

CBSE Class 12 Chemistry Question Paper 2004 with Solution PDF-Set 56/1 (Foreign)



Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) All questions are compulsory.
- (ii) Marks for each question are indicated against it.
- (iii) Question numbers 1 to 5 are very short-answer, carrying 1 mark each. Answer these in one word or about one-sentence each.
- (iv) Question numbers 6 to 12 are short-answer, carrying 2 marks each. Answer these in about 30 words each.
- (v) Question numbers 13 to 24 are short-answer questions of 3 marks each. Answer these in about 40 words each.
- (vi) Question numbers 25 and 27 are long-answer questions of 5 marks each. Answer these in about 70 words each.
- (vii) Use Log Tables, if necessary. Use of calculators is not permitted.

1. What is coordination number of a metal atom in ccp structure?

[1 mark]

Solution:

Concept:

- Coordination number is the number of nearest neighbouring atoms in direct contact with a chosen atom.
- Cubic close packing (ccp) has the same arrangement as a face-centred cubic (fcc) lattice.

Step 1: Identify the nearest neighbours In a close-packed layer, a metal atom touches six atoms in its own layer. Close packing places three atoms of the layer above and three atoms of the layer below in contact with it.

Step 2: Count all contacts The total number of nearest neighbours is therefore $6 + 3 + 3 = 12$. Count contacts in all three layers, rather than only the six visible in a single plane.

Step 3: Conclusion The coordination number of a metal atom in ccp is $\boxed{12}$.

Quick Tip to Solve: For ccp or hcp, count six neighbours in the same layer and three on either side.

2. State Raoult's law for a solution of volatile liquids.

[1 mark]

Solution:

Concept:

- Raoult's law applies to an ideal solution of volatile liquids at a fixed temperature.
- For component i , x_i is its liquid-phase mole fraction and p_i^0 is the vapour pressure of the pure liquid at that temperature.

Step 1: State the proportionality The partial vapour pressure of each volatile component over the solution is directly proportional to its mole fraction in the liquid solution.

Step 2: Write the mathematical relation Thus $p_i = x_i p_i^0$. For a binary solution, $p_A = x_A p_A^0$ and $p_B = x_B p_B^0$; the total pressure is the sum of these partial pressures, $p = p_A + p_B$.

Step 3: Conclusion Raoult's law: $\boxed{p_i = x_i p_i^0}$ for each volatile component of an ideal solution.

Quick Tip to Solve: Use the liquid mole fraction in Raoult's law; each component has its own pure-liquid vapour pressure.

3. Write the Arrhenius equation which relates the rate constant with temperature.

[1 mark]

Solution:

Concept:

- The Arrhenius equation expresses the temperature dependence of the reaction rate constant k .
- E_a is activation energy, R the gas constant, T absolute temperature and A the pre-exponential (frequency) factor.

Step 1: Relate energy and temperature The exponential factor $e^{-E_a/(RT)}$ represents the activation-

energy dependence. The exponent is dimensionless, so E_a and R must use consistent energy units, and T must be in kelvin.

Step 2: State the equation Multiplying this exponential factor by A gives the rate constant:

$$k = A \exp\left(-\frac{E_a}{RT}\right).$$

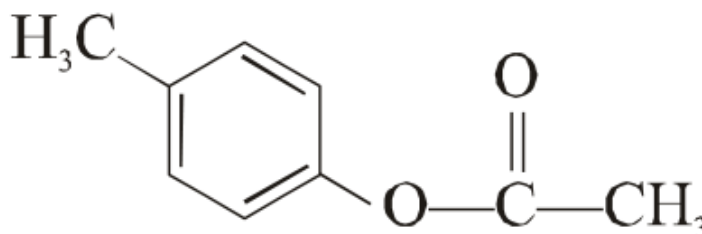
For positive activation energy, increasing temperature makes the exponent less negative and increases k .

Step 3: Conclusion $k = Ae^{-E_a/(RT)}$, with T measured in kelvin.

Quick Tip to Solve: Remember the negative sign in the exponent and always substitute temperature in kelvin.

4. Write the IUPAC name of the following:

[1 mark]



Solution:

Concept:

- An ester RCOOR' is named by naming the group attached to oxygen, followed by the carboxylate part.
- For a substituted phenyl group, assign position 1 to the ring carbon bonded to the ester oxygen.

Step 1: Identify the oxygen-linked group The oxygen bonded to the benzene ring is attached to a phenyl group bearing a methyl substituent opposite it. This is the para arrangement, so this group is named 4-methylphenyl.

Step 2: Identify the acid-derived part The carbonyl carbon is bonded to CH_3 , giving the acid-derived fragment $\text{CH}_3\text{COO}-$. Its systematic name is ethanoate. Combining the oxygen-linked group and acid-derived name gives the ester name.

Step 3: Conclusion The IUPAC name is 4-methylphenyl ethanoate.

Quick Tip to Solve: Start ring numbering at the carbon bonded to oxygen; the opposite methyl group is at position 4.

5. Arrange the following in the order of their increasing basic character in solution:

NH_3 , EtNH_2 , Et_2NH , Et_3N .

[1 mark]

Solution:

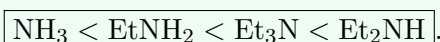
Concept:

- Basic strength in aqueous solution depends on electron donation to nitrogen and on the solvation of the conjugate acid.
- For ethylamines in water, the combined inductive and solvation effects give secondary amine greater basicity than tertiary, followed by primary amine.

Step 1: Compare with ammonia Ethyl groups donate electron density by the positive inductive effect, making the nitrogen lone pair more available for protonation. All three ethylamines listed are therefore stronger bases than ammonia in aqueous solution.

Step 2: Account for aqueous solvation Solvation stabilises the protonated amines. Although triethylamine has three electron-donating ethyl groups, its protonated ion is less effectively solvated than that of diethylamine. For these ethylamines, the observed order is diethylamine, then triethylamine, then ethylamine in decreasing basicity.

Step 3: Conclusion The increasing order is



Quick Tip to Solve: For ethylamines in water remember the order secondary > tertiary > primary > ammonia; include solvation.

6(a). Describe mathematically the formation of molecular orbitals in homonuclear diatomic hydrogen molecule by LCAO method.

[2 marks]

Solution:

Concept:

- In the linear combination of atomic orbitals (LCAO) method, atomic wave functions of comparable energy and suitable symmetry combine to form molecular wave functions.
- Let ϕ_A and ϕ_B be the normalized $1s$ atomic wave functions of the two hydrogen atoms. The overlap integral is $S = \int \phi_A \phi_B d\tau$.

Step 1: Construct the bonding molecular orbital Constructive addition of the two atomic wave functions gives the bonding orbital:

$$\psi_{\sigma 1s} = \frac{\phi_A + \phi_B}{\sqrt{2(1 + S)}}.$$

The positive cross term in $|\psi_{\sigma 1s}|^2$ increases electron density between the nuclei. Both nuclei attract this shared density, so the bonding orbital has lower energy than the separated atomic orbitals.

Step 2: Construct the antibonding orbital and fill the orbitals Destructive subtraction gives the

antibonding orbital:

$$\psi_{\sigma^*1s} = \frac{\phi_A - \phi_B}{\sqrt{2(1 - S)}}$$

Cancellation produces a node between the nuclei, and this orbital has higher energy. Thus two atomic orbitals produce two molecular orbitals. The two electrons of H_2 occupy the lower bonding orbital with opposite spins, giving $(\sigma 1s)^2$.

Step 3: Conclusion The sum $\phi_A + \phi_B$ forms bonding $\sigma 1s$, while the difference $\phi_A - \phi_B$ forms antibonding $\sigma^* 1s$; the ground state of H_2 is $(\sigma 1s)^2$.

Quick Tip to Solve: Remember addition means enhanced internuclear density, while subtraction introduces an internuclear node.

OR

6(b). Compare the relative stability of the following species and indicate their magnetic (diamagnetic or paramagnetic) behaviour:

B_2 and O_2^{2-}

[2 marks]

Solution:

Concept:

- Bond order is $BO = (N_b - N_a)/2$, where N_b and N_a count electrons in bonding and antibonding molecular orbitals.
- An unpaired electron makes a species paramagnetic; if all electrons are paired, it is diamagnetic. Equal bond orders imply equal stability in the usual bond-order comparison.

Step 1: Determine the bonding and magnetism of boron B_2 has ten electrons. Its configuration is

$$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^1(\pi 2p_y)^1.$$

For boron, the bonding $\pi 2p$ levels lie below $\sigma 2p$. Hund's rule puts the last two electrons separately in the degenerate π orbitals. Hence $N_b = 6$, $N_a = 4$, and $BO = 1$. There are two unpaired electrons, so it is paramagnetic.

Step 2: Determine the bonding and magnetism of peroxide O_2^{2-} has eighteen electrons. Its valence configuration is

$$(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x)^2(\pi 2p_y)^2(\pi^* 2p_x)^2(\pi^* 2p_y)^2.$$

The filled core bonding and antibonding levels cancel in the bond order. The valence counts are eight bonding and six antibonding electrons, so $BO = (8 - 6)/2 = 1$. All electrons are paired; therefore the ion is diamagnetic.

Step 3: Conclusion Both species have bond order 1, so they have equal relative stability on the bond-order criterion. B_2 is paramagnetic, whereas O_2^{2-} is diamagnetic.

Quick Tip to Solve: Add the two extra electrons of peroxide to the antibonding pi orbitals before checking the spin pairing.

7. Describe a Leclanche cell with special reference to (i) the electrodes used and (ii) the reactions occurring at the electrodes in the cell. [2 marks]

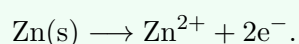
Solution:

Concept:

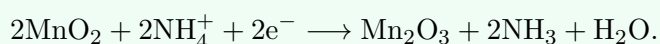
- A Leclanche cell is a primary galvanic cell: zinc undergoes oxidation at the negative anode and reduction takes place at the positive cathode.
- The electrolyte is ammonium chloride solution or a moist paste containing NH_4Cl and ZnCl_2 . Manganese dioxide acts as the cathodic oxidant (depolarizer).

Step 1: Identify the electrodes The anode is zinc, present as a zinc rod in the wet cell or as the zinc container in the dry form. The positive electrode consists of a graphite (carbon) rod surrounded by a mixture of manganese dioxide and powdered carbon. Graphite conducts electrons; manganese dioxide participates in the reduction.

Step 2: Write the electrode reactions At the anode, zinc supplies electrons by oxidation:



A conventional representation of the cathode process is



Here manganese is reduced from oxidation state +4 to +3. The ammonia produced can combine with zinc chloride, so the actual electrolyte contains zinc ammine species. The half-reactions show electron production and consumption explicitly.

Step 3: Conclusion The cell uses a zinc anode and a carbon cathode surrounded by MnO_2 . Zinc is oxidized and manganese dioxide is reduced in the ammonium chloride electrolyte.

Quick Tip to Solve: Write zinc oxidation first, then balance the cathode reaction with ammonium ions, ammonia and water.

8(a). Write the chemical equation for the reactions which occur when:

(i) R_2SiCl_2 is subjected to hydrolysis.

(ii) Sodium iodate, NaIO_3 is reduced with sodium hydrogen sulphite.

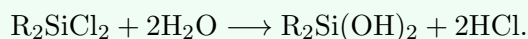
[2 marks]

Solution:

Concept:

- Hydrolysis replaces each $\text{Si} - \text{Cl}$ bond by $\text{Si} - \text{OH}$; the resulting silanediol condenses to form $\text{Si} - \text{O} - \text{Si}$ linkages.
- In iodate reduction, iodine changes from +5 to 0, while sulphur in hydrogen sulphite is oxidized from +4 to +6.

Step 1: Hydrolyse the organosilicon chloride The initial hydrolysis equation is

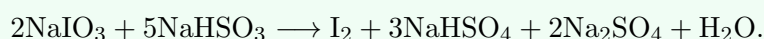


The two hydroxyl groups allow condensation with neighbouring molecules to form silicone chains. For a linear chain, an exact finite-chain equation is



Thus water first produces the silanediol, and elimination of water subsequently makes siloxane bonds.

Step 2: Reduce sodium iodate with sodium hydrogen sulphite The balanced equation for liberation of iodine is



Two iodine atoms together gain ten electrons, while five sulphur atoms together lose ten electrons. This verifies the redox coefficients. The equation also conserves sodium, hydrogen and oxygen; hydrogen sulphite is the reducing agent.

Step 3: Conclusion Hydrolysis gives $\text{R}_2\text{Si}(\text{OH})_2$, followed by silicone formation. Iodate reduction is $2\text{NaIO}_3 + 5\text{NaHSO}_3 \rightarrow \text{I}_2 + 3\text{NaHSO}_4 + 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$.

Quick Tip to Solve: For iodate to iodine, match the ten electrons gained by two iodines with five hydrogen sulphite ions.

OR

8(b). Write the chemical equation for the reactions which occur when:

(i) XeF_4 is subjected to hydrolysis.

(ii) SO_2 reacts with hydrogen sulphide (H_2S).

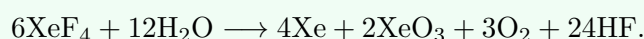
[2 marks]

Solution:

Concept:

- Hydrolysis replaces fluorine by oxygen-containing products; xenon tetrafluoride also undergoes disproportionation.
- In the reaction of sulphur dioxide with hydrogen sulphide, sulphur in oxidation states +4 and -2 forms elemental sulphur.

Step 1: (i) Hydrolysis of xenon tetrafluoride Complete hydrolysis of XeF_4 produces xenon, xenon trioxide, oxygen and hydrogen fluoride:



The equation conserves six xenon atoms, twenty-four fluorine atoms, twenty-four hydrogen atoms and twelve oxygen atoms. Xenon is partly reduced from +4 to zero and partly oxidised to +6.

Step 2: (ii) Reaction of sulphur dioxide with hydrogen sulphide Sulphur dioxide oxidises hydrogen

sulphide to sulphur while itself being reduced to sulphur:



The sulphur atom of SO_2 gains four electrons; each of the two sulphur atoms of H_2S loses two electrons. Thus the reactants are required in the molar ratio 1 : 2.

Step 3: Conclusion The required equations are $6\text{XeF}_4 + 12\text{H}_2\text{O} \rightarrow 4\text{Xe} + 2\text{XeO}_3 + 3\text{O}_2 + 24\text{HF}$ and $\text{SO}_2 + 2\text{H}_2\text{S} \rightarrow 3\text{S} + 2\text{H}_2\text{O}$.

Quick Tip to Solve: For the sulphur reaction, balance electron transfer first: one sulphur at +4 requires two sulphur atoms at -2.

9. The outer electronic configurations of two transition metals are (i) $3d^5 4s^2$ and (ii) $3d^6 4s^2$ respectively. Based on this information predict the relative stability of +2 and +3 oxidation states of these metals. Which one of the two exhibits larger number of oxidation states? [2 marks]

Solution:

Concept:

- For transition-metal cations, the $4s$ electrons are removed before the $3d$ electrons.
- A half-filled $3d^5$ subshell has enhanced stability; oxidation-state preferences can be predicted by comparing the resulting ionic configurations.

Step 1: Compare the +2 and +3 states Metal (i) is manganese, Mn, with outer configuration $3d^5 4s^2$. Its ions are $\text{Mn}^{2+} : 3d^5$ and $\text{Mn}^{3+} : 3d^4$. The +2 state is relatively more stable because it retains the half-filled subshell; oxidation to +3 removes this advantage. Metal (ii) is iron, Fe, with outer configuration $3d^6 4s^2$. Its ions are $\text{Fe}^{2+} : 3d^6$ and $\text{Fe}^{3+} : 3d^5$. The +3 state gains half-filled-shell stability and is favoured on this electronic-configuration basis.

Step 2: Compare the range of oxidation states Manganese exhibits the larger number of oxidation states. Its five $3d$ electrons and two $4s$ electrons allow a broad range, commonly +2, +3, +4, +5, +6, +7. Iron most commonly exhibits +2 and +3, with fewer commonly encountered higher states. The maximum common oxidation state of manganese, +7, corresponds to participation of all seven outer electrons.

Step 3: Conclusion Metal (i), manganese, favours +2; metal (ii), iron, gains extra stability in +3. Manganese exhibits the larger number of oxidation states.

Quick Tip to Solve: Remove the two $4s$ electrons first, then check which ion has the especially stable $3d^5$ configuration.

10. Explain the terms (i) asymmetric molecule and (ii) R and S notations.

[2 marks]

Solution:

Concept:

- Chirality describes a molecule whose mirror image cannot be superimposed on it.
- The Cahn–Ingold–Prelog priority rules give the absolute configuration of a stereogenic centre as *R* or *S*.

Step 1: (i) Asymmetric molecule An asymmetric molecule is one whose mirror image is non-superimposable on the original molecule; it is chiral. A typical example contains a tetrahedral carbon bonded to four different groups, such as $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$. Its central carbon carries H, OH, CH_3 and COOH. These arrangements give a pair of enantiomers. Merely having a carbon atom is insufficient: the four attached groups must be distinguishable in this simple case.

Step 2: (ii) R and S notations Assign priorities $1 > 2 > 3 > 4$ to the groups attached to the stereogenic centre using the Cahn–Ingold–Prelog rules: higher atomic number has higher priority, and ties are resolved at the first point of difference. View the molecule with the lowest-priority group, 4, pointing away. If the order $1 \rightarrow 2 \rightarrow 3$ is clockwise, the configuration is *R* (rectus); if anticlockwise, it is *S* (sinister). These symbols specify spatial configuration and do not predict the sign of optical rotation.

Step 3: Conclusion An asymmetric molecule is non-superimposable on its mirror image. With group 4 directed away, clockwise $1 \rightarrow 2 \rightarrow 3$ gives *R*, and anticlockwise gives *S*.

Quick Tip to Solve: Always point priority 4 away before reading the turn; R and S do not mean dextrorotatory and laevorotatory.

11. Describe the mechanism by which the hydroxyl group attached to an aromatic ring is more acidic than the hydroxyl group attached to an alkyl group. How does the presence of a nitro group in phenol affect its acidic character?

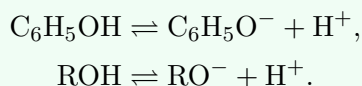
[2 marks]

Solution:

Concept:

- An acid is stronger when its conjugate base is more stable: $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$.
- Resonance delocalisation and electron-withdrawing groups stabilise a negative charge; electron-releasing alkyl groups tend to destabilise it.

Step 1: Explain the greater acidity of phenol Phenol and an alcohol lose a proton from their hydroxyl group:



In phenoxide, the oxygen lone pair conjugates with the aromatic ring. The negative charge is delocalised over oxygen and the ortho and para ring positions through resonance. In an alkoxide, the charge remains largely localised on oxygen; the alkyl group also releases electron density by its $+I$ effect. Phenoxide is therefore better stabilised relative to its parent acid, so phenol loses a proton more readily than an alcohol.

Step 2: Explain the effect of a nitro substituent A nitro group, $-\text{NO}_2$, withdraws electron density by its $-I$ effect and increases the acidity of phenol by stabilising the phenoxide ion. At ortho and para positions, its $-R$ effect additionally allows the anionic charge to be delocalised towards the nitro group. At the meta position, the principal stabilisation is inductive. Thus nitrophenols are more acidic than phenol.

Step 3: Conclusion Phenol is more acidic than an alcohol because its phenoxide conjugate base is resonance-stabilised. A nitro group increases acidity by withdrawing electron density and stabilising that base.

Quick Tip to Solve: Compare conjugate bases: spread-out negative charge favours acidity, and a nitro substituent stabilises phenoxide further.

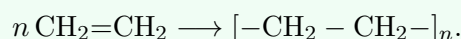
12. Distinguish between homopolymers and copolymers and give one example for each. [2 marks]

Solution:

Concept:

- A monomer is a small molecule that joins repeatedly to form a polymer. The distinction concerns the number of chemically different monomer species used.
- Repetition of one monomer species gives a homopolymer; polymerisation of two or more different monomer species together gives a copolymer.

Step 1: Homopolymer A homopolymer is formed from only one kind of monomer. For example, polyethene is obtained by addition polymerisation of ethene:



Every repeat unit comes from ethene. Many molecules of the same monomer are used, but there is only one monomer species.

Step 2: Copolymer A copolymer is formed by polymerising two or more different kinds of monomers together. For example, Buna-S is obtained from 1,3-butadiene, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, and styrene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$. Its polymer chains contain units derived from both monomers. This is incorporation into a polymer chain, rather than merely mixing two finished polymers.

Step 3: Conclusion Homopolymers use one monomer species (polyethene from ethene); copolymers use two or more different monomer species (Buna-S from butadiene and styrene).

Quick Tip to Solve: Count different monomer species, not the number of monomer molecules or the elements they contain.

13. What do you understand by (i) Radial probability density, R^2 and (ii) Radial probability function, $4\pi r^2 R^2$? Draw the curves obtained by plotting radial probability function versus r of the electron from the nucleus for 1s and 2s orbitals for hydrogen atom. [3 marks]

Solution:

Concept:

- For a hydrogen s orbital the electron density is spherically symmetric. In the notation of the question, $R^2(r)$ is the probability density per unit volume at distance r from the nucleus.
- A thin spherical shell of radius r and thickness dr has volume $4\pi r^2 dr$. The probability in that shell is $P(r)dr = 4\pi r^2 R^2(r)dr$, where $P(r)$ is the radial probability function.

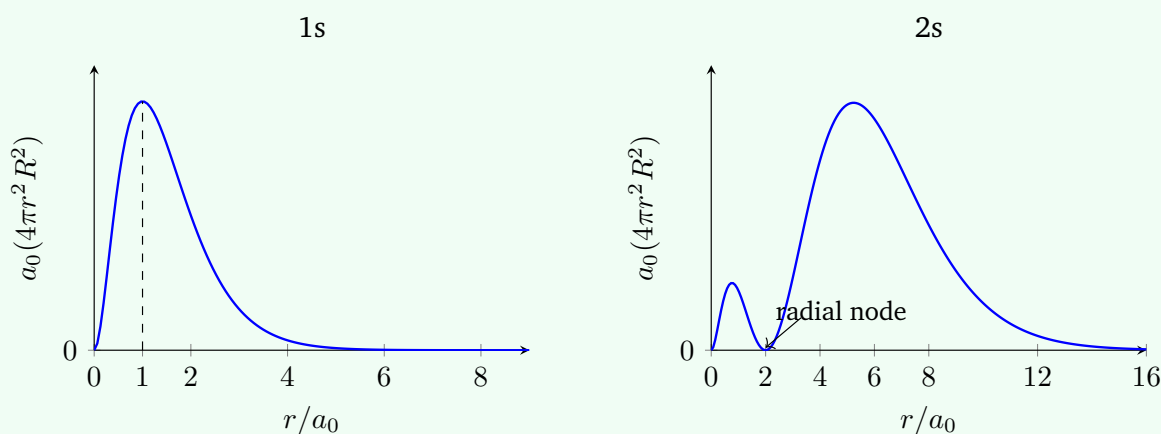
Step 1: Distinguish density from shell probability (i) R^2 , the radial probability density used here, describes the probability per unit volume at a given distance from the nucleus. Thus $R^2 dV$ gives the probability in a small volume dV . (ii) The radial probability function $4\pi r^2 R^2$ includes all points in the spherical shell at that distance. The probability of finding the electron between r and $r + dr$ is this function multiplied by dr . The area under its curve over a radial interval is the probability in that interval; the total area from zero to infinity is unity.

Step 2: Hydrogen 1s and 2s curves Put $x = r/a_0$, where a_0 is the Bohr radius. The normalised radial distributions are

$$a_0 P_{1s}(r) = 4x^2 e^{-2x},$$

$$a_0 P_{2s}(r) = \frac{1}{8} x^2 (2 - x)^2 e^{-x}.$$

Both curves start at zero because of the shell factor r^2 , even though the s-orbital density at the nucleus is nonzero. The 1s curve has one maximum at $r = a_0$, no radial node, and tends to zero at large r . The 2s curve has two maxima, separated by a radial node at $r = 2a_0$; its larger outer maximum lies farther from the nucleus. Both distributions approach zero asymptotically.



Radial probability distributions for hydrogen 1s and 2s orbitals; horizontal coordinate is distance in units of the Bohr radius.

Step 3: Conclusion R^2 gives density per unit volume, whereas $4\pi r^2 R^2$ gives probability per unit radial distance. The 1s distribution has one peak and no radial node; the 2s distribution has two peaks and one radial node at $2a_0$.

Quick Tip to Solve: Multiply the local density by the spherical-shell factor before sketching: every radial distribution starts at zero.

14. Calculate the density of silver which is known to crystallise in face-centred cubic form. The distance between the nearest metal atoms is 287 pm.

(Molar mass of Ag = 107.87 g mol⁻¹, N_A = 6.02 × 10²³ mol⁻¹)

[3 marks]

Solution:

Concept:

- An FCC unit cell contains $Z = 8(1/8) + 6(1/2) = 4$ atoms: corner atoms are shared by eight cells and face-centred atoms by two cells.
- In FCC, nearest neighbours touch along a face diagonal. If d is their separation and a the cell edge, $a\sqrt{2} = 2d$. Density is $\rho = ZM/(N_A a^3)$, where M is molar mass and N_A is the Avogadro constant.

Step 1: Find the unit-cell edge The given nearest-neighbour distance is $d = 287$ pm; it is not the cube edge. A face diagonal joins a corner, a face-centred atom and the opposite corner, so it contains two nearest-neighbour separations. Hence

$$a = \sqrt{2}d = \sqrt{2}(287) = 405.88 \text{ pm} = 4.0588 \times 10^{-8} \text{ cm}.$$

We use centimetres because the molar mass is given in grams and the required density can then be expressed in grams per cubic centimetre.

Step 2: Calculate the mass and volume of one cell The mass of four silver atoms and the volume of the cubic cell are

$$m_{\text{cell}} = \frac{4(107.87)}{6.02 \times 10^{23}} = 7.1674 \times 10^{-22} \text{ g}, \quad V_{\text{cell}} = (4.0588 \times 10^{-8})^3 = 6.6866 \times 10^{-23} \text{ cm}^3.$$

Therefore

$$\rho = \frac{7.1674 \times 10^{-22}}{6.6866 \times 10^{-23}} = 10.719 \text{ g cm}^{-3}.$$

The FCC atom count and the conversion of a length before cubing are both essential to this calculation.

Step 3: Conclusion The density of silver is 10.7 g cm^{-3} (approximately $1.07 \times 10^4 \text{ kg m}^{-3}$).

Quick Tip to Solve: For FCC, first convert nearest-neighbour distance to the edge using $a = \sqrt{2}d$; never substitute d directly into the cell volume.

15. Two elements A and B form compounds having molecular formulae AB₂ and AB₄. When dissolved in 20 g of benzene, 1 g of AB₂ lowers the freezing point by 2.3 K, whereas 1.0 g of AB₄ lowers it by 1.3 K. The molar depression constant for benzene is 5.1 K kg mol⁻¹. Calculate the atomic masses of A and B.

[3 marks]

Solution:

Concept:

- For a molecular solute without association or dissociation, freezing-point depression is $\Delta T_f = K_f m$, where m is moles of solute per kilogram of solvent.
- For solute mass w , solvent mass W in grams and solute molar mass M , $M = 1000K_f w / (\Delta T_f W)$.

The atomic masses of A and B add according to the molecular formula.

Step 1: Find the two compound molar masses Here $W = 20 \text{ g} = 0.020 \text{ kg}$ and each solute sample has mass 1.0 g . Applying the colligative-property relation separately gives

$$M(\text{AB}_2) = \frac{5.1 \times 1.0}{2.3 \times 0.020} = 110.87 \text{ g mol}^{-1},$$
$$M(\text{AB}_4) = \frac{5.1 \times 1.0}{1.3 \times 0.020} = 196.15 \text{ g mol}^{-1}.$$

The larger molecule produces the smaller depression because the same sample mass supplies fewer dissolved molecules.

Step 2: Solve for the atomic masses Let the numerical atomic masses of A and B be x and y , respectively. The formulae give

$$x + 2y = 110.87, \quad x + 4y = 196.15.$$

Subtracting the first equation from the second eliminates A:

$$2y = 85.28, \quad y = 42.64.$$

Substitution into the first equation then yields

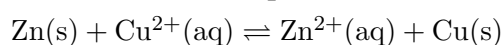
$$x = 110.87 - 2(42.64) = 25.59.$$

As a check, these values reconstruct both measured molar masses: $25.59 + 2(42.64) = 110.87$ and $25.59 + 4(42.64) = 196.15$. Atomic masses are quoted in u, while the corresponding molar masses have units of grams per mole.

Step 3: Conclusion The atomic masses are $A \approx 25.6 \text{ u}, \quad B \approx 42.6 \text{ u}$.

Quick Tip to Solve: Calculate each compound molar mass first; subtract the two formula-mass equations to isolate the two extra B atoms.

16. Calculate the equilibrium constant for the reaction:



Given: $E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.763 \text{ V}$ and $E_{\text{Cu}^{2+}/\text{Cu}}^\circ = +0.34 \text{ V}$.

[3 marks]

Solution:

Concept:

- The standard cell potential is the cathode reduction potential minus the anode reduction potential:
 $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$.
- The thermodynamic relations $\Delta G^\circ = -nFE_{\text{cell}}^\circ$ and $\Delta G^\circ = -RT \ln K$ imply $\log_{10} K = nE_{\text{cell}}^\circ / 0.0591$ at 298 K. Here n counts transferred electrons.

Step 1: Identify the half-reactions and cell potential Zinc is oxidised: $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$.

Copper ions are reduced: $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$. Thus $n = 2$. Using the given reduction potentials without multiplying them by electron coefficients,

$$E_{\text{cell}}^{\circ} = 0.340 - (-0.763) = 1.103 \text{ V}.$$

The positive sign is consistent with the spontaneous forward reaction under standard conditions.

Step 2: Relate the standard potential to equilibrium Using the conventional temperature $T = 298 \text{ K}$ for the standard electrode data,

$$\log_{10} K = \frac{2(1.103)}{0.0591} = 37.3266.$$

Taking the antilogarithm gives

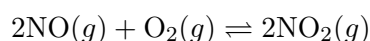
$$K = 10^{37.3266} = 2.12 \times 10^{37}.$$

Pure zinc and copper solids have unit activity, so the equilibrium constant corresponds to $K = a(\text{Zn}^{2+})/a(\text{Cu}^{2+})$. Its very large value shows that equilibrium strongly favours zinc ions and copper metal. The numerical result is sensitive to rounding in the voltage-to-logarithm constant, so an order-of-magnitude-consistent value obtained with 0.0592 V is equivalent within that approximation.

Step 3: Conclusion At 298 K, the equilibrium constant is $K \approx 2.1 \times 10^{37}$, using 0.0591 V in the logarithmic relation.

Quick Tip to Solve: Count two transferred electrons and subtract the zinc reduction potential with its negative sign before calculating $\log K$.

17. Define order of a reaction. The following reaction occurs in one step:



How will the rate of the above reaction change if the volume of the reaction vessel is diminished to one-third of its original volume? Calculate the extent to which the change will occur. [3 marks]

Solution:

Concept:

- The order of a reaction is the sum of the powers of the reactant concentrations in its experimentally determined rate law.
- For an elementary reaction occurring in one step, the powers in the forward rate law equal the stoichiometric coefficients of the reactants.

Step 1: Write the rate law For the given single-step forward reaction, two molecules of NO react with one molecule of O_2 . Hence the forward rate is

$$r = k[\text{NO}]^2[\text{O}_2].$$

Its overall order is $2 + 1 = 3$. The single-step condition is essential: coefficients cannot in general be used to obtain the rate law of a multistep reaction.

Step 2: Apply the volume change Let the original volume be V , and let the amounts of the gases remain unchanged during the compression at constant temperature. Since concentration is amount divided by volume, changing the volume to $V/3$ triples each concentration:

$$[\text{NO}]' = 3[\text{NO}], \quad [\text{O}_2]' = 3[\text{O}_2].$$

The temperature is unchanged, so the rate constant k is unchanged.

Step 3: Calculate the rate factor The new forward rate immediately after compression is

$$r' = k(3[\text{NO}])^2(3[\text{O}_2]) = 27k[\text{NO}]^2[\text{O}_2] = 27r.$$

Thus the increase in forward rate is $r' - r = 26r$. Although the printed equation is reversible, this elementary reactant rate law describes the forward reaction; a net rate would additionally require the reverse rate and the product concentration.

Step 4: Conclusion The order is the sum of the concentration exponents in the rate law. Here the forward reaction is third order, and reducing the volume to one-third makes its rate 27 times the original rate.

Quick Tip to Solve: For a fixed-temperature compression, multiply every gaseous reactant concentration by the volume ratio and raise that factor to the overall order.

18(a). Explain the following terms:

- (i) Peptisation
- (ii) Electrophoresis
- (iii) Hardy-Schulze rule

[3 marks]

Solution:

Concept:

- Colloidal particles carry surface charge and remain dispersed when repulsion prevents aggregation.
- An electric field reveals particle charge, while oppositely charged electrolyte ions can neutralise it and cause coagulation.

Step 1: (i) Peptisation Peptisation is the conversion of a freshly prepared precipitate into a colloidal sol by shaking it with the dispersion medium in the presence of a small amount of a suitable electrolyte, called a peptising agent. Ions from this electrolyte are adsorbed on the precipitate particles. The particles acquire similar charges, repel one another and disperse as colloidal particles. For example, a little FeCl_3 peptises freshly precipitated $\text{Fe}(\text{OH})_3$; adsorption of Fe^{3+} gives positively charged particles.

Step 2: (ii) Electrophoresis Electrophoresis is the movement of charged colloidal particles towards the oppositely charged electrode when an electric field is applied to a sol. Positively charged particles move towards the cathode, whereas negatively charged particles move towards the anode. The direction of movement therefore indicates the sign of the charge on the colloidal particles. It is the dispersed particles that migrate in this phenomenon.

Step 3: (iii) Hardy-Schulze rule The coagulating power of an electrolyte depends chiefly on the

valency of the ion whose charge is opposite to that of the colloidal particles. The greater the valency of this counter-ion, the greater its coagulating power and the smaller the concentration needed for coagulation. For a negatively charged sol, the typical order is $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^{+}$. For a positively charged sol, anions are the effective coagulating ions.

Step 4: Conclusion Peptisation produces a sol from a fresh precipitate; electrophoresis is field-induced migration of charged sol particles; the Hardy-Schulze rule relates coagulating power to counter-ion valency.

Quick Tip to Solve: For the Hardy-Schulze rule, identify the charge of the sol first, then compare only the ions of opposite charge.

OR

18(b). Explain the following terms:

(i) Tyndall effect

(ii) Shape-selective catalysis

(iii) Coagulation

[3 marks]

Solution:

Concept:

- Colloidal particles scatter light and can aggregate when the forces stabilising the sol are removed.
- In porous catalysts, molecular dimensions and pore geometry can determine which molecules react.

Step 1: (i) Tyndall effect The Tyndall effect is the scattering of light by colloidal particles, which makes the path of a light beam visible through a sol as a bright cone. The particles scatter incident light in different directions, allowing an observer to see the beam from the side. A true solution does not normally show this visible light path because its dissolved particles are too small to produce appreciable scattering under the same conditions. A beam through a colloidal sol therefore reveals its heterogeneous nature.

Step 2: (ii) Shape-selective catalysis Shape-selective catalysis is catalysis in which the pore size and shape of the catalyst, together with the sizes and shapes of reactant and product molecules, determine which reactions occur. Molecules of suitable dimensions enter the pores and reach the active sites; larger or unsuitable molecules are excluded, or cannot form the required transition state inside the pores. Zeolites, which are porous aluminosilicates with regular cavities and channels, are common shape-selective catalysts. Thus their structure provides selectivity in addition to catalytic activity.

Step 3: (iii) Coagulation Coagulation is the aggregation of colloidal particles into larger particles that separate from the dispersion medium, usually as a precipitate. In a charged sol, addition of a suitable electrolyte supplies counter-ions that reduce or neutralise the particle charge. Repulsion between particles decreases, so collisions allow them to stick together and form aggregates. The sol consequently loses its stability; this process is also called flocculation.

Step 4: Conclusion Tyndall effect is light scattering by a sol; shape-selective catalysis depends on

molecular and pore geometry; coagulation is the aggregation and separation of colloidal particles.

Quick Tip to Solve: Keep the three causes distinct: light scattering, access to catalyst pores, and loss of colloidal stability.

19. (a) Write the complete chemical equations for the reactions when (i) alkaline KMnO_4 reacts with KI and when (ii) mercury (II) chloride reacts with aqueous ammonia.

(b) Which property of the transition metals makes them good catalysts?

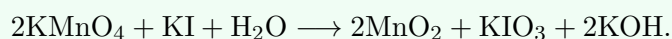
[3 marks]

Solution:

Concept:

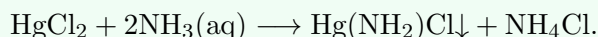
- In alkaline medium, permanganate oxidises iodide to iodate and is reduced to manganese dioxide. Oxidation and reduction must balance both atoms and charge.
- Transition metals can exhibit variable oxidation states and form intermediate complexes, allowing a reaction to proceed by a pathway of lower activation energy.

Step 1: (a)(i) Reaction of alkaline permanganate with potassium iodide Iodine changes from oxidation state -1 in I^- to $+5$ in IO_3^- , losing six electrons. Each manganese atom changes from $+7$ in permanganate to $+4$ in MnO_2 , gaining three electrons. Hence two permanganate ions are required per iodide ion. The complete equation is



The brown product is manganese dioxide; iodide is oxidised to iodate in the alkaline solution.

Step 2: (a)(ii) Reaction of mercury(II) chloride with aqueous ammonia Aqueous ammonia produces a white precipitate of mercury(II) amidochloride, $\text{Hg}(\text{NH}_2)\text{Cl}$, together with ammonium chloride:



One ammonia molecule supplies the amido group and the other accepts a proton. This accounts for both nitrogen atoms and all six hydrogen atoms.

Step 3: (b) Catalytic property of transition metals Their variable oxidation states enable transition metals to accept and donate electrons during successive reaction steps. Their ability to form intermediate complexes also brings reactants together and facilitates bond breaking and bond formation. The catalyst is regenerated at the end of the sequence. For heterogeneous catalysts, adsorption on the metal surface further assists the reaction by weakening bonds in the adsorbed reactants.

Step 4: Conclusion The balanced equations are $2\text{KMnO}_4 + \text{KI} + \text{H}_2\text{O} \rightarrow 2\text{MnO}_2 + \text{KIO}_3 + 2\text{KOH}$ and $\text{HgCl}_2 + 2\text{NH}_3 \rightarrow \text{Hg}(\text{NH}_2)\text{Cl} + \text{NH}_4\text{Cl}$. Variable oxidation states and intermediate-complex formation explain catalytic activity.

Quick Tip to Solve: For the alkaline permanganate equation, match the six-electron oxidation of iodide with two three-electron reductions of manganese.

20. (a) Draw a figure to show the splitting of degenerate d orbitals in octahedral field.

(b) Write the IUPAC name and draw the structure of coordination entities of $[\text{PtCl}(\text{NH}_3)_5]\text{Cl}_3$.

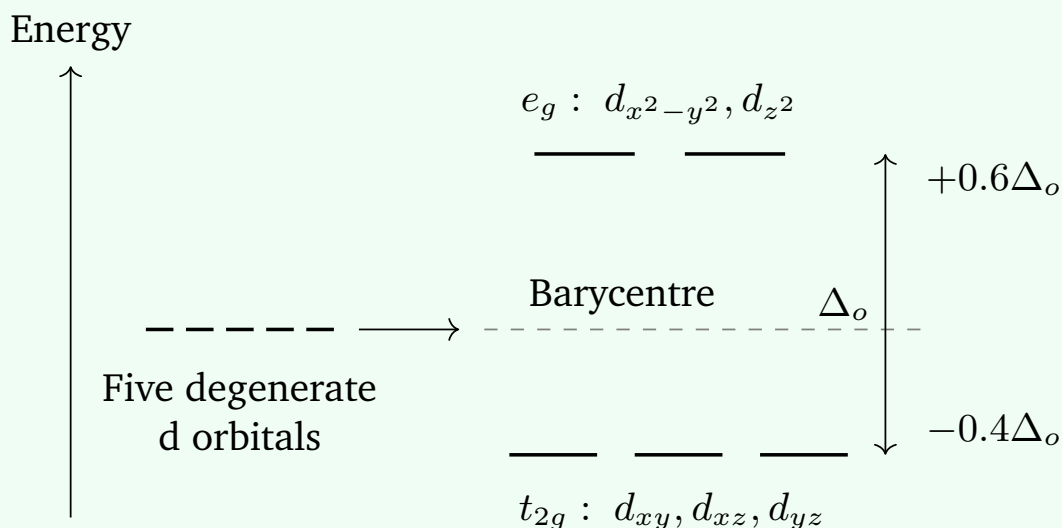
[3 marks]

Solution:

Concept:

- In an octahedral ligand field, the five initially degenerate d orbitals split into lower-energy t_{2g} and higher-energy e_g sets separated by Δ_o .
- The coordination sphere contains only the species inside square brackets. Ammine ligands are neutral and chlorido has charge -1 ; the counterions determine the charge of the complex.

Step 1: (a) Octahedral splitting of the d orbitals Six ligands approach the metal along the Cartesian axes. The $d_{x^2-y^2}$ and d_{z^2} orbitals point towards these ligands, suffer greater repulsion, and form the upper e_g set. The d_{xy} , d_{xz} , and d_{yz} orbitals point between the axes and form the lower t_{2g} set. Relative to the barycentre, each t_{2g} orbital lies at $-0.4\Delta_o$ and each e_g orbital at $+0.6\Delta_o$. Thus $3(-0.4\Delta_o) + 2(0.6\Delta_o) = 0$; the average energy is conserved. The diagram shows energy levels without assigning electrons, since part (a) asks for orbital splitting.



Splitting of the five d orbitals in an octahedral field

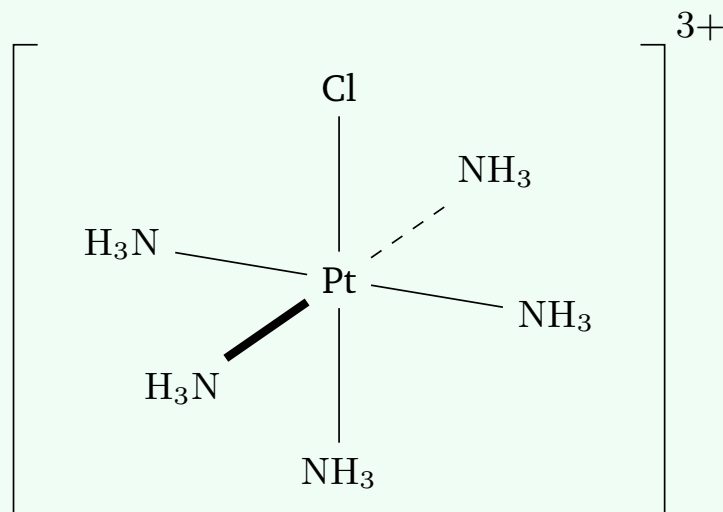
Step 2: (b) Determine the oxidation state and name The three chloride ions outside the brackets have total charge -3 , so the coordination entity is $[\text{PtCl}(\text{NH}_3)_5]^{3+}$. Let the oxidation state of platinum be x . Then

$$x + (-1) + 5(0) = +3 \Rightarrow x = +4.$$

There are five ammine ligands and one chlorido ligand, listed alphabetically with numerical prefixes ignored. The complete salt is named **pentaamminechloridoplatinum(IV) chloride**. The coordination cation itself is the **pentaamminechloridoplatinum(IV) ion**.

Step 3: (b) Draw the coordination entity Platinum has coordination number six because each of the five ammonia molecules and the chloride ligand supplies one donor atom. The coordination entity is octahedral, with platinum at the centre, four ligands in an equatorial plane and two in opposite

axial positions. The diagram places chloride at one axial position and ammonia at the remaining five positions. The three chloride counterions are outside the coordination sphere and are not bonded to platinum.



Octahedral coordination cation $[\text{PtCl}(\text{NH}_3)_5]^{3+}$

Step 4: Conclusion The octahedral field gives lower t_{2g} and upper e_g levels. The salt is pentaamminechloridoplatinum(IV) chloride, containing the octahedral cation $[\text{PtCl}(\text{NH}_3)_5]^{3+}$.

Quick Tip to Solve: Count only ligands inside the brackets: five neutral amines and one chlorido give coordination number six and platinum(IV).

21. Complete the following nuclear reactions:

(i) $^{133}_{56}\text{Ba}$ undergoes K-capture

(ii) $^{238}_{92}\text{U}$ undergoes α -decay

(iii) $^{234}_{91}\text{Pa}$ undergoes β -decay

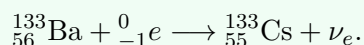
(Note: Use symbol 'X' where name of the element is not known in the nuclear reaction) [3 marks]

Solution:

Concept:

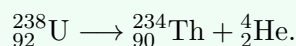
- In a nuclear equation both mass number A , the number of nucleons, and atomic number Z , the nuclear charge number, are conserved.
- K-capture absorbs an inner-shell electron; alpha emission removes a helium nucleus; beta-minus emission converts a neutron into a proton.

Step 1: (i) K-capture by barium A K-shell electron is captured by a proton: $p + e^- \rightarrow n + \nu_e$. Thus the mass number remains 133 while the atomic number decreases from 56 to 55. The daughter is caesium:



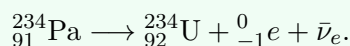
The mass-number balance is $133 + 0 = 133$, and the charge-number balance is $56 - 1 = 55$.

Step 2: (ii) Alpha decay of uranium An alpha particle is ${}^4_2\text{He}$. Subtract its mass number and atomic number from those of uranium: $A = 238 - 4 = 234$ and $Z = 92 - 2 = 90$. Hence



Thorium is the daughter; the sums on the right are $234 + 4 = 238$ and $90 + 2 = 92$.

Step 3: (iii) Beta decay of protactinium In beta-minus decay, $n \rightarrow p + e^- + \bar{\nu}_e$; the nucleon count stays fixed and the nuclear charge increases by one. Thus



The daughter has mass number 234 and atomic number 92. Charge is conserved because $92 - 1 = 91$; the antineutrino has zero electric charge and zero nucleon number.

Step 4: Conclusion The daughter nuclei are (i) ${}^{133}_{55}\text{Cs}$, (ii) ${}^{234}_{90}\text{Th}$, and (iii) ${}^{234}_{92}\text{U}$, with the emitted or captured particles shown above.

Quick Tip to Solve: For each nuclear equation, balance the upper numbers and lower numbers separately before identifying the daughter element.

22. Write one chemical equation each to exemplify the following reactions:

(i) Aldol condensation

(ii) Cannizzaro's reaction

(iii) Hell-Volhard-Zelinsky reaction

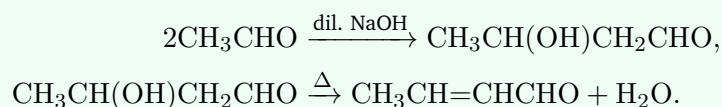
[3 marks]

Solution:

Concept:

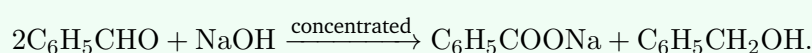
- Aldol condensation needs an aldehyde or ketone with an alpha hydrogen; dilute base gives a beta-hydroxy carbonyl compound, which loses water on heating.
- Cannizzaro disproportionation uses an aldehyde without alpha hydrogens and concentrated alkali. The HVZ reaction halogenates the alpha carbon of a carboxylic acid.

Step 1: (i) Aldol condensation Ethanal contains alpha hydrogens. In dilute sodium hydroxide, two molecules combine to give 3-hydroxybutanal (aldol). Heating dehydrates it to but-2-enal:



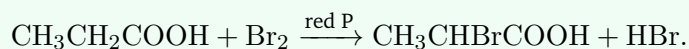
The carbonyl group remains in the product, and the new double bond is conjugated with it.

Step 2: (ii) Cannizzaro reaction Benzaldehyde has no alpha hydrogen and undergoes self-oxidation and self-reduction with concentrated aqueous sodium hydroxide:



One molecule becomes sodium benzoate by oxidation; the other becomes benzyl alcohol by reduction. The carboxyl product remains a salt in the alkaline medium.

Step 3: (iii) Hell-Volhard-Zelinsky reaction Propanoic acid has alpha hydrogens. Bromine in the presence of a small amount of red phosphorus replaces an alpha hydrogen by bromine:



The product is 2-bromopropanoic acid. Bromination occurs at the carbon immediately next to the carboxyl group, rather than at the terminal methyl group.

Step 4: Conclusion The examples give but-2-enal by aldol condensation, sodium benzoate and benzyl alcohol by Cannizzaro reaction, and 2-bromopropanoic acid by the HVZ reaction.

Quick Tip to Solve: Check alpha hydrogens first: they are needed for aldol and HVZ reactions, but must be absent for a self-Cannizzaro example.

23. Write the chemical equation and the condition for preparing each of the following:

(i) Ethyl amine from ethyl bromide

(ii) Sulphanilic acid from aniline

(iii) Phenol from aniline

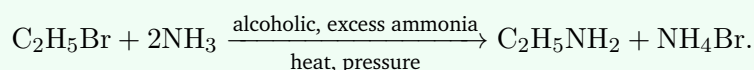
[3 marks]

Solution:

Concept:

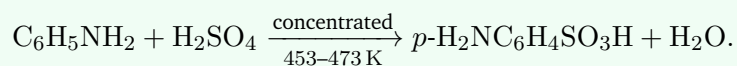
- Alkyl halides undergo nucleophilic substitution with ammonia. Excess ammonia favours formation of the primary amine over further alkylation.
- Aniline undergoes sulphonation with concentrated sulphuric acid. Diazotisation followed by hydrolysis replaces its amino group by a hydroxyl group.

Step 1: (i) Ethylamine from ethyl bromide Heat ethyl bromide with excess alcoholic ammonia in a sealed tube (under pressure). The overall equation is



Ammonia first forms an ethylammonium salt; another ammonia molecule removes a proton. Using excess ammonia reduces further alkylation of the ethylamine product.

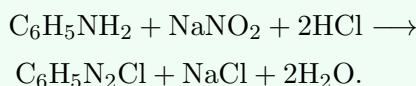
Step 2: (ii) Sulphanilic acid from aniline Treat aniline with concentrated sulphuric acid and heat at 453–473 K. Anilinium hydrogen sulphate forms initially; on heating it gives sulphanilic acid, with the sulphonc acid group para to the amino group:



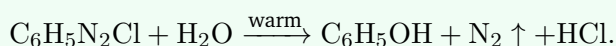
Sulphanilic acid is commonly present as the zwitterion $p\text{-}^+\text{H}_3\text{NC}_6\text{H}_4\text{SO}_3^-$.

Step 3: (iii) Phenol from aniline First diazotise aniline with sodium nitrite and dilute hydrochloric

acid at 273–278 K:



The low temperature preserves the benzenediazonium chloride. Warm its aqueous solution to hydrolyse it:



Nitrogen gas escapes, and phenol is obtained.

Step 4: Conclusion The required conditions are (i) excess alcoholic ammonia with heat and pressure, (ii) concentrated sulphuric acid at 453–473 K, and (iii) cold diazotisation followed by warming with water.

Quick Tip to Solve: For phenol from aniline, keep diazotisation cold, then warm only in the hydrolysis stage; write both equations.

24. Describe the following with examples:

(i) Antifertility drugs

(ii) Antioxidants

(iii) Biliquid propellant

[3 marks]

Solution:

Concept:

- Antifertility drugs control conception by interfering with reproductive processes, commonly by preventing ovulation.
- Antioxidants retard oxidation, whereas a propellant produces expanding gases that provide thrust in a rocket engine.

Step 1: (i) Antifertility drugs These are drugs used to prevent pregnancy and thus help in family planning. Oral contraceptive preparations commonly contain synthetic hormones related to progesterone, alone or together with an estrogen. They suppress ovulation and also make conditions less favourable for fertilisation and implantation. Norethindrone is an example of a synthetic progestogen used in oral contraceptives; ethynylestradiol is an estrogen component used in combination pills. Their contraceptive action is different from the action of antibiotics, which treat bacterial infections.

Step 2: (ii) Antioxidants Antioxidants are substances that inhibit or slow oxidation by oxygen. They are added to foods containing fats and oils to retard oxidative rancidity, thereby helping preserve flavour and extend storage life. They interrupt oxidation reactions or are preferentially oxidised, protecting the food constituents. Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) are common examples used as food antioxidants. Thus their role is to prevent chemical deterioration by oxidation, rather than simply to mask the smell of rancid food.

Step 3: (iii) Biliquid propellant A biliquid propellant is a rocket-propellant system in which the fuel and the oxidiser are both liquids. They are stored in separate tanks and fed into the combustion chamber, where their reaction generates hot gases. The gases expand and escape through a nozzle,

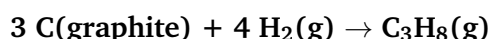
producing thrust. An example is liquid hydrogen as the fuel with liquid oxygen as the oxidiser. Another example is hydrazine as fuel with dinitrogen tetroxide as oxidiser. The oxidiser is carried on board, so combustion does not depend on atmospheric oxygen.

Step 4: Conclusion Antifertility drugs prevent conception, for example norethindrone; antioxidants inhibit oxidation, for example BHA or BHT; and a biliquid propellant uses a liquid fuel with a liquid oxidiser, for example liquid hydrogen with liquid oxygen.

Quick Tip to Solve: For each term give its function and a named example; for biliquid propellants explicitly identify both the fuel and the oxidiser.

25. (a) Taking a suitable example show that ΔS_{total} is a criterion for spontaneity of a change.

(b) Calculate the standard Gibbs energy change for the formation of propane at 298 K.



$\Delta_f H^\circ$ for propane is $-103.85 \text{ kJ mol}^{-1}$ and $S^\circ_m \text{ C}_3\text{H}_8(\text{g}) = 270.2 \text{ J K}^{-1} \text{ mol}^{-1}$, $S^\circ_m \text{ C(graphite)} = 5.70 \text{ J K}^{-1} \text{ mol}^{-1}$ and $S^\circ_m \text{ H}_2(\text{g}) = 130.68 \text{ J K}^{-1} \text{ mol}^{-1}$. [5 marks]

Solution:

Concept:

- The total entropy change is $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$. A spontaneous change has $\Delta S_{\text{total}} > 0$; at equilibrium the total entropy change is zero.
- At constant temperature and pressure, $\Delta G = \Delta H - T\Delta S_{\text{system}} = -T\Delta S_{\text{total}}$, with T the absolute temperature.
- The standard reaction entropy is the sum of standard molar entropies of products minus that of reactants, each multiplied by its stoichiometric coefficient.

Step 1: (a) Apply the total-entropy criterion Consider freezing liquid water below its normal freezing temperature at atmospheric pressure. Freezing produces more ordered ice, so the entropy of the water decreases: $\Delta S_{\text{system}} < 0$. Nevertheless freezing is spontaneous under these conditions because the released heat increases the entropy of the surroundings by more than the decrease in the water's entropy. Thus the entropy of the system alone cannot decide spontaneity; the system and surroundings must be considered together.

Step 2: Show the criterion quantitatively for freezing Let $L > 0$ be the molar latent heat of fusion at the melting temperature T_m . Over a small temperature interval below T_m , neglecting heat-capacity corrections, freezing one mole gives

$$\Delta S_{\text{system}} \simeq -\frac{L}{T_m}, \quad \Delta S_{\text{surroundings}} \simeq \frac{L}{T}.$$

Therefore

$$\Delta S_{\text{total}} \simeq L \left(\frac{1}{T} - \frac{1}{T_m} \right).$$

Below the melting point, $T < T_m$, this is positive and freezing is spontaneous. At $T = T_m$, it is zero and ice and water are in equilibrium. Above T_m , it is negative for freezing, so the reverse change,

melting, is spontaneous. This example illustrates the second-law criterion that a spontaneous change increases total entropy, even when the system's entropy decreases.

Step 3: (b) Calculate the standard entropy of formation of propane For $3\text{C}(\text{graphite}) + 4\text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g})$, one mole of propane is formed. Using the supplied standard molar entropies,

$$\begin{aligned}\Delta_f S^\circ &= S_m^\circ(\text{C}_3\text{H}_8) - [3S_m^\circ(\text{C}) + 4S_m^\circ(\text{H}_2)] \\ &= 270.2 - [3(5.70) + 4(130.68)] \\ &= 270.2 - 539.82 \\ &= -269.62 \text{ J K}^{-1}\text{mol}^{-1} \\ &= -0.26962 \text{ kJ K}^{-1}\text{mol}^{-1}.\end{aligned}$$

The negative sign is consistent with combining four moles of gaseous hydrogen into one mole of gaseous propane, together with consumption of solid carbon.

Step 4: Substitute in the Gibbs energy relation at 298 K The given standard enthalpy of formation is $\Delta_f H^\circ = -103.85 \text{ kJ mol}^{-1}$. Converting entropy to kilojoules before subtraction gives

$$\begin{aligned}\Delta_f G^\circ &= \Delta_f H^\circ - T\Delta_f S^\circ \\ &= -103.85 - 298(-0.26962) \\ &= -103.85 + 80.34676 \\ &= -23.50324 \text{ kJ mol}^{-1}.\end{aligned}$$

Here the negative entropy change makes $-T\Delta S^\circ$ positive, opposing the favourable negative enthalpy contribution. At 298 K the enthalpy contribution is larger in magnitude, leaving a negative standard Gibbs energy change.

Step 5: Conclusion (a) A change is spontaneous when $\Delta S_{\text{total}} > 0$, as shown by freezing water below its melting point despite a decrease in the water's entropy. (b) The standard Gibbs energy of formation of propane at 298 K is $\Delta_f G^\circ = -23.50 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: Multiply every molar entropy by its reaction coefficient, then convert J to kJ before evaluating the enthalpy-minus-temperature-entropy expression.

26. (a) Assign reasons for each of the following:

- (i) Sulphur in vapour state exhibits some paramagnetic behaviour.
- (ii) Anhydrous aluminium chloride acts as a catalyst in many organic reactions.
- (iii) The bond energy of F–F bond is less than that of Cl–Cl bond.

(b) Draw the structures of the following species:

- (i) PCl_5 (s)
- (ii) XeF_4

[5 marks]

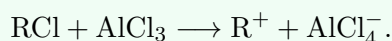
Solution:

Concept:

- Paramagnetism is caused by unpaired electrons. Sulphur vapour contains molecular species whose proportions vary with temperature.
- A Lewis acid accepts an electron pair; an electron-deficient aluminium centre can therefore activate reagents in organic reactions.
- Molecular shapes follow the number of bond pairs and lone pairs around the central atom. Solid phosphorus pentachloride is ionic.

Step 1: (a)(i) Paramagnetism of sulphur vapour At high temperature, sulphur vapour contains some diatomic S_2 molecules formed by dissociation of larger sulphur molecules. Like O_2 , S_2 has two unpaired electrons in its antibonding π^* molecular orbitals. These unpaired electrons cause attraction towards a magnetic field, so sulphur vapour exhibits some paramagnetic behaviour.

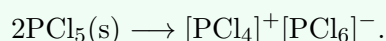
Step 2: (a)(ii) Catalytic action of anhydrous aluminium chloride In AlCl_3 , aluminium has an incomplete octet and can accept an electron pair. Thus anhydrous aluminium chloride acts as a Lewis acid. It coordinates with a reagent and facilitates the generation of a reactive electrophile, thereby catalysing reactions such as Friedel–Crafts alkylation and acylation. For example, activation of an alkyl chloride is commonly represented as



Aluminium chloride is regenerated during the catalytic reaction cycle.

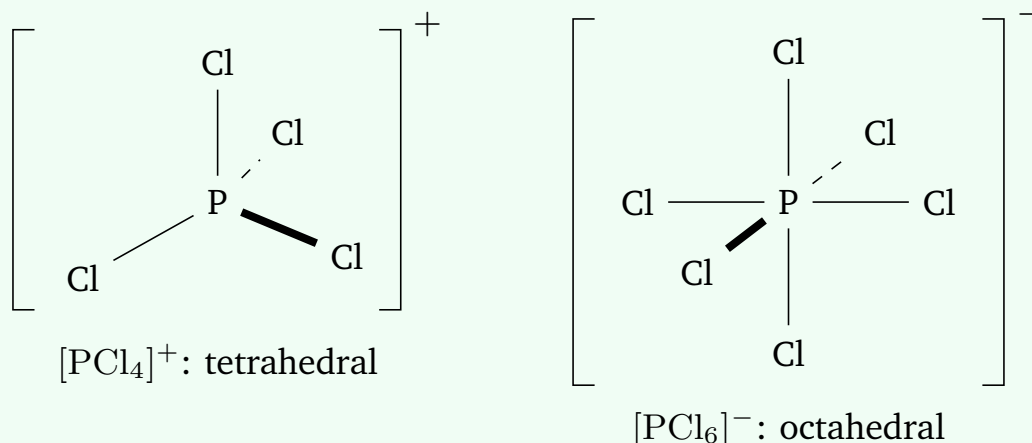
Step 3: (a)(iii) Comparison of fluorine and chlorine bond energies Each halogen atom in F_2 or Cl_2 carries three lone pairs. The fluorine atom is very small, so the non-bonding electron pairs on the two fluorine atoms lie close together in the short F – F bond. Strong lone-pair–lone-pair repulsions weaken this bond. In Cl_2 , the larger chlorine atoms keep these electron pairs farther apart, reducing this repulsion. Consequently, the bond dissociation energy of F – F is lower than that of Cl – Cl, despite the shorter fluorine bond.

Step 4: (b)(i) Structure of solid phosphorus pentachloride In the solid state, phosphorus pentachloride exists as an ionic lattice containing $[\text{PCl}_4]^+$ and $[\text{PCl}_6]^-$ ions:



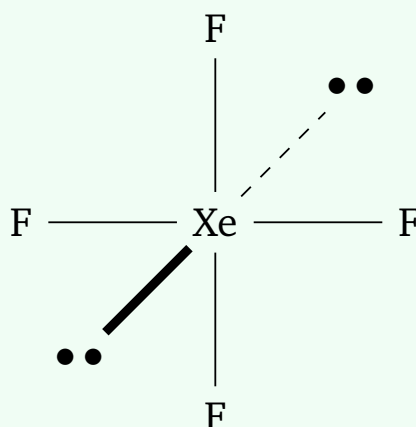
The $[\text{PCl}_4]^+$ ion is tetrahedral, with four P–Cl bonds directed towards the vertices of a tetrahedron. The $[\text{PCl}_6]^-$ ion is octahedral, with six P–Cl bonds directed towards the vertices of an octahedron.

Both ions are shown below; a trigonal-bipyramidal molecule describes gaseous PCl_5 , whereas the question asks about the solid.



Tetrahedral and octahedral ions in solid phosphorus pentachloride

Step 5: (b)(ii) Structure of xenon tetrafluoride Xenon has eight valence electrons. Four Xe–F bonds leave two lone pairs on xenon, giving six electron-pair domains. Their electron-pair arrangement is octahedral. The two lone pairs occupy opposite positions to minimise repulsion, leaving the four fluorine atoms in one plane. Thus XeF_4 is square planar, with adjacent F–Xe–F angles of 90° and opposite F–Xe–F angles of 180° .



Opposite lone pairs (out of plane)

Square-planar XeF_4 ; the two xenon lone pairs lie above and below the molecular plane

Step 6: Conclusion Sulphur vapour is paramagnetic because of unpaired electrons in S_2 ; anhydrous AlCl_3 is a Lewis-acid catalyst; strong lone-pair repulsion weakens F – F. Solid PCl_5 contains tetrahedral $[\text{PCl}_4]^+$ and octahedral $[\text{PCl}_6]^-$ ions, while XeF_4 is square planar.

Quick Tip to Solve: Check the state symbol before drawing PCl_5 : the solid contains two different ions. For XeF_4 , place the two xenon lone pairs opposite each other before drawing the four bonds.

27(a). What is mutarotation? Explain occurrence of mutarotation in D-glucose.

(b) How are lipids classified? Give one example of each class.

[5 marks]

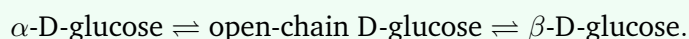
Solution:

Concept:

- Mutarotation is the gradual change in the specific optical rotation of a freshly prepared solution of a sugar until a constant equilibrium value is attained.
- The cyclic hemiacetal forms of D-glucose differ in configuration at the anomeric carbon, C_1 . Opening and reclosing the ring allows their interconversion in aqueous solution.
- Lipids are classified by their chemical composition and hydrolysis products as simple lipids, compound lipids and derived lipids.

Step 1: (a) Observe the change in optical rotation Freshly dissolved α -D-glucose has a specific rotation of approximately $+112^\circ$, whereas freshly dissolved β -D-glucose has a specific rotation of approximately $+19^\circ$. On standing in water, the rotation of the former decreases and that of the latter increases. Both solutions eventually reach the same constant specific rotation, approximately $+52.5^\circ$. This spontaneous change towards the equilibrium rotation is mutarotation.

Step 2: Explain interconversion through the open-chain form In water, the cyclic hemiacetal ring of either anomer can open to give the open-chain aldehydic form. When the hydroxyl group at C_5 adds again to the aldehyde group at C_1 , ring closure can produce either configuration at C_1 . Thus,



The equilibrium mixture contains approximately 36% of the α anomer and 64% of the β anomer, with only a very small amount of open-chain glucose. Its fixed composition explains the final constant rotation. The change involves the anomeric carbon; D-glucose is not converted into L-glucose.

Step 3: (b) Classify lipids and give examples **Simple lipids:** These are esters of fatty acids with alcohols. On hydrolysis they yield fatty acids and the alcohol only. Fats and oils are esters with glycerol; for example, tristearin is a simple lipid. Waxes, such as beeswax, are another group of simple lipids containing long-chain monohydric alcohols.

Compound lipids: In addition to fatty acids and an alcohol, these contain another group such as phosphate or carbohydrate. For example, lecithin (phosphatidylcholine) is a phospholipid and contains a phosphate-containing group.

Derived lipids: These include substances obtained by hydrolysis of simple or compound lipids and related lipid substances. For example, stearic acid is a fatty acid obtained on hydrolysis of suitable fats. Sterols such as cholesterol are also included in this class.

Step 4: Conclusion D-glucose undergoes mutarotation because its α and β cyclic forms interconvert through the open-chain form, producing an equilibrium rotation of about $+52.5^\circ$. Lipids are classified as simple (tristearin), compound (lecithin) and derived (stearic acid).

Quick Tip to Solve: Link mutarotation to a free anomeric hemiacetal group and ring opening; classify lipids by what hydrolysis produces, then attach one named example to each class.

27(b). How does DNA replicate? Describe the mechanism of replication. How is the process responsible for preservation of heredity? [5 marks]

Solution:

Concept:

- DNA replication is the formation of two identical DNA molecules from one parental DNA molecule before cell division. It is semiconservative: each daughter molecule contains one parental strand and one newly synthesised strand.
- Complementary base pairing determines the sequence of a new strand: adenine pairs with thymine ($A - T$) and guanine pairs with cytosine ($G - C$). The sequence of bases in DNA stores hereditary information.

Step 1: Unwind and separate the parental strands Replication begins at an origin of replication. The DNA double helix unwinds, and the hydrogen bonds between complementary bases break, separating the two strands. The covalent sugar-phosphate backbone of each parental strand remains intact. The exposed strands serve as separate templates for synthesis of complementary strands.

Step 2: Form complementary strands on the templates Free deoxyribonucleotides pair with the exposed template bases according to the base-pairing rule: a template A directs incorporation of T , T directs A , G directs C , and C directs G . DNA polymerase joins the incoming nucleotides by phosphodiester bonds, producing the sugar-phosphate backbone of the new strand. Synthesis proceeds in the $5'$ to $3'$ direction, starting from a primer. Because the template strands are antiparallel, one new strand is synthesised continuously, while the other is formed in short fragments that are subsequently joined by DNA ligase after primer removal and replacement with DNA.

Step 3: Produce two semiconservative daughter molecules Each original strand becomes paired with its newly formed complementary strand, and the strands form double helices. Thus one parental DNA molecule yields two daughter DNA molecules with the same base sequence as the original, provided copying occurs accurately. Each daughter DNA has one old strand and one new strand; the parental DNA is therefore conserved strand by strand, rather than remaining wholly together in only one daughter molecule.

Step 4: Explain preservation of heredity The specific pairing of bases makes the sequence of each new strand depend on that of its parental template. For example, a template segment $5' - ATGC - 3'$ directs the complementary segment $3' - TACG - 5'$. Copying the complementary strand restores the original sequence. Hence the same genetic information is reproduced in the daughter DNA molecules. When the replicated DNA is distributed to daughter cells during cell division, each receives the hereditary instructions carried by the parent cell. Accurate replication, aided by proofreading and repair, therefore maintains genetic continuity from cell to cell and through generations. Occasional unrepaired copying errors are mutations, so preservation describes the normal faithful process rather than an absolute absence of variation.

Step 5: Conclusion DNA replicates by separation of its strands followed by template-directed synthesis of complementary strands. Replication is semiconservative, and faithful complementary base pairing preserves the base sequence and thus the hereditary information in the daughter DNA molecules.

Quick Tip to Solve: State both features explicitly: each daughter DNA has one old strand, and complementary base pairing preserves the genetic sequence.