zn is low (no unpaired d electrons).
Atomic/ionic radii	Decrease slowly across the series, then become almost constant, because the added d electrons shield poorly but also repel each other.
Ionisation enthalpy	Increases gradually across the series (higher than s-block, lower than p-block).
Variable oxidation states	Because ns and (n-1)d electrons have similar energies. Mn shows +2 to +7 (maximum in the series). Highest states are found in oxides/fluorides (MnO_4^- , CrO_4^{2-}).
Colour	Due to d-d transitions : an electron absorbs visible light and jumps between split d orbitals; the complementary colour is seen. Ions with d^0 (Sc^{3+} , Ti^{4+}) or d^{10} (Zn^{2+} , Cu^+) are colourless. Cu^{2+} blue, Fe^{3+} yellow, Ni^{2+} green, MnO_4^- purple (charge transfer).
Magnetic properties	Unpaired electrons $\rightarrow$ paramagnetic. Magnetic moment $\mu = \sqrt{n(n+2)}$ BM, n = unpaired electrons. Fe, Co, Ni are ferromagnetic.
Catalytic property	Variable oxidation states and large surface area / ability to form complexes. Fe in Haber process, V_2O_5 in contact process, Ni in hydrogenation of oils, Pt in Ostwald process.
Interstitial compounds	Small atoms (H, C, N) trapped in the metal lattice (TiC , Fe_3H , Mn_4N): hard, high melting, retain metallic conductivity, chemically inert.
Alloy formation	Similar atomic sizes allow one metal to replace another in the lattice: brass (Cu + Zn), bronze (Cu + Sn), stainless steel (Fe + Cr + Ni).
Complex formation	Small, highly charged ions with vacant d orbitals form complexes: $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

Example. Calculate the magnetic moment of Fe^{2+} (Z = 26) and Mn^{2+} (Z = 25).

Fe^{2+} : $3d^6 \rightarrow 4$ unpaired $\Rightarrow \mu = \sqrt{24} = \mathbf{4.90 \text{ BM}}$. Mn^{2+} : $3d^5 \rightarrow 5$ unpaired $\Rightarrow \mu = \sqrt{35} = \mathbf{5.92 \text{ BM}}$.

Potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$

Preparation (from chromite ore):

1. Fusion with sodium carbonate in air: $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$
2. Acidification: $2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ (yellow chromate $\rightarrow$ orange dichromate)
3. Treat with KCl: $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$ (orange crystals)

Properties: orange crystals; strong oxidising agent in acid: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ (orange $\rightarrow$ green). Oxidises I^- to I_2 , Fe^{2+} to Fe^{3+} , H_2S to S , Sn^{2+} to Sn^{4+} . Chromate-dichromate equilibrium depends on pH: $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$. **Uses:** leather tanning, volumetric analysis (primary standard), breath-analyser test for alcohol.

Potassium permanganate, KMnO_4

Preparation: (i) Fuse pyrolusite (MnO_2) with KOH and an oxidant (KNO_3/air): $2\text{MnO}_2 + 4\text{KOH} + \text{O}_2 \rightarrow 2\text{K}_2\text{MnO}_4$ (green manganate) + $2\text{H}_2\text{O}$. (ii) Manganate disproportionates in neutral/acid solution or is oxidised electrolytically: $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$.

Properties: dark purple crystals; powerful oxidising agent.

- Acidic medium: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ (purple $\rightarrow$ colourless). Oxidises Fe^{2+} , oxalate (to CO_2), I^- , H_2S , SO_2 .
- Neutral/weakly alkaline: $\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$ (brown ppt).
- Uses: disinfectant, titrations (self-indicator), bleaching, Baeyer's reagent.

Lanthanoids (4f series, Ce to Lu)

- Configuration: $[\text{Xe}] 4f^{1-14} 5d^{0-1} 6s^2$.
- Common oxidation state **+3**; some show +2 (Eu, Yb) and +4 (Ce) to attain f^0 , f^7 or f^{14} stability.
- Reactive metals; tarnish in air, react with water to give H_2 , burn to form Ln_2O_3 , react with acids.
- **Lanthanoid contraction:** steady decrease in atomic and ionic size from La to Lu, because 4f electrons shield the increasing nuclear charge very poorly.
- **Consequences:** (1) 2nd and 3rd transition series have almost the same size (Zr 160 pm, Hf 159 pm), so Zr and Hf are very similar and hard to separate; (2) basicity of $\text{Ln}(\text{OH})_3$ decreases from La to Lu; (3) lanthanoids are difficult to separate from each other.

Actinoids (5f series, Th to Lr)

- Configuration $[\text{Rn}] 5f^{1-14} 6d^{0-1} 7s^2$. All are **radioactive**; elements after U are man-made.
- Show a **wider range** of oxidation states (+3 to +7; e.g. U +6, Np/Pu +7) because 5f, 6d and 7s orbitals have similar energies.
- **Comparison with lanthanoids:** both show contraction and +3 state; but actinoids show more oxidation states, are radioactive, form complexes more readily and actinoid contraction is greater (poorer shielding by 5f).

XII-5. Coordination Compounds

Idea: Coordination compounds contain a central metal atom/ion bonded to a fixed number of ions or molecules (ligands) by coordinate bonds. Haemoglobin (Fe), chlorophyll (Mg) and vitamin B₁₂ (Co) are coordination compounds.

TERMS

- **Ligand:** ion or molecule donating an electron pair to the metal. **Unidentate** (one donor atom): Cl^- , H_2O , NH_3 , CN^- . **Bidentate:** ethane-1,2-diamine (en), oxalate ($\text{C}_2\text{O}_4^{2-}$). **Polydentate:** EDTA^{4-} (hexadentate). **Ambidentate:** can bind through two different atoms (NO_2^- via N or O; SCN^- via S or N).
- **Chelate:** a ring formed when a polydentate ligand binds; chelates are extra stable.
- **Coordination number (CN):** number of donor atoms bonded to the metal. In $[\text{Co}(\text{NH}_3)_6]^{3+}$, CN = 6.
- **Coordination sphere:** metal + ligands in square brackets; ions outside are counter ions.
- **Oxidation number of metal:** charge it would have if all ligands were removed with their electron pairs.
- **Homoleptic** (one type of ligand) and **heteroleptic** (more than one type).

Werner's theory (1893)

1. Metals show two types of valency: **primary** (ionisable, = oxidation state, satisfied by negative ions) and **secondary** (non-ionisable, = coordination number, satisfied by ligands).
2. Secondary valencies are directed in space, giving definite geometry (6 → octahedral, 4 → tetrahedral or square planar).

Example: $\text{CoCl}_3 \cdot 6\text{NH}_3 = [\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ gives 3 mol AgCl; $\text{CoCl}_3 \cdot 5\text{NH}_3 = [\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ gives 2 mol AgCl; $\text{CoCl}_3 \cdot 4\text{NH}_3 = [\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ gives 1 mol AgCl.

IUPAC nomenclature rules

1. Cation is named first, then anion.
2. Inside the complex, ligands are named alphabetically before the metal; prefixes di-, tri- (or bis-, tris- for complex ligands) are ignored in alphabetising.
3. Anionic ligands end in -o: chlorido, cyanido, hydroxido, oxalato, nitrito-N. Neutral: aqua (H_2O), ammine (NH_3), carbonyl (CO), nitrosyl (NO).
4. Oxidation state of metal in Roman numerals in brackets.
5. If the complex is an anion, the metal name ends in -ate (ferrate, cuprate, argentate, cobaltate).

Formula	IUPAC name
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	Hexaamminecobalt(III) chloride
$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	Diamminedichloridoplatinum(II)
$\text{K}_4[\text{Fe}(\text{CN})_6]$	Potassium hexacyanidoferrate(II)
$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$	Potassium trioxalatoferrate(III)
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	Pentaamminechloridocobalt(III) chloride
$[\text{Ni}(\text{CO})_4]$	Tetracarbonylnickel(0)
$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$	Tetraamminecopper(II) sulphate

Isomerism

Structural isomerism: ionisation ($[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$), linkage ($-\text{NO}_2$ vs $-\text{ONO}$), coordination, hydrate (solvate). **Stereoisomerism: geometrical** (cis-trans) in square planar MA_2B_2 like $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and octahedral MA_4B_2 ; fac-mer in MA_3B_3 ; **optical** isomers (non-superimposable mirror images) in $[\text{Co}(\text{en})_3]^{3+}$ and cis- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$.

Valence Bond Theory (VBT)

The metal uses hybridised empty orbitals to accept ligand electron pairs.

CN	Hybridisation	Shape	Example	Magnetic
4	sp^3	Tetrahedral	$[\text{NiCl}_4]^{2-}$	Paramagnetic (2 unpaired)
4	dsp^2	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$	Diamagnetic
6	d^2sp^3 (inner orbital, low spin)	Octahedral	$[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$	Dia / 1 unpaired
6	sp^3d^2 (outer orbital, high spin)	Octahedral	$[\text{CoF}_6]^{3-}$	Paramagnetic (4 unpaired)

Limitations of VBT: does not explain colour, gives no quantitative magnetic data, cannot distinguish weak and strong ligands properly.

Crystal Field Theory (CFT)

Ligands are treated as point charges. In an **octahedral** field, the five d orbitals split into a lower set t_{2g} (3 orbitals: d_{xy} , d_{yz} , d_{xz}) and a higher set e_g (2 orbitals: $\text{d}_{x^2-y^2}$, d_{z^2}). The energy gap is Δ_o . In a tetrahedral field the order is reversed and $\Delta_t = (4/9)\Delta_o$.

Spectrochemical series (increasing field strength): $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^- < \text{OH}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$. Strong-field ligands (CN^- , CO) give large $\Delta_o \rightarrow$ electrons pair up in $\text{t}_{2g} \rightarrow$ **low spin**. Weak-field ligands give small $\Delta_o \rightarrow$ **high spin**.

Colour: an electron absorbs light to jump from t_{2g} to e_g (d-d transition); the complementary colour is seen. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorbs green-yellow light and looks violet. Anhydrous CuSO_4 is white because there are no water ligands to split the d orbitals.

Importance of coordination compounds

- **Qualitative analysis:** Ni^{2+} with dimethylglyoxime $\rightarrow$ red ppt; $\text{Cu}^{2+} + \text{NH}_3 \rightarrow$ deep blue $[\text{Cu}(\text{NH}_3)_4]^{2+}$; $\text{Fe}^{3+} + \text{K}_4[\text{Fe}(\text{CN})_6] \rightarrow$ Prussian blue.
- **Extraction of metals:** silver and gold extracted as $[\text{Ag}(\text{CN})_2]^-$, $[\text{Au}(\text{CN})_2]^-$ (cyanide process); nickel purified via $[\text{Ni}(\text{CO})_4]$ (Mond process).
- **Biological systems:** chlorophyll (Mg), haemoglobin (Fe), vitamin B_{12} (Co).
- **Medicine:** cis-platin treats cancer; EDTA removes lead poisoning. **Water hardness** is estimated by titration with EDTA.

Example. Explain $[\text{Fe}(\text{CN})_6]^{3-}$ using VBT.

Fe^{3+} : $3d^5$. CN^- is strong field, so the 5 electrons pair into three 3d orbitals (one unpaired). Two empty 3d, one 4s and three 4p orbitals form d^2sp^3 hybrids $\rightarrow$ octahedral, inner-orbital, low-spin, paramagnetic (1 unpaired electron, $\mu = 1.73 \text{ BM}$).

Exam Q&A - d/f Block & Coordination Compounds

Q1. Why are Zn, Cd, Hg not regarded as transition elements? [2]

They have completely filled d^{10} orbitals in the ground state and in their common oxidation state (+2).

Q2. Why do transition metals form coloured compounds? [2]

Due to d-d transitions of unpaired electrons in partly filled d orbitals, which absorb part of visible light.

Q3. What is lanthanoid contraction? Give one consequence. [2]

Gradual decrease in size of lanthanoids with increasing atomic number due to poor shielding by 4f electrons. Consequence: Zr and Hf have nearly identical radii and properties.

Q4. Write the IUPAC name of $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$. [1]

Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride.

Q5. What is the coordination number and oxidation state of Fe in $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$? [2]

Oxalate is bidentate, so CN = 6. Oxidation state: $3(+1) + x + 3(-2) = 0 \Rightarrow x = +3$.

Q6. Why does KMnO_4 act as a self-indicator? [1]

Its purple colour disappears when reduced to Mn^{2+} ; the first excess drop gives a permanent pink colour at the end point.

XII-6. Haloalkanes and Haloarenes

Idea: When a hydrogen of a hydrocarbon is replaced by a halogen (F, Cl, Br, I) we get a **haloalkane** (alkyl halide, R-X) or a **haloarene** (aryl halide, Ar-X). Examples: chloroform, iodoform, DDT, chlorobenzene.

Nomenclature and classification

Structure	Common name	IUPAC name	Type
$\text{CH}_3\text{CH}_2\text{Br}$	Ethyl bromide	Bromoethane	1°
$(\text{CH}_3)_2\text{CHCl}$	Isopropyl chloride	2-Chloropropane	2°
$(\text{CH}_3)_3\text{CBr}$	tert-Butyl bromide	2-Bromo-2-methylpropane	3°
$\text{CH}_2=\text{CHCl}$	Vinyl chloride	Chloroethene	Vinylic
$\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$	Allyl chloride	3-Chloroprop-1-ene	Allylic
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	Benzyl chloride	(Chloromethyl)benzene	Benzylic
$\text{C}_6\text{H}_5\text{Cl}$	Chlorobenzene	Chlorobenzene	Aryl

Nature of the C-X bond

Halogen is more electronegative than carbon, so the C-X bond is **polar**: $\text{C}^{\delta+}-\text{X}^{\delta-}$. The carbon is electron-deficient and is attacked by nucleophiles. Bond length: $\text{C-F} < \text{C-Cl} < \text{C-Br} < \text{C-I}$; bond strength decreases in the same order, so reactivity is $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$.

Physical properties

Boiling points are higher than those of parent alkanes (polarity, larger mass); $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$; boiling point decreases with branching. Only slightly soluble in water (cannot form H-bonds well), soluble in organic solvents. Iodo and bromo compounds are denser than water.

Preparation

- From alcohols: $\text{R-OH} + \text{HCl} (\text{ZnCl}_2, \text{Lucas reagent}) \rightarrow \text{R-Cl}$; $\text{R-OH} + \text{PCl}_5 \rightarrow \text{R-Cl} + \text{POCl}_3 + \text{HCl}$; $\text{R-OH} + \text{SOCl}_2 \rightarrow \text{R-Cl} + \text{SO}_2 \uparrow + \text{HCl} \uparrow$ (best — by-products are gases).
- From alkenes: addition of HX (Markovnikov).
- Halogen exchange: **Finkelstein** $\text{R-Cl} + \text{NaI} (\text{acetone}) \rightarrow \text{R-I} + \text{NaCl}$; **Swarts** $\text{R-Br} + \text{AgF} \rightarrow \text{R-F} + \text{AgBr}$.
- Haloarenes: $\text{C}_6\text{H}_6 + \text{Cl}_2 (\text{FeCl}_3) \rightarrow \text{C}_6\text{H}_5\text{Cl}$; **Sandmeyer reaction** from diazonium salt: $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{CuCl} \rightarrow \text{C}_6\text{H}_5\text{Cl} + \text{N}_2$.

Chemical reactions of haloalkanes

(a) Nucleophilic substitution: $R-X + Nu^- \rightarrow R-Nu + X^-$. With aq. KOH $\rightarrow$ alcohol; KCN $\rightarrow$ nitrile ($R-CN$); AgCN $\rightarrow$ isocyanide ($R-NC$); $NH_3 \rightarrow$ amine; $NaOR' \rightarrow$ ether (Williamson synthesis); $KNO_2 \rightarrow$ alkyl nitrite; $AgNO_2 \rightarrow$ nitroalkane.

Feature	S_N2	S_N1
Steps	One step; nucleophile attacks from the back as X leaves	Two steps; carbocation formed first (slow step), then nucleophile attacks
Rate law	Rate = $k[RX][Nu^-]$ (second order)	Rate = $k[RX]$ (first order)
Reactivity	$CH_3X > 1^\circ > 2^\circ > 3^\circ$ (steric hindrance)	$3^\circ > 2^\circ > 1^\circ > CH_3X$ (carbocation stability)
Stereochemistry	Inversion of configuration (Walden inversion)	Racemisation (attack from both sides of planar carbocation)
Solvent	Polar aprotic (acetone)	Polar protic (water, alcohol)

Optical activity (needed for mechanisms)

A carbon attached to four different groups is **chiral** (asymmetric). Such molecules exist as two non-superimposable mirror images called **enantiomers**, which rotate plane-polarised light equally but in opposite directions — **dextrorotatory (d, +)** and **laevorotatory (l, -)**. Rotation is measured with a **polarimeter**. An equimolar mixture of d and l is a **racemic mixture** (optically inactive, dl or $\pm$). Example: butan-2-ol, 2-chlorobutane, lactic acid.

(b) Elimination (dehydrohalogenation): with alcoholic KOH, H and X are removed from adjacent carbons $\rightarrow$ alkene. **Saytzeff rule:** the more substituted alkene (fewer H on double-bond carbons) is the major product. 2-Bromobutane $\rightarrow$ but-2-ene (major, 80%) + but-1-ene.

(c) With metals: Grignard reagent $R-X + Mg$ (dry ether) $\rightarrow RMgX$; Wurtz reaction $2RX + 2Na \rightarrow R-R + 2NaX$.

Haloarenes - nature of C-X bond and reactions

Haloarenes are much **less reactive** towards nucleophilic substitution because: (1) **resonance** gives the C-Cl bond partial double-bond character; (2) carbon is sp^2 (more electronegative, shorter stronger bond); (3) phenyl cation is unstable; (4) the electron-rich ring repels nucleophiles. Substitution occurs only under drastic conditions: $C_6H_5Cl + NaOH$ (623 K, 300 atm) $\rightarrow$ phenol (Dow process). Electron-withdrawing $-NO_2$ groups at ortho/para positions make it easier.

Electrophilic substitution in haloarenes: halogen is **deactivating** ($-I$) but **ortho/para directing** ($+R$). Chlorobenzene on nitration gives 1-chloro-2-nitrobenzene + 1-chloro-4-nitrobenzene (major); on Friedel-Crafts methylation gives 2- and 4-chlorotoluene; with $Cl_2/FeCl_3$ gives 1,2- and 1,4-dichlorobenzene. **Wurtz-Fittig:** $C_6H_5Cl + CH_3Cl + 2Na \rightarrow C_6H_5CH_3 + 2NaCl$. **Fittig:** $2C_6H_5Cl + 2Na \rightarrow C_6H_5-C_6H_5$ (biphenyl).

Uses and environmental effects of polyhalogen compounds

Compound	Uses	Effects
Dichloromethane (CH_2Cl_2)	Solvent, paint remover, aerosol propellant	Harms nervous system; dizziness, nausea; skin and eye irritation
Trichloromethane (chloroform, CHCl_3)	Solvent for fats, alkaloids; earlier an anaesthetic	Depresses nervous system; liver/kidney damage. In air and light forms poisonous phosgene (COCl_2) — stored in dark coloured bottles filled to the brim
Tetrachloromethane (CCl_4)	Making refrigerants and propellants; earlier fire extinguisher, cleaning fluid	Liver cancer suspected; nerve damage; depletes the ozone layer
Iodoform (CHI_3)	Antiseptic (releases iodine)	Objectionable smell — replaced by other antiseptics
Freons (CFCs, CCl_2F_2)	Refrigerants, air conditioners, aerosol propellants	Reach the stratosphere, release $\text{Cl}\cdot$ radicals that destroy the ozone layer
DDT (p,p'-dichlorodiphenyltrichloroethane)	First chlorinated insecticide; controlled malaria-carrying mosquitoes	Not biodegradable; accumulates in fat tissues of animals and moves up the food chain (biomagnification); harmful to birds and fish — banned in many countries

XII-7. Alcohols, Phenols and Ethers

Alcohols (R-OH)

Classification: mono-, di-, trihydric by number of -OH; 1° , 2° , 3° by the carbon bearing -OH. **Names:** CH_3OH methanol; $\text{C}_2\text{H}_5\text{OH}$ ethanol; $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ propan-2-ol; $(\text{CH}_3)_3\text{COH}$ 2-methylpropan-2-ol; $\text{HOCH}_2\text{CH}_2\text{OH}$ ethane-1,2-diol (glycol); glycerol propane-1,2,3-triol.

Preparation:

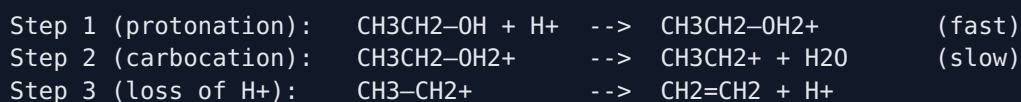
- From alkenes: acid-catalysed hydration (Markovnikov); hydroboration-oxidation with B_2H_6 then $\text{H}_2\text{O}_2/\text{OH}^-$ (anti-Markovnikov).
- Reduction of aldehydes/ketones (H_2/Pd , NaBH_4 , LiAlH_4): aldehyde $\rightarrow 1^\circ$ alcohol; ketone $\rightarrow 2^\circ$ alcohol. Carboxylic acids/esters with $\text{LiAlH}_4 \rightarrow 1^\circ$ alcohol.
- From Grignard reagents: $\text{HCHO} \rightarrow 1^\circ$ alcohol; other aldehydes $\rightarrow 2^\circ$; ketones $\rightarrow 3^\circ$.
- Hydrolysis of alkyl halides with aq. KOH.

Physical properties: high boiling points due to **intermolecular hydrogen bonding**; lower alcohols are soluble in water (H-bonding with water); solubility decreases as the alkyl part grows.

Chemical properties:

- **Acidic nature:** $2\text{ROH} + 2\text{Na} \rightarrow 2\text{RONa} + \text{H}_2$. Acidity: $1^\circ > 2^\circ > 3^\circ$ (+I effect of alkyl groups reduces acidity). Alcohols are weaker acids than water.
- **Esterification:** $\text{ROH} + \text{R}'\text{COOH} \rightleftharpoons \text{R}'\text{COOR} + \text{H}_2\text{O}$ (conc. H_2SO_4).
- **With HX, PX_3 , PCl_5 , SOCl_2** $\rightarrow$ alkyl halides.
- **Dehydration** (conc. H_2SO_4 , 443 K) $\rightarrow$ alkene; ease $3^\circ > 2^\circ > 1^\circ$.
- **Oxidation:** $1^\circ \rightarrow$ aldehyde (PCC or Cu/573 K) $\rightarrow$ carboxylic acid ($\text{KMnO}_4/\text{K}_2\text{Cr}_2\text{O}_7$); $2^\circ \rightarrow$ ketone; $3^\circ \rightarrow$ resist oxidation (with hot Cu, give alkene).

Mechanism of dehydration of ethanol



Distinguishing 1° , 2° and 3° alcohols

Test	1°	2°	3°
Lucas test (conc. HCl + anhyd. ZnCl_2)	No turbidity at room temperature	Turbidity in about 5 minutes	Turbidity immediately
Victor Meyer test	Blood red colour	Blue colour	Colourless
Oxidation / Cu at 573 K	Aldehyde	Ketone	Alkene

Uses — methanol: solvent, making formaldehyde, antifreeze; **poisonous** — small amounts cause blindness, large amounts death. **Ethanol:** alcoholic beverages, solvent, fuel (blended with petrol), antiseptic, preparation of many chemicals. **Denatured alcohol** is ethanol made unfit to drink by adding CuSO_4 and pyridine. Ethanol is made by **fermentation** of molasses using yeast enzymes (invertase, zymase).

Phenols (Ar-OH)

Preparation: (i) from chlorobenzene (Dow process, NaOH at 623 K, 300 atm, then acid); (ii) from benzenesulphonic acid fused with NaOH; (iii) from diazonium salts by warming with water; (iv) from cumene (isopropylbenzene) by air oxidation and acid hydrolysis — also gives acetone (industrial).

Acidic nature: phenol is more acidic than alcohols and water because the phenoxide ion is stabilised by resonance (negative charge spread into the ring); it dissolves in NaOH but not in NaHCO_3 (weaker than carboxylic acids). Electron-withdrawing groups ($-\text{NO}_2$) at o/p increase acidity (p-nitrophenol > phenol; picric acid is strongly acidic); electron-donating groups ($-\text{CH}_3$) decrease it.

Electrophilic substitution (–OH is strongly activating, o/p directing):

- Dilute $\text{HNO}_3 \rightarrow$ o- and p-nitrophenol (separated by steam distillation — ortho is steam-volatile due to intramolecular H-bond). Conc. $\text{HNO}_3 \rightarrow$ 2,4,6-trinitrophenol (picric acid).
- Bromine water $\rightarrow$ **2,4,6-tribromophenol** (white ppt) — a test for phenol. Br_2 in CS_2 at low temperature $\rightarrow$ mono-bromophenols.
- **Kolbe's reaction:** sodium phenoxide + CO_2 (4–7 atm, 400 K), then acid $\rightarrow$ salicylic acid (used to make aspirin).
- **Reimer-Tiemann reaction:** phenol + CHCl_3 + aq. $\text{NaOH} \rightarrow$ salicylaldehyde.
- With zinc dust $\rightarrow$ benzene. FeCl_3 test: violet colour.

Uses: antiseptic and disinfectant (carbolic acid), making Bakelite, dyes, drugs (aspirin), explosives (picric acid).

Ethers (R-O-R')

Names: CH_3OCH_3 methoxymethane (dimethyl ether); $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ ethoxyethane (diethyl ether); $\text{C}_6\text{H}_5\text{OCH}_3$ methoxybenzene (anisole).

Preparation: (i) dehydration of alcohols with conc. H_2SO_4 at 413 K ($2\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{H}_2\text{O}$); (ii) **Williamson synthesis:** $\text{R-X} + \text{R}'\text{-ONa} \rightarrow \text{R-O-R}' + \text{NaX}$ (use a primary alkyl halide; with 3° halides elimination occurs instead).

Properties: low boiling points (no H-bonding between ether molecules), similar to alkanes; slightly soluble in water. Cleaved by HI : $\text{R-O-R}' + \text{HI} \rightarrow \text{R-I} + \text{R}'\text{-OH}$; with excess HI both become iodides. Anisole + $\text{HI} \rightarrow$ phenol + CH_3I . Anisole undergoes o/p electrophilic substitution ($-\text{OCH}_3$ is activating).

Uses: diethyl ether as a solvent and earlier as an anaesthetic; anisole in perfumes.

Exam Q&A - Haloalkanes, Alcohols, Phenols, Ethers

Q1. Why is chloroform stored in dark bottles? [1]

In light and air it oxidises to poisonous phosgene (COCl_2).

Q2. Why are haloarenes less reactive than haloalkanes towards nucleophilic substitution? [2]

Resonance gives partial double-bond character to C-X, the carbon is sp^2 , the phenyl cation is unstable and the ring repels nucleophiles.

Q3. Phenol is more acidic than ethanol. Why? [2]

Phenoxide ion is stabilised by resonance; ethoxide ion has no resonance and is destabilised by the +I effect of the ethyl group.

Q4. How will you distinguish between ethanol and phenol? [2]

Phenol gives violet colour with neutral FeCl_3 and white ppt with bromine water; ethanol does not. (Ethanol gives the iodoform test.)

Q5. Write the $\text{S}_{\text{N}}1$ mechanism for hydrolysis of tert-butyl bromide. [3]

Step 1 (slow): $(\text{CH}_3)_3\text{C}-\text{Br} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Br}^-$. Step 2 (fast): $(\text{CH}_3)_3\text{C}^+ + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{C}-\text{OH}$. Rate = $k[(\text{CH}_3)_3\text{CBr}]$.

Q6. Give the Reimer-Tiemann reaction. [2]

Phenol + CHCl_3 + aq. NaOH (340 K), then acid $\rightarrow$ salicylaldehyde (2-hydroxybenzaldehyde).

XII-8. Aldehydes, Ketones and Carboxylic Acids

Nomenclature

Formula	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
CH ₃ CHO	Acetaldehyde	Ethanal
C ₆ H ₅ CHO	Benzaldehyde	Benzenecarbaldehyde
CH ₃ COCH ₃	Acetone	Propanone
CH ₃ COC ₂ H ₅	Ethyl methyl ketone	Butan-2-one
C ₆ H ₅ COCH ₃	Acetophenone	1-Phenylethanone
HCOOH	Formic acid	Methanoic acid
CH ₃ COOH	Acetic acid	Ethanoic acid
C ₆ H ₅ COOH	Benzoic acid	Benzenecarboxylic acid

Nature of the carbonyl group

The C=O carbon is sp² hybridised; the group is planar (bond angles ≈ 120°). Oxygen is more electronegative, so the bond is polar: C^{δ+}=O^{δ-}. The carbon is attacked by **nucleophiles**; hence aldehydes and ketones give **nucleophilic addition** reactions. Aldehydes are more reactive than ketones — (1) two alkyl groups in ketones push electrons (+I) and reduce δ+ on carbon; (2) two groups crowd the carbon (steric hindrance).

Preparation of aldehydes and ketones

- Oxidation of alcohols: 1° → aldehyde (PCC); 2° → ketone (K₂Cr₂O₇/H⁺).
- Dehydrogenation: alcohol vapours over Cu at 573 K.
- Ozonolysis of alkenes; hydration of alkynes (HgSO₄/H₂SO₄): ethyne → ethanal; other alkynes → ketones.
- **Rosenmund reduction:** RCOCl + H₂ (Pd/BaSO₄) → RCHO.
- **Stephen reaction:** RCN + SnCl₂/HCl → imine → hydrolysis → RCHO.
- From nitriles with Grignard reagent → ketone. Etard reaction (toluene + CrO₂Cl₂) → benzaldehyde. Friedel-Crafts acylation → aromatic ketone.

Physical properties

Boiling points higher than hydrocarbons/ethers of similar mass (dipole-dipole forces) but lower than alcohols (no intermolecular H-bonding). Lower members are water-soluble (H-bonds with water). Many have pleasant smells (vanillin, cinnamaldehyde).

Chemical reactions

(A) Nucleophilic addition

- $\text{HCN} \rightarrow$ cyanohydrin (base catalysed).
- $\text{NaHSO}_3 \rightarrow$ crystalline bisulphite adduct (used to purify aldehydes/ketones).
- Grignard reagent $\rightarrow$ alcohols after hydrolysis.
- Alcohols $\rightarrow$ hemiacetal and acetal (aldehydes); ketals with ethylene glycol.
- **Ammonia derivatives (addition-elimination)** $\text{Z-NH}_2 \rightarrow \text{C=N-Z}$: hydroxylamine $\rightarrow$ oxime; hydrazine $\rightarrow$ hydrazone; phenylhydrazine $\rightarrow$ phenylhydrazone; 2,4-DNP $\rightarrow$ orange/yellow 2,4-dinitrophenylhydrazone (test for C=O); semicarbazide $\rightarrow$ semicarbazone.

Mechanism of nucleophilic addition (e.g. HCN)

Step 1: $\text{HCN} + \text{OH}^- \rightarrow \text{CN}^- + \text{H}_2\text{O}$ (nucleophile generated)
 Step 2: CN^- attacks the δ^+ carbon of C=O ; the π electrons move to O, forming a tetrahedral alkoxide ion
 Step 3: the alkoxide takes H^+ from $\text{HCN/H}_2\text{O} \rightarrow$ cyanohydrin $\text{R}_2\text{C(OH)CN}$

(B) Reduction: $\text{NaBH}_4/\text{LiAlH}_4 \rightarrow$ alcohols. **Clemmensen** ($\text{Zn-Hg}/\text{conc. HCl}$) and **Wolff-Kishner** (NH_2NH_2 , then $\text{KOH}/\text{ethylene glycol}$, heat) reduce C=O to CH_2 .

(C) Oxidation: aldehydes are easily oxidised to acids, so they are **reducing agents**:

- **Tollens' test:** aldehyde + ammoniacal $\text{AgNO}_3 \rightarrow$ bright **silver mirror**.
- **Fehling's test:** aliphatic aldehyde + Fehling's solution $\rightarrow$ **red-brown ppt of Cu_2O** (benzaldehyde does not respond).
- Ketones do not give these tests (distinguish aldehydes from ketones).
- **Haloform reaction:** compounds with $\text{CH}_3\text{CO-}$ group (and $\text{CH}_3\text{CH(OH)-}$ group) + NaOI (I_2/NaOH) $\rightarrow$ yellow ppt of **iodoform CHI_3** . Ethanal, propanone, ethanol, acetophenone give it; methanal and propanal don't.

(D) Reactions due to α -hydrogen (H on the carbon next to C=O is acidic because the carbanion/enolate is resonance-stabilised):

- **Aldol condensation:** aldehydes/ketones having α -H, with dilute NaOH , give β -hydroxy aldehydes/ketones (aldols), which lose water on heating to give α,β -unsaturated compounds. $2\text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CH(OH)CH}_2\text{CHO}$ (aldol) $\rightarrow \text{CH}_3\text{CH=CHCHO}$ (but-2-enal).
- **Cross aldol** between two different carbonyl compounds gives a mixture.

(E) Cannizzaro reaction: aldehydes **without α -H** (HCHO , $\text{C}_6\text{H}_5\text{CHO}$) with conc. NaOH undergo self oxidation-reduction: $2\text{HCHO} + \text{conc. NaOH} \rightarrow \text{CH}_3\text{OH} + \text{HCOONa}$.

(F) Electrophilic substitution in aromatic aldehydes/ketones: $-\text{CHO}$, $-\text{COR}$ are meta-directing and deactivating.

Uses: formalin (40% HCHO) preserves biological specimens; HCHO makes Bakelite; acetone is a common solvent (nail-polish remover); benzaldehyde in perfumes and dyes.

Carboxylic Acids (R-COOH)

Preparation: oxidation of 1° alcohols/aldehydes (KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$); oxidation of alkylbenzenes with $\text{KMnO}_4 \rightarrow$ benzoic acid; hydrolysis of nitriles and amides; Grignard reagent + CO_2 (dry ice), then acid; hydrolysis of esters.

Physical properties: very high boiling points because they form **dimers** by hydrogen bonding; lower members are water-soluble.

Acidic nature: $\text{RCOOH} \rightleftharpoons \text{RCOO}^- + \text{H}^+$. The carboxylate ion is stabilised by resonance (two equivalent C-O bonds), so carboxylic acids are stronger acids than phenols and alcohols; they liberate CO_2 from NaHCO_3 (test). **Effect of substituents:** electron-withdrawing groups increase acidity, electron-donating groups decrease it.

Order: $\text{CF}_3\text{COOH} > \text{CCl}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{HCOOH} > \text{C}_6\text{H}_5\text{COOH} > \text{CH}_3\text{COOH}$.

Chemical reactions:

- With metals/alkalis/carbonates $\rightarrow$ salts ($2\text{RCOOH} + \text{Na}_2\text{CO}_3 \rightarrow 2\text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2$).
- With PCl_5 , PCl_3 , $\text{SOCl}_2 \rightarrow$ acid chlorides (RCOCl).
- Esterification with alcohols (conc. H_2SO_4) $\rightarrow$ fruity-smelling esters.
- With $\text{NH}_3 \rightarrow$ ammonium salt $\rightarrow$ amide (on heating).
- Dehydration with $\text{P}_2\text{O}_5 \rightarrow$ acid anhydrides.
- Reduction with $\text{LiAlH}_4 \rightarrow$ 1° alcohols.
- **Decarboxylation:** sodium salt + soda lime $\rightarrow$ alkane; Kolbe electrolysis.
- **Hell-Volhard-Zelinsky (HVZ) reaction:** acids with $\alpha\text{-H} + \text{Cl}_2/\text{Br}_2$ (red P) $\rightarrow$ α -halo acids.
- Ring substitution in benzoic acid: $-\text{COOH}$ is meta-directing (gives m-nitrobenzoic acid). Benzoic acid does not give Friedel-Crafts reaction.

Uses: methanoic acid in rubber, textile and leather industries; ethanoic acid as vinegar (6-8%) and in making cellulose acetate; benzoic acid and sodium benzoate as food preservatives; higher fatty acids for soaps.

Example. An organic compound $\text{C}_3\text{H}_6\text{O}$ gives a positive iodoform test but does not reduce Tollens' reagent. Identify it.

Not an aldehyde (no Tollens); iodoform positive $\rightarrow$ has $\text{CH}_3\text{CO}-$. The compound is **propanone, CH_3COCH_3** .

XII-9. Amines

Idea: Amines are derivatives of ammonia in which one or more H atoms are replaced by alkyl or aryl groups. 1° R-NH_2 ; 2° R_2NH ; 3° R_3N . Examples: methanamine CH_3NH_2 ; N-

methylmethanamine $(\text{CH}_3)_2\text{NH}$; N,N-dimethylmethanamine $(\text{CH}_3)_3\text{N}$; aniline (benzenamine) $\text{C}_6\text{H}_5\text{NH}_2$.

Structure: nitrogen is sp^3 hybridised with one lone pair; pyramidal shape; C-N-C angle $\approx 108^\circ$.

Preparation

- **Reduction of nitro compounds:** $\text{C}_6\text{H}_5\text{NO}_2 + \text{Fe}/\text{HCl}$ (or Sn/HCl , or H_2/Ni) $\rightarrow$ $\text{C}_6\text{H}_5\text{NH}_2$.
- **Ammonolysis of alkyl halides:** $\text{R-X} + \text{NH}_3 \rightarrow$ mixture of 1° , 2° , 3° amines and quaternary salt.
- Reduction of nitriles (LiAlH_4 or H_2/Ni) $\rightarrow$ 1° amines (one extra carbon); reduction of amides (LiAlH_4).
- **Gabriel phthalimide synthesis** $\rightarrow$ pure 1° aliphatic amines (not aromatic).
- **Hoffmann bromamide degradation:** $\text{RCONH}_2 + \text{Br}_2 + 4\text{NaOH} \rightarrow \text{RNH}_2 + \text{Na}_2\text{CO}_3 + 2\text{NaBr} + 2\text{H}_2\text{O}$ — amine has **one carbon less** than the amide.

Physical properties

Lower aliphatic amines are gases with a fishy smell. 1° and 2° amines form intermolecular H-bonds; 3° cannot. Boiling point order: $1^\circ > 2^\circ > 3^\circ$. Lower amines are water-soluble.

Basic character

The lone pair on N accepts H^+ , so amines are bases. In water (aqueous phase), basicity of methyl amines: $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$ (combined effect of +I, solvation by H-bonding and steric hindrance). **Aniline is a much weaker base** than ammonia and aliphatic amines because its lone pair is delocalised into the benzene ring by resonance and is less available.

Chemical reactions

- Salt formation with acids: $\text{C}_6\text{H}_5\text{NH}_2 + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-$.
- Alkylation and acylation (with $\text{CH}_3\text{COCl} \rightarrow$ N-substituted amide). Benzoylation with $\text{C}_6\text{H}_5\text{COCl}$.
- **Carbylamine reaction** (isocyanide test): only **1° amines** (aliphatic and aromatic) heated with CHCl_3 and alcoholic KOH give foul-smelling isocyanides: $\text{RNH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{RNC} + 3\text{KCl} + 3\text{H}_2\text{O}$.
- **With nitrous acid ($\text{NaNO}_2 + \text{HCl}$):** 1° aliphatic amines give alcohol + N_2 gas (bubbles); aromatic 1° amines at 273–278 K give **diazonium salts**.
- Aniline: $-\text{NH}_2$ is strongly activating. With bromine water $\rightarrow$ 2,4,6-tribromoaniline (white ppt). To get mono-substitution, first acetylate ($-\text{NHCOCH}_3$ is less activating). Direct nitration gives m-nitroaniline too, because in acid, $-\text{NH}_3^+$ (meta-directing)

forms. Sulphonation → sulphanilic acid. Aniline does not undergo Friedel-Crafts (it forms a salt with AlCl_3).

Identification of 1°, 2°, 3° amines - Hinsberg's test

Amine	With benzenesulphonyl chloride (Hinsberg reagent)	Product in KOH
1°	Forms N-alkylbenzenesulphonamide	Soluble (acidic H on N)
2°	Forms N,N-dialkylbenzenesulphonamide	Insoluble (no H on N)
3°	No reaction	—

Diazonium salts ($\text{Ar-N}_2^+\text{X}^-$)

Preparation (diazotisation): $\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + 2\text{HCl} (273-278 \text{ K}) \rightarrow \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{NaCl} + 2\text{H}_2\text{O}$. Benzene diazonium chloride is used immediately because it is unstable above 278 K. Aromatic diazonium salts are more stable than aliphatic ones due to resonance.

Reactions (N_2 replaced):

Reagent	Product	Name
CuCl/HCl or CuBr/HBr	$\text{C}_6\text{H}_5\text{Cl}$ / $\text{C}_6\text{H}_5\text{Br}$	Sandmeyer reaction
$\text{Cu powder} + \text{HCl/HBr}$	$\text{C}_6\text{H}_5\text{Cl}$ / Br	Gattermann reaction
CuCN/KCN	$\text{C}_6\text{H}_5\text{CN}$	Sandmeyer
KI	$\text{C}_6\text{H}_5\text{I}$	—
HBF_4 , heat	$\text{C}_6\text{H}_5\text{F}$	Balz-Schiemann
H_3PO_2 or ethanol	C_6H_6	Reduction
Warm water	$\text{C}_6\text{H}_5\text{OH}$	Hydrolysis

Coupling reactions (N_2 retained): with phenol (in alkali) → p-hydroxyazobenzene (orange dye); with aniline (in acid) → p-aminoazobenzene (yellow dye). These **azo dyes** are important industrially.

Importance: diazonium salts are versatile intermediates to introduce -F, -Cl, -Br, -I, -CN, -OH, -H into the benzene ring, including groups that cannot be put in by direct substitution.

XII-10. Biomolecules

Carbohydrates

Optically active polyhydroxy aldehydes or ketones, or compounds that give these on hydrolysis. General formula often $\text{C}_x(\text{H}_2\text{O})_y$.

Class	Meaning	Examples
Monosaccharides	Cannot be hydrolysed further	Glucose, fructose, ribose
Oligosaccharides	2-10 monosaccharide units (disaccharides most common)	Sucrose, lactose, maltose
Polysaccharides	Many units	Starch, cellulose, glycogen

Aldoses contain -CHO (glucose: aldohexose); **ketoses** contain >C=O (fructose: ketohexose). Sugars that reduce Tollens'/Fehling's are **reducing sugars** (all monosaccharides, maltose, lactose); sucrose is non-reducing.

Glucose ($\text{C}_6\text{H}_{12}\text{O}_6$): prepared by hydrolysis of sucrose or starch. Evidence for open-chain structure: with $\text{HI} \rightarrow$ n-hexane (straight chain of 6 C); with $\text{NH}_2\text{OH} \rightarrow$ oxime (C=O present); with Br_2 water $\rightarrow$ gluconic acid (-CHO present); acetylation gives pentaacetate (5 -OH groups); with $\text{HNO}_3 \rightarrow$ saccharic acid. But glucose does not give Schiff's test or react with NaHSO_3 — explained by its **cyclic (pyranose) structure**, which exists as α and β forms (anomers).

D-L configuration: refers to the position of -OH on the lowest asymmetric carbon compared with glyceraldehyde: -OH on the right $\rightarrow$ D; on the left $\rightarrow$ L. Natural glucose is D-(+)-glucose. (D/L has nothing to do with the direction of rotation, + or -.)

Fructose: ketohexose, laevorotatory, five-membered (furanose) ring; found in fruits and honey.

Disaccharide	Units	Notes
Sucrose (cane sugar)	α -D-glucose + β -D-fructose (C1-C2 link)	Non-reducing; hydrolysis gives "invert sugar" (rotation changes from + to -)
Maltose	2 α -D-glucose (C1-C4)	Reducing
Lactose (milk sugar)	β -D-galactose + β -D-glucose (C1-C4)	Reducing

Polysaccharides: **starch** (plant food store) = amylose (15-20%, water-soluble, unbranched) + amylopectin (80-85%, branched). **Cellulose** (plant cell walls) = linear chains of β -D-glucose; humans cannot digest it. **Glycogen** ("animal starch") = highly branched, stored in liver and muscles.

Importance: main source of energy (glucose), energy storage (starch, glycogen), structural material (cellulose in wood, cotton), part of nucleic acids (ribose, deoxyribose), honey, paper and textile industries.

Proteins

Amino acids contain -NH_2 and -COOH groups: $\text{R-CH(NH}_2\text{)-COOH}$. About 20 occur in proteins. **Essential** amino acids (valine, leucine, lysine...) must come from food; **non-**

essential ones (glycine, alanine) are made in the body. In solution they exist as **zwitterions** ($\text{H}_3\text{N}^+-\text{CHR}-\text{COO}^-$), so they are amphoteric with high melting points.

Peptide bond: the amide link $-\text{CO}-\text{NH}-$ formed between $-\text{COOH}$ of one amino acid and $-\text{NH}_2$ of another with loss of water. Two amino acids $\rightarrow$ dipeptide; many $\rightarrow$ **polypeptide**; polypeptides with more than ~ 100 amino acids (mass $> 10,000$ u) are **proteins**.

Structure level	Meaning
Primary	Sequence of amino acids in the chain
Secondary	Folding into α -helix (H-bonds within the chain) or β -pleated sheet (H-bonds between chains)
Tertiary	Overall 3-D folding of the chain — fibrous or globular shape; held by H-bonds, disulphide links, ionic and van der Waals forces
Quaternary	Arrangement of two or more polypeptide sub-units (e.g. haemoglobin has 4)

Fibrous proteins (keratin in hair, myosin in muscle) are insoluble; **globular proteins** (insulin, albumin) are soluble.

Denaturation: loss of biological activity when a protein's secondary and tertiary structures are destroyed by heat, pH change or chemicals, while the primary structure remains. Examples: boiling an egg (albumin coagulates), curdling of milk.

Enzymes: biological catalysts, mostly globular proteins, highly specific, work at body temperature and pH. Examples: invertase (sucrose $\rightarrow$ glucose + fructose), maltase, pepsin and trypsin (proteins), amylase (starch).

Hormones (elementary idea)

Chemical messengers produced by endocrine glands and carried by blood to target organs. Types: **steroids** (oestrogen, testosterone), **polypeptides** (insulin, glucagon), **amino-acid derivatives** (thyroxine, adrenaline). Insulin and glucagon regulate blood sugar; thyroxine controls metabolism (deficiency $\rightarrow$ goitre); adrenaline prepares the body for emergencies.

Vitamins

Vitamin	Type	Source	Deficiency disease
A	Fat-soluble	Carrots, milk, fish-liver oil	Night blindness, xerophthalmia
B ₁ (thiamine)	Water-soluble	Cereals, yeast	Beri-beri
B ₂ (riboflavin)	Water-soluble	Milk, eggs	Cracked lips, cheilosis
B ₆	Water-soluble	Yeast, cereals	Convulsions
B ₁₂	Water-soluble	Meat, fish, eggs	Pernicious anaemia
C (ascorbic acid)	Water-soluble	Citrus fruits, amla	Scurvy (bleeding gums)
D	Fat-soluble	Sunlight, fish, egg yolk	Rickets, osteomalacia
E	Fat-soluble	Vegetable oils, wheat germ	Fragile red blood cells, muscle weakness
K	Fat-soluble	Green leafy vegetables	Delayed blood clotting

Fat-soluble vitamins (A, D, E, K) are stored in the liver and fat tissues; water-soluble ones (B, C) are excreted and must be taken regularly (B₁₂ is an exception and is stored).

Nucleic acids

Long polymers of **nucleotides**. A nucleotide = **nitrogenous base + pentose sugar + phosphate**. A nucleoside = base + sugar.

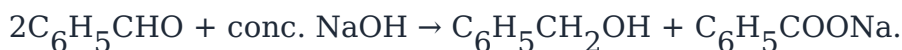
Feature	DNA	RNA
Sugar	2-Deoxyribose	Ribose
Bases	A, G, C, T (thymine)	A, G, C, U (uracil)
Structure	Double helix (Watson and Crick, 1953); A pairs with T, G with C by H-bonds	Usually single-stranded
Function	Stores genetic information; replicates itself	Protein synthesis (mRNA, tRNA, rRNA)

Exam Q&A - Organic II and Biomolecules

Q1. Why are aldehydes more reactive than ketones towards nucleophilic addition? [2]

Ketones have two electron-releasing alkyl groups (reduce δ^+ on carbon) and more steric hindrance.

Q2. Write the Cannizzaro reaction of benzaldehyde. [2]



Q3. Why is aniline a weaker base than methylamine? [2]

In aniline, the lone pair on N is delocalised into the benzene ring by resonance, so it is less available; in methylamine the +I effect of CH_3 increases electron density on N.

Q4. How will you convert aniline into chlorobenzene? [2]

Diazotise ($\text{NaNO}_2 + \text{HCl}$, 273–278 K) to benzene diazonium chloride, then treat with CuCl/HCl (Sandmeyer).

Q5. What is a peptide bond? [1]

The $-\text{CO}-\text{NH}-$ amide linkage between two amino acids formed with loss of water.

Q6. Name the deficiency diseases of vitamin C and vitamin D. [1]

Scurvy; rickets.

Q7. What is denaturation of protein? Give an example. [2]

Loss of biological activity due to destruction of secondary/tertiary structure by heat, pH or chemicals; e.g. coagulation of egg white on boiling.

Chemistry Practical – Class XII (30 marks)

Item	Marks
Salt analysis – basic radical (Dry 5 + Wet 7)	12
Crystallisation / Double titration / Bench acid / Redox titration / Organic compound	10
Viva-voce	5
Record	3

Group analysis of basic radicals

Group	Radicals	Group reagent	Precipitate
Zero	NH_4^+	NaOH , heat	NH_3 gas (white fumes with HCl ; Nessler's reagent brown)
I	Ag^+ , Pb^{2+} , Hg_2^{2+}	Dil. HCl	Chlorides (white)
II	Hg^{2+} , Cu^{2+} , Bi^{3+} , As^{3+} , Sb^{3+} , $\text{Sn}^{2+}/\text{Sn}^{4+}$	H_2S in presence of dil. HCl	Sulphides (CuS black, As_2S_3 yellow, Sb_2S_3 orange)
III A	Fe^{3+} , Al^{3+} , Cr^{3+}	$\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$	Hydroxides ($\text{Fe}(\text{OH})_3$ reddish-brown, $\text{Al}(\text{OH})_3$ white gelatinous, $\text{Cr}(\text{OH})_3$ green)
III B (IV)	Co^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+}	H_2S in ammoniacal medium	Sulphides (ZnS white, MnS buff, CoS/NiS black)
IV (V)	Ba^{2+} , Sr^{2+} , Ca^{2+}	$(\text{NH}_4)_2\text{CO}_3 + \text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$	Carbonates (white)
V (VI)	Mg^{2+} , Na^+ , K^+ , NH_4^+	No common reagent	Mg: white ppt with Na_2HPO_4 ; Na: golden yellow flame; K: lilac flame

Flame test colours: Ca – brick red; Sr – crimson red; Ba – apple green; Cu – bluish green; Na – golden yellow; K – lilac/violet.

Redox titration (KMnO₄ vs oxalic acid)

Reaction: $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$. Done in dil. H_2SO_4 at 60–70 °C. KMnO_4 is a self-indicator; end point = permanent light pink. Use $M_1V_1/n_1 = M_2V_2/n_2$ ($n_{\text{KMnO}_4} = 2$, $n_{\text{oxalic}} = 5$) or $N_1V_1 = N_2V_2$.

Organic functional group tests

Group	Test	Observation
Unsaturation	Bromine water / Baeyer's reagent	Colour discharged
Aromatic vs aliphatic	Copper foil / ignition test	Aromatic burns with sooty flame
Carboxylic acid	NaHCO_3	Brisk effervescence (CO_2)
Phenol	Neutral FeCl_3	Violet colour
Aldehyde	Tollens' / Fehling's	Silver mirror / red ppt
Ketone	Sodium nitroprusside + NaOH ; 2,4-DNP	Red colour; orange ppt
Alcohol	Ceric ammonium nitrate; Na metal	Red colour; H_2 gas

Chemistry Question Bank – How to Use It

The following pages contain **chapter-wise question banks** for every chapter of the CHSE +2 2nd Year Chemistry syllabus. Each bank has five parts: **Key points** (a one-look revision list), **A. Multiple choice questions** (1 mark each), **B. Very short answer questions** (1–2 marks), **C. Short answer questions** (3 marks) and **D. Long answer questions** (5–7 marks) with complete step-by-step solutions.

STUDY PLAN

Read the key points first. Try every MCQ yourself before looking at the answer. Write the short answers in your own words in a notebook. For numericals, always write (1) the formula, (2) the values with units, (3) the substitution and (4) the final answer with unit – CHSE examiners give step marks for each.

SYLLABUS NOTE

The present CHSE Class XII syllabus (rationalised, in line with NCERT) has ten theory units: Solutions, Electrochemistry, Chemical Kinetics, d- and f-Block Elements, Coordination Compounds, Haloalkanes and Haloarenes, Alcohols Phenols and Ethers, Aldehydes Ketones and Carboxylic Acids, Amines, and Biomolecules. "Solid State", "Surface Chemistry", "Polymers" and "Chemistry in Everyday Life" are no longer in the theory syllabus, so they are not covered here. Always check the latest syllabus booklet issued by CHSE for your session.

QB-1. Solutions

Key points

- Molarity (M) = moles of solute per litre of solution – changes with temperature (volume changes). Molality (m) = moles of solute per kg of solvent – independent of temperature.
- Mole fraction: $x_A + x_B = 1$ for a binary solution.
- Henry's law: $p = K_H \cdot x$. Greater K_H means lower solubility of the gas. Gas solubility falls as temperature rises.
- Raoult's law: $p_A = p_A^\circ \cdot x_A$. Relative lowering of vapour pressure = mole fraction of solute.
- Ideal solution: $\Delta H_{\text{mix}} = 0$, $\Delta V_{\text{mix}} = 0$. Positive deviation forms minimum-boiling azeotropes (ethanol–water, 95.6% ethanol); negative deviation forms maximum-boiling azeotropes (HNO_3 –water, 68% HNO_3).
- Colligative properties depend only on the **number** of solute particles: relative lowering of vapour pressure, elevation of boiling point ($\Delta T_b = K_b \cdot m$), depression of freezing point ($\Delta T_f = K_f \cdot m$) and osmotic pressure ($\pi = CRT$).
- Osmotic pressure is the best method for finding the molar mass of proteins and polymers (measured at room temperature; large values even for dilute solutions).
- Isotonic solutions have the same osmotic pressure. 0.9% NaCl (normal saline) is isotonic with blood. Hypertonic solution shrinks a cell (plasmolysis); hypotonic solution swells it.
- van't Hoff factor i = observed colligative property/calculated value = normal molar mass/abnormal molar mass. $i > 1$ for dissociation, $i < 1$ for association.
- Degree of dissociation $\alpha = (i - 1)/(n - 1)$; degree of association $\alpha = (1 - i)/(1 - 1/n)$.

A. Multiple choice questions

1. Which concentration term does not change with temperature? (a) Molarity (b) Normality (c) Molality (d) Formality

(c) Molality – it involves mass, not volume.

2. The van't Hoff factor for $\text{K}_4[\text{Fe}(\text{CN})_6]$ assuming complete dissociation is (a) 2 (b) 4 (c) 5 (d) 10

(c) $4\text{K}^+ + [\text{Fe}(\text{CN})_6]^{4-} = 5$ ions.

3. A mixture of chloroform and acetone shows (a) positive deviation (b) negative deviation (c) ideal behaviour (d) no change

(b) H-bonding between CHCl_3 and acetone makes A–B attraction stronger.

4. Which colligative property is used to find the molar mass of proteins? (a) ΔT_b (b) ΔT_f (c) Osmotic pressure (d) Relative lowering of vapour pressure

(c).

5. The unit of ebullioscopic constant K_b is (a) K kg mol^{-1} (b) mol kg K^{-1} (c) K mol kg^{-1} (d) kg mol^{-1}

(a).

6. Which 0.1 m aqueous solution has the lowest freezing point? (a) glucose (b) NaCl (c) CaCl_2 (d) urea

(c) $i = 3$, so largest ΔT_f .

7. Acetic acid in benzene has van't Hoff factor close to (a) 2 (b) 1 (c) 0.5 (d) 3

(c) It dimerises by hydrogen bonding.

8. Henry's law constant increases with temperature. This means solubility of the gas (a) increases (b) decreases (c) is unchanged (d) first increases then decreases

(b).

9. Normal saline is (a) 0.9% NaCl (b) 9% NaCl (c) 0.09% NaCl (d) 5% glucose

(a).

10. An azeotrope of ethanol and water boils (a) above both components (b) below both components (c) between them (d) at 100°C

(b) Minimum-boiling azeotrope (positive deviation).

B. Very short answer questions

1. Define molality. [1]

Number of moles of solute dissolved in 1 kg of solvent.

2. State Henry's law. [1]

At constant temperature, the partial pressure of a gas in vapour phase is proportional to its mole fraction in the solution: $p = K_H x$.

3. What are isotonic solutions? [1]

Solutions having the same osmotic pressure at a given temperature.

4. Why do we sprinkle common salt on roads in snowfall? [1]

Salt depresses the freezing point of water, so the ice melts at a lower temperature and roads are cleared.

5. What is reverse osmosis? Give one use. [2]

When a pressure greater than the osmotic pressure is applied on the solution side, pure solvent flows from solution to solvent through the semipermeable membrane. Used in desalination of sea water.

6. Why are aquatic species more comfortable in cold water? [1]

Solubility of O_2 in water is higher at lower temperature (K_H is smaller).

7. Give one example each of positive and negative deviation. [2]

Positive: ethanol + acetone (or ethanol + water). Negative: chloroform + acetone (or HNO_3 + water).

8. What is the value of i for $\text{Al}_2(\text{SO}_4)_3$ on complete dissociation? [1]



C. Short answer questions

1. Calculate the molarity of a solution containing 5 g of NaOH in 450 mL of solution.

Moles of NaOH = $5/40 = 0.125$ mol. Volume = 0.450 L. $M = 0.125/0.450 = \mathbf{0.278\ M}$.

2. Calculate the mole fraction of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) in a solution containing 20% of it by mass.

In 100 g solution: glycol = 20 g, water = 80 g. $n(\text{glycol}) = 20/62 = 0.3226$ mol;
 $n(\text{water}) = 80/18 = 4.444$ mol. $x(\text{glycol}) = 0.3226/(0.3226 + 4.444) = \mathbf{0.068}$; $x(\text{water}) = 0.932$.

3. 18 g of glucose is dissolved in 1 kg of water. At what temperature will the solution boil? ($K_b = 0.52\ \text{K kg mol}^{-1}$)

$m = (18/180)/1 = 0.1\ \text{mol kg}^{-1}$. $\Delta T_b = K_b m = 0.52 \times 0.1 = 0.052\ \text{K}$. Boiling point = $373.15 + 0.052 = \mathbf{373.202\ K}$.

4. 1.00 g of a non-electrolyte dissolved in 50 g of benzene lowered its freezing point by 0.40 K. Find the molar mass of the solute. (K_f of benzene = $5.12\ \text{K kg mol}^{-1}$)

$M_2 = (K_f \times w_2 \times 1000)/(\Delta T_f \times w_1) = (5.12 \times 1.00 \times 1000)/(0.40 \times 50) = \mathbf{256\ g\ mol}^{-1}$.

5. The partial pressure of N_2 over water is 0.987 bar at 293 K. K_H for N_2 is 76.48 kbar. Find the millimoles of N_2 dissolved in 1 litre of water.

$x(\text{N}_2) = p/K_H = 0.987/76480 = 1.29 \times 10^{-5}$. 1 L water = $1000/18 = 55.5$ mol. Since x is very small, $n(\text{N}_2) \approx x \times 55.5 = 7.16 \times 10^{-4}\ \text{mol} = \mathbf{0.716\ mmol}$.

6. A 5% solution of cane sugar ($M = 342$) is isotonic with a 0.877% solution of substance X. Find the molar mass of X.

Isotonic $\Rightarrow$ equal molar concentration: $(5/342) = (0.877/M)$. $M = 0.877 \times 342/5 = \mathbf{60\ g\ mol}^{-1}$ (X may be urea).

7. Calculate the freezing point depression of 0.1 m NaCl, assuming complete dissociation ($K_f = 1.86\ \text{K kg mol}^{-1}$).

$i = 2$. $\Delta T_f = i K_f m = 2 \times 1.86 \times 0.1 = \mathbf{0.372\ K}$. Freezing point = $-0.372\ ^\circ\text{C}$.

D. Long answer questions

1. (a) State Raoult's law for a solution of a non-volatile solute and show that relative lowering of vapour pressure is a colligative property. (b) The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile solute weighing 2.175 g is added to 39.08 g of benzene; the vapour pressure becomes 600 mm Hg. Find the molar mass of the solute.

(a) For a solution of non-volatile solute, vapour pressure comes only from the solvent: $p = p^\circ x_1$. Since $x_1 = 1 - x_2$, $p = p^\circ(1 - x_2)$, so $(p^\circ - p)/p^\circ = x_2 = n_2/(n_1 + n_2)$. The relative lowering depends only on the number of moles of solute particles, not on their nature - hence it is colligative.

(b) For a dilute solution, $(p^\circ - p)/p^\circ = (w_2 M_1)/(w_1 M_2)$. $(640 - 600)/640 = (2.175 \times 78)/(39.08 \times M_2)$. $M_2 = (2.175 \times 78 \times 640)/(39.08 \times 40) = \mathbf{69.5 \text{ g mol}^{-1}}$.

2. (a) What is osmotic pressure? Derive the relation used to find molar mass from it. (b) 200 cm³ of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure at 300 K is 2.57×10^{-3} bar. Calculate the molar mass. ($R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$)

(a) Osmotic pressure is the extra pressure that must be applied on the solution side to just stop the flow of solvent into it through a semipermeable membrane. $\pi = CRT = (n_2/V)RT = (w_2 RT)/(M_2 V)$, so $M_2 = w_2 RT/(\pi V)$.

(b) $M_2 = (1.26 \times 0.083 \times 300)/(2.57 \times 10^{-3} \times 0.200) = 31.37/(5.14 \times 10^{-4}) \approx \mathbf{6.1 \times 10^4 \text{ g mol}^{-1}}$ (61,039 g mol⁻¹).

3. 0.6 mL of acetic acid (density 1.06 g mL⁻¹) is dissolved in 1 litre of water. The depression in freezing point observed is 0.0205 °C. Calculate the van't Hoff factor and the degree of dissociation. ($K_f = 1.86 \text{ K kg mol}^{-1}$)

Mass of acid = $0.6 \times 1.06 = 0.636 \text{ g}$; moles = $0.636/60 = 0.0106 \text{ mol}$. Taking 1 L water $\approx 1 \text{ kg}$, $m = 0.0106 \text{ mol kg}^{-1}$.

Calculated $\Delta T_f = 1.86 \times 0.0106 = 0.0197 \text{ K}$.

$i = \text{observed/calculated} = 0.0205/0.0197 = \mathbf{1.04}$.

$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$ ($n = 2$): $\alpha = (i - 1)/(n - 1) = \mathbf{0.04 \text{ (about 4%)}}$.

$K_a = c\alpha^2/(1 - \alpha) = 0.0106 \times (0.0398)^2/0.96 \approx 1.75 \times 10^{-5}$.

4. Explain ideal and non-ideal solutions with vapour-pressure diagrams in words.**What are azeotropes?**

Ideal solution: obeys Raoult's law over the entire range; A-B attractions equal A-A and B-B attractions; $\Delta H_{\text{mix}} = 0$, $\Delta V_{\text{mix}} = 0$. The total vapour pressure graph is a straight line joining p_A° and p_B° . Example: benzene + toluene.

Positive deviation: A-B attractions are weaker, molecules escape easily, vapour pressure is higher than predicted, curve lies above the straight line, $\Delta H_{\text{mix}} > 0$, $\Delta V_{\text{mix}} > 0$. Example: ethanol + acetone.

Negative deviation: A-B attractions are stronger, vapour pressure is lower, curve lies below the line, $\Delta H_{\text{mix}} < 0$, $\Delta V_{\text{mix}} < 0$. Example: chloroform + acetone.

Azeotropes are binary mixtures that boil at constant temperature with the same composition in liquid and vapour, so they cannot be separated by fractional distillation. Minimum-boiling: ethanol 95.6% + water. Maximum-boiling: HNO_3 68% + water.

QB-2. Electrochemistry

Key points

- Galvanic cell converts chemical energy to electrical energy; anode (–) is where oxidation occurs, cathode (+) is where reduction occurs. In an electrolytic cell anode is +.
- $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ (both reduction potentials). Positive $E^\circ_{\text{cell}} \Rightarrow$ spontaneous reaction.
- Standard hydrogen electrode (SHE): $\text{Pt}, \text{H}_2(1 \text{ bar}) \mid \text{H}^+(1 \text{ M}); E^\circ = 0.00 \text{ V}$.
- Nernst equation (298 K): $E = E^\circ - (0.059/n) \log Q$. For $\text{M}^{n+} + n\text{e}^- \rightarrow \text{M}$, $E = E^\circ - (0.059/n) \log (1/[\text{M}^{n+}])$.
- $\Delta G^\circ = -nFE^\circ_{\text{cell}}$; $\Delta G^\circ = -2.303RT \log K$; $\log K = nE^\circ/0.059$ at 298 K. $F = 96500 \text{ C mol}^{-1}$.
- Conductance $G = 1/R$ (S). Conductivity $\kappa = G \times (l/A) = \text{cell constant}/R$. Molar conductivity $\Lambda_m = \kappa \times 1000/C$ ($\text{S cm}^2 \text{ mol}^{-1}$, κ in S cm^{-1} , C in mol L^{-1}).
- On dilution κ decreases (fewer ions per cm^3) but Λ_m increases. For strong electrolytes $\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$ (Debye-Hückel-Onsager).
- Kohlrausch's law: $\Lambda^\circ_m = \nu_+ \lambda^\circ_+ + \nu_- \lambda^\circ_-$. Used to find Λ°_m of weak electrolytes, $\alpha = \Lambda_m/\Lambda^\circ_m$, and $K_a = C\alpha^2/(1 - \alpha)$.
- Faraday's first law: $w = ZIt = (M/nF) \times I \times t$. Second law: $w_1/w_2 = E_1/E_2$ (equivalent masses) for the same charge.
- Electrolysis products: aqueous NaCl gives H_2 at cathode, Cl_2 at anode (overpotential of O_2), NaOH in solution. Dilute H_2SO_4 gives O_2 at anode; concentrated gives $\text{S}_2\text{O}_8^{2-}$.
- Batteries: dry cell (1.5 V), mercury cell (1.35 V, constant), lead storage (2 V per cell, rechargeable), nickel-cadmium; H_2 - O_2 fuel cell (Apollo space programme). Corrosion of iron is electrochemical: $\text{Fe} \rightarrow \text{Fe}^{2+}$ at anodic spot, $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ at cathodic spot; rust = $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$.

A. Multiple choice questions

- The unit of molar conductivity is (a) S cm^{-1} (b) $\text{S cm}^2 \text{ mol}^{-1}$ (c) S mol cm^{-2} (d) $\Omega \text{ cm}$ (b).
- E° values: $\text{Zn}^{2+}/\text{Zn} = -0.76 \text{ V}$, $\text{Cu}^{2+}/\text{Cu} = +0.34 \text{ V}$. E°_{cell} of Daniell cell is (a) 0.42 V (b) 1.10 V (c) –1.10 V (d) 0.34 V
(b) $0.34 - (-0.76) = 1.10 \text{ V}$.
- Charge on one mole of electrons is (a) 96500 C (b) $1.6 \times 10^{-19} \text{ C}$ (c) $6.022 \times 10^{23} \text{ C}$ (d) 9650 C

(a).

4. Which of the following is used in the Apollo space programme? (a) Dry cell (b) $\text{H}_2\text{-O}_2$ fuel cell (c) Lead storage cell (d) Mercury cell

(b).

5. On dilution, the conductivity of an electrolyte solution (a) increases (b) decreases (c) remains same (d) becomes zero

(b).

6. The electrolyte used in the lead storage battery is (a) dil. HCl (b) 38% H_2SO_4 (c) KOH (d) NH_4Cl paste

(b).

7. The number of Faradays needed to reduce 1 mol of MnO_4^- to Mn^{2+} is (a) 2 (b) 3 (c) 5 (d) 7

(c) Mn changes from +7 to +2.

8. For a spontaneous cell reaction (a) $\Delta G < 0$, $E > 0$ (b) $\Delta G > 0$, $E < 0$ (c) $\Delta G = 0$, $E = 0$ (d) $\Delta G > 0$, $E > 0$

(a).

9. Which metal is used for sacrificial protection of iron? (a) Cu (b) Zn (c) Ag (d) Sn

(b) Zn has lower reduction potential, so it corrodes first.

10. The potential of hydrogen electrode in a solution of pH = 10 is (a) 0.59 V (b) -0.59 V (c) 0 V (d) -0.059 V

(b) $E = -0.059 \text{ pH} = -0.59 \text{ V}$.

B. Very short answer questions

1. Define cell constant. [1]

Ratio of the distance between the electrodes to the area of cross-section (l/A); unit cm^{-1} .

2. State Kohlrausch's law. [1]

Limiting molar conductivity of an electrolyte is the sum of the limiting molar conductivities of its cation and anion, each multiplied by the number of ions.

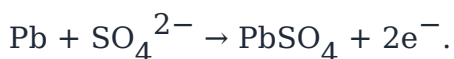
3. What is the function of the salt bridge? [2]

It completes the internal circuit and keeps both half-cells electrically neutral; it also minimises liquid-junction potential.

4. Why does a mercury cell give constant voltage? [1]

Its overall reaction $\text{Zn(Hg)} + \text{HgO} \rightarrow \text{ZnO} + \text{Hg}$ involves no ion in solution whose concentration changes.

5. Write the anode reaction in a lead storage battery during discharge. [1]



6. Why can't Λ_m° of CH_3COOH be found by extrapolation? [2]

For a weak electrolyte, Λ_m rises steeply at low concentration (α increases sharply), so the graph does not meet the axis as a straight line; Kohlrausch's law is used instead.

7. Give the relation between ΔG° and E° . [1]

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

8. Name the products of electrolysis of aqueous NaCl. [2]

H₂ at cathode, Cl₂ at anode, NaOH left in solution.

C. Short answer questions

1. Calculate ΔG° for the Daniell cell: $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$; $E^\circ_{\text{cell}} = 1.10 \text{ V}$.

$$n = 2. \Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.10 = -212300 \text{ J} = \mathbf{-212.3 \text{ kJ mol}^{-1}}.$$

2. The resistance of 0.001 M KCl in a cell is 1500 Ω . Its conductivity is $0.146 \times 10^{-3} \text{ S cm}^{-1}$. Find the cell constant.

$$\text{Cell constant } G^* = \kappa \times R = 0.146 \times 10^{-3} \times 1500 = \mathbf{0.219 \text{ cm}^{-1}}.$$

3. The conductivity of 0.20 M KCl is 0.0248 S cm^{-1} . Calculate its molar conductivity.

$$\Lambda_m = \kappa \times 1000/C = 0.0248 \times 1000/0.20 = \mathbf{124 \text{ S cm}^2 \text{ mol}^{-1}}.$$

4. Given Λ°_m of HCl = 425.9, CH₃COONa = 91.0 and NaCl = 126.4 $\text{S cm}^2 \text{ mol}^{-1}$. Find Λ°_m of CH₃COOH.

$$\Lambda^\circ(\text{CH}_3\text{COOH}) = \Lambda^\circ(\text{HCl}) + \Lambda^\circ(\text{CH}_3\text{COONa}) - \Lambda^\circ(\text{NaCl}) = 425.9 + 91.0 - 126.4 = \mathbf{390.5 \text{ S cm}^2 \text{ mol}^{-1}}.$$

5. A CuSO₄ solution is electrolysed for 10 minutes with a current of 1.5 A. What mass of copper is deposited? (Cu = 63.5)

$$Q = I \times t = 1.5 \times 600 = 900 \text{ C. } \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu: } 2 \times 96500 \text{ C deposit 63.5 g. Mass} = 900 \times 63.5/193000 = \mathbf{0.296 \text{ g}}.$$

6. Calculate the equilibrium constant of $\text{Cu} + 2\text{Ag}^+ \rightarrow \text{Cu}^{2+} + 2\text{Ag}$; $E^\circ_{\text{cell}} = 0.46 \text{ V}$.

$$\log K = nE^\circ/0.059 = 2 \times 0.46/0.059 = 15.59. K = 10^{15.59} = \mathbf{3.9 \times 10^{15}}.$$

D. Long answer questions

1. (a) Derive the Nernst equation for a metal electrode. (b) Calculate the emf of the cell $\text{Zn} | \text{Zn}^{2+} (0.001 \text{ M}) || \text{Ag}^+ (0.1 \text{ M}) | \text{Ag}$. $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$, $E^\circ(\text{Ag}^+/\text{Ag}) = 0.80 \text{ V}$.

(a) For $\text{M}^{n+}(\text{aq}) + n\text{e}^- \rightarrow \text{M}(\text{s})$, $\Delta G = \Delta G^\circ + RT \ln Q$ with $Q = 1/[\text{M}^{n+}]$. Putting $\Delta G = -nFE$ and $\Delta G^\circ = -nFE^\circ$: $-nFE = -nFE^\circ + RT \ln(1/[\text{M}^{n+}])$. Dividing by $-nF$: $E = E^\circ - (RT/nF) \ln(1/[\text{M}^{n+}])$. At 298 K, $2.303RT/F = 0.059 \text{ V}$, so $E = E^\circ - (0.059/n) \log(1/[\text{M}^{n+}])$.

(b) Cell reaction: $\text{Zn} + 2\text{Ag}^+ \rightarrow \text{Zn}^{2+} + 2\text{Ag}$; $n = 2$.

$$E^\circ_{\text{cell}} = 0.80 - (-0.76) = 1.56 \text{ V.}$$

$$E = E^\circ - (0.059/2) \log([\text{Zn}^{2+}]/[\text{Ag}^+]^2) = 1.56 - 0.0295 \log(0.001/0.01) = 1.56 - 0.0295 \times (-1) = \mathbf{1.5895 \text{ V} \approx 1.59 \text{ V}}.$$

2. The molar conductivity of 0.001028 M acetic acid is $48.15 \text{ S cm}^2 \text{ mol}^{-1}$. Using $\Lambda^\circ_{\text{m}} = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$, find its degree of dissociation and dissociation constant. Also explain variation of molar conductivity with concentration.

$$\alpha = \Lambda_{\text{m}}/\Lambda^\circ_{\text{m}} = 48.15/390.5 = \mathbf{0.1233}.$$

$$K_{\text{a}} = C\alpha^2/(1 - \alpha) = 0.001028 \times (0.1233)^2/(1 - 0.1233) = \mathbf{1.78 \times 10^{-5} \text{ mol L}^{-1}}.$$

Variation: Molar conductivity increases with dilution for all electrolytes. For a strong electrolyte (KCl) the increase is small and linear in $\sqrt{C}$, because interionic attractions decrease; extrapolating to $C = 0$ gives Λ°_{m} . For a weak electrolyte (CH_3COOH) the increase is very large at low concentration because the degree of dissociation increases sharply.

3. Describe the construction and working of the lead storage battery with reactions during discharging and charging.

Anode: lead grid; cathode: grid packed with PbO_2 ; electrolyte: 38% H_2SO_4 (density 1.30 g mL^{-1}).

Discharge: Anode: $\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2\text{e}^-$. Cathode: $\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$. Overall: $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$. Acid is consumed so density falls.

Charging: the reaction is reversed by passing current: $2\text{PbSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4$. Each cell gives about 2 V; six cells give 12 V for vehicles.

4. Explain the mechanism of rusting of iron and two methods of preventing it.

A water drop with dissolved O_2 and CO_2 acts as electrolyte. At the anodic spot: $2Fe \rightarrow 2Fe^{2+} + 4e^-$ ($E^\circ = -0.44$ V). At the cathodic spot: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ ($E^\circ = 1.23$ V). Overall: $2Fe + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O$, $E^\circ_{\text{cell}} = 1.67$ V. Fe^{2+} is further oxidised by air to Fe^{3+} forming rust $Fe_2O_3 \cdot xH_2O$.

Prevention: (i) barrier protection - paint, oil, grease or electroplating; (ii) sacrificial protection/galvanisation - coating with Zn or Mg, which are oxidised in preference to iron; (iii) using anti-rust solutions (bisphenol).

QB-3. Chemical Kinetics

Key points

- Average rate = $-\Delta[R]/\Delta t = +\Delta[P]/\Delta t$. For $aA + bB \rightarrow cC + dD$: rate = $-(1/a) d[A]/dt = (1/c) d[C]/dt$.
- Rate law: rate = $k[A]^x[B]^y$; order = $x + y$ (found experimentally, may be zero or fraction). Molecularity = number of species in an elementary step (always a whole number, 1, 2 or 3).
- Units of k : zero order $\text{mol L}^{-1} \text{s}^{-1}$; first order s^{-1} ; second order $\text{L mol}^{-1} \text{s}^{-1}$. General: $(\text{mol L}^{-1})^{1-n} \text{s}^{-1}$.
- Zero order: $[R] = [R]_0 - kt$; $t_{1/2} = [R]_0/2k$ (depends on initial concentration). Example: decomposition of NH_3 on hot Pt.
- First order: $k = (2.303/t) \log([R]_0/[R])$; $t_{1/2} = 0.693/k$ (independent of initial concentration). Examples: radioactive decay, decomposition of N_2O_5 .
- Pseudo first order: hydrolysis of ester in excess water, inversion of cane sugar.
- Arrhenius equation: $k = A e^{-E_a/RT}$; $\log(k_2/k_1) = (E_a/2.303R)[(T_2 - T_1)/(T_1 T_2)]$. Plot of $\ln k$ vs $1/T$ has slope $-E_a/R$.
- Rate roughly doubles for every 10 K rise. A catalyst lowers E_a by giving an alternative path; it does not change ΔG or equilibrium constant.
- Collision theory: rate = $P Z_{AB} e^{-E_a/RT}$; only collisions with enough energy and proper orientation are effective.

A. Multiple choice questions

1. Unit of rate constant of a first-order reaction is (a) $\text{mol L}^{-1} \text{s}^{-1}$ (b) s^{-1} (c) $\text{L mol}^{-1} \text{s}^{-1}$ (d) mol s^{-1}
(b).
2. Half-life of a zero-order reaction is (a) $0.693/k$ (b) $[R]_0/2k$ (c) $1/k[R]_0$ (d) independent of $[R]_0$
(b).
3. For rate = $k[A][B]^2$, if both concentrations are doubled, rate becomes (a) 2 times (b) 4 times (c) 6 times (d) 8 times
(d) $2 \times 2^2 = 8$.
4. Inversion of cane sugar is a reaction of (a) zero order (b) second order (c) pseudo first order (d) third order
(c).
5. Slope of the plot of $\log k$ vs $1/T$ is (a) $-E_a/R$ (b) $-E_a/2.303R$ (c) E_a/R (d) $2.303R/E_a$
(b).

- 6. A catalyst increases rate by (a) increasing E_a (b) decreasing E_a (c) increasing ΔH (d) shifting equilibrium**
(b).
- 7. After three half-lives, the fraction of a first-order reactant left is (a) $1/3$ (b) $1/6$ (c) $1/8$ (d) $1/9$**
(c) $(1/2)^3$.
- 8. Molecularity of a reaction can be (a) zero (b) 1.5 (c) 2 (d) negative**
(c).
- 9. The order of the reaction $H_2 + Cl_2 \rightarrow 2HCl$ (in sunlight) is (a) 0 (b) 1 (c) 2 (d) 3**
(a) Photochemical, zero order.
- 10. In Arrhenius equation, A is called (a) activation energy (b) frequency (pre-exponential) factor (c) rate constant (d) collision number**
(b).

B. Very short answer questions

1. Define order of a reaction. [1]

Sum of the powers of the concentration terms in the experimentally determined rate law.

2. Define half-life. [1]

Time in which the concentration of a reactant falls to half its initial value.

3. What is activation energy? [1]

The minimum extra energy that reactant molecules must absorb to form the activated complex (energy of activated complex – energy of reactants).

4. Why is molecularity not applicable to complex reactions? [2]

A complex reaction occurs in several steps; molecularity is defined only for each elementary step. The overall rate is governed by the slowest (rate-determining) step.

5. Write the unit of k for a second-order gaseous reaction in terms of atm. [1]

$\text{atm}^{-1} \text{s}^{-1}$.

6. Give one example of a zero-order reaction. [1]

$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$ on hot platinum surface at high pressure.

7. What is a pseudo first-order reaction? [2]

A reaction that is actually of higher order but behaves as first order because one reactant is in large excess, e.g., $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$ (H^+), rate = k' [ester].

C. Short answer questions

1. A first-order reaction has $t_{1/2} = 30$ min. Calculate k and the time for 90% completion.

$k = 0.693/30 = 0.0231 \text{ min}^{-1}$. For 90% completion $[\text{R}]_0/[\text{R}] = 100/10 = 10$. $t = (2.303/0.0231) \log 10 = 99.7 \text{ min} \approx 100 \text{ min}$.

2. Show that for a first-order reaction the time for 99.9% completion is about 10 half-lives.

$$t_{99.9\%} = (2.303/k) \log(100/0.1) = (2.303/k) \times 3 = 6.909/k. \quad t_{1/2} = 0.693/k. \quad \text{Ratio} = 6.909/0.693 = \mathbf{9.97 \approx 10}.$$

3. For a first-order reaction, concentration falls from 0.8 M to 0.2 M in 40 min. Find $t_{1/2}$ and k .

$$0.8 \rightarrow 0.4 \rightarrow 0.2 \text{ is two half-lives, so } 2t_{1/2} = 40 \text{ min; } t_{1/2} = \mathbf{20 \text{ min}}. \quad k = 0.693/20 = \mathbf{0.0347 \text{ min}^{-1}}.$$

4. For the reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, the rate of formation of NO_2 is $2.8 \times 10^{-3} \text{ M s}^{-1}$. Find the rate of disappearance of N_2O_5 and rate of formation of O_2 .

$$\begin{aligned} \text{Rate} &= -(1/2) d[\text{N}_2\text{O}_5]/dt = (1/4) d[\text{NO}_2]/dt = d[\text{O}_2]/dt. \\ -d[\text{N}_2\text{O}_5]/dt &= (2/4) \times 2.8 \times 10^{-3} = \mathbf{1.4 \times 10^{-3} \text{ M s}^{-1}}; \quad d[\text{O}_2]/dt = 2.8 \times 10^{-3}/4 = \mathbf{7.0 \times 10^{-4} \text{ M s}^{-1}}. \end{aligned}$$

5. Rate of a reaction doubles when temperature rises from 298 K to 308 K. Calculate E_a .

$$\log 2 = (E_a/2.303 \times 8.314) \times (10/(298 \times 308)). \quad E_a = 0.3010 \times 2.303 \times 8.314 \times 298 \times 308/10 = 52903 \text{ J mol}^{-1} = \mathbf{52.9 \text{ kJ mol}^{-1}}.$$

D. Long answer questions

1. Derive the integrated rate equation for a first-order reaction and show that its half-life is independent of initial concentration.

For $\text{R} \rightarrow \text{P}$, rate $= -d[\text{R}]/dt = k[\text{R}]$. Separating: $d[\text{R}]/[\text{R}] = -k dt$. Integrating: $\ln[\text{R}] = -kt + I$. At $t = 0$, $[\text{R}] = [\text{R}]_0$, so $I = \ln[\text{R}]_0$. Hence $\ln([\text{R}]_0/[\text{R}]) = kt$, or $k = (2.303/t) \log([\text{R}]_0/[\text{R}])$.

At $t = t_{1/2}$, $[\text{R}] = [\text{R}]_0/2$: $k = (2.303/t_{1/2}) \log 2 \Rightarrow t_{1/2} = 0.693/k$. Since $[\text{R}]_0$ does not appear, half-life is independent of initial concentration.

Graph: $\ln[\text{R}]$ vs t is a straight line with slope $-k$; $\log([\text{R}]_0/[\text{R}])$ vs t is a straight line through the origin with slope $k/2.303$.

2. The rate constants of a reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} . Calculate E_a and A .

$$\log(k_2/k_1) = (E_a/2.303R)[(T_2 - T_1)/(T_1 T_2)].$$

$$\log(0.07/0.02) = \log 3.5 = 0.5441 = (E_a/19.147) \times (200/350000).$$

$$E_a = 0.5441 \times 19.147 \times 1750 = \mathbf{18230 \text{ J mol}^{-1} \approx 18.2 \text{ kJ mol}^{-1}}.$$

$$A = k/e^{-E_a/RT}: \text{ at 500 K, } E_a/RT = 18230/(8.314 \times 500) = 4.385; e^{-4.385} = 0.01246. A = 0.02/0.01246 = \mathbf{1.61 \text{ s}^{-1}}.$$

3. Distinguish between order and molecularity. Derive the integrated rate law for a zero-order reaction.

Order	Molecularity
Sum of powers in the experimental rate law	Number of species colliding in an elementary step
Can be 0, fraction or whole number	Always a whole number (1, 2, 3)
Defined for overall reaction	Defined for elementary steps only
Found by experiment	Theoretical concept

Zero order: $-d[R]/dt = k[R]^0 = k$. $d[R] = -k dt$. Integrating: $[R] = -kt + I$; at $t = 0$, $I = [R]_0$. So $[R] = [R]_0 - kt$, $k = ([R]_0 - [R])/t$. Half-life: $t_{1/2} = [R]_0/2k$. Graph of $[R]$ vs t is a straight line of slope $-k$.

4. Explain the effect of temperature on rate using the Arrhenius equation and energy distribution curve.

$k = A e^{-E_a/RT}$. The factor $e^{-E_a/RT}$ is the fraction of molecules having energy $\geq E_a$.

According to the Maxwell-Boltzmann distribution, when temperature increases by 10 K the curve flattens and shifts to higher energy; the area beyond E_a (molecules able to react) roughly doubles. Therefore the rate approximately doubles for every 10 K rise.

Taking logs: $\ln k = \ln A - E_a/RT$, so a plot of $\ln k$ vs $1/T$ is a straight line with slope $-E_a/R$ and intercept $\ln A$, from which E_a is calculated.

QB-4. d- and f-Block Elements

Key points

- Transition elements: partly filled d orbitals in the atom or in a common ion. General configuration $(n-1)d^{1-10} ns^{1-2}$. Exceptions: Cr $3d^5 4s^1$, Cu $3d^{10} 4s^1$ (half-filled/filled stability).
- Zn, Cd, Hg (d^{10}) are not regarded as transition elements; they are soft, low-melting and form colourless compounds.
- Characteristic properties: variable oxidation states, coloured ions (d-d transition), paramagnetism, catalytic activity, complex formation, interstitial compounds, alloy formation, high melting points (except Zn, Cd, Hg).
- Magnetic moment (spin only): $\mu = \sqrt{n(n+2)}$ BM, n = number of unpaired electrons. $n = 1 \rightarrow 1.73$, $2 \rightarrow 2.83$, $3 \rightarrow 3.87$, $4 \rightarrow 4.90$, $5 \rightarrow 5.92$ BM.
- Mn shows the maximum number of oxidation states (+2 to +7) in the 3d series. Highest oxidation states are seen in oxides and fluorides (Mn_2O_7 , CrO_3).
- $E^\circ(M^{2+}/M)$ of Cu is positive (+0.34 V), so Cu does not liberate H_2 from acids. Mn^{2+} (d^5) and Zn^{2+} (d^{10}) are especially stable.
- $K_2Cr_2O_7$ from chromite ore $FeCr_2O_4$: fusion with Na_2CO_3 in air $\rightarrow Na_2CrO_4 \rightarrow$ acidify $\rightarrow Na_2Cr_2O_7 \rightarrow + KCl \rightarrow K_2Cr_2O_7$. Chromate (yellow) $\rightleftharpoons$ dichromate (orange) depending on pH.
- $KMnO_4$ from pyrolusite MnO_2 : fusion with $KOH + O_2 \rightarrow K_2MnO_4$ (green) $\rightarrow$ oxidation (electrolytic or Cl_2/O_3) $\rightarrow KMnO_4$ (purple).
- Lanthanoid contraction: steady decrease in size from La to Lu due to poor shielding by 4f electrons. Consequences: Zr/Hf have almost equal radii; basicity of $Ln(OH)_3$ decreases from $La(OH)_3$ to $Lu(OH)_3$; difficulty in separating lanthanoids.
- Lanthanoids mainly show +3; Ce^{4+} is a good oxidant, Eu^{2+} and Yb^{2+} are reductants. Actinoids show a wider range of oxidation states (+3 to +7), are radioactive, and show greater (actinoid) contraction.
- Misch metal = 95% lanthanoid + 5% Fe + traces of S, C, Ca, Al; used in lighter flints and Mg-based alloys for bullets.

A. Multiple choice questions

1. Which ion is colourless? (a) Ti^{3+} (b) Cu^{2+} (c) Sc^{3+} (d) Fe^{3+}

(c) Sc^{3+} is $3d^0$.

2. The spin-only magnetic moment of Fe^{2+} ($Z = 26$) is (a) 2.83 BM (b) 4.90 BM (c) 5.92 BM (d) 3.87 BM

(b) $3d^6$, 4 unpaired: $\sqrt{24} = 4.90$.

3. The element showing the highest number of oxidation states in the 3d series is (a) Fe (b) Cr (c) Mn (d) V

(c).

4. In acidic medium, the equivalent weight of KMnO_4 ($M = 158$) is (a) 158 (b) 52.7 (c) 31.6 (d) 79

(c) 158/5.

5. Lanthanoid contraction is due to (a) poor shielding by 4f electrons (b) good shielding by 4f electrons (c) increase in nuclear size (d) radioactivity

(a).

6. Which pair has almost identical atomic radii? (a) Ti, Zr (b) Zr, Hf (c) Cu, Ag (d) Fe, Ru
(b).

7. Colour change in $\text{K}_2\text{Cr}_2\text{O}_7$ when alkali is added is (a) orange to yellow (b) yellow to orange (c) green to orange (d) purple to green

(a) $\text{Cr}_2\text{O}_7^{2-} + 2\text{OH}^- \rightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$.

8. The common oxidation state of lanthanoids is (a) +2 (b) +3 (c) +4 (d) +6

(b).

9. Which element is not a transition element by definition? (a) Cu (b) Zn (c) Fe (d) Ni

(b).

10. Interstitial compounds are formed when small atoms like ___ are trapped in metal lattices. (a) Na (b) H, C, N (c) Cl (d) Ar

(b).

B. Very short answer questions

1. Write the electronic configuration of Cr ($Z = 24$). [1]

$[\text{Ar}] 3d^5 4s^1$.

2. Why is Cu^+ unstable in aqueous solution? [2]

Cu^{2+} has a much higher (more negative) hydration enthalpy that more than compensates for the second ionisation enthalpy, so $2\text{Cu}^+ \rightarrow \text{Cu}^{2+} + \text{Cu}$ (disproportionation).

3. What is misch metal? [1]

An alloy of about 95% lanthanoid metals, 5% iron and traces of S, C, Ca and Al; used in lighter flints.

4. Why do transition metals act as good catalysts? [2]

They show variable oxidation states and can form unstable intermediate compounds; they also provide a large surface for adsorption. Examples: V_2O_5 in contact process, Fe in Haber process, Ni in hydrogenation.

5. Why is Mn^{2+} more stable than Fe^{2+} towards oxidation? [2]

Mn^{2+} is $3d^5$ (half-filled, extra stable); Fe^{2+} ($3d^6$) becomes Fe^{3+} ($3d^5$) on losing one electron, so it is easily oxidised.

6. Name the ores of chromium and manganese. [1]

Chromite FeCr_2O_4 ; pyrolusite MnO_2 .

7. Why do actinoids show more oxidation states than lanthanoids? [2]

The 5f, 6d and 7s orbitals are of comparable energy, so electrons from all three can take part in bonding.

C. Short answer questions

1. Calculate the spin-only magnetic moment of Mn^{2+} ($Z = 25$) and Cu^{2+} ($Z = 29$).

Mn^{2+} : $3d^5$, $n = 5$; $\mu = \sqrt{5 \times 7} = \sqrt{35} = \mathbf{5.92 \text{ BM}}$.

Cu^{2+} : $3d^9$, $n = 1$; $\mu = \sqrt{1 \times 3} = \mathbf{1.73 \text{ BM}}$.

2. Write the ionic equations for the reaction of acidified $\text{K}_2\text{Cr}_2\text{O}_7$ with (i) iodide (ii) Fe^{2+} (iii) H_2S .

Half reaction: $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$.

(i) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{I}^- \rightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$

(ii) $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$

(iii) $\text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ + 3\text{H}_2\text{S} \rightarrow 2\text{Cr}^{3+} + 3\text{S} + 7\text{H}_2\text{O}$

3. Write the reactions of acidified KMnO_4 with (i) Fe^{2+} (ii) oxalate (iii) SO_2 .

Half reaction: $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$.

(i) $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$

(ii) $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$

(iii) $2\text{MnO}_4^- + 5\text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Mn}^{2+} + 5\text{SO}_4^{2-} + 4\text{H}^+$

4. What is lanthanoid contraction? Write any three consequences.

The gradual decrease in atomic and ionic (M^{3+}) radii from La to Lu is called lanthanoid contraction. It occurs because the added 4f electrons shield each other poorly from the increasing nuclear charge.

Consequences: (1) The second (4d) and third (5d) transition series have nearly equal radii, e.g. Zr 160 pm and Hf 159 pm, so they occur together and are hard to separate. (2) Basic strength of hydroxides decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$. (3) Lanthanoids have very similar properties, so their separation is difficult (ion-exchange is used).

5. Explain why transition metals form interstitial compounds and state their properties.

Small atoms like H, C, N, B fit into the voids (interstices) of the metal crystal lattice, e.g. TiC , Mn_4N , Fe_3H , $\text{TiH}_{1.7}$. These are non-stoichiometric. Properties: very hard, high melting points (higher than the pure metal), retain metallic conductivity, chemically inert.

D. Long answer questions

1. Describe the preparation of potassium dichromate from chromite ore. Explain the effect of pH on dichromate ion and write its structure.

Step 1 (fusion): $4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$.

Step 2 (acidification): $2\text{Na}_2\text{CrO}_4 + 2\text{H}^+ \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Na}^+ + \text{H}_2\text{O}$.

Step 3 (conversion): $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$. $\text{K}_2\text{Cr}_2\text{O}_7$ is less soluble and crystallises out as orange crystals.

Effect of pH: 2CrO_4^{2-} (yellow) + $2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}$ (orange) + H_2O . In acid the equilibrium shifts right; in alkali, left.

Structure: chromate is tetrahedral; dichromate consists of two tetrahedra sharing one corner oxygen, Cr-O-Cr angle 126° .

2. Compare lanthanoids and actinoids under: configuration, oxidation states, radioactivity, complex formation, and contraction.

Property	Lanthanoids	Actinoids
Configuration	$[\text{Xe}] 4f^{1-14} 5d^{0-1} 6s^2$	$[\text{Rn}] 5f^{1-14} 6d^{0-1} 7s^2$
Oxidation states	Mainly +3 (some +2, +4)	+3 to +7 (U +6, Np/Pu +7)
Radioactivity	Non-radioactive except Pm	All radioactive
Complex formation	Less tendency	Greater tendency
Contraction	Lanthanoid contraction (smaller)	Actinoid contraction (greater, poorer 5f shielding)
Oxocations	Not formed	Formed, e.g. UO_2^{2+} , PuO_2^{2+}

3. Explain with reasons: (a) transition metals form coloured ions (b) they are paramagnetic (c) they have high enthalpy of atomisation (d) they form alloys.

(a) In the presence of ligands the d orbitals split into groups of different energy. An unpaired d electron absorbs a particular wavelength of visible light and jumps to a higher d level (d-d transition); the complementary colour is seen. Example:

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is violet.

(b) Unpaired electrons have spin and orbital magnetic moments, so the ion is attracted by a magnetic field. $\mu = \sqrt{n(n+2)} \text{ BM}$.

(c) Large number of unpaired d electrons take part in strong metallic bonding, so enthalpy of atomisation is high (maximum near the middle of the series).

(d) Atoms of different transition metals have similar radii (within 15%), so they easily replace each other in the crystal lattice - e.g. brass (Cu-Zn), bronze (Cu-Sn), stainless steel (Fe-Cr-Ni).

QB-5. Coordination Compounds

Key points

- Werner's theory: metal shows primary valency (oxidation state, ionisable, satisfied by anions) and secondary valency (coordination number, non-ionisable, directional – gives geometry).
- Ligands: unidentate (Cl^- , NH_3 , H_2O , CN^-), bidentate (en, $\text{C}_2\text{O}_4^{2-}$), hexadentate (EDTA^{4-}), ambidentate ($\text{NO}_2^-/\text{ONO}^-$, $\text{SCN}^-/\text{NCS}^-$). A chelate ring makes the complex extra stable (chelate effect).
- IUPAC order: cation first then anion; inside the sphere, ligands in alphabetical order, then metal with oxidation state in Roman numerals; anionic complex ends in "-ate" (ferrate, cuprate, argentate, aurate, plumbate, stannate).
- Isomerism: structural (ionisation, linkage, coordination, hydrate/solvate) and stereo (geometrical cis-trans and fac-mer; optical). Tetrahedral complexes do not show geometrical isomerism; square planar $[\text{MA}_2\text{B}_2]$ and octahedral $[\text{MA}_4\text{B}_2]$, $[\text{MA}_3\text{B}_3]$ do.
- VBT: CN 4 $\rightarrow \text{sp}^3$ (tetrahedral) or dsp^2 (square planar); CN 6 $\rightarrow \text{d}^2\text{sp}^3$ (inner orbital, low spin) or sp^3d^2 (outer orbital, high spin).
- CFT: in an octahedral field d orbitals split into t_{2g} (lower, $-0.4\Delta_o$) and e_g (higher, $+0.6\Delta_o$). Tetrahedral splitting $\Delta_t = (4/9)\Delta_o$, so tetrahedral complexes are always high spin.
- Spectrochemical series (increasing field strength): $\text{I}^- < \text{Br}^- < \text{SCN}^- < \text{Cl}^- < \text{S}^{2-} < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{edta}^{4-} < \text{NH}_3 < \text{en} < \text{CN}^- < \text{CO}$.
- If $\Delta_o > P$ (pairing energy) $\rightarrow$ low spin (strong field); if $\Delta_o < P \rightarrow$ high spin (weak field).
- Metal carbonyls: synergic bonding – σ donation from CO to metal plus π back-donation from filled metal d orbitals to empty π^* of CO. Ni(CO)_4 tetrahedral, Fe(CO)_5 trigonal bipyramidal, Cr(CO)_6 octahedral.
- Uses: EDTA titration for hardness (Ca^{2+} , Mg^{2+}); cis-platin in cancer therapy; Wilkinson's catalyst $[\text{RhCl(PPh}_3)_3]$ for hydrogenation; chlorophyll (Mg), haemoglobin (Fe), vitamin B_{12} (Co); extraction of Ag and Au as $[\text{Ag(CN)}_2]^-$, $[\text{Au(CN)}_2]^-$.

A. Multiple choice questions

1. The coordination number of Co in $[\text{Co(en)}_3]^{3+}$ is (a) 3 (b) 4 (c) 6 (d) 2

(c) en is bidentate: $3 \times 2 = 6$.

2. The oxidation state of Fe in $\text{K}_4[\text{Fe(CN)}_6]$ is (a) +2 (b) +3 (c) +4 (d) 0

(a) $4 + x - 6 = 0 \Rightarrow x = +2$.

3. Which is an ambidentate ligand? (a) NH_3 (b) en (c) NO_2^- (d) H_2O

(c).

4. $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ are (a) linkage (b) ionisation (c) coordination (d) optical isomers

(b).

5. Hybridisation of Ni in $[\text{Ni}(\text{CN})_4]^{2-}$ is (a) sp^3 (b) dsp^2 (c) sp^3d^2 (d) d^2sp^3

(b) CN^- is strong field; square planar, diamagnetic.

6. The strongest field ligand among the following is (a) F^- (b) H_2O (c) NH_3 (d) CO

(d).

7. Number of ions produced by $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ in water is (a) 2 (b) 3 (c) 4 (d) 6

(c) $[\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$.

8. Cis-platin is (a) $\text{cis-}[\text{PtCl}_2(\text{NH}_3)_2]$ (b) $\text{trans-}[\text{PtCl}_2(\text{NH}_3)_2]$ (c) $[\text{PtCl}_4]^{2-}$ (d) $[\text{Pt}(\text{NH}_3)_4]^{2+}$

(a) Used as an anticancer drug.

9. In an octahedral field, the e_g set consists of (a) d_{xy}, d_{yz} (b) $d_{x^2-y^2}, d_{z^2}$ (c) d_{xz}, d_{yz} (d) $d_{xy}, d_{x^2-y^2}$

(b) They point directly at the ligands.

10. Denticity of EDTA is (a) 2 (b) 4 (c) 5 (d) 6

(d).

B. Very short answer questions

1. Write the IUPAC name of $\text{K}_3[\text{Fe}(\text{CN})_6]$. [1]

Potassium hexacyanidoferrate(III).

2. Write the IUPAC name of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. [1]

Pentaamminechloridocobalt(III) chloride.

3. Write the formula of tetraamminediaquacobalt(III) chloride. [1]

$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Cl}_3$.

4. What is a chelate? [1]

A complex in which a polydentate ligand binds the metal through two or more donor atoms forming a ring, e.g. $[\text{Co}(\text{en})_3]^{3+}$.

5. Why is $[\text{NiCl}_4]^{2-}$ paramagnetic but $[\text{Ni}(\text{CN})_4]^{2-}$ diamagnetic? [2]

Ni^{2+} is 3d^8 . Cl^- is a weak ligand, no pairing, sp^3 , two unpaired electrons. CN^- is strong, forces pairing, dsp^2 , no unpaired electron.

6. What is the spectrochemical series? [1]

The arrangement of ligands in increasing order of their crystal-field splitting power.

7. Name a coordination compound used in the treatment of lead poisoning. [1]

Ca-EDTA (calcium disodium edetate).

8. Write the IUPAC name of $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$. [1]

Diamminechloridonitrito-N-platinum(II).

C. Short answer questions

1. Write the IUPAC names: (i) $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$ (ii) $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ (iii) $\text{Na}_2[\text{Ni}(\text{CN})_4]$ (iv) $[\text{Ni}(\text{CO})_4]$ (v) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$

- (i) Diamminesilver(I) dicyanidoargentate(I)
 (ii) Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
 (iii) Sodium tetracyanonickelate(II)
 (iv) Tetracarbonylnickel(0)
 (v) Hexaaquachromium(III) chloride

2. Draw/describe the isomers of $[\text{CoCl}_2(\text{en})_2]^+$. How many stereoisomers are there?

Geometrical: **cis** (two Cl on adjacent positions) and **trans** (two Cl opposite). The trans form has a plane of symmetry and is optically inactive. The cis form has no plane of symmetry and exists as two non-superimposable mirror images (d and l). Total stereoisomers = **3** (trans + d-cis + l-cis).

3. Using VBT explain the geometry and magnetic behaviour of $[\text{Co}(\text{NH}_3)_6]^{3+}$.

Co ($Z = 27$): $3d^7 4s^2$; Co^{3+} : $3d^6$. NH_3 (strong field here) pairs the six electrons into three 3d orbitals, leaving two 3d orbitals empty. Two 3d + one 4s + three 4p $\rightarrow d^2 sp^3$ hybridisation; six NH_3 donate lone pairs. Geometry: octahedral; inner-orbital, low-spin complex; no unpaired electron $\Rightarrow$ **diamagnetic**.

4. Explain $[\text{CoF}_6]^{3-}$ by VBT and compare it with $[\text{Co}(\text{NH}_3)_6]^{3+}$.

Co^{3+} $3d^6$. F^- is a weak ligand; no pairing occurs, four 3d electrons remain unpaired. Hybridisation uses 4s, 4p and 4d: **$sp^3 d^2$** , outer-orbital, high-spin, octahedral, **paramagnetic** with 4 unpaired electrons ($\mu = 4.90 \text{ BM}$). $[\text{Co}(\text{NH}_3)_6]^{3+}$ is inner-orbital ($d^2 sp^3$) and diamagnetic.

5. Explain the bonding in metal carbonyls.

The M-C bond has both σ and π character. (1) CO donates its lone pair on carbon into a vacant metal orbital (σ bond). (2) The metal donates electrons from a filled d orbital into the vacant antibonding π^* orbital of CO (π back-bonding). This mutual (synergic) bonding strengthens the M-C bond and slightly weakens the $\text{C}\equiv\text{O}$ bond.

6. Write the limitations of VBT.

(1) It does not explain the colour of complexes. (2) It gives no quantitative interpretation of magnetic data. (3) It cannot predict whether a 4-coordinate complex is tetrahedral or square planar. (4) It does not distinguish between weak and strong ligands. (5) It does not explain the thermodynamic or kinetic stability of complexes.

D. Long answer questions

1. Explain crystal field splitting in an octahedral complex. How does it explain (a) high spin and low spin complexes (b) colour of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$?

In a free ion, the five d orbitals have the same energy. When six ligands (treated as point negative charges) approach along the x, y, z axes, the $d_{x^2-y^2}$ and d_{z^2} orbitals, which point at the ligands, are repelled more and rise in energy (e_g set, $+0.6\Delta_o$). The d_{xy} , d_{yz} , d_{xz} orbitals, lying between the axes, are lowered (t_{2g} set, $-0.4\Delta_o$). The energy gap is Δ_o .

(a) For d^4 to d^7 , the fourth electron can either pair in t_{2g} (costs pairing energy P) or go to e_g (costs Δ_o). With weak-field ligands $\Delta_o < P$, so it enters e_g : **high spin** ($t_{2g}^3 e_g^1$). With strong-field ligands $\Delta_o > P$, so it pairs: **low spin** ($t_{2g}^4 e_g^0$).

(b) Ti^{3+} is $3d^1$ (t_{2g}^1). It absorbs green-yellow light (about 498 nm) to promote the electron to e_g . The complementary colour, violet, is seen. If ligands are absent, no splitting occurs and the substance is colourless (anhydrous CuSO_4 is white, hydrated is blue).

2. Discuss the types of structural isomerism in coordination compounds with one example each.

(i) Ionisation isomerism: exchange of an ion between inside and outside the coordination sphere, giving different ions in solution: $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ (gives Br^- , yellow ppt with AgNO_3) and $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ (gives SO_4^{2-} , white ppt with BaCl_2).

(ii) Linkage isomerism: ambidentate ligand binds through different atoms: $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ (yellow, N-bonded) and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ (red, O-bonded).

(iii) Coordination isomerism: interchange of ligands between cationic and anionic complexes: $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$.

(iv) Solvate (hydrate) isomerism: water inside or outside the sphere: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet), $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (blue-green), $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (dark green).

3. State the postulates of Werner's theory. Explain the structures of $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$ and $\text{CoCl}_3 \cdot 4\text{NH}_3$ on its basis.

Postulates: (1) Metals show two types of valency – primary (ionisable, equals oxidation state) and secondary (non-ionisable, equals coordination number). (2) Primary valencies are satisfied by negative ions; secondary by neutral molecules or negative ions. (3) Secondary valencies are directed in space and decide the geometry.

Compound	Formula	Moles AgCl with AgNO_3	Ions
$\text{CoCl}_3 \cdot 6\text{NH}_3$ (yellow)	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	3	4
$\text{CoCl}_3 \cdot 5\text{NH}_3$ (purple)	$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	2	3
$\text{CoCl}_3 \cdot 4\text{NH}_3$ (green/violet)	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	1	2

In each, the coordination number of Co is 6 (octahedral) and the oxidation state is +3. The two forms of $\text{CoCl}_3 \cdot 4\text{NH}_3$ (green trans and violet cis) are geometrical isomers.

NAMING CHECKLIST

(1) Ligand names: Cl^- chlorido, CN^- cyanido, OH^- hydroxido, NO_2^- nitrito-N, ONO^- nitrito-O, H_2O aqua, NH_3 ammine, CO carbonyl, en ethane-1,2-diamine. (2) Use di, tri, tetra for simple ligands; bis, tris, tetrakis for ligands whose names already contain a number. (3) Alphabetical order ignores prefixes. (4) Anionic complexes: iron → ferrate, copper → cuprate, silver → argentate, gold → aurate, lead → plumbate, tin → stannate.

QB-6. Haloalkanes and Haloarenes

Key points

- Classification: 1°, 2°, 3° alkyl halides; allylic (X on carbon next to C=C), benzylic (X on carbon next to benzene ring), vinylic (X on C=C carbon), aryl (X on ring carbon).
- C-X bond is polar ($C^{\delta+}-X^{\delta-}$). Bond strength: $C-F > C-Cl > C-Br > C-I$; reactivity: $R-I > R-Br > R-Cl > R-F$.
- Preparation: from alcohols ($HX/ZnCl_2$, PCl_5 , PCl_3 , $SOCl_2$ - best, as by-products SO_2 and HCl are gases); from alkenes (HX , Markovnikov; HBr + peroxide, anti-Markovnikov); Finkelstein ($R-Cl + NaI/acetone \rightarrow R-I$); Swarts ($R-Br + AgF \rightarrow R-F$); Sandmeyer for haloarenes.
- Boiling point increases with molar mass ($RI > RBr > RCl > RF$) and decreases with branching. Para-dichlorobenzene has a higher melting point than ortho and meta (symmetry, better packing).
- S_N2 : one step, rate = $k[RX][Nu^-]$, backside attack, **inversion** of configuration (Walden inversion); reactivity $CH_3X > 1^\circ > 2^\circ > 3^\circ$ (steric hindrance).
- S_N1 : two steps via carbocation, rate = $k[RX]$, **racemisation**; reactivity $3^\circ > 2^\circ > 1^\circ > CH_3X$ (carbocation stability); favoured by polar protic solvents. Allylic and benzylic halides react fast by S_N1 (resonance-stabilised cation).
- Elimination (dehydrohalogenation) with alcoholic KOH follows **Saytzeff rule**: the more substituted alkene is the major product. Aqueous KOH gives alcohol (substitution).
- KCN gives alkyl cyanide (C attacks); $AgCN$ gives isocyanide (N attacks). KNO_2 gives alkyl nitrite; $AgNO_2$ gives nitroalkane.
- Haloarenes are much less reactive to nucleophilic substitution: resonance gives partial double-bond character to C-X, sp^2 carbon, phenyl cation unstable, repulsion of the electron-rich ring. $-NO_2$ groups at ortho/para positions increase reactivity.
- Halogen in haloarenes is deactivating but **ortho/para directing** ($-I$ effect deactivates, $+R$ effect directs).
- Named reactions: Wurtz ($2RX + 2Na \rightarrow R-R$), Wurtz-Fittig ($ArX + RX + 2Na \rightarrow Ar-R$), Fittig ($2ArX + 2Na \rightarrow Ar-Ar$), Grignard reagent ($RX + Mg$ in dry ether $\rightarrow RMgX$).
- Polyhalogen compounds: $CHCl_3$ (stored in dark coloured bottles filled to the brim because it forms poisonous phosgene $COCl_2$ in air and light), CHI_3 (antiseptic), CCl_4 , freons (deplete ozone), DDT (non-biodegradable, accumulates in food chains).

A. Multiple choice questions

1. Which is most reactive towards S_N2 ? (a) CH_3Cl (b) $(CH_3)_2CHCl$ (c) $(CH_3)_3CCl$ (d) C_2H_5Cl

(a) Least steric hindrance.

2. Which is most reactive towards S_N1 ? (a) CH_3Br (b) C_2H_5Br (c) $(CH_3)_3CBr$ (d) $(CH_3)_2CHBr$

(c) Tertiary carbocation is most stable.

3. $R-Br + AgF \rightarrow R-F + AgBr$ is called (a) Finkelstein (b) Swarts (c) Sandmeyer (d) Wurtz
(b).

4. Chlorobenzene on reaction with $Cl_2/FeCl_3$ mainly gives (a) m-dichlorobenzene (b) o- and p-dichlorobenzene (c) benzene (d) hexachlorobenzene
(b).

5. Alkyl halide + alcoholic KOH gives (a) alcohol (b) alkene (c) ether (d) alkane
(b).

6. Alkyl halide + $AgCN$ gives mainly (a) nitrile (b) isocyanide (c) amine (d) amide
(b) $AgCN$ is covalent; N donates its lone pair.

7. The compound used as an anaesthetic in the past and now known to damage the liver is (a) $CHCl_3$ (b) CHI_3 (c) CCl_4 (d) DDT
(a).

8. Which halide has the highest boiling point? (a) CH_3Cl (b) CH_3Br (c) CH_3I (d) CH_3F
(c).

9. S_N2 reaction of an optically active halide gives (a) racemic mixture (b) retention (c) inversion (d) no product
(c).

10. Grignard reagent is prepared in dry ether because (a) ether is acidic (b) Grignard reagent reacts with water (c) ether is a catalyst (d) it increases yield of alkane
(b) $RMgX + H_2O \rightarrow RH + Mg(OH)X$.

B. Very short answer questions

1. Write the IUPAC name of $(CH_3)_3CBr$. [1]

2-Bromo-2-methylpropane.

2. Why is thionyl chloride preferred for preparing alkyl chlorides from alcohols? [1]

The by-products SO_2 and HCl are gases and escape, leaving pure alkyl chloride.

3. What is a racemic mixture? [1]

An equimolar mixture of d and l enantiomers; optically inactive due to external compensation.

4. Why are haloalkanes insoluble in water though polar? [2]

Energy released by forming new attractions between haloalkane and water is less than the energy needed to break the hydrogen bonds between water molecules.

5. What is the full form of DDT? [1]

p,p'-Dichlorodiphenyltrichloroethane.

6. What are enantiomers? [1]

Non-superimposable mirror-image stereoisomers.

7. Write the Finkelstein reaction. [1]

$\text{CH}_3\text{CH}_2\text{Br} + \text{NaI}$ (dry acetone) $\rightarrow \text{CH}_3\text{CH}_2\text{I} + \text{NaBr}$. NaBr precipitates and drives the reaction forward.

8. What is a chiral carbon? [1]

A carbon attached to four different groups (asymmetric carbon), e.g. C-2 of butan-2-ol.

C. Short answer questions

1. Write the mechanism of $\text{S}_{\text{N}}1$ reaction of tert-butyl bromide with aqueous KOH.

Step 1 (slow, rate-determining): $(\text{CH}_3)_3\text{C}-\text{Br} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Br}^-$ (ionisation forming a planar carbocation).

Step 2 (fast): $(\text{CH}_3)_3\text{C}^+ + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{C}-\text{OH}$.

Rate = $k[(\text{CH}_3)_3\text{CBr}]$ - first order. Since the nucleophile can attack the planar carbocation from either face, an optically active substrate gives a racemic product.

2. Write the $\text{S}_{\text{N}}2$ mechanism of CH_3Cl with OH^- .

OH^- attacks carbon from the side opposite to Cl. A transition state forms in which C is partly bonded to both OH and Cl: $[\text{HO}\cdots\text{CH}_3\cdots\text{Cl}]^-$. Cl^- leaves while the other three groups flip like an umbrella in the wind. Product CH_3OH has inverted configuration.

Rate = $k[\text{CH}_3\text{Cl}][\text{OH}^-]$ - second order, one step.

3. Explain why chlorobenzene is less reactive than chloroethane towards nucleophilic substitution.

(i) Resonance: the lone pair on Cl is delocalised into the ring, giving the C-Cl bond partial double-bond character, making it hard to break. (ii) Carbon in chlorobenzene is sp^2 (more s character, more electronegative) so the C-Cl bond is shorter and stronger. (iii) The phenyl cation formed by $\text{S}_{\text{N}}1$ is not resonance-stabilised. (iv) Backside attack is blocked by the electron-rich ring.

4. Predict the major product with reasons: 2-bromobutane + alcoholic KOH.

Dehydrohalogenation can give but-1-ene ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_3$) or but-2-ene ($\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$). By the Saytzeff rule, the more substituted alkene is more stable and predominates: **but-2-ene (about 80%)**.

5. How will you convert (i) chlorobenzene to biphenyl (ii) chlorobenzene to toluene (iii) ethyl bromide to propanenitrile?

(i) Fittig: $2\text{C}_6\text{H}_5\text{Cl} + 2\text{Na}$ (dry ether) $\rightarrow \text{C}_6\text{H}_5-\text{C}_6\text{H}_5 + 2\text{NaCl}$.

(ii) Wurtz-Fittig: $\text{C}_6\text{H}_5\text{Cl} + \text{CH}_3\text{Cl} + 2\text{Na} \rightarrow \text{C}_6\text{H}_5\text{CH}_3 + 2\text{NaCl}$.

(iii) $\text{C}_2\text{H}_5\text{Br} + \text{KCN}$ (alc.) $\rightarrow \text{C}_2\text{H}_5\text{CN} + \text{KBr}$.

D. Long answer questions

1. Compare S_N1 and S_N2 mechanisms. Arrange the following in order of S_N1 and S_N2 reactivity: CH_3Br , C_2H_5Br , $(CH_3)_2CHBr$, $(CH_3)_3CBr$.

Point	S_N1	S_N2
Steps	Two (carbocation intermediate)	One (transition state)
Kinetics	First order, rate = $k[RX]$	Second order, rate = $k[RX][Nu]$
Stereochemistry	Racemisation	Inversion
Favoured substrate	$3^\circ > 2^\circ > 1^\circ$	$1^\circ > 2^\circ > 3^\circ$
Solvent	Polar protic (water, alcohol)	Polar aprotic (acetone, DMSO)
Rearrangement	Possible	Not possible

S_N1 : $(CH_3)_3CBr > (CH_3)_2CHBr > C_2H_5Br > CH_3Br$.

S_N2 : $CH_3Br > C_2H_5Br > (CH_3)_2CHBr > (CH_3)_3CBr$.

2. Describe the electrophilic substitution reactions of chlorobenzene (halogenation, nitration, sulphonation, Friedel-Crafts). Why is Cl ortho/para directing yet deactivating?

Chlorobenzene + Cl_2 /anhyd. $FeCl_3 \rightarrow$ 1,2- and 1,4-dichlorobenzene.

+ conc. HNO_3 /conc. $H_2SO_4 \rightarrow$ 1-chloro-2-nitrobenzene (minor) + 1-chloro-4-nitrobenzene (major).

+ conc. $H_2SO_4 \rightarrow$ 2- and 4-chlorobenzenesulphonic acid.

+ CH_3Cl /anhyd. $AlCl_3 \rightarrow$ 2- and 4-chlorotoluene; + $CH_3COCl/AlCl_3 \rightarrow$ 2- and 4-chloroacetophenone.

Reason: Cl withdraws electrons by the $-I$ effect, reducing electron density in the whole ring (deactivation). But its lone pairs are donated by $+R$ (resonance) effect, increasing electron density specifically at ortho and para positions, so the electrophile attacks there. The para product dominates because of less steric hindrance.

3. Write notes on (a) Wurtz reaction (b) Sandmeyer reaction (c) Grignard reagent and its use.

(a) **Wurtz:** two molecules of alkyl halide react with sodium in dry ether to give a higher alkane with double the carbon atoms: $2CH_3Br + 2Na \rightarrow CH_3-CH_3 + 2NaBr$.

(b) **Sandmeyer:** benzenediazonium chloride with $CuCl/HCl$ or $CuBr/HBr$ gives chlorobenzene or bromobenzene: $C_6H_5N_2^+Cl^- + CuCl \rightarrow C_6H_5Cl + N_2$; with $CuCN/KCN$ gives benzonitrile.

(c) **Grignard reagent:** $RX + Mg$ (dry ether) $\rightarrow RMgX$. The C-Mg bond is highly polar (carbanion character), so $RMgX$ is a strong nucleophile and base. Uses: with $HCHO \rightarrow 1^\circ$ alcohol; with other aldehydes $\rightarrow 2^\circ$ alcohol; with ketones $\rightarrow 3^\circ$ alcohol (after hydrolysis); with $CO_2 \rightarrow$ carboxylic acid; with water $\rightarrow$ alkane.

QB-7. Alcohols, Phenols and Ethers

Key points

- Preparation of alcohols: hydration of alkenes (acid-catalysed, Markovnikov), hydroboration-oxidation (anti-Markovnikov), reduction of aldehydes/ketones (NaBH_4 , LiAlH_4 , H_2/Pd), Grignard reagent with carbonyl compounds.
- Preparation of phenol: from haloarene (Dow's process: NaOH at 623 K, 300 atm), from benzenesulphonic acid (fusion with NaOH), from diazonium salt (warm water), from cumene (cumene hydroperoxide $\rightarrow$ phenol + acetone - industrial).
- Boiling points of alcohols are high because of intermolecular hydrogen bonding; solubility in water decreases as the alkyl chain grows.
- Acidity: phenol ($\text{pK}_a \approx 10$) is more acidic than alcohol ($\text{pK}_a \approx 16$) and water, because phenoxide ion is resonance-stabilised. Electron-withdrawing groups ($-\text{NO}_2$) increase acidity; electron-donating groups ($-\text{CH}_3$) decrease it. 2,4,6-trinitrophenol (picric acid) is strongly acidic.
- Lucas test (conc. HCl + anhyd. ZnCl_2): 3° alcohol - turbidity immediately; 2° - in about 5 minutes; 1° - no turbidity at room temperature.
- Dehydration of alcohols (conc. H_2SO_4): ease $3^\circ > 2^\circ > 1^\circ$. Ethanol at 443 K $\rightarrow$ ethene; at 413 K with excess alcohol $\rightarrow$ diethyl ether.
- Oxidation: 1° alcohol $\rightarrow$ aldehyde (PCC) $\rightarrow$ acid (KMnO_4); $2^\circ \rightarrow$ ketone; 3° resists. Over hot Cu at 573 K: $1^\circ \rightarrow$ aldehyde, $2^\circ \rightarrow$ ketone, $3^\circ \rightarrow$ alkene.
- Phenol reactions: bromine water $\rightarrow$ 2,4,6-tribromophenol (white ppt); dil. $\text{HNO}_3 \rightarrow$ o- and p-nitrophenol (separated by steam distillation; ortho is steam-volatile due to intramolecular H-bond); Kolbe's reaction $\rightarrow$ salicylic acid; Reimer-Tiemann $\rightarrow$ salicylaldehyde; Zn dust $\rightarrow$ benzene; neutral $\text{FeCl}_3 \rightarrow$ violet colour.
- Ethers: Williamson synthesis $\text{R-ONa} + \text{R'-X} \rightarrow \text{R-O-R'}$ (use 1° halide; 3° halides give alkene). Cleavage with HI: for methyl tert-butyl ether, products are CH_3OH and $(\text{CH}_3)_3\text{CI}$ ($\text{S}_{\text{N}}1$). For anisole: phenol + CH_3I (the $\text{O-C}_6\text{H}_5$ bond is stronger).
- Anisole undergoes electrophilic substitution at ortho/para positions ($-\text{OCH}_3$ is activating).

A. Multiple choice questions

1. Which is most acidic? (a) ethanol (b) phenol (c) p-nitrophenol (d) p-cresol

(c) $-\text{NO}_2$ stabilises the phenoxide ion.

2. Lucas reagent is (a) conc. HCl + anhyd. ZnCl_2 (b) conc. HNO_3 + H_2SO_4 (c) Br_2 water (d) alkaline KMnO_4

(a).

3. Phenol + CHCl_3 + NaOH , then acid, gives (a) salicylic acid (b) salicylaldehyde (c) benzaldehyde (d) picric acid

(b) Reimer-Tiemann reaction.

4. The industrial method of preparing phenol along with acetone is from (a) chlorobenzene (b) cumene (c) aniline (d) benzoic acid

(b).

5. Which alcohol gives turbidity immediately with Lucas reagent? (a) propan-1-ol (b) propan-2-ol (c) 2-methylpropan-2-ol (d) methanol

(c) 3° alcohol.

6. Anisole + HI gives (a) $C_6H_5I + CH_3OH$ (b) $C_6H_5OH + CH_3I$ (c) $C_6H_6 + CH_3OH$ (d) $C_6H_5I + CH_3I$

(b).

7. Ortho-nitrophenol is steam volatile because of (a) intermolecular H-bond (b) intramolecular H-bond (c) high molar mass (d) ionic character

(b).

8. Kolbe's reaction product is (a) salicylic acid (b) benzoic acid (c) phenol (d) aspirin

(a) Sodium phenoxide + CO_2 (4–7 atm, 400 K) then H^+ .

9. Methylated spirit contains ethanol denatured with (a) methanol (b) propanol (c) acetone (d) glycerol

(a) Plus pyridine and copper sulphate.

10. Hydroboration-oxidation of propene gives (a) propan-1-ol (b) propan-2-ol (c) propanal (d) propanone

(a) Anti-Markovnikov addition of water.

B. Very short answer questions

1. Write the IUPAC name of $CH_3-CH(OH)-CH_2-CH_3$. [1]

Butan-2-ol.

2. Why does phenol give a violet colour with $FeCl_3$? [1]

It forms a violet coloured iron-phenoxide complex, $[Fe(OC_6H_5)_6]^{3-}$.

3. What is absolute alcohol? [1]

100% pure ethanol (free from water).

4. Why are alcohols more soluble in water than hydrocarbons of comparable mass? [1]

They form hydrogen bonds with water molecules.

5. Name the reagent used to oxidise a primary alcohol to aldehyde only. [1]

Pyridinium chlorochromate (PCC) in CH_2Cl_2 .

6. Why is phenol acidic but ethanol is practically neutral? [2]

Phenoxide ion is stabilised by resonance (negative charge spread over the ring); ethoxide ion has no resonance and is destabilised by +I effect of the ethyl group.

7. Write the product of phenol with bromine in CS_2 at low temperature. [1]

Mixture of o-bromophenol and p-bromophenol (p major); in water 2,4,6-tribromophenol forms.

8. What is Williamson synthesis? [1]

Preparation of ethers by S_N2 reaction of sodium alkoxide with a primary alkyl halide:
 $C_2H_5ONa + CH_3Br \rightarrow C_2H_5OCH_3 + NaBr$.

C. Short answer questions

1. Explain the mechanism of acid-catalysed dehydration of ethanol to ethene.

Step 1: Protonation - $CH_3CH_2-OH + H^+ \rightarrow CH_3CH_2-OH_2^+$ (fast).

Step 2: Loss of water forms carbocation - $CH_3CH_2-OH_2^+ \rightarrow CH_3CH_2^+ + H_2O$ (slow, rate-determining).

Step 3: Loss of a proton - $CH_3CH_2^+ \rightarrow CH_2=CH_2 + H^+$. Conditions: conc. H_2SO_4 , 443 K.

2. Write the cumene process for phenol.

Benzene + propene (H_3PO_4) $\rightarrow$ cumene (isopropylbenzene). Cumene + O_2 (air) $\rightarrow$ cumene hydroperoxide $C_6H_5C(CH_3)_2OOH$. Treatment with dilute acid:

$C_6H_5C(CH_3)_2OOH \rightarrow C_6H_5OH + CH_3COCH_3$. Advantage: acetone is a valuable by-product.

3. Why is the preparation of di-tert-butyl ether or methyl tert-butyl ether from tert-butyl bromide by Williamson synthesis not possible? Give the correct method.

With a 3° halide, the strongly basic alkoxide causes elimination ($E2$), giving 2-methylpropene instead of ether. Correct method for methyl tert-butyl ether: $(CH_3)_3C-ONa + CH_3-Br \rightarrow (CH_3)_3C-O-CH_3 + NaBr$ (use the 1° halide and the 3° alkoxide).

4. Distinguish by chemical tests: (i) ethanol and phenol (ii) propan-1-ol and propan-2-ol (iii) methanol and ethanol.

(i) Neutral $FeCl_3$: phenol violet, ethanol no colour. Bromine water: phenol gives white ppt.

(ii) Lucas test: propan-2-ol turbid in about 5 min, propan-1-ol not at room temperature. Also iodoform test: propan-2-ol gives yellow CHI_3 .

(iii) Iodoform test ($I_2 + NaOH$, warm): ethanol gives yellow ppt of CHI_3 ; methanol does not.

5. Arrange in increasing order of acidity with reason: phenol, p-nitrophenol, p-cresol, ethanol.

ethanol < p-cresol < phenol < p-nitrophenol. Ethanol has no resonance in its anion. In p-cresol, $-CH_3$ (+I, hyperconjugation) destabilises phenoxide. $-NO_2$ ($-I$, $-R$) spreads the negative charge further and stabilises the anion most.

D. Long answer questions

1. Describe the electrophilic substitution reactions of phenol with equations: nitration, bromination, Kolbe's reaction, Reimer-Tiemann reaction.

-OH is strongly activating and o/p directing (+R effect).

Nitration: with dilute HNO_3 at 298 K $\rightarrow$ o-nitrophenol + p-nitrophenol; with conc. $\text{HNO}_3 \rightarrow$ 2,4,6-trinitrophenol (picric acid).

Bromination: in $\text{CS}_2/\text{CHCl}_3$ at low temperature $\rightarrow$ mono-bromophenols (p major); with bromine water $\rightarrow$ 2,4,6-tribromophenol, white precipitate (test for phenol).

Kolbe's reaction: $\text{C}_6\text{H}_5\text{ONa} + \text{CO}_2$ (400 K, 4-7 atm) $\rightarrow$ sodium salicylate $\rightarrow (\text{H}^+)$ salicylic acid (2-hydroxybenzoic acid). Phenoxide is a stronger activator than phenol, so even the weak electrophile CO_2 attacks.

Reimer-Tiemann: phenol + CHCl_3 + aq. NaOH (340 K) $\rightarrow$ intermediate benzal chloride $\rightarrow$ hydrolysis/acidification $\rightarrow$ salicylaldehyde (2-hydroxybenzaldehyde). Electrophile: dichlorocarbene $:\text{CCl}_2$.

2. How are primary, secondary and tertiary alcohols prepared from Grignard reagent? How are they distinguished by oxidation and by heated copper?

$\text{HCHO} + \text{CH}_3\text{MgBr} \rightarrow \text{CH}_3\text{CH}_2\text{OMgBr} \rightarrow (\text{H}_2\text{O}) \text{CH}_3\text{CH}_2\text{OH}$ (1°).

$\text{CH}_3\text{CHO} + \text{CH}_3\text{MgBr} \rightarrow (\text{CH}_3)_2\text{CHOMgBr} \rightarrow (\text{H}_2\text{O})$ propan-2-ol (2°).

$\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{MgBr} \rightarrow (\text{CH}_3)_3\text{COMgBr} \rightarrow (\text{H}_2\text{O})$ 2-methylpropan-2-ol (3°).

Heated Cu at 573 K: $1^\circ \rightarrow$ aldehyde + H_2 (dehydrogenation); $2^\circ \rightarrow$ ketone + H_2 ; $3^\circ \rightarrow$ alkene + H_2O (dehydration).

Acidified $\text{K}_2\text{Cr}_2\text{O}_7$: $1^\circ \rightarrow$ aldehyde $\rightarrow$ carboxylic acid with same C atoms; $2^\circ \rightarrow$ ketone; $3^\circ \rightarrow$ not oxidised in normal conditions (orange colour stays).

3. Write the preparation and reactions of anisole (methoxybenzene).

Preparation: $\text{C}_6\text{H}_5\text{ONa} + \text{CH}_3\text{I} \rightarrow \text{C}_6\text{H}_5\text{OCH}_3 + \text{NaI}$ (Williamson).

Cleavage: $\text{C}_6\text{H}_5\text{OCH}_3 + \text{HI} \rightarrow \text{C}_6\text{H}_5\text{OH} + \text{CH}_3\text{I}$.

Halogenation: + Br_2 in ethanoic acid $\rightarrow$ p-bromoanisole (major) + o-bromoanisole.

Friedel-Crafts alkylation: + $\text{CH}_3\text{Cl}/\text{AlCl}_3 \rightarrow$ 2- and 4-methoxytoluene. **Acylation:** + $\text{CH}_3\text{COCl}/\text{AlCl}_3 \rightarrow$ 2- and 4-methoxyacetophenone.

Nitration: + conc. $\text{HNO}_3/\text{H}_2\text{SO}_4 \rightarrow$ 2- and 4-nitroanisole. The $-\text{OCH}_3$ group activates the ring and directs the electrophile to ortho and para positions.

QB-8. Aldehydes, Ketones and Carboxylic Acids

Key points

- Carbonyl carbon is sp^2 , trigonal planar; $C=O$ is polar ($C^{\delta+}$). Aldehydes are more reactive than ketones towards nucleophilic addition (less steric hindrance, only one electron-releasing alkyl group).
- Preparation: oxidation of alcohols; Rosenmund reduction ($RCOCl + H_2/Pd-BaSO_4 \rightarrow RCHO$); Stephen reaction ($RCN + SnCl_2/HCl$, then $H_2O \rightarrow RCHO$); Etard reaction (toluene + $CrO_2Cl_2 \rightarrow$ benzaldehyde); Gattermann-Koch (benzene + $CO + HCl/AlCl_3 \rightarrow$ benzaldehyde); Friedel-Crafts acylation for aromatic ketones; DIBAL-H reduction of nitriles/esters.
- Nucleophilic addition: HCN (cyanohydrin), $NaHSO_3$ (crystalline bisulphite adduct, used for purification), Grignard reagent, alcohols (hemiacetal/acetal), NH_2-Z derivatives (oxime with NH_2OH , hydrazone, phenylhydrazone, 2,4-DNP derivative - orange/yellow ppt, semicarbazone).
- Reduction: Clemmensen ($Zn-Hg/conc. HCl$) and Wolff-Kishner ($NH_2NH_2, KOH/$ ethylene glycol) convert $C=O$ to CH_2 .
- Aldol condensation: aldehydes/ketones with α -hydrogen + dil. $NaOH \rightarrow \beta$ -hydroxy aldehyde/ketone $\rightarrow$ (heat) α,β -unsaturated compound. Cannizzaro reaction: aldehydes **without** α -hydrogen ($HCHO, C_6H_5CHO$) + conc. $NaOH \rightarrow$ alcohol + salt of acid (disproportionation).
- Tests for aldehydes: Tollens' reagent (silver mirror), Fehling's solution (red ppt of Cu_2O ; aromatic aldehydes do not respond). Iodoform test: compounds with CH_3CO- or $CH_3CH(OH)-$ group.
- Carboxylic acids: preparation by oxidation of 1° alcohols/aldehydes, alkylbenzenes ($KMnO_4 \rightarrow$ benzoic acid), hydrolysis of nitriles, Grignard + CO_2 .
- Acidity: carboxylate ion is resonance stabilised (two equivalent structures). EWG increases acidity: $F_3C-COOH > Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > HCOOH > CH_3COOH$. $HCOOH$ is stronger than CH_3COOH (no +I group).
- Reactions of acids: with $PCl_5/SOCl_2 \rightarrow$ acid chloride; with alcohol/ $H^+ \rightarrow$ ester (esterification); with $NH_3 \rightarrow$ amide; decarboxylation (sodalime) $\rightarrow$ alkane with one less C; Kolbe electrolysis; Hell-Volhard-Zelinsky (HVZ) reaction - α -halogenation with $X_2/red P$; reduction with $LiAlH_4 \rightarrow 1^\circ$ alcohol.
- $-COOH$ is deactivating and meta-directing in benzoic acid; benzoic acid does not undergo Friedel-Crafts reaction.
- Carboxylic acids have higher boiling points than alcohols of similar mass because they form dimers by hydrogen bonding.

A. Multiple choice questions

1. Which does not give Cannizzaro reaction? (a) HCHO (b) $\text{C}_6\text{H}_5\text{CHO}$ (c) CH_3CHO (d) $(\text{CH}_3)_3\text{CCHO}$
(c) It has α -hydrogens; it gives aldol.
2. Rosenmund reduction converts (a) acid chloride to aldehyde (b) ketone to alkane (c) nitrile to aldehyde (d) ester to alcohol
(a).
3. Which gives a positive iodoform test? (a) CH_3OH (b) HCHO (c) CH_3COCH_3 (d) $\text{C}_6\text{H}_5\text{CHO}$
(c).
4. Clemmensen reduction uses (a) Zn-Hg/HCl (b) LiAlH_4 (c) $\text{NH}_2\text{NH}_2/\text{KOH}$ (d) H_2/Pd
(a).
5. The strongest acid among the following is (a) CH_3COOH (b) ClCH_2COOH (c) Cl_2CHCOOH (d) Cl_3CCOOH
(d).
6. Fehling's solution is not reduced by (a) HCHO (b) CH_3CHO (c) $\text{C}_6\text{H}_5\text{CHO}$ (d) glucose
(c).
7. HVZ reaction gives (a) α -halo acid (b) acid chloride (c) β -halo acid (d) alkyl halide
(a).
8. Benzaldehyde + conc. NaOH gives (a) benzyl alcohol + sodium benzoate (b) benzoic acid only (c) benzophenone (d) toluene
(a) Cannizzaro reaction.
9. Ethanal + dil. NaOH gives (a) 3-hydroxybutanal (b) ethanol (c) acetic acid (d) acetone
(a) Aldol.
10. Toluene + CrO_2Cl_2 then hydrolysis gives benzaldehyde. This is (a) Etard reaction (b) Stephen reaction (c) Gattermann-Koch (d) Rosenmund
(a).

B. Very short answer questions

1. Write the IUPAC name of $\text{CH}_3\text{CH}=\text{CHCHO}$. [1]

But-2-enal.

2. What is Tollens' reagent? [1]

Ammoniacal silver nitrate solution, $[\text{Ag}(\text{NH}_3)_2]^+$.

3. Why does the carbonyl carbon undergo nucleophilic attack? [1]

Oxygen is more electronegative, so carbon carries a partial positive charge.

4. Write the structure of 2,4-DNP. [1]

2,4-Dinitrophenylhydrazine: $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{NHNH}_2$ (nitro groups at 2 and 4 positions).

5. Why is formic acid stronger than acetic acid? [1]

The $-\text{CH}_3$ group in acetic acid releases electrons (+I) and destabilises the acetate ion.

6. What is the role of BaSO_4 in Rosenmund reduction? [1]

It poisons the Pd catalyst so that the aldehyde is not further reduced to alcohol.

7. Name the reaction: $\text{CH}_3\text{COONa} + \text{NaOH (CaO, heat)} \rightarrow \text{CH}_4 + \text{Na}_2\text{CO}_3$. [1]

Decarboxylation.

8. Why do carboxylic acids not give reactions of the carbonyl group? [2]

Lone pair on the -OH oxygen is in resonance with C=O, reducing the electrophilic character of the carbonyl carbon.

C. Short answer questions

1. Write the mechanism of nucleophilic addition of HCN to a carbonyl compound.

Step 1: $\text{HCN} + \text{OH}^- \rightarrow \text{CN}^- + \text{H}_2\text{O}$ (base generates the strong nucleophile).

Step 2: CN^- attacks the carbonyl carbon; the π electrons move to oxygen giving a tetrahedral alkoxide intermediate $\text{R}_2\text{C}(\text{O}^-)\text{CN}$.

Step 3: The alkoxide takes a proton from water/HCN: $\text{R}_2\text{C}(\text{OH})\text{CN}$ (cyanohydrin). The carbon changes from sp^2 (planar) to sp^3 (tetrahedral).

2. Write the aldol condensation of ethanal with mechanism outline.

OH^- removes an $\alpha\text{-H}$: $\text{CH}_3\text{CHO} \rightarrow ^-\text{CH}_2\text{CHO}$ (enolate). The carbanion attacks the carbonyl carbon of another CH_3CHO forming $\text{CH}_3\text{CH}(\text{O}^-)\text{CH}_2\text{CHO}$, which takes a proton: $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$ (3-hydroxybutanal, aldol). On heating it loses water: $\text{CH}_3\text{CH}=\text{CHCHO}$ (but-2-enal).

3. Distinguish: (i) propanal and propanone (ii) acetophenone and benzophenone (iii) benzoic acid and phenol.

(i) Tollens' test - propanal gives silver mirror, propanone does not. (Iodoform: propanone positive.)

(ii) Iodoform test - acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$) gives yellow CHI_3 ; benzophenone does not.

(iii) NaHCO_3 - benzoic acid gives brisk effervescence of CO_2 ; phenol does not. FeCl_3 - phenol violet, benzoic acid buff precipitate.

4. Write the Cannizzaro reaction of formaldehyde and explain why it is called disproportionation.

$2\text{HCHO} + \text{conc. NaOH} \rightarrow \text{CH}_3\text{OH} + \text{HCOONa}$. One molecule is oxidised (to formate, C oxidation state +2) and the other reduced (to methanol, -2), from the same compound (0) - hence disproportionation (self oxidation-reduction).

5. Arrange in increasing order of reactivity towards nucleophilic addition: ethanal, propanal, propanone, butanone.

butanone < propanone < propanal < ethanal. Larger alkyl groups increase steric hindrance and push electrons (+I) into the carbonyl carbon, reducing its positive character.

D. Long answer questions

1. An organic compound A (C_3H_6O) gives a yellow precipitate with $I_2/NaOH$ but does not reduce Tollens' reagent. It gives an orange precipitate with 2,4-DNP. Identify A and write all reactions. What does A give with CH_3MgBr followed by hydrolysis?

Positive 2,4-DNP $\Rightarrow$ carbonyl compound. Negative Tollens $\Rightarrow$ ketone. Positive iodoform $\Rightarrow$ CH_3CO- group. Hence **A = propanone, CH_3COCH_3 .**

Iodoform: $CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CHI_3 \downarrow + CH_3COONa + 3NaI + 3H_2O$.

2,4-DNP: $(CH_3)_2C=O + H_2N-NH-C_6H_3(NO_2)_2 \rightarrow (CH_3)_2C=N-NH-C_6H_3(NO_2)_2 + H_2O$.

With CH_3MgBr then H_2O : $(CH_3)_3C-OH$ (2-methylpropan-2-ol, a 3° alcohol).

2. Explain the acidity of carboxylic acids. Why are they stronger than phenols? Explain the effect of substituents with examples.

$R-COOH \rightleftharpoons R-COO^- + H^+$. The carboxylate ion has two equivalent resonance structures; the negative charge is shared equally by two electronegative oxygen atoms, so it is highly stable. In phenoxide ion, the negative charge is delocalised onto less electronegative carbon atoms, and the structures are not equivalent; so phenoxide is less stable and phenol is a weaker acid.

Substituent effect: Electron-withdrawing groups ($-Cl$, $-F$, $-NO_2$, $-CN$) disperse the negative charge and increase acidity; the effect is greater with more groups and when nearer to $-COOH$. $ClCH_2COOH$ (pK_a 2.9) $>$ CH_3COOH (4.76). Electron-donating groups (alkyl) decrease acidity: $HCOOH$ (3.75) $>$ CH_3COOH . In benzoic acids, p-nitrobenzoic acid is stronger than benzoic acid; p-methoxybenzoic acid is weaker.

3. How will you bring about: (i) benzene to benzaldehyde (ii) ethanenitrile to ethanal (iii) ethanoic acid to 2-chloroethanoic acid (iv) benzoic acid to m-nitrobenzoic acid (v) propanone to propane?

(i) Gattermann-Koch: $\text{C}_6\text{H}_6 + \text{CO} + \text{HCl} (\text{anhyd. AlCl}_3/\text{CuCl}) \rightarrow \text{C}_6\text{H}_5\text{CHO}$.

(ii) Stephen: $\text{CH}_3\text{CN} + \text{SnCl}_2 + \text{HCl} \rightarrow \text{CH}_3\text{CH}=\text{NH}\cdot\text{HCl} \rightarrow (\text{H}_3\text{O}^+) \text{CH}_3\text{CHO}$.

(iii) HVZ: $\text{CH}_3\text{COOH} + \text{Cl}_2 (\text{red P}) \rightarrow \text{ClCH}_2\text{COOH} + \text{HCl}$.

(iv) $\text{C}_6\text{H}_5\text{COOH} + \text{conc. HNO}_3/\text{conc. H}_2\text{SO}_4 \rightarrow \text{m-O}_2\text{NC}_6\text{H}_4\text{COOH}$ (-COOH is meta-directing).

(v) Clemmensen: $\text{CH}_3\text{COCH}_3 + 4[\text{H}] (\text{Zn-Hg/conc. HCl}) \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$ (or Wolff-Kishner).

QB-9. Amines

Key points

- Amines are derivatives of NH_3 : 1° (RNH_2), 2° (R_2NH), 3° (R_3N). Nitrogen is sp^3 , pyramidal.
- Preparation: reduction of nitro compounds (Sn/HCl or Fe/HCl), ammonolysis of alkyl halides (mixture), reduction of nitriles and amides (LiAlH_4), Gabriel phthalimide synthesis (pure 1° aliphatic amines; not for aromatic amines), Hoffmann bromamide degradation ($\text{RCONH}_2 + \text{Br}_2 + 4\text{NaOH} \rightarrow \text{RNH}_2$; one carbon less).
- Basicity in water (aqueous phase): for methyl: $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$; for ethyl: $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$. (Combination of +I effect, solvation, steric hindrance.)
- Aniline is a much weaker base than NH_3 (lone pair delocalised into ring). pK_b : aniline 9.38, NH_3 4.75, CH_3NH_2 3.38.
- Carbylamine test (1° amines only): $\text{RNH}_2 + \text{CHCl}_3 + 3\text{KOH (alc.)} \rightarrow \text{RNC}$ (foul-smelling isocyanide) + $3\text{KCl} + 3\text{H}_2\text{O}$.
- Nitrous acid: 1° aliphatic amine $\rightarrow$ alcohol + $\text{N}_2 \uparrow$; aniline at 273–278 K $\rightarrow$ benzenediazonium chloride (diazotisation).
- Hinsberg's reagent (benzenesulphonyl chloride): $1^\circ \rightarrow$ sulphonamide soluble in alkali; $2^\circ \rightarrow$ sulphonamide insoluble in alkali; $3^\circ \rightarrow$ no reaction.
- Aniline with bromine water $\rightarrow$ 2,4,6-tribromoaniline (white ppt). To get mono-substitution, protect $-\text{NH}_2$ by acetylation. Direct nitration gives 47% meta product because anilinium ion (meta-directing) forms in acid. Aniline does not undergo Friedel-Crafts (forms salt with AlCl_3).
- Diazonium salt reactions: Sandmeyer (CuCl , CuBr , CuCN), Gattermann (Cu powder/ HX), $\text{KI} \rightarrow$ iodobenzene, $\text{HBF}_4/\text{heat} \rightarrow$ fluorobenzene (Balz-Schiemann), $\text{H}_3\text{PO}_2 \rightarrow$ benzene, warm water $\rightarrow$ phenol, coupling with phenol (orange dye p-hydroxyazobenzene) and with aniline (yellow dye p-aminoazobenzene).

A. Multiple choice questions

- Which is the strongest base in aqueous solution? (a) NH_3 (b) CH_3NH_2 (c) $(\text{CH}_3)_2\text{NH}$ (d) $\text{C}_6\text{H}_5\text{NH}_2$
(c).
- Carbylamine test is given by (a) 1° amines (b) 2° amines (c) 3° amines (d) all
(a).
- Hoffmann bromamide reaction converts acetamide into (a) ethylamine (b) methylamine (c) acetic acid (d) acetonitrile
(b) One carbon less.

4. Gabriel synthesis is used for preparing (a) 1° aromatic amines (b) 1° aliphatic amines (c) 2° amines (d) 3° amines

(b).

5. Hinsberg's reagent is (a) $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ (b) $\text{C}_6\text{H}_5\text{COCl}$ (c) $\text{CHCl}_3 + \text{KOH}$ (d) $\text{NaNO}_2 + \text{HCl}$

(a).

6. Aniline + NaNO_2/HCl at 273 K gives (a) phenol (b) benzenediazonium chloride (c) nitrobenzene (d) chlorobenzene

(b).

7. Benzenediazonium chloride + H_3PO_2 gives (a) phenol (b) benzene (c) aniline (d) chlorobenzene

(b).

8. Coupling of benzenediazonium chloride with phenol in alkaline medium gives (a) orange dye (b) yellow dye (c) white ppt (d) blue colour

(a) p-Hydroxyazobenzene.

9. Aniline is less basic than methylamine because (a) of resonance of lone pair with ring (b) of +I effect (c) it is aromatic only (d) it has no lone pair

(a).

10. Which amine gives an alkali-insoluble product with Hinsberg's reagent? (a) CH_3NH_2 (b) $(\text{CH}_3)_2\text{NH}$ (c) $(\text{CH}_3)_3\text{N}$ (d) $\text{C}_6\text{H}_5\text{NH}_2$

(b).

B. Very short answer questions

1. Write the IUPAC name of $\text{CH}_3\text{NHC}_2\text{H}_5$. [1]

N-Methylethanamine.

2. Why are aliphatic amines stronger bases than ammonia? [1]

Alkyl groups release electrons (+I effect), increasing electron density on nitrogen.

3. Why must diazotisation be done at 273-278 K? [1]

Diazonium salts are unstable and decompose to phenol at higher temperature.

4. Why does aniline not undergo Friedel-Crafts reaction? [2]

Aniline (a Lewis base) forms a salt with AlCl_3 (Lewis acid); the positive N then strongly deactivates the ring.

5. Why do primary amines have higher boiling points than tertiary amines of equal mass? [1]

1° amines have two N-H bonds for intermolecular H-bonding; 3° amines have none.

6. Why is benzenediazonium salt more stable than an alkyl diazonium salt? [1]

It is stabilised by resonance with the benzene ring.

7. Write the Hoffmann bromamide reaction for benzamide. [1]



C. Short answer questions

1. Describe Gabriel phthalimide synthesis. Why can't it make aniline?

Phthalimide + ethanolic KOH → potassium phthalimide. This is heated with alkyl halide R-X → N-alkylphthalimide. Hydrolysis with NaOH (or hydrazine) → RNH₂ + sodium phthalate. Aryl halides do not undergo nucleophilic substitution with the phthalimide anion, so aniline cannot be prepared.

2. Explain why -NH₂ is o/p directing but nitration of aniline gives a large amount of m-nitroaniline. How is p-nitroaniline prepared?

In strongly acidic nitrating mixture, aniline is protonated to anilinium ion C₆H₅NH₃⁺, which is meta-directing; products: p 51%, m 47%, o 2%. To get p-nitroaniline: aniline + (CH₃CO)₂O → acetanilide (protected, moderately activating) → nitration → p-nitroacetanilide (major) → acid/alkali hydrolysis → p-nitroaniline.

3. Arrange in increasing order of basic strength: C₆H₅NH₂, C₂H₅NH₂, (C₂H₅)₂NH, NH₃.

C₆H₅NH₂ < NH₃ < C₂H₅NH₂ < (C₂H₅)₂NH.

4. Complete: (i) C₆H₅N₂Cl + KI → (ii) C₆H₅N₂Cl + CuCN → (iii) C₆H₅N₂Cl + H₂O (warm) → (iv) C₆H₅N₂Cl + HBF₄, heat →

(i) C₆H₅I + KCl + N₂ (ii) C₆H₅CN + N₂ (+ CuCl) (iii) C₆H₅OH + N₂ + HCl (iv) C₆H₅N₂⁺BF₄⁻ → C₆H₅F + BF₃ + N₂.

D. Long answer questions

1. Explain Hinsberg's test for distinguishing 1°, 2° and 3° amines with equations.

Reagent: benzenesulphonyl chloride C₆H₅SO₂Cl.

1° amine: C₆H₅SO₂Cl + H₂N-C₂H₅ → C₆H₅SO₂NH-C₂H₅ + HCl. The H on N is acidic (strong electron-withdrawing sulphonyl group), so the product dissolves in KOH.

2° amine: C₆H₅SO₂Cl + HN(C₂H₅)₂ → C₆H₅SO₂N(C₂H₅)₂ + HCl. No H on N, so insoluble in alkali.

3° amine: no H on N, no reaction.

(Nowadays p-toluenesulphonyl chloride is used in place of benzenesulphonyl chloride.)

2. Starting from benzene, how will you prepare (i) aniline (ii) phenol (iii) chlorobenzene (iv) benzonitrile (v) p-hydroxyazobenzene?

(i) $\text{C}_6\text{H}_6 + \text{HNO}_3 (\text{H}_2\text{SO}_4) \rightarrow \text{C}_6\text{H}_5\text{NO}_2 \rightarrow (\text{Sn}/\text{HCl}, \text{ then NaOH}) \text{C}_6\text{H}_5\text{NH}_2$.

(ii) Aniline $\rightarrow (\text{NaNO}_2/\text{HCl}, 273 \text{ K}) \text{C}_6\text{H}_5\text{N}_2\text{Cl} \rightarrow (\text{warm H}_2\text{O}) \text{C}_6\text{H}_5\text{OH}$.

(iii) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{CuCl}/\text{HCl} \rightarrow \text{C}_6\text{H}_5\text{Cl}$ (Sandmeyer).

(iv) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{CuCN}/\text{KCN} \rightarrow \text{C}_6\text{H}_5\text{CN}$.

(v) $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_6\text{H}_5\text{OH} (\text{NaOH}, \text{ pH } 9-10) \rightarrow \text{p-HO-C}_6\text{H}_4\text{-N=N-C}_6\text{H}_5$ (orange dye).

QB-10. Biomolecules

Key points

- Carbohydrates: polyhydroxy aldehydes or ketones. Monosaccharides (glucose, fructose), disaccharides (sucrose, maltose, lactose), polysaccharides (starch, cellulose, glycogen). Reducing sugars reduce Fehling's/Tollens' (all monosaccharides, maltose, lactose); sucrose is non-reducing.
- Glucose: $C_6H_{12}O_6$, aldohexose. Evidence for open chain: HI $\rightarrow$ n-hexane (straight chain); $NH_2OH \rightarrow$ oxime ($C=O$); acetylation $\rightarrow$ pentaacetate (five $-OH$); Br_2 water $\rightarrow$ gluconic acid ($-CHO$); $HNO_3 \rightarrow$ saccharic acid ($1^\circ -OH$).
- Open-chain structure fails to explain: no reaction with $NaHSO_3$ and Schiff's reagent, pentaacetate does not react with NH_2OH , existence of α and β forms. Cyclic (pyranose) structure explains these. α and β glucose are **anomers** (differ at C-1). Mutarotation: specific rotation changes to an equilibrium value of $+52.5^\circ$.
- Sucrose = α -D-glucose + β -D-fructose linked C1-C2 (both reducing groups used, so non-reducing). Hydrolysis gives invert sugar (laevorotatory). Maltose = two α -glucose (C1-C4). Lactose = β -galactose + β -glucose (C1-C4).
- Starch = amylose (15-20%, water soluble, linear, C1-C4 α -links) + amylopectin (80-85%, branched, C1-C6 at branches). Cellulose: β -D-glucose units linked C1-C4, straight chains; humans cannot digest it.
- Proteins: polymers of α -amino acids joined by peptide bonds ($-CO-NH-$). Essential amino acids must come from food (valine, leucine, isoleucine, lysine, etc.). Amino acids exist as zwitterions; isoelectric point.
- Structure of proteins: primary (sequence), secondary (α -helix, β -pleated sheet - hydrogen bonds), tertiary (folding - fibrous/globular), quaternary (subunits). Denaturation (heat, pH) destroys secondary and tertiary structure but not primary, e.g. boiling egg, curdling of milk.
- Enzymes: biological catalysts (proteins), highly specific (e.g., maltase, invertase, pepsin).
- Vitamins: fat-soluble A, D, E, K (stored in liver/adipose tissue); water-soluble B group and C (must be supplied regularly; B_{12} exception - stored). Deficiency: A - night blindness; B_1 - beriberi; B_2 - cheilosis; B_6 - convulsions; B_{12} - pernicious anaemia; C - scurvy; D - rickets; E - fragility of RBCs; K - increased blood clotting time.
- Nucleic acids: polymers of nucleotides (base + pentose sugar + phosphate). DNA - deoxyribose, bases A, G, C, T, double helix ($A=T$, $G\equiv C$); RNA - ribose, A, G, C, U, single strand; types m-RNA, r-RNA, t-RNA. DNA is the genetic material; RNA helps in protein synthesis.

A. Multiple choice questions

1. Which is a non-reducing sugar? (a) glucose (b) maltose (c) sucrose (d) lactose (c).

2. α -D-glucose and β -D-glucose are (a) enantiomers (b) anomers (c) epimers at C-4 (d) structural isomers

(b).

3. The linkage in proteins is (a) glycosidic (b) peptide (c) phosphodiester (d) ester

(b).

4. Deficiency of vitamin C causes (a) rickets (b) scurvy (c) beriberi (d) night blindness

(b).

5. Which base is found in RNA but not in DNA? (a) adenine (b) guanine (c) thymine (d) uracil

(d).

6. Glucose + HI (prolonged heating) gives (a) n-hexane (b) gluconic acid (c) sorbitol (d) saccharic acid

(a).

7. Amylopectin is branched through (a) C1-C4 α -links (b) C1-C6 α -links (c) C1-C4 β -links (d) C1-C2 links

(b).

8. The α -helix is held by (a) disulphide bonds (b) hydrogen bonds (c) ionic bonds (d) peptide bonds

(b).

9. Which vitamin is water soluble? (a) A (b) D (c) K (d) B₁

(d).

10. Base pairing in DNA is (a) A-G, C-T (b) A-T, G-C (c) A-U, G-C (d) A-C, G-T

(b).

B. Very short answer questions

1. What are reducing sugars? [1]

Sugars that reduce Fehling's solution and Tollens' reagent because they have a free aldehyde or ketone group.

2. What is invert sugar? [1]

The equimolar mixture of glucose (+52.5°) and fructose (−92.4°) formed by hydrolysis of sucrose; it is laevorotatory, so the sign of rotation is inverted.

3. What is a zwitterion? [1]

A dipolar ion $\text{H}_3\text{N}^+-\text{CHR}-\text{COO}^-$ formed by an amino acid in water, carrying both charges.

4. What is denaturation of protein? [1]

Loss of biological activity due to destruction of secondary and tertiary structure by heat or change of pH; primary structure remains.

5. Name the sugar present in DNA and RNA. [1]

DNA: β -D-2-deoxyribose; RNA: β -D-ribose.

6. Why can vitamin C not be stored in our body? [1]

It is water soluble and is excreted in urine.

7. What is a glycosidic linkage? [1]

The oxide (-O-) link joining two monosaccharide units with loss of water.

C. Short answer questions**1. Give evidence that glucose contains (i) a straight chain (ii) five -OH groups (iii) an aldehyde group.**

- (i) Prolonged heating with HI gives n-hexane - all six carbons in a straight chain.
 (ii) With acetic anhydride it forms glucose pentaacetate - five -OH groups.
 (iii) Bromine water oxidises it to gluconic acid (six carbon acid) - the carbonyl is an aldehyde. Also it gives oxime with NH_2OH and cyanohydrin with HCN (carbonyl present).

2. Distinguish between DNA and RNA.

DNA	RNA
Sugar: 2-deoxyribose	Sugar: ribose
Bases A, G, C, T	Bases A, G, C, U
Double helix	Single strand
Replicates; carries genetic information	Does not replicate; helps in protein synthesis

3. Distinguish fibrous and globular proteins with examples.

Fibrous: polypeptide chains run parallel, held by H-bonds and disulphide bonds, fibre-like, insoluble in water - keratin (hair, wool), myosin (muscle). Globular: chains coil into spherical shapes, soluble in water - insulin, albumin.

D. Long answer questions

1. Discuss the open-chain structure of glucose and its limitations. How does the cyclic structure explain them?

Open chain: $\text{CHO}-(\text{CHOH})_4-\text{CH}_2\text{OH}$, established by the reactions with HI, acetic anhydride, Br_2 water, HNO_3 , NH_2OH and HCN (see C-1).

Limitations: (1) despite having $-\text{CHO}$, glucose does not give Schiff's test or the 2,4-DNP test and does not form a hydrogensulphite addition product with NaHSO_3 ; (2) glucose pentaacetate does not react with NH_2OH , showing no free $-\text{CHO}$; (3) glucose exists in two crystalline forms: α (m.p. 419 K, $[\alpha] = +111^\circ$) and β (m.p. 423 K, $[\alpha] = +19.2^\circ$), and each changes in solution to an equilibrium value of $+52.5^\circ$ (mutarotation).

Cyclic structure: the $-\text{OH}$ at C-5 adds to the $-\text{CHO}$ group forming a six-membered ring (pyranose) hemiacetal. C-1 becomes a new chiral centre, giving α ($-\text{OH}$ on C-1 on the same side as ring O in Fischer projection; down in Haworth) and β forms – anomers. The free $-\text{CHO}$ is absent in the ring form, explaining the negative Schiff's and bisulphite tests; in solution a small equilibrium amount of open chain exists, and α and β interconvert through it (mutarotation).

2. Describe the four levels of protein structure.

Primary: the specific sequence of amino acids in the polypeptide chain; a change of even one amino acid can change the function (sickle-cell anaemia).

Secondary: shape of the chain due to H-bonds between $\text{C}=\text{O}$ and $\text{N}-\text{H}$ of peptide groups: α -helix (right-handed coil, H-bond between every fourth amino acid) and β -pleated sheet (chains side by side, H-bonded).

Tertiary: overall folding of the chain due to H-bonds, disulphide bridges, van der Waals and electrostatic forces – gives fibrous or globular shape.

Quaternary: spatial arrangement of two or more polypeptide subunits, e.g. haemoglobin has four subunits.

Named Reactions – Conditions and Products

Named reactions are asked almost every year in CHSE (2-3 marks each: name, equation, condition). The table below adds full conditions for reactions that are often confused; Finkelstein, Swarts, Williamson, Reimer-Tiemann, Kolbe, Rosenmund, Stephen, Etard, Cannizzaro, HVZ and carbylamine reactions are listed in the Name Reactions table of the Practice section and in the model papers.

Name	Reaction (reagents / conditions)	Product
Wurtz	$2 \text{ R-X} + 2 \text{ Na}$, dry ether	$\text{R-R} + 2 \text{ NaX}$
Wurtz-Fittig	$\text{Ar-X} + \text{R-X} + 2 \text{ Na}$, dry ether	Ar-R (e.g. toluene from $\text{C}_6\text{H}_5\text{Br} + \text{CH}_3\text{Br}$)
Fittig	$2 \text{ Ar-X} + 2 \text{ Na}$, dry ether	Ar-Ar (biphenyl)
Sandmeyer	$\text{ArN}_2^+\text{Cl}^- + \text{CuCl/HCl}$, CuBr/HBr or CuCN/KCN	Ar-Cl , Ar-Br , $\text{Ar-CN} + \text{N}_2$
Gattermann (halide)	$\text{ArN}_2^+\text{Cl}^- + \text{Cu powder} / \text{HCl}$ or HBr	Ar-Cl , Ar-Br
Friedel-Crafts alkylation	$\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl}$, anhyd. AlCl_3	Toluene + HCl
Friedel-Crafts acylation	$\text{C}_6\text{H}_6 + \text{CH}_3\text{COCl}$, anhyd. AlCl_3	Acetophenone + HCl
Gattermann-Koch	$\text{C}_6\text{H}_6 + \text{CO} + \text{HCl}$, anhyd. $\text{AlCl}_3/\text{CuCl}$	Benzaldehyde
Clemmensen reduction	$>\text{C=O} + \text{Zn-Hg} / \text{conc. HCl}$	$>\text{CH}_2$
Wolff-Kishner reduction	$>\text{C=O} + \text{NH}_2\text{NH}_2$, then $\text{KOH} / \text{ethylene glycol}$, heat	$>\text{CH}_2 + \text{N}_2$

Name	Reaction (reagents / conditions)	Product
Aldol condensation	2 CH ₃ CHO, dil. NaOH (needs α-H)	CH ₃ CH(OH)CH ₂ CHO → on heating CH ₃ CH=CHCHO (but-2-enal)
Cross aldol	Two different carbonyls with α-H, dil. NaOH	Mixture of four products
Kolbe electrolysis	Electrolysis of aq. CH ₃ COONa	C ₂ H ₆ at anode + CO ₂ ; H ₂ at cathode
Decarboxylation	R-COONa + NaOH/CaO (soda lime), heat	R-H + Na ₂ CO ₃
Hoffmann bromamide degradation	R-CONH ₂ + Br ₂ + 4 NaOH	R-NH ₂ (one C less) + Na ₂ CO ₃ + 2 NaBr + 2 H ₂ O
Gabriel phthalimide	Phthalimide + KOH, then R-X, then NaOH(aq)	Pure 1° amine R-NH ₂ (not aromatic amines)
Hinsberg test	Amine + C ₆ H ₅ SO ₂ Cl	1°: product soluble in KOH; 2°: insoluble; 3°: no reaction
Diazotisation	C ₆ H ₅ NH ₂ + NaNO ₂ + 2 HCl, 273–278 K	C ₆ H ₅ N ₂ ⁺ Cl [−] + NaCl + 2 H ₂ O
Coupling reaction	C ₆ H ₅ N ₂ ⁺ Cl [−] + phenol (pH 9–10) or aniline (pH 4–5)	p-hydroxyazobenzene (orange) / p-aminoazobenzene (yellow)

EXAM TIP

For a named reaction, always write (1) the name, (2) a balanced equation with a specific example (for example, use CH₃CHO rather than only R-CHO), and (3) the condition or catalyst above the arrow. Missing the catalyst usually costs half a mark.

Organic Conversions – Solved Bank

Each conversion is written as a chain of steps. Reagents are given in brackets over each arrow.

1. Ethanol to propanenitrile.

$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{(\text{SOCl}_2 \text{ or } \text{PCl}_5)} \text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{(\text{alc. KCN})} \text{CH}_3\text{CH}_2\text{CN}$. The carbon chain increases by one carbon.

2. Ethanol to but-1-yne.

$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{(\text{SOCl}_2)} \text{CH}_3\text{CH}_2\text{Cl}$. Separately, $\text{HC}\equiv\text{CH} + \text{NaNH}_2 \rightarrow \text{HC}\equiv\text{C}^-\text{Na}^+$. Then $\text{HC}\equiv\text{CNa} + \text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{HC}\equiv\text{C-CH}_2\text{CH}_3 + \text{NaCl}$.

3. Benzene to 4-bromonitrobenzene.

$\text{C}_6\text{H}_6 \xrightarrow{(\text{Br}_2/\text{FeBr}_3)} \text{C}_6\text{H}_5\text{Br} \xrightarrow{(\text{conc. HNO}_3 + \text{conc. H}_2\text{SO}_4)} \text{p-BrC}_6\text{H}_4\text{NO}_2$ (major, with some ortho). Bromination is done first because Br is o/p-directing; $-\text{NO}_2$ is m-directing.

4. Toluene to benzyl alcohol.

$\text{C}_6\text{H}_5\text{CH}_3 \xrightarrow{(\text{Cl}_2, h\nu)} \text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{(\text{aq. KOH})} \text{C}_6\text{H}_5\text{CH}_2\text{OH}$.

5. Propene to propan-1-ol.

$\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow{(\text{B}_2\text{H}_6, \text{ then } \text{H}_2\text{O}_2/\text{OH}^-)} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (hydroboration-oxidation gives anti-Markovnikov product).

6. Propene to propan-2-ol.

$\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow{(\text{H}_2\text{O}, \text{H}_2\text{SO}_4)} \text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ (Markovnikov addition of water).

7. Phenol to aspirin.

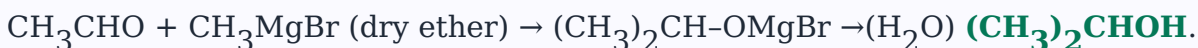
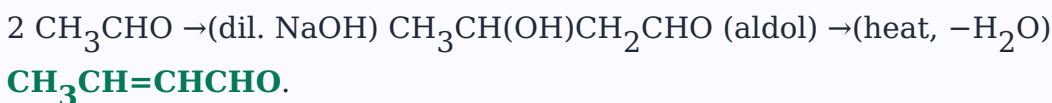
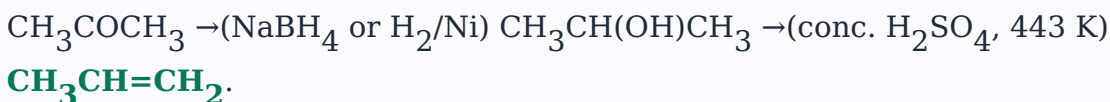
$\text{C}_6\text{H}_5\text{OH} \xrightarrow{(\text{NaOH})} \text{C}_6\text{H}_5\text{ONa} \xrightarrow{(\text{CO}_2, 400 \text{ K}, 4-7 \text{ atm}; \text{H}^+)} \text{salicylic acid} \xrightarrow{((\text{CH}_3\text{CO})_2\text{O}, \text{H}^+)} \text{acetylsalicylic acid (aspirin)}$.

8. Phenol to benzene.

$\text{C}_6\text{H}_5\text{OH} + \text{Zn (dust, heat)} \rightarrow \text{C}_6\text{H}_6 + \text{ZnO}$.

9. Phenol to picric acid.

$\text{C}_6\text{H}_5\text{OH} \xrightarrow{(\text{conc. H}_2\text{SO}_4)} \text{phenol-2,4-disulphonic acid} \xrightarrow{(\text{conc. HNO}_3)} \text{2,4,6-trinitrophenol}$. Sulphonation first avoids oxidation of phenol by conc. HNO_3 .

10. Ethanal to propan-2-ol.**11. Ethanal to but-2-enal.****12. Propanone to propene.**

"Give Reasons" Bank – Physical and Inorganic

1. Molality is preferred to molarity in colligative property work.

Molality uses mass of solvent, which does not change with temperature; molarity uses volume, which expands or contracts with temperature.

2. Aquatic animals feel more comfortable in cold water than in warm water.

Solubility of O_2 in water decreases with rise of temperature (K_{H} increases), so cold water holds more dissolved oxygen.

3. Scuba divers use air diluted with helium.

At high pressure underwater, more N_2 dissolves in blood (Henry's law); on rising it forms bubbles (the bends). Helium is much less soluble in blood, so it reduces this danger.

4. Common salt is spread on icy roads in winter.

NaCl depresses the freezing point of water, so ice melts at temperatures below 0°C .

5. A raw mango placed in concentrated salt solution shrivels.

Salt solution is hypertonic; water moves out of the mango cells by osmosis (exosmosis).

6. Osmotic pressure method is preferred for finding molar mass of proteins.

Proteins are unstable at high temperature, and their solutions give very small ΔT_{b} or ΔT_{f} . Osmotic pressure is measured at room temperature and is large enough to measure accurately even for dilute solutions.

7. Abnormal molar mass is obtained for acetic acid in benzene.

Acetic acid dimerises in benzene by hydrogen bonding, so the number of particles halves ($i \approx 0.5$) and the observed molar mass is nearly double (about 120 g mol^{-1}).

8. Conductivity of an electrolyte decreases on dilution, but molar conductivity increases.

Conductivity is conductance of 1 cm^3 ; on dilution the number of ions per cm^3 falls. Molar conductivity $\Lambda_{\text{m}} = \kappa \times 1000/C$ refers to the whole solution containing 1 mol; the volume increases faster than κ falls, and interionic attraction decreases, so Λ_{m} rises.

9. Λ_{m}° of a weak electrolyte cannot be found by extrapolation.

For a weak electrolyte, Λ_m rises steeply at very low concentration and the curve does not become linear, so extrapolation to $C = 0$ is not possible. Kohlrausch's law is used instead.

10. In the electrolysis of aqueous NaCl, H_2 (not Na) is liberated at the cathode.

E° of H_2O/H_2 (-0.83 V) is much higher than E° of Na^+/Na (-2.71 V), so water is reduced more easily.

"Give Reasons" Bank – Organic Chemistry

1. Haloalkanes are only slightly soluble in water though they are polar.

Energy needed to break the H-bonds among water molecules is not compensated by the weak dipole interactions formed between haloalkane and water.

2. Boiling points: $CH_3I > CH_3Br > CH_3Cl > CH_3F$.

Molecular size and mass increase, so van der Waals forces increase.

3. Among isomeric butyl bromides, the tert-isomer has the lowest boiling point.

Branching makes the molecule more spherical; surface area and hence van der Waals forces decrease.

4. Haloarenes are less reactive than haloalkanes towards nucleophilic substitution.

(i) Resonance gives the C-X bond partial double-bond character; (ii) the carbon is sp^2 (more electronegative, shorter bond); (iii) the phenyl cation is unstable; (iv) the π -electron cloud repels the incoming nucleophile.

5. A nitro group at ortho or para position increases the reactivity of chlorobenzene towards nucleophiles.

The $-NO_2$ group withdraws electron density and stabilises the negatively charged carbanion intermediate by resonance; meta $-NO_2$ cannot do so.

6. Chloroform is stored in dark coloured, completely filled bottles.

In light and air it is oxidised to poisonous phosgene: $2 CHCl_3 + O_2 \rightarrow 2 COCl_2 + 2 HCl$. A full bottle leaves no air.

7. Grignard reagents must be prepared under anhydrous conditions.

They react with even traces of water to give alkanes: $RMgX + H_2O \rightarrow RH + Mg(OH)X$.

8. S_N1 reactions of optically active halides give racemic mixtures.

The planar carbocation intermediate can be attacked from both faces equally.

9. Reactivity order for S_N2 : $CH_3X > 1^\circ > 2^\circ > 3^\circ$.

Bulky groups hinder the back-side attack of the nucleophile (steric hindrance).

10. Alcohols have higher boiling points than ethers or alkanes of similar mass.

Alcohol molecules are associated by intermolecular hydrogen bonding.

11. Phenol is more acidic than ethanol.

Phenoxide ion is resonance stabilised (negative charge delocalised over the ring); ethoxide ion has no resonance and is destabilised by the +I effect of the ethyl group.

12. o-Nitrophenol is more volatile than p-nitrophenol.

o-Nitrophenol has intramolecular H-bonding; p-nitrophenol has intermolecular H-bonding (molecules associated). So o-isomer is steam volatile.

Distinction Tests (How will you distinguish?)

Pair	Reagent	Observation
Ethanol / methanol	$I_2 + NaOH$, warm (iodoform test)	Ethanol: yellow CHI_3 . Methanol: none.
Propan-2-ol / propan-1-ol	Iodoform test	Propan-2-ol: yellow ppt. Propan-1-ol: none.
1°, 2°, 3° alcohols	Lucas reagent (conc. $HCl + anhyd. ZnCl_2$)	3°: turbidity at once; 2°: in about 5 minutes; 1°: no turbidity at room temperature.
Phenol / ethanol	Neutral $FeCl_3$	Phenol: violet colour. Ethanol: none.
Phenol / benzoic acid	$NaHCO_3$	Benzoic acid: brisk effervescence (CO_2). Phenol: none.
Ethanal / propanone	Tollens' reagent	Ethanal: silver mirror. Propanone: none.
Benzaldehyde / acetaldehyde	Fehling's solution	Acetaldehyde: red ppt of Cu_2O . Benzaldehyde: none.
Propanal / propanone	Iodoform test or Fehling's	Propanone: yellow CHI_3 . Propanal: red ppt with Fehling's.
Formic acid / acetic acid	Tollens' reagent	Formic acid: silver mirror.
Methylamine / dimethylamine	Carbylamine test	Methylamine: foul smell of isocyanide.
Aniline / benzylamine	HNO_2 (0-5 °C) then β -naphthol	Aniline: orange-red azo dye. Benzylamine: N_2 gas, no dye.
Aniline / N-methylaniline	Carbylamine test	Aniline only gives isocyanide smell.
Chlorobenzene / benzyl chloride	Aq. $NaOH$, then $HNO_3 + AgNO_3$	Benzyl chloride: white ppt of $AgCl$. Chlorobenzene: none.
Glucose / sucrose	Fehling's or Tollens'	Glucose: positive. Sucrose: negative.
Starch / glucose	Iodine solution	Starch: blue-black colour.

ODOFORM TEST - WHO GIVES IT?

Compounds containing CH_3CO- or $CH_3CH(OH)-$ groups: ethanol, ethanal, propan-2-ol, propanone, butan-2-ol, butan-2-one, acetophenone. Methanol, formaldehyde, propanal, propan-1-ol, benzaldehyde and pentan-3-one do **not** give it.

Model Paper 1 (Solved)

PATTERN USED

Full marks 70, time 3 hours. Section A: $14 \times 1 = 14$ (7 MCQs + 7 very short answers).
Section B: $7 \times 2 = 14$ (answer any 7 of 9). Section C: $6 \times 3 = 18$ (answer any 6 of 8).
Section D: $4 \times 6 = 24$ (answer any 4, with internal choice). This follows the usual CHSE layout; always confirm the blueprint printed in the current year's syllabus booklet.

Section A (1 mark each)

1. Which of the following aqueous solutions has the highest boiling point? (a) 0.1 M glucose (b) 0.1 M NaCl (c) 0.1 M BaCl₂ (d) 0.1 M urea

(c) BaCl₂ gives 3 ions ($i = 3$), the largest number of particles.

2. The unit of rate constant of a first-order reaction is (a) mol L⁻¹ s⁻¹ (b) s⁻¹ (c) L mol⁻¹ s⁻¹ (d) unitless

(b) s⁻¹.

3. The IUPAC name of [Co(NH₃)₅Cl]Cl₂ is

Pentaamminechloridocobalt(III) chloride.

4. Which lanthanoid shows +4 oxidation state? (a) La (b) Ce (c) Gd (d) Lu

(b) Ce ($4f^0$ in Ce⁴⁺).

5. The reagent used to convert an alcohol into an alkyl chloride with only gaseous by-products is

Thionyl chloride, SOCl₂ (by-products SO₂ and HCl).

6. Which amine gives the carbylamine test? (a) (CH₃)₂NH (b) (CH₃)₃N (c) C₆H₅NH₂ (d) C₆H₅NHCH₃

(c) Only primary amines.

7. The linkage joining monosaccharide units in a disaccharide is called

Glycosidic linkage.

8. Define molal elevation constant.

The elevation in boiling point produced when 1 mol of a non-volatile solute is dissolved in 1 kg of solvent.

9. What is the oxidation state of Cr in K₂Cr₂O₇?

+6.

10. Write the formula of the iodoform-forming group in ketones.

CH₃CO- (methyl ketone group).

11. Why is phenol acidic?

Its conjugate base, phenoxide ion, is stabilised by resonance.

12. Name the vitamin whose deficiency causes scurvy.

Vitamin C (ascorbic acid).

13. What is the molecularity of an elementary reaction $2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$?

2 (bimolecular).

14. Give one example of an ambidentate ligand.

NO_2^- (bonds through N or O); also SCN^- .

Section B (2 marks each)**15. State Henry's law and give one application.**

The partial pressure of a gas in the vapour phase is proportional to its mole fraction in solution: $p = K_{\text{H}} x$. Application: soft drink bottles are sealed under high CO_2 pressure to increase the solubility of CO_2 .

16. What is a fuel cell? Write the electrode reactions of the H_2 - O_2 fuel cell.

A galvanic cell converting the energy of combustion of a fuel directly into electricity.

Anode: $2 \text{H}_2 + 4 \text{OH}^- \rightarrow 4 \text{H}_2\text{O} + 4 \text{e}^-$. Cathode: $\text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^-$.

17. Calculate the spin-only magnetic moment of Fe^{2+} ($Z = 26$).

$\text{Fe}^{2+} = 3\text{d}^6$, $n = 4$ unpaired. $\mu = \sqrt{n(n+2)} = \sqrt{24} = \mathbf{4.90 \text{ BM}}$.

18. Write the Finkelstein reaction.

$\text{CH}_3\text{CH}_2\text{Br} + \text{NaI} \rightarrow (\text{dry acetone}) \text{CH}_3\text{CH}_2\text{I} + \text{NaBr} \downarrow$. NaBr is insoluble in acetone, so the equilibrium shifts forward.

19. Write the Reimer-Tiemann reaction.

$\text{C}_6\text{H}_5\text{OH} + \text{CHCl}_3 + \text{aq. NaOH (340 K)} \rightarrow \text{intermediate, then } \text{H}^+ \rightarrow \text{salicylaldehyde (o-HOC}_6\text{H}_4\text{CHO)}$.

20. Distinguish between ethanal and propanone by a chemical test.

Tollens' test: ethanal gives a silver mirror; propanone does not. (Iodoform: both positive, so it cannot be used here.)

21. Why is aniline less basic than ethylamine?

In aniline the N lone pair is delocalised into the ring; in ethylamine the +I effect of C_2H_5 increases electron density on N.

22. What are essential amino acids? Give two examples.

Amino acids not synthesised in the body and supplied through diet, e.g., valine, leucine (also lysine, threonine).

23. What is the effect of a catalyst on activation energy and on equilibrium?

It lowers activation energy by providing an alternative path; it does not change ΔG or the equilibrium constant, only helps reach equilibrium faster.

Section C (3 marks each)

24. 10 g of urea ($M = 60$) is dissolved in 250 g of water. Calculate the depression in freezing point. ($K_f = 1.86 \text{ K kg mol}^{-1}$)

$m = (10/60)/0.250 = 0.667 \text{ mol kg}^{-1}$. $\Delta T_f = 1.86 \times 0.667 = \mathbf{1.24 \text{ K}}$. Freezing point = 271.91 K ($-1.24 \text{ }^\circ\text{C}$).

25. Calculate the emf of the cell $\text{Zn} | \text{Zn}^{2+}(0.1 \text{ M}) || \text{Cu}^{2+}(0.01 \text{ M}) | \text{Cu}$ at 298 K . ($E^\circ_{\text{cell}} = 1.10 \text{ V}$)

$\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$, $n = 2$. $E = E^\circ - (0.0591/2) \log([\text{Zn}^{2+}]/[\text{Cu}^{2+}]) = 1.10 - 0.02955 \times \log 10 = \mathbf{1.07 \text{ V}}$.

26. A first-order reaction is 30% complete in 40 minutes. Calculate its half-life.

$k = (2.303/40) \log(100/70) = (2.303/40) \times 0.1549 = 8.92 \times 10^{-3} \text{ min}^{-1}$. $t_{1/2} = 0.693/k = \mathbf{77.7 \text{ min}}$.

27. Explain, using valence bond theory, the geometry and magnetic nature of $[\text{Co}(\text{NH}_3)_6]^{3+}$.

$\text{Co}^{3+} = 3d^6$. NH_3 here acts as a strong-field ligand, so the six d electrons pair into three 3d orbitals, leaving two 3d orbitals empty. Hybridisation d^2sp^3 (inner orbital), **octahedral, diamagnetic** (no unpaired electron).

28. Write the mechanism of S_N1 hydrolysis of tert-butyl bromide.

Step 1 (slow, rate-determining): $(\text{CH}_3)_3\text{C}-\text{Br} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Br}^-$. Step 2 (fast): $(\text{CH}_3)_3\text{C}^+ + \text{OH}^- \rightarrow (\text{CH}_3)_3\text{C}-\text{OH}$. Rate = $k[(\text{CH}_3)_3\text{CBr}]$; first order. The 3° carbocation is stabilised by hyperconjugation and +I effect; polar protic solvents favour the reaction.

29. How is phenol prepared from cumene? Why is this method important?

Cumene + $\text{O}_2 \rightarrow$ cumene hydroperoxide; then dil. $\text{H}_2\text{SO}_4 \rightarrow$ phenol + acetone. It is the main industrial method; the by-product acetone is also valuable.

30. Write the Cannizzaro reaction and aldol condensation, one example each.

$2 \text{HCHO} + \text{conc. NaOH} \rightarrow \text{CH}_3\text{OH} + \text{HCOONa}$. $2 \text{CH}_3\text{CHO} \xrightarrow{(\text{dil. NaOH})} \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO} \xrightarrow{(\text{heat})} \text{CH}_3\text{CH}=\text{CHCHO} + \text{H}_2\text{O}$.

31. What is denaturation of proteins? Give one example.

Loss of biological activity due to disruption of secondary and tertiary structure by heat, pH change or chemicals; primary structure remains. Examples: coagulation of egg white on boiling, curdling of milk.

Section D (6 marks each)

32. (a) State Kohlrausch's law and give two applications. (b) Calculate ΔG° for the Daniell cell ($E^\circ = 1.10$ V).

(a) At infinite dilution each ion contributes a definite amount to the molar conductivity of the electrolyte: $\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$. Applications: (i) Λ_m° of weak electrolytes, e.g., $\Lambda^\circ(\text{CH}_3\text{COOH}) = \Lambda^\circ(\text{CH}_3\text{COONa}) + \Lambda^\circ(\text{HCl}) - \Lambda^\circ(\text{NaCl})$; (ii) degree of dissociation $\alpha = \Lambda_m / \Lambda_m^\circ$ and dissociation constant $K_a = C\alpha^2 / (1 - \alpha)$. (b) $\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.10 = -212300 \text{ J} = -212.3 \text{ kJ mol}^{-1}$.

33. Describe the preparation of KMnO_4 from pyrolusite. Write its reactions with (i) Fe^{2+} and (ii) oxalate in acid medium.

Fusion: $2 \text{MnO}_2 + 4 \text{KOH} + \text{O}_2 \rightarrow 2 \text{K}_2\text{MnO}_4 + 2 \text{H}_2\text{O}$. Oxidation: $3 \text{MnO}_4^{2-} + 4 \text{H}^+ \rightarrow 2 \text{MnO}_4^- + \text{MnO}_2 + 2 \text{H}_2\text{O}$ (or electrolytic oxidation). (i) $\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 5 \text{Fe}^{3+} + 4 \text{H}_2\text{O}$. (ii) $2 \text{MnO}_4^- + 16 \text{H}^+ + 5 \text{C}_2\text{O}_4^{2-} \rightarrow 2 \text{Mn}^{2+} + 10 \text{CO}_2 + 8 \text{H}_2\text{O}$.

34. (a) Write Hoffmann bromamide and Gabriel phthalimide reactions. (b) How will you convert aniline to phenol and to benzonitrile?

(a) $\text{CH}_3\text{CONH}_2 + \text{Br}_2 + 4 \text{NaOH} \rightarrow \text{CH}_3\text{NH}_2 + \text{Na}_2\text{CO}_3 + 2 \text{NaBr} + 2 \text{H}_2\text{O}$. Phthalimide + KOH $\rightarrow$ potassium phthalimide; + $\text{C}_2\text{H}_5\text{Br} \rightarrow$ N-ethylphthalimide; + NaOH(aq) $\rightarrow$ $\text{C}_2\text{H}_5\text{NH}_2$ + sodium phthalate. (b) Aniline $\rightarrow$ (NaNO_2/HCl , 273–278 K) $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$; warm with water $\rightarrow$ phenol; with CuCN/KCN $\rightarrow$ benzonitrile.

35. Describe the open-chain structure of glucose with evidence. Why is the cyclic structure needed?

Evidence: (i) HI $\rightarrow$ n-hexane (6 C straight chain); (ii) $\text{NH}_2\text{OH} \rightarrow$ oxime, HCN $\rightarrow$ cyanohydrin (C=O present); (iii) Br_2 water $\rightarrow$ gluconic acid ($-\text{CHO}$); (iv) acetic anhydride $\rightarrow$ pentaacetate (five $-\text{OH}$); (v) $\text{HNO}_3 \rightarrow$ saccharic acid ($1^\circ -\text{OH}$). Cyclic form needed because glucose does not give Schiff's test, does not form NaHSO_3 adduct, its pentaacetate does not react with NH_2OH , and it exists as α and β anomers (mutarotation). The C5 $-\text{OH}$ adds to the $-\text{CHO}$ forming a six-membered pyranose ring.

Model Paper 2 (Solved)

Section A (1 mark each)

1. Azeotropes showing negative deviation have (a) minimum boiling point (b) maximum boiling point (c) no fixed composition (d) zero vapour pressure

(b) Maximum boiling point.

2. For a zero-order reaction, $t_{1/2}$ is (a) independent of $[R]_0$ (b) proportional to $[R]_0$ (c) proportional to $1/[R]_0$ (d) constant

(b) $t_{1/2} = [R]_0/2k$.

3. The coordination number of Fe in $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ is (a) 3 (b) 4 (c) 6 (d) 8

(c) 6 (oxalate is bidentate).

4. Which is the strongest acid? (a) CH_3COOH (b) ClCH_2COOH (c) Cl_2CHCOOH (d) Cl_3CCOOH

(d) Three $-I$ chlorine atoms.

5. Which reagent converts acid chlorides to aldehydes? (a) LiAlH_4 (b) $\text{H}_2/\text{Pd}-\text{BaSO}_4$ (c) NaBH_4 (d) $\text{Zn}-\text{Hg}/\text{HCl}$

(b) Rosenmund reduction.

6. Mutarotation is shown by (a) sucrose (b) glucose (c) starch (d) cellulose

(b) Glucose.

7. The $\text{S}_{\text{N}}2$ reaction proceeds with (a) racemisation (b) retention (c) inversion of configuration (d) no change

(c) Inversion (Walden inversion).

8. What is the SI unit of molar conductivity?

$\text{S m}^2 \text{ mol}^{-1}$.

9. Which transition metal of 3d series has the highest melting point?

Chromium (Cr).

10. Name the product when ethanol reacts with conc. H_2SO_4 at 413 K.

Diethyl ether (ethoxyethane).

11. Write the structure of Hinsberg's reagent.

$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ (benzenesulphonyl chloride).

12. Which base is present in RNA but not in DNA?

Uracil.

13. What is the value of van't Hoff factor for K_2SO_4 on complete dissociation?

3.

14. What is the hybridisation of Ni in $[\text{Ni}(\text{CO})_4]$?

sp^3 (tetrahedral, diamagnetic).

Section B (2 marks each)

15. Calculate the osmotic pressure of a 0.1 M glucose solution at 27 °C. ($R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$)

$\pi = CRT = 0.1 \times 0.0821 \times 300 = 2.46 \text{ atm}$.

16. The conductivity of 0.20 M KCl is 0.0248 S cm^{-1} . Calculate its molar conductivity.

$\Lambda_{\text{m}} = \kappa \times 1000/C = 0.0248 \times 1000/0.20 = 124 \text{ S cm}^2 \text{ mol}^{-1}$.

17. What is lanthanoid contraction? Give one consequence.

Steady decrease in size of atoms and Ln^{3+} ions from La to Lu due to imperfect shielding by 4f electrons. Consequence: Zr and Hf have nearly identical radii.

18. Write any two differences between $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$.

$\text{S}_{\text{N}}1$: two steps, carbocation intermediate, first order, racemisation, favoured by 3° halides. $\text{S}_{\text{N}}2$: one step, transition state, second order, inversion, favoured by 1° halides.

19. Write the Williamson ether synthesis. Why can't tert-butyl bromide be used with sodium methoxide?

$\text{CH}_3\text{ONa} + \text{CH}_3\text{CH}_2\text{Br} \rightarrow \text{CH}_3\text{OCH}_2\text{CH}_3 + \text{NaBr}$. With a 3° halide, the strongly basic alkoxide causes elimination, giving 2-methylpropene.

20. Write the Clemmensen and Wolff-Kishner reductions.

$\text{CH}_3\text{COCH}_3 + 4[\text{H}] \xrightarrow{(\text{Zn-Hg/conc. HCl})} \text{CH}_3\text{CH}_2\text{CH}_3 + \text{H}_2\text{O}$. $\text{CH}_3\text{COCH}_3 \xrightarrow{(\text{NH}_2\text{NH}_2; \text{KOH, ethylene glycol, heat})} \text{CH}_3\text{CH}_2\text{CH}_3 + \text{N}_2$.

21. Write the coupling reaction of benzene diazonium chloride with phenol.

$\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{C}_6\text{H}_5\text{OH} \xrightarrow{(\text{OH}^-, \text{pH } 9-10)} \text{p-HO-C}_6\text{H}_4\text{-N=N-C}_6\text{H}_5$ (orange dye) + HCl .

22. What are reducing sugars? Give one example.

Sugars with a free aldehyde or ketone group that reduce Fehling's and Tollens' reagents, e.g., glucose, maltose.

23. What is pseudo first-order reaction? Give an example.

A reaction of higher molecularity which behaves as first order because one reactant is in large excess, e.g., acid hydrolysis of ethyl acetate in water: $\text{rate} = k'[\text{ester}]$.

Section C (3 marks each)

24. A current of 1.5 A is passed through AgNO_3 solution for 10 minutes. Calculate the mass of silver deposited. ($\text{Ag} = 108$)

$Q = It = 1.5 \times 600 = 900 \text{ C}$. $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$, so 96500 C deposit 108 g. $\text{Mass} = 900 \times 108/96500 = \mathbf{1.007 \text{ g}}$.

25. The rate constant of a reaction doubles when temperature rises from 300 K to 310 K. Calculate E_a .

$\log(k_2/k_1) = (E_a/2.303R)(T_2 - T_1)/(T_1T_2)$. $\log 2 = 0.3010 = E_a \times 10/(2.303 \times 8.314 \times 300 \times 310)$. $E_a = 53604 \text{ J} = \mathbf{53.6 \text{ kJ mol}^{-1}}$.

26. A first-order reaction has $k = 1.15 \times 10^{-3} \text{ s}^{-1}$. How long will 5 g of reactant take to reduce to 3 g?

$t = (2.303/k) \log([R]_0/[R]) = (2.303/1.15 \times 10^{-3}) \log(5/3) = 2003 \times 0.2218 = \mathbf{444 \text{ s}}$ (about 7.4 min).

27. Calculate the equilibrium constant of $\text{Cu} + 2 \text{Ag}^+ \rightleftharpoons \text{Cu}^{2+} + 2 \text{Ag}$. ($E^\circ_{\text{Ag}^+/\text{Ag}} = 0.80 \text{ V}$, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V}$)

$$E^\circ_{\text{cell}} = 0.80 - 0.34 = 0.46 \text{ V}, n = 2. \log K = nE^\circ/0.0591 = 2 \times 0.46/0.0591 = 15.57. K = 3.7 \times 10^{15}.$$

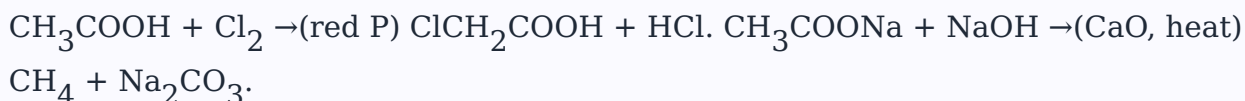
28. Explain crystal field splitting in an octahedral complex. Why is $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ violet?

Six ligands approach along the axes. The e_g orbitals ($d_{x^2-y^2}$, d_{z^2}) pointing at the ligands are raised by $0.6 \Delta_o$; the t_{2g} orbitals (d_{xy} , d_{yz} , d_{xz}) are lowered by $0.4 \Delta_o$. Ti^{3+} ($3d^1$) electron in t_{2g} absorbs green-yellow light (about 498 nm) and jumps to e_g ; the complementary violet colour is seen.

29. Explain why chlorobenzene undergoes electrophilic substitution at ortho and para positions though Cl is deactivating.

–I effect of Cl withdraws electrons from the whole ring, so the rate is slower than benzene (deactivation). But +R effect of the Cl lone pair increases electron density specifically at ortho and para positions, so the electrophile enters there. Example: chlorination gives 1,2- and 1,4-dichlorobenzene.

30. Write the HVZ reaction and decarboxylation reaction.



31. Distinguish between DNA and RNA (any three points).

DNA: sugar 2-deoxyribose, bases A, G, C, T, double helix, responsible for heredity.

RNA: sugar ribose, bases A, G, C, U, single strand, controls protein synthesis.

Section D (6 marks each)

32. (a) Explain Raoult's law for a solution of two volatile liquids with a graph description. (b) What are positive and negative deviations? Give one example of each.

(a) $p_A = p^\circ_A x_A$, $p_B = p^\circ_B x_B$, $p_{\text{total}} = p^\circ_A + (p^\circ_B - p^\circ_A)x_B$. Plotting against x_B , the partial pressures and total pressure are straight lines; total lies between p°_A and p°_B .

(b) Positive deviation: A-B attraction weaker than A-A and B-B; p higher than predicted, $\Delta H_{\text{mix}} > 0$, $\Delta V_{\text{mix}} > 0$; e.g., ethanol + acetone. Negative deviation: A-B attraction stronger; p lower, $\Delta H_{\text{mix}} < 0$, $\Delta V_{\text{mix}} < 0$; e.g., chloroform + acetone.

33. Compare the lanthanoids and actinoids (four points). Write the general electronic configuration of the f-block.

General configuration: $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$. Comparison: (i) Lanthanoids mainly +3; actinoids show +3 to +7. (ii) Most lanthanoids are non-radioactive (except Pm); all actinoids are radioactive. (iii) Actinoid contraction is greater than lanthanoid contraction (poorer shielding by 5f). (iv) Actinoids form complexes more readily and form oxocations such as UO_2^{2+} .

34. An organic compound A (C_2H_4O) gives a silver mirror with Tollens' reagent and a yellow precipitate with $I_2/NaOH$. A on treatment with dilute NaOH gives B, which on heating gives C (C_4H_6O). Identify A, B and C with equations.

A gives both Tollens' and iodoform tests with formula C_2H_4O : **A = ethanal, CH_3CHO** .
 $2 CH_3CHO \xrightarrow{\text{dil. NaOH}}$ **B = $CH_3CH(OH)CH_2CHO$** (3-hydroxybutanal, aldol)
 $\xrightarrow{\text{heat, } -H_2O}$ **C = $CH_3CH=CHCHO$** (but-2-enal, C_4H_6O). Tests: $CH_3CHO + 2[Ag(NH_3)_2]^+ + 3 OH^- \rightarrow CH_3COO^- + 2 Ag + 4 NH_3 + 2 H_2O$; $CH_3CHO + 3 I_2 + 4 NaOH \rightarrow CHI_3 + HCOONa + 3 NaI + 3 H_2O$.

35. (a) Describe the classification of amines with examples. (b) Arrange in increasing order of basic strength in water: $C_6H_5NH_2$, NH_3 , $(C_2H_5)_2NH$, $C_2H_5NH_2$. Justify.

(a) Primary $R-NH_2$ (ethylamine), secondary R_2NH (diethylamine), tertiary R_3N (triethylamine); aryl amines such as aniline $C_6H_5NH_2$. (b) **$C_6H_5NH_2 < NH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$** . Aniline is weakest due to resonance of the lone pair with the ring; alkyl groups (+I) raise electron density on N; the 2° amine benefits from two alkyl groups while still being well solvated.

SELF-CHECK

Time yourself: 3 hours for each paper. Mark with the solutions and note the chapters where you lost marks; revise those question banks again.

100+ MCQs with Answers

Chapter-wise objective questions. Cover the answer column, attempt all questions, then check.

Solutions

No.	Question	Ans
1	Molality is expressed in (a) mol L^{-1} (b) mol kg^{-1} (c) g L^{-1} (d) mol	(b)
2	Which is a colligative property? (a) Surface tension (b) Viscosity (c) Osmotic pressure (d) Refractive index	(c)
3	Normal saline is (a) 0.9% NaCl (b) 9% NaCl (c) 0.09% NaCl (d) 1.9% NaCl	(a)
4	van't Hoff factor for acetic acid in benzene is about (a) 2 (b) 1 (c) 0.5 (d) 3	(c)
5	Ethanol-water azeotrope shows (a) negative deviation (b) positive deviation (c) ideal behaviour (d) no deviation	(b)
6	Gas solubility in a liquid with rise of temperature (a) increases (b) decreases (c) stays same (d) first rises then falls	(b)
7	Relative lowering of vapour pressure equals (a) mole fraction of solvent (b) mole fraction of solute (c) molality (d) molarity	(b)
8	K_f of water is (a) 0.52 (b) 1.86 (c) 5.12 (d) $3.9 \text{ K kg mol}^{-1}$	(b)
9	Reverse osmosis is used for (a) desalination (b) distillation (c) electrolysis (d) chromatography	(a)
10	A solution with higher osmotic pressure than blood is (a) isotonic (b) hypotonic (c) hypertonic (d) neutral	(c)

Electrochemistry

No.	Question	Ans
11	1 Faraday equals (a) 9650 C (b) 96500 C (c) 965 C (d) 6.02×10^{23} C	(b)
12	Salt bridge contains (a) KCl or KNO_3 in agar (b) NaOH (c) H_2SO_4 (d) CuSO_4	(a)
13	E° of SHE is (a) 1 V (b) 0.0 V (c) -0.76 V (d) 0.34 V	(b)
14	Unit of conductivity κ is (a) S cm^{-1} (b) $\text{S cm}^2 \text{ mol}^{-1}$ (c) $\Omega \text{ cm}$ (d) S	(a)
15	Cell constant equals (a) A/l (b) l/A (c) $l \times A$ (d) $R \times A$	(b)
16	Rusting of iron is (a) reduction (b) electrochemical oxidation (c) neutralisation (d) hydrolysis	(b)
17	Mercury cell gives a constant voltage of about (a) 1.35 V (b) 2.0 V (c) 1.5 V (d) 12 V	(a)
18	Lead storage battery anode is (a) PbO_2 (b) Pb (c) PbSO_4 (d) H_2SO_4	(b)
19	A cell reaction is spontaneous when (a) $E_{\text{cell}} < 0$ (b) $\Delta G > 0$ (c) $E_{\text{cell}} > 0$ (d) $K < 1$	(c)
20	Strongest reducing agent among the following: (a) Li (b) Na (c) K (d) Zn	(a)

Chemical Kinetics

No.	Question	Ans
21	Order of radioactive decay is (a) 0 (b) 1 (c) 2 (d) 3	(b)
22	Half-life of a first-order reaction (a) depends on $[R]_0$ (b) is independent of $[R]_0$ (c) is $1/k$ (d) is $2/k$	(b)
23	Unit of k for a zero-order reaction is (a) s^{-1} (b) $\text{mol L}^{-1} s^{-1}$ (c) $\text{L mol}^{-1} s^{-1}$ (d) none	(b)
24	Slope of $\ln k$ vs $1/T$ plot is (a) E_a/R (b) $-E_a/R$ (c) $-E_a/2.303R$ (d) A	(b)
25	A catalyst changes (a) ΔH (b) equilibrium constant (c) activation energy (d) ΔG	(c)
26	Molecularity can never be (a) 1 (b) 2 (c) 3 (d) fractional	(d)
27	Inversion of cane sugar is (a) zero order (b) pseudo first order (c) second order (d) third order	(b)
28	For a first-order reaction $t_{99\%}$ is about (a) $2 t_{1/2}$ (b) $5 t_{1/2}$ (c) $6.64 t_{1/2}$ (d) $10 t_{1/2}$	(c)
29	Rate of reaction generally doubles for a rise of (a) 1 K (b) 10 K (c) 50 K (d) 100 K	(b)
30	Arrhenius factor A is also called (a) frequency factor (b) rate factor (c) energy factor (d) order	(a)

d- and f-Block Elements

No.	Question	Ans
31	Which ion is colourless? (a) Cu^{2+} (b) Ti^{3+} (c) Zn^{2+} (d) Fe^{3+}	(c)
32	Highest oxidation state of Mn is (a) +4 (b) +6 (c) +7 (d) +8	(c)
33	Colour of $\text{K}_2\text{Cr}_2\text{O}_7$ is (a) yellow (b) orange (c) green (d) purple	(b)
34	Equivalent weight of KMnO_4 in acid medium ($M = 158$) is (a) 158 (b) 52.7 (c) 31.6 (d) 79	(c)
35	Most common oxidation state of lanthanoids is (a) +2 (b) +3 (c) +4 (d) +5	(b)
36	Misch metal contains mainly (a) lanthanoid metal with Fe (b) Cu and Zn (c) Ni and Cr (d) Hg and Sn	(a)
37	Which has the maximum number of unpaired electrons? (a) Fe^{3+} (b) Fe^{2+} (c) Co^{2+} (d) Ni^{2+}	(a)
38	Zr and Hf have similar size due to (a) actinoid contraction (b) lanthanoid contraction (c) inert pair effect (d) shielding by s electrons	(b)
39	Interstitial compounds are (a) very soft (b) hard with high melting points (c) gases (d) ionic	(b)
40	Catalyst in contact process is (a) Fe (b) Ni (c) V_2O_5 (d) Pt only	(c)

Coordination Compounds

No.	Question	Ans
41	EDTA is a (a) monodentate (b) bidentate (c) tetradentate (d) hexadentate ligand	(d)
42	Oxidation state of Fe in $K_4[Fe(CN)_6]$ is (a) +2 (b) +3 (c) +4 (d) 0	(a)
43	$[Pt(NH_3)_2Cl_2]$ shows (a) optical isomerism (b) geometrical isomerism (c) ionisation isomerism (d) linkage isomerism	(b)
44	Strongest field ligand: (a) Cl^- (b) H_2O (c) NH_3 (d) CN^-	(d)
45	Hybridisation in $[Ni(CN)_4]^{2-}$ is (a) sp^3 (b) dsp^2 (c) d^2sp^3 (d) sp^3d^2	(b)
46	Number of ions from $[Co(NH_3)_6]Cl_3$ in water (a) 2 (b) 3 (c) 4 (d) 6	(c)
47	Wilkinson's catalyst contains (a) Rh (b) Pt (c) Fe (d) Ti	(a)
48	Chlorophyll contains (a) Fe (b) Co (c) Mg (d) Cu	(c)
49	$[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$ are (a) linkage (b) ionisation (c) hydrate (d) coordination isomers	(a)
50	Vitamin B_{12} contains (a) Fe (b) Co (c) Mg (d) Zn	(b)

Haloalkanes and Haloarenes

No.	Question	Ans
51	Freon-12 is (a) CCl_4 (b) CCl_2F_2 (c) $CHCl_3$ (d) CF_4	(b)
52	S_N2 is fastest for (a) CH_3Br (b) 1° bromide (c) 2° bromide (d) 3° bromide	(a)
53	Alkyl halide + alc. KOH gives (a) alcohol (b) alkene (c) ether (d) alkane	(b)
54	Saytzeff rule predicts (a) less substituted alkene (b) more substituted alkene (c) alkyne (d) alcohol	(b)
55	Chloroform in air and light forms (a) CO_2 (b) phosgene (c) CCl_4 (d) methanol	(b)
56	DDT is (a) an antibiotic (b) an insecticide (c) a dye (d) a polymer	(b)
57	Racemic mixture is (a) optically active (b) optically inactive by external compensation (c) meso (d) achiral molecule	(b)
58	Product of $C_2H_5Br + AgCN$ is (a) C_2H_5CN (b) C_2H_5NC (c) C_2H_5OH (d) C_2H_6	(b)
59	Chlorobenzene + $Cl_2/FeCl_3$ gives mainly (a) m-dichlorobenzene (b) o- and p-dichlorobenzene (c) benzene (d) phenol	(b)
60	Iodoform is used as (a) anaesthetic (b) antiseptic (c) solvent (d) refrigerant	(b)

Alcohols, Phenols and Ethers

No.	Question	Ans
61	Wood spirit is (a) ethanol (b) methanol (c) propanol (d) glycerol	(b)
62	Lucas reagent is (a) conc. HCl + anhyd. ZnCl_2 (b) conc. $\text{HNO}_3 + \text{H}_2\text{SO}_4$ (c) $\text{NaOH} + \text{I}_2$ (d) KMnO_4	(a)
63	Most acidic: (a) phenol (b) p-nitrophenol (c) p-cresol (d) ethanol	(b)
64	Phenol + Br_2 water gives (a) o-bromophenol (b) 2,4,6-tribromophenol (white ppt) (c) p-bromophenol only (d) no reaction	(b)
65	Phenol with neutral FeCl_3 gives (a) violet colour (b) red ppt (c) white ppt (d) no change	(a)
66	Anisole is (a) $\text{C}_6\text{H}_5\text{OCH}_3$ (b) $\text{C}_6\text{H}_5\text{OH}$ (c) $\text{C}_6\text{H}_5\text{CHO}$ (d) $\text{C}_6\text{H}_5\text{CH}_3$	(a)
67	Ethanol to ethene: conc. H_2SO_4 at (a) 413 K (b) 443 K (c) 273 K (d) 373 K	(b)
68	Denatured alcohol contains (a) CuSO_4 and pyridine (b) NaCl (c) glycerol (d) acetone	(a)
69	Hydroboration-oxidation of propene gives (a) propan-2-ol (b) propan-1-ol (c) propanal (d) propanone	(b)
70	Kolbe's reaction product is (a) salicylaldehyde (b) salicylic acid (c) benzoic acid (d) picric acid	(b)

Aldehydes, Ketones and Carboxylic Acids

No.	Question	Ans
71	Formalin is a 40% aqueous solution of (a) HCHO (b) CH_3CHO (c) HCOOH (d) CH_3OH	(a)
72	Tollens' reagent is (a) ammoniacal AgNO_3 (b) alkaline CuSO_4 (c) KMnO_4 (d) $\text{K}_2\text{Cr}_2\text{O}_7$	(a)
73	Cannizzaro reaction is given by (a) CH_3CHO (b) $\text{C}_6\text{H}_5\text{CHO}$ (c) CH_3COCH_3 (d) $\text{CH}_3\text{CH}_2\text{CHO}$	(b)
74	Ketones do not reduce (a) Tollens' (b) Fehling's (c) both (d) neither	(c)
75	2,4-DNP gives with carbonyls (a) yellow-orange ppt (b) white ppt (c) blue colour (d) gas	(a)
76	Strongest acid: (a) HCOOH (b) CH_3COOH (c) $\text{C}_2\text{H}_5\text{COOH}$ (d) $\text{C}_3\text{H}_7\text{COOH}$	(a)
77	Vinegar contains (a) 6-8% acetic acid (b) 40% formic acid (c) oxalic acid (d) citric acid only	(a)
78	Etard reagent is (a) CrO_2Cl_2 (b) KMnO_4 (c) SnCl_2 (d) PCl_5	(a)
79	Benzoic acid on nitration gives (a) o-nitro (b) m-nitrobenzoic acid (c) p-nitro (d) mixture of o and p	(b)
80	Acetone with CH_3MgBr then H_2O gives (a) 1° alcohol (b) 2° alcohol (c) 3° alcohol (d) ketone	(c)

Amines

No.	Question	Ans
81	Most basic in water: (a) NH_3 (b) CH_3NH_2 (c) $(\text{CH}_3)_2\text{NH}$ (d) $\text{C}_6\text{H}_5\text{NH}_2$	(c)
82	Diazotisation is done at (a) 273–278 K (b) 373 K (c) 300 K (d) 473 K	(a)
83	Hinsberg's reagent distinguishes (a) 1° , 2° , 3° amines (b) aldehydes and ketones (c) acids (d) sugars	(a)
84	Aniline + CHCl_3 + alc. KOH gives (a) phenyl isocyanide (b) chlorobenzene (c) benzonitrile (d) phenol	(a)
85	Reduction of nitrobenzene with Sn/HCl gives (a) aniline (b) azobenzene (c) phenol (d) benzene	(a)
86	Hoffmann bromamide degradation decreases carbon number by (a) 0 (b) 1 (c) 2 (d) 3	(b)
87	Tertiary amines with HNO_2 (aliphatic) form (a) N_2 gas (b) nitrite salts (c) alcohols (d) diazonium salts	(b)
88	Coupling with aniline is carried out at (a) pH 4–5 (b) pH 9–10 (c) pH 13 (d) pH 7 exactly	(a)
89	Sulphanilic acid exists as (a) zwitterion (b) free acid only (c) gas (d) anion only	(a)
90	Acetanilide is prepared from aniline by (a) acetylation (b) nitration (c) diazotisation (d) reduction	(a)

Biomolecules

No.	Question	Ans
91	Glucose is (a) aldohexose (b) ketohexose (c) aldopentose (d) disaccharide	(a)
92	Sucrose on hydrolysis gives (a) glucose + fructose (b) glucose + galactose (c) 2 glucose (d) fructose only	(a)
93	Amylose has (a) α -1,4 links, unbranched (b) β -1,4 links (c) α -1,6 branches only (d) peptide bonds	(a)
94	Peptide bond is (a) $-\text{CO}-\text{NH}-$ (b) $-\text{COO}-$ (c) $-\text{O}-$ (d) $-\text{NH}-\text{NH}-$	(a)
95	α -Helix is stabilised by (a) H-bonds (b) ionic bonds (c) disulphide bonds only (d) metallic bonds	(a)
96	Enzymes are mainly (a) carbohydrates (b) proteins (c) lipids (d) vitamins	(b)
97	Fat-soluble vitamins are (a) A, D, E, K (b) B and C (c) B only (d) C only	(a)
98	Deficiency of vitamin D causes (a) scurvy (b) rickets (c) beri-beri (d) night blindness	(b)
99	In DNA, adenine pairs with (a) guanine (b) cytosine (c) thymine (d) uracil	(c)
100	Nucleotide = (a) base + sugar (b) base + sugar + phosphate (c) sugar + phosphate (d) base + phosphate	(b)
101	Optically inactive amino acid: (a) glycine (b) alanine (c) valine (d) lysine	(a)
102	Insulin regulates (a) blood sugar (b) blood pressure (c) calcium (d) iodine	(a)

Practical Guide – Salt Analysis

PRACTICAL EXAM PLAN

Practical carries 30 marks (usual split: salt analysis, volumetric titration, organic functional group test, project or record, and viva). Write observations in a three-column table: Experiment | Observation | Inference.

Preliminary tests

Test	Observation	Inference
Colour of salt	Blue / green	Cu^{2+} / Ni^{2+} , Fe^{2+}
	Light pink / white	Mn^{2+} / Zn^{2+} , Al^{3+} , Ca^{2+} , Ba^{2+} , NH_4^+
Flame test (with conc. HCl paste)	Brick red / crimson / apple green / bluish green	Ca^{2+} / Sr^{2+} / Ba^{2+} / Cu^{2+}
Salt + NaOH, warm	Smell of ammonia; white fumes with HCl rod	NH_4^+

Anions (acid radicals)

Salt + reagent	Observation	Confirmatory test
Dil. H_2SO_4	Brisk effervescence, gas turns lime water milky	CO_3^{2-} : with MgSO_4 solution, white ppt
Dil. H_2SO_4	Rotten-egg smell, lead acetate paper turns black	S^{2-} : sodium nitroprusside gives purple/violet colour
Dil. H_2SO_4	Light brown fumes	NO_2^- : KI + starch turns blue
Dil. H_2SO_4	Vinegar smell	CH_3COO^- : neutral FeCl_3 gives blood-red colour

Salt + reagent	Observation	Confirmatory test
Conc. H_2SO_4	Colourless pungent gas, white fumes with NH_3 rod	Cl^- : AgNO_3 gives white ppt soluble in NH_4OH ; chromyl chloride test (red vapours)
Conc. H_2SO_4	Reddish brown vapours	Br^- : AgNO_3 gives pale yellow ppt, partly soluble in NH_4OH ; CCl_4 layer turns orange with Cl_2 water
Conc. H_2SO_4	Violet vapours	I^- : AgNO_3 gives yellow ppt insoluble in NH_4OH ; CCl_4 layer violet
Conc. H_2SO_4 + Cu turnings	Brown fumes (NO_2)	NO_3^- : brown ring test with FeSO_4 and conc. H_2SO_4
Independent test	BaCl_2 : white ppt insoluble in conc. HCl	SO_4^{2-} : lead acetate gives white ppt soluble in ammonium acetate
Independent test	Ammonium molybdate + conc. HNO_3 , warm: canary yellow ppt	PO_4^{3-}

Cations (basic radicals) – group separation

Group	Group reagent	Ions	Precipitate
0	NaOH , heat	NH_4^+	NH_3 gas (Nessler's reagent: brown ppt)
I	Dil. HCl	Pb^{2+}	PbCl_2 (white, soluble in hot water; yellow with KI or K_2CrO_4)
II	H_2S in dil. HCl	Cu^{2+} , Pb^{2+} , As^{3+}	CuS black (blue solution with NH_4OH ; chocolate ppt with $\text{K}_4[\text{Fe}(\text{CN})_6]$); As_2S_3 yellow
III	NH_4OH + NH_4Cl	Fe^{3+} , Al^{3+}	$\text{Fe}(\text{OH})_3$ brown (Prussian blue with $\text{K}_4[\text{Fe}(\text{CN})_6]$); $\text{Al}(\text{OH})_3$ white gelatinous (blue lake test)
IV	H_2S in NH_4OH	Zn^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+}	ZnS white, MnS buff/pink, NiS and CoS black (Ni: red ppt with dimethylglyoxime)
V	$(\text{NH}_4)_2\text{CO}_3$ in NH_4OH	Ba^{2+} , Sr^{2+} , Ca^{2+}	White carbonates; Ba: yellow ppt with K_2CrO_4 ; Ca: white ppt with ammonium oxalate
VI	No group reagent	Mg^{2+}	White ppt with Na_2HPO_4 + NH_4OH

WHY NH_4Cl IN GROUP III?

Common-ion effect: NH_4Cl suppresses ionisation of NH_4OH , so $[\text{OH}^-]$ is just enough to precipitate Group III hydroxides (very low K_{sp}) but not Group IV, V or Mg hydroxides. Similarly HCl suppresses H_2S ionisation in Group II so that only the very insoluble Group II sulphides precipitate.

Practical Guide – Titration and Organic Tests

Redox titration with KMnO_4

- KMnO_4 is a self-indicator: end point is the first **permanent light pink** colour.
- Medium: dil. H_2SO_4 only. HCl is not used (it is oxidised to Cl_2); HNO_3 is not used (it is itself an oxidant).
- Oxalic acid titration is done at 60–70 °C because the reaction is slow at room temperature; Mn^{2+} formed acts as autocatalyst. Mohr's salt titration is done cold (heat would oxidise Fe^{2+} by air).
- Molar ratio: $\text{MnO}_4^- : \text{C}_2\text{O}_4^{2-} = 2 : 5$; $\text{MnO}_4^- : \text{Fe}^{2+} = 1 : 5$. Formula: $a_1M_1V_1 = a_2M_2V_2$, where a = electrons exchanged per formula unit (KMnO_4 5, oxalic acid 2, Mohr's salt 1).

1. How much oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, $M = 126$) is needed to prepare 250 mL of 0.05 M solution?

Mass = $M \times V(\text{L}) \times \text{molar mass} = 0.05 \times 0.250 \times 126 = \mathbf{1.575 \text{ g}}$.

2. 10 mL of 0.05 M oxalic acid needs 20 mL of KMnO_4 . Find the molarity and strength of KMnO_4 .

$5 \times M \times 20 = 2 \times 0.05 \times 10$, so $M = \mathbf{0.01 \text{ M}}$. Strength = $0.01 \times 158 = \mathbf{1.58 \text{ g L}^{-1}}$.

3. Mass of Mohr's salt ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, $M = 392$) for 250 mL of 0.05 M solution? If 20 mL of it needs 20 mL KMnO_4 , find $M(\text{KMnO}_4)$.

Mass = $0.05 \times 0.250 \times 392 = \mathbf{4.9 \text{ g}}$. $5 \times M \times 20 = 1 \times 0.05 \times 20$, so $M = \mathbf{0.01 \text{ M}}$.

Organic functional group tests

Group	Test	Positive result
Unsaturation (C=C)	Br ₂ in CCl ₄ ; Baeyer's reagent (cold dil. alkaline KMnO ₄)	Bromine colour discharged; pink colour discharged, brown MnO ₂
Alcohol (-OH)	Ceric ammonium nitrate; sodium metal	Red colour; H ₂ effervescence
Phenol	Neutral FeCl ₃ ; Liebermann's nitroso test	Violet colour; deep blue/green with NaOH
Aldehyde and ketone	2,4-DNP	Yellow-orange ppt
Aldehyde only	Tollens', Fehling's, Schiff's reagent	Silver mirror; red ppt; pink colour restored
Methyl ketone	Iodoform test (I ₂ + NaOH)	Yellow ppt of CHI ₃
Carboxylic acid	NaHCO ₃ ; ester test (ethanol + conc. H ₂ SO ₄)	Effervescence of CO ₂ ; fruity smell
1° amine (aromatic)	Azo dye test (NaNO ₂ /HCl at 0-5 °C, then alkaline β-naphthol)	Orange-red dye
1° amine (any)	Carbylamine test	Offensive isocyanide smell
Carbohydrate	Molisch's test (α-naphthol + conc. H ₂ SO ₄)	Violet ring at junction
Protein	Biuret test (NaOH + dil. CuSO ₄); xanthoproteic test	Violet colour; yellow with conc. HNO ₃
Starch	Iodine solution	Blue-black colour

Viva voce – quick answers

1. Why is dil. HCl, not conc. HCl, used as Group I reagent?

Excess Cl⁻ from conc. HCl would dissolve PbCl₂ as the complex [PbCl₄]²⁻.

2. Why is the original solution boiled with conc. HNO₃ before Group III?

To oxidise Fe²⁺ to Fe³⁺; Fe(OH)₂ is not completely precipitated by NH₄OH.

3. What is the brown ring in the nitrate test?

[Fe(H₂O)₅NO]²⁺ (nitrosoferrous sulphate).

4. What is Nessler's reagent?

Alkaline solution of K₂[HgI₄]; gives brown ppt (iodide of Millon's base) with NH₄⁺.

RECORD WRITING FORMAT

Aim, apparatus and chemicals, theory (with balanced equations), procedure, observation table (burette readings with at least three concordant values), calculation and result with unit.

Concordant readings differ by not more than 0.1 mL.

PRACTICE & REVISION

Chemistry · +2 2nd Year (Class XII)

Chemistry – Numerical Problem Bank (Class XII)

1. Calculate the mole fraction of benzene in a solution containing 30% by mass of benzene in CCl_4 .

100 g: 30 g C_6H_6 (78) = 0.385 mol; 70 g CCl_4 (154) = 0.455 mol. $x = 0.385/0.840 =$ **0.459**.

2. 45 g ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) is mixed with 600 g water. Find the freezing point depression ($K_f = 1.86$).

$n = 45/62 = 0.726$ mol; $m = 0.726/0.6 = 1.21$. $\Delta T_f = 1.86 \times 1.21 =$ **2.25 K**.

3. Find the osmotic pressure of 0.1 M glucose at 27 °C ($R = 0.0821$).

$\pi = CRT = 0.1 \times 0.0821 \times 300 =$ **2.46 atm**.

4. Calculate E_{cell} of $\text{Ni} | \text{Ni}^{2+}(0.001 \text{ M}) || \text{Ag}^+(0.1 \text{ M}) | \text{Ag}$. $E^\circ(\text{Ni}) = -0.25 \text{ V}$, $E^\circ(\text{Ag}) = 0.80 \text{ V}$.

$E^\circ = 0.80 + 0.25 = 1.05 \text{ V}$. $\text{Ni} + 2\text{Ag}^+ \rightarrow \text{Ni}^{2+} + 2\text{Ag}$, $n = 2$. $E = 1.05 - (0.059/2) \log(0.001/0.01) = 1.05 - 0.0295(-1) =$ **1.0795 V**.

5. How much charge is needed to reduce 1 mol of MnO_4^- to Mn^{2+} ?

Mn: +7 $\rightarrow$ +2, 5 electrons. $Q = 5F =$ **482500 C**.

6. Λ°_m of acetic acid is $390.5 \text{ S cm}^2/\text{mol}$ and Λ_m at 0.001 M is 48.15. Find α and K_a .

$\alpha = 48.15/390.5 = 0.1233$. $K_a = C\alpha^2/(1 - \alpha) = 0.001 \times 0.0152/0.8767 =$ **1.73×10^{-5}** .

7. A first-order reaction is 20% complete in 10 min. Find k and the time for 75% completion.

$$k = (2.303/10) \log(100/80) = 0.2303 \times 0.0969 = 0.0223 \text{ min}^{-1}. t_{75} = (2.303/0.0223) \log 4 = 103.3 \times 0.602 = \approx \mathbf{62 \text{ min.}}$$

8. The half-life of a zero-order reaction is 20 min when $[R]_0 = 0.4 \text{ M}$. Find k.

$$t_{1/2} = [R]_0/2k \Rightarrow k = 0.4/40 = \mathbf{0.01 \text{ M min}^{-1}}.$$

9. Calculate the spin-only magnetic moment of Cr^{3+} ($Z = 24$).

$$\text{Cr}^{3+}: 3d^3, n = 3. \mu = \sqrt{15} = \mathbf{3.87 \text{ BM.}}$$

Chemistry – Name Reactions & Conversions (Class XII)

Name	Reaction
Finkelstein	$\text{R-Cl} + \text{NaI (acetone)} \rightarrow \text{R-I} + \text{NaCl}$
Swarts	$\text{R-Br} + \text{AgF} \rightarrow \text{R-F} + \text{AgBr}$
Sandmeyer	$\text{ArN}_2^+ \text{Cl}^- + \text{CuCl/CuBr/CuCN} \rightarrow \text{ArCl/ArBr/ArCN}$
Wurtz-Fittig	$\text{ArX} + \text{RX} + 2\text{Na} \rightarrow \text{Ar-R}$
Williamson	$\text{RX} + \text{R'ONa} \rightarrow \text{R-O-R'}$
Kolbe's (phenol)	Sodium phenoxide + $\text{CO}_2 \rightarrow$ salicylic acid
Reimer-Tiemann	Phenol + $\text{CHCl}_3 + \text{NaOH} \rightarrow$ salicylaldehyde
Rosenmund	$\text{RCOCl} + \text{H}_2 \text{ (Pd/BaSO}_4) \rightarrow \text{RCHO}$
Stephen	$\text{RCN} + \text{SnCl}_2/\text{HCl}, \text{H}_3\text{O}^+ \rightarrow \text{RCHO}$
Etard	Toluene + $\text{CrO}_2\text{Cl}_2 \rightarrow$ benzaldehyde
Clemmensen / Wolff-Kishner	$\text{C=O} \rightarrow \text{CH}_2$
Aldol condensation	$2\text{CH}_3\text{CHO (dil. NaOH)} \rightarrow \text{aldol} \rightarrow \text{but-2-enal}$
Cannizzaro	$2\text{HCHO} + \text{conc. NaOH} \rightarrow \text{CH}_3\text{OH} + \text{HCOONa}$
HVZ	$\text{RCH}_2\text{COOH} + \text{X}_2/\text{red P} \rightarrow \text{RCHXCOOH}$
Hoffmann bromamide	$\text{RCONH}_2 + \text{Br}_2 + 4\text{NaOH} \rightarrow \text{RNH}_2 \text{ (one C less)}$
Gabriel phthalimide	Phthalimide $\rightarrow$ pure 1° amine
Carbylamine	$\text{RNH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{RNC (foul smell)}$
Coupling	$\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{phenol} \rightarrow \text{p-hydroxyazobenzene (orange dye)}$

Distinction tests (very important)

Pair	Test
Ethanol vs methanol	Iodoform test: ethanol gives yellow ppt
Phenol vs ethanol	FeCl_3 : phenol violet
Ethanal vs propanone	Tollens'/Fehling's: ethanal positive
Propanal vs propanone	Tollens' (propanal); iodoform (propanone)
Benzaldehyde vs acetaldehyde	Fehling's: only acetaldehyde gives red ppt
Ethanoic acid vs phenol	NaHCO_3 : acid gives effervescence
1°, 2°, 3° amines	Hinsberg test; carbylamine (1° only)
Aniline vs ethylamine	Azo-dye test: aniline (diazotise + β -naphthol $\rightarrow$ orange-red dye)

Chemistry – Important Long-Answer Questions (Model Answers)**Q1. What are colligative properties? Show that elevation of boiling point is a colligative property and derive the formula for molar mass. [5]**

Colligative properties depend only on the number of solute particles, not on their nature. When a non-volatile solute is added, the vapour pressure of the solvent falls, so the solution must be heated to a higher temperature for its vapour pressure to equal atmospheric pressure. Experimentally, $\Delta T_b \propto m$, i.e. $\Delta T_b = K_b m$, where m depends only on the number of moles of solute. Since $m = (w_2/M_2) \times 1000/w_1$, we get $\Delta T_b = K_b \times w_2 \times 1000/(M_2 \times w_1)$, so $M_2 = K_b \times w_2 \times 1000/(\Delta T_b \times w_1)$.

Q2. Derive the integrated rate equation for a first-order reaction and show that its half-life is independent of initial concentration. [5]

For $R \rightarrow P$, rate = $-d[R]/dt = k[R]$. Rearranging: $d[R]/[R] = -k dt$. Integrating: $\ln[R] = -kt + I$. At $t = 0$, $[R] = [R]_0$, so $I = \ln[R]_0$. Hence $\ln([R]_0/[R]) = kt$, or $k = (2.303/t) \log([R]_0/[R])$. At $t = t_{1/2}$, $[R] = [R]_0/2$: $k = (2.303/t_{1/2}) \log 2 \Rightarrow t_{1/2} = 0.693/k$, which does not contain $[R]_0$.

Q3. Describe the construction and working of the lead storage battery. [5]

Anode: spongy lead; cathode: grid of lead packed with PbO_2 ; electrolyte: 38% H_2SO_4 .

Discharge: anode $\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2e^-$; cathode $\text{PbO}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$; overall $\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$. The acid is used up and density falls. **Charging:** an external current reverses the reaction, regenerating Pb , PbO_2 and H_2SO_4 . Each cell gives about 2 V; six cells give 12 V for vehicles and inverters.

Q4. Explain the crystal field splitting in an octahedral complex. How does it explain the colour and magnetic behaviour of complexes? [5]

In an octahedral complex, six ligands approach along the axes. The $d_{x^2-y^2}$ and d_{z^2} orbitals (e_g) point directly at the ligands and are raised in energy; d_{xy} , d_{yz} , d_{zx} (t_{2g}) lie

between the axes and are lowered. The gap is Δ_o . **Colour:** an electron in t_{2g} absorbs visible light of energy Δ_o and jumps to e_g ; the complementary colour is seen. **Magnetism:** with strong-field ligands (large Δ_o), electrons pair in t_{2g} (low spin, fewer unpaired electrons); with weak-field ligands they occupy e_g before pairing (high spin, more unpaired electrons, more paramagnetic). E.g. $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic while $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ has 4 unpaired electrons.

Q5. Explain the mechanism of S_N2 reaction with an example. Why does it lead to inversion? [5]

Example: $\text{CH}_3\text{Cl} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{Cl}^-$. The nucleophile OH^- attacks the carbon from the side opposite to Cl (back-side attack). In a single step a transition state forms in which carbon is partly bonded to both OH and Cl and the three H atoms lie in one plane. As the C-OH bond forms, the C-Cl bond breaks. The three groups flip over like an umbrella in a strong wind, so the configuration is inverted (Walden inversion). Rate = $k[\text{CH}_3\text{Cl}][\text{OH}^-]$ — second order. Reactivity: $\text{CH}_3\text{X} > 1^\circ > 2^\circ > 3^\circ$ due to steric hindrance.

Q6. Discuss the structure of glucose. What evidence shows that it has an aldehyde group and five -OH groups? Why is a cyclic structure needed? [5]

Molecular formula $\text{C}_6\text{H}_{12}\text{O}_6$; with HI it gives n-hexane (six carbons in a straight chain). With hydroxylamine it forms an oxime and with HCN a cyanohydrin (carbonyl present). Bromine water oxidises it to gluconic acid with the same number of carbons (the carbonyl is an aldehyde). Acetylation gives a pentaacetate (five -OH groups). However, glucose does not give Schiff's test or the NaHSO_3 addition product, and its pentaacetate does not react with NH_2OH . Also it exists in two forms (α and β) with different rotations (mutarotation). These facts are explained by a six-membered cyclic hemiacetal (pyranose) structure formed by reaction of the C5 -OH with the -CHO group.

Last-Minute Exam Tips

Chemistry

- Always write units: K kg mol^{-1} , $\text{S cm}^2 \text{ mol}^{-1}$, s^{-1} , V, J mol^{-1} .
- In Nernst equation questions, write the balanced cell reaction first to find n and Q.
- For organic conversions, write reagent and condition above the arrow (e.g. "alc. KOH, Δ ").
- Learn IUPAC names of complexes by practising 10 examples; alphabetical order of ligands is the most common mistake.
- Distinction tests: write the test, the observation for each compound and the equation if possible.
- In the practical, record observations in a three-column table: Experiment - Observation - Inference.

THE NIGHT BEFORE THE EXAM

Revise only formula boxes, name reactions, grammar rules and your own mistake list. Sleep well — a fresh mind solves problems faster than a tired one. Carry admit card, two pens, pencil, scale, eraser and a geometry box. Good luck!