

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



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. Name a substance which on addition to AgCl causes cation vacancy in it.

[1 mark]

Solution:

Concept:

- An impurity cation of higher charge can replace a host cation in an ionic crystal.
- Electrical neutrality requires the total positive and negative charges of the crystal to remain equal.

Step 1: Choose a divalent chloride Cadmium chloride, CdCl_2 , supplies Cd^{2+} ions when added as an impurity to silver chloride.

Step 2: Account for the vacancy A Cd^{2+} ion replaces one Ag^+ ion at a normal cation site. Its extra positive charge is compensated by leaving one other Ag^+ site vacant. Thus each incorporated cadmium ion produces one cation vacancy while the crystal remains electrically neutral.

Step 3: Conclusion Cadmium chloride, CdCl_2 , causes cation vacancies in AgCl.

Quick Tip to Solve: For a divalent dopant in a monovalent cation lattice, count one cation vacancy per dopant ion.

2. Mention a large scale use of the phenomenon called 'reverse osmosis'.

[1 mark]

Solution:

Concept:

- Osmosis is solvent flow through a semipermeable membrane from a dilute solution towards a concentrated solution.
- When pressure greater than the osmotic pressure is applied to the solution, the solvent flows in the reverse direction.

Step 1: Identify the industrial application Reverse osmosis is used on a large scale for desalination of seawater to obtain fresh water.

Step 2: Explain the separation Pressure greater than the osmotic pressure is applied on the seawater side of a semipermeable membrane. Water is forced through the membrane, while dissolved salts are retained mainly on the seawater side. The collected permeate is therefore fresh water with a much lower salt content.

Step 3: Conclusion An important large-scale use is desalination of seawater.

Quick Tip to Solve: Link reverse osmosis to pressure-driven removal of dissolved salts from seawater.

3. Give an example of a pseudo first order reaction.

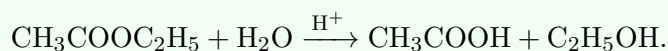
[1 mark]

Solution:

Concept:

- A pseudo first order reaction is a reaction of higher actual order that behaves kinetically as first order under specified conditions.
- A reactant taken in large excess has an effectively constant concentration, which is included in the observed rate constant.

Step 1: Give the reaction Acid-catalysed hydrolysis of ethyl acetate in excess water is an example:



Step 2: Explain the apparent order At fixed acid concentration, the rate may be written as $r = k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$. Water is present in such large excess that its concentration changes negligibly. Hence $r = k_{\text{obs}}[\text{CH}_3\text{COOC}_2\text{H}_5]$, where $k_{\text{obs}} = k[\text{H}_2\text{O}]$, giving apparent first order behaviour.

Step 3: Conclusion Hydrolysis of ethyl acetate in excess water is a pseudo first order reaction.

Quick Tip to Solve: Always state excess water and fixed acid concentration when using ester hydrolysis as this example.

4. Write the IUPAC name of the following: $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$

[1 mark]

Solution:

Concept:

- The parent chain must contain the principal functional group and the carbon-carbon double bond.
- Number the chain to give the ketone carbonyl the lowest possible locant; the ketone is named with the suffix -one.

Step 1: Select and number the chain Rewrite the compound as $\text{CH}_3\text{COCH}=\text{C}(\text{CH}_3)_2$. The longest chain containing the carbonyl group and the double bond has five carbon atoms. Numbering from the carbonyl end places the ketone group at carbon 2.

Step 2: Locate the other structural features The double bond lies between carbon atoms 3 and 4, giving pent-3-en-2-one as the parent name. The additional methyl group is attached to carbon 4. Combining the substituent and parent names gives the required systematic name.

Step 3: Conclusion The IUPAC name is 4-methylpent-3-en-2-one.

Quick Tip to Solve: Give the ketone group priority over the double bond when choosing the numbering direction.

5. Mention two properties of acetonitrile by which it acts as a good solvent.

[1 mark]

Solution:

Concept:

- Acetonitrile, CH_3CN , is a polar molecular solvent containing a strongly polar nitrile group.
- A high dielectric constant reduces the electrostatic attraction between oppositely charged ions in a solution.

Step 1: State the first property Acetonitrile has a high dielectric constant. It therefore weakens the attraction between ions, helping suitable ionic substances dissolve and remain separated in solution.

Step 2: State the second property Acetonitrile has a high dipole moment due to the polar nitrile group. Its molecules can interact effectively with charged and polar solute particles through ion-dipole and dipole-dipole attractions. These interactions help stabilise such particles in solution and contribute to its solvent ability.

Step 3: Conclusion The two properties are high dielectric constant and high dipole moment.

Quick Tip to Solve: For acetonitrile, connect solvent power to its dielectric constant and the polarity of the nitrile group.

6. Draw a diagram showing the formation of bonding and antibonding molecular orbitals by the LCAO in homonuclear hydrogen molecule.

[2 marks]

Solution:

Concept:

- The linear combination of atomic orbitals (LCAO) combines the hydrogen $1s$ wave functions ϕ_A and ϕ_B by addition or subtraction.
- Constructive overlap gives a lower-energy bonding orbital σ_{1s} ; destructive overlap gives a higher-energy antibonding orbital σ_{1s}^* . The signs in the diagram denote wave-function phase, not electric charge.

Step 1: Form the bonding molecular orbital Adding the same-phase atomic orbitals gives

$$\psi_{\sigma_{1s}} = N_+(\phi_A + \phi_B),$$

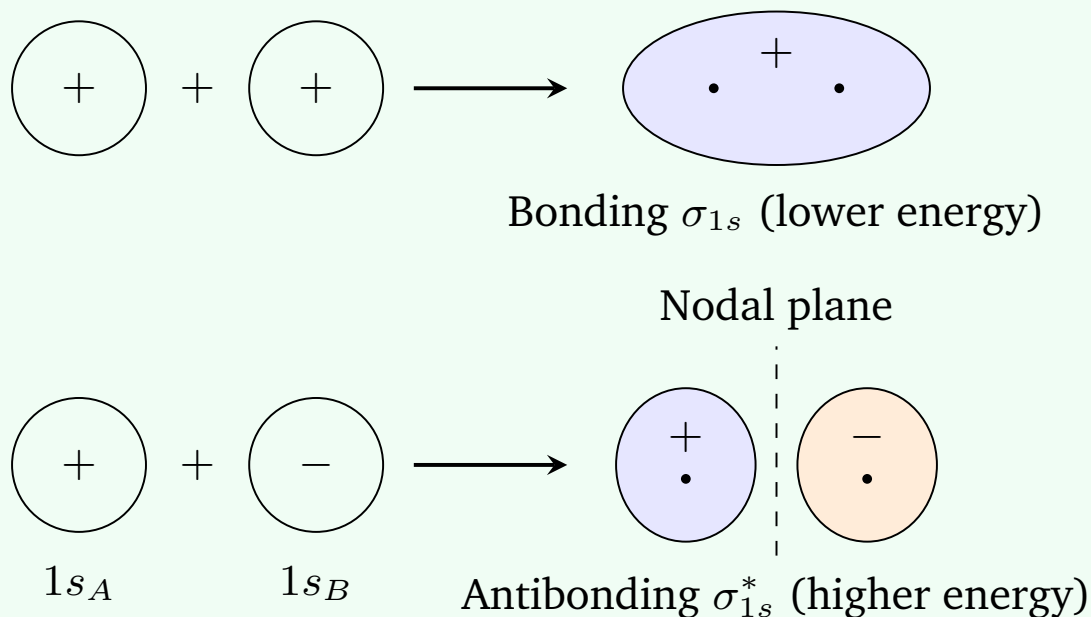
where N_+ is a normalisation constant. Electron density increases between the nuclei, attracting both nuclei and stabilising the molecule. The overlapping orbitals form one continuous bonding region, as shown in the upper row.

Step 2: Form the antibonding molecular orbital Subtracting the atomic wave functions gives

$$\psi_{\sigma_{1s}^*} = N_-(\phi_A - \phi_B),$$

where N_- is a normalisation constant. Opposite phases cancel between the nuclei, producing a nodal plane with zero electron density. This orbital is less stable. In ground-state H_2 , both electrons occupy σ_{1s} with opposite spins; σ_{1s}^* remains empty.

Quick Tip to Solve: Show a continuous region between nuclei for bonding and a labelled central nodal plane for antibonding; plus and minus indicate phase.



LCAO formation of hydrogen molecular orbitals (schematic phase diagrams)

Step 3: Conclusion LCAO forms bonding σ_{1s} by constructive overlap and antibonding σ_{1s}^* by destructive overlap; H_2 has configuration $(\sigma_{1s})^2$.

Quick Tip to Solve: Show a continuous region between nuclei for bonding and a labelled central nodal plane for antibonding; plus and minus indicate phase.

7. Taking a specific example show that ΔS_{total} is a criterion for spontaneity of a change.

[2 marks]

Solution:

Concept:

- Total entropy change includes both system and surroundings:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

- A change is spontaneous when $\Delta S_{\text{total}} > 0$, and equilibrium corresponds to $\Delta S_{\text{total}} = 0$. A proposed direction with negative total entropy change is non-spontaneous.

Step 1: Consider melting of ice above its melting point Let one mole of ice melt at constant pressure in contact with surroundings at a temperature T slightly above $T_m = 273.15 \text{ K}$. The process is



Near the melting point, neglecting the small heat-capacity correction, the system gains entropy $\Delta S_{\text{system}} \simeq \Delta H_{\text{fus}}/T_m$, where $\Delta H_{\text{fus}} > 0$ is the molar enthalpy of fusion. The surroundings supply this heat, so $\Delta S_{\text{surroundings}} \simeq -\Delta H_{\text{fus}}/T$.

Quick Tip to Solve: Add the entropy lost by the surroundings to the entropy gained by ice; the system's entropy increase alone cannot decide spontaneity.

Step 2: Apply the total entropy criterion Therefore,

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

For $T > T_m$, this is positive, so ice melts spontaneously. At $T = T_m$, it is zero and ice and water coexist in equilibrium. Slightly below T_m , melting gives a negative value; the reverse change, freezing, is spontaneous and increases total entropy.

Step 3: Conclusion Melting of ice above 273.15 K illustrates that a spontaneous change increases the total entropy of system and surroundings: $\Delta S_{\text{total}} > 0$.

Quick Tip to Solve: Add the entropy lost by the surroundings to the entropy gained by ice; the system's entropy increase alone cannot decide spontaneity.

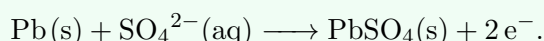
8. Write the cell reactions which occur in lead storage battery (i) when the battery is in use (ii) when the battery is on charging. [2 marks]

Solution:

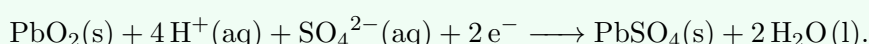
Concept:

- A lead storage battery has a lead electrode, a lead dioxide electrode and aqueous sulphuric acid as electrolyte. During discharge, lead is oxidised and lead dioxide is reduced; both form lead sulphate.
- Charging uses an external direct-current source to reverse these reactions, regenerating Pb, PbO₂ and sulphuric acid.

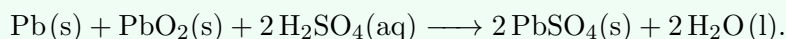
Step 1: Battery in use: discharge reactions At the negative electrode (anode during discharge),



At the positive electrode (cathode during discharge),

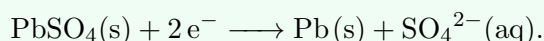


Adding cancels the electrons and gives

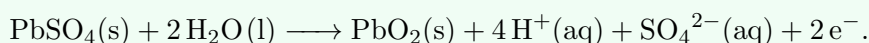


Sulphuric acid is consumed, so its concentration decreases during use.

Step 2: Battery on charging: reverse the reactions At the negative electrode, lead sulphate is reduced:



At the positive electrode, lead sulphate is oxidised:



Quick Tip to Solve: Both plates become lead sulphate on discharge; reverse every half-reaction, including the electrons, to obtain charging reactions.

The overall charging reaction is



Thus charging restores the original electrode materials and increases the acid concentration.

Step 3: Conclusion In use, $\text{Pb} + \text{PbO}_2 + 2 \text{H}_2\text{SO}_4 \longrightarrow 2 \text{PbSO}_4 + 2 \text{H}_2\text{O}$; on charging, the overall reaction proceeds in the reverse direction.

Quick Tip to Solve: Both plates become lead sulphate on discharge; reverse every half-reaction, including the electrons, to obtain charging reactions.

9. Give chemical reaction in support of each of the following statements:

(i) The +1 oxidation state gets stabilised progressively from Ga to Tl in Group 13.

(ii) All the bonds in PCl_5 molecule are not equivalent.

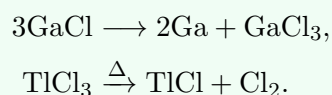
[2 marks]

Solution:

Concept:

- The inert-pair effect is the decreasing tendency of the outer ns^2 pair to participate in bonding down Group 13; thus the +1 state becomes more stable relative to +3.
- Gaseous PCl_5 is trigonal bipyramidal, with three equatorial and two longer, weaker axial P – Cl bonds.

Step 1: Support the increasing stability of the +1 state Gallium(I) chloride tends to disproportionate, whereas thallium(III) chloride readily gives the more stable thallium(I) chloride:



The first reaction shows the instability of Ga(I); the second shows the preference of Tl for the +1 state. These endpoint reactions support the progressive stabilisation of the +1 state from Ga to Tl.

Step 2: Support the non-equivalence of bonds in phosphorus pentachloride On heating, phosphorus pentachloride dissociates:



The two weaker axial bonds are preferentially broken in this dissociation. Axial bonds experience greater repulsion from the three equatorial bond pairs and are longer than equatorial bonds; therefore all five bonds are not equivalent.

Step 3: Conclusion The reactions illustrate the greater stability of Tl(I) compared with Ga(I), and the easier cleavage of the two axial bonds in PCl_5 .

Quick Tip to Solve: For the first statement compare Ga(I) disproportionation with Tl(III) decomposition; for the second identify the two axial bonds.

10. Explain the following terms:

(i) Asymmetric molecule

(ii) R and S notations

[2 marks]

Solution:

Concept:

- Chirality means that a molecule cannot be superimposed on its mirror image.
- The Cahn–Ingold–Prelog (CIP) rules assign substituent priorities to specify absolute configuration at a stereogenic centre.

Step 1: Define an asymmetric molecule An asymmetric molecule is one whose mirror image is not superimposable on it; it has no improper symmetry element such as a plane of symmetry. A familiar example is butan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$, whose second carbon is bonded to four different groups: H, OH, methyl and ethyl. Such a tetrahedral carbon is called an asymmetric carbon atom. The two mirror-image arrangements form a pair of enantiomers.

Step 2: Explain R and S notations The symbols *R* (rectus) and *S* (sinister) describe the absolute configuration. Rank the four groups attached to the stereogenic carbon from 1 (highest) to 4 (lowest) by the CIP rules: the higher atomic number at the first point of difference has higher priority. View the centre with group 4 directed away from the observer. The sequence $1 \rightarrow 2 \rightarrow 3$ clockwise is *R*, while anticlockwise is *S*. These symbols do not specify the sign of optical rotation, which is measured experimentally.

Step 3: Conclusion An asymmetric molecule has a non-superimposable mirror image. With the lowest-priority group away, clockwise priority order denotes *R* and anticlockwise denotes *S*.

Quick Tip to Solve: Always put priority 4 behind the stereogenic carbon before reading the 1-to-2-to-3 direction; otherwise reverse the result.

11. Write the names of the reagents and equations in the conversion of

(i) phenol to salicylaldehyde

(ii) anisole to p-methoxyacetophenone

[2 marks]

Solution:

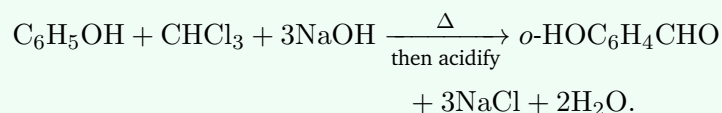
Concept:

- The Reimer–Tiemann reaction introduces a formyl group, $-\text{CHO}$, chiefly ortho to the phenolic hydroxyl group.
- Anisole undergoes Friedel–Crafts acylation; its methoxy group directs electrophilic substitution to the ortho and para positions.

Step 1: Convert phenol into salicylaldehyde Use chloroform and aqueous sodium hydroxide, heat, and then acidify with dilute acid. This is the Reimer–Tiemann reaction. The net equation after acid

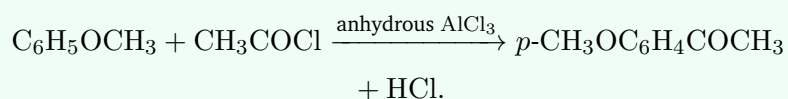
Quick Tip to Solve: Use formylation for phenol to make CHO , and acetylation for anisole to make COCH_3 ; retain the original oxygen substituent.

work-up is



The major product is salicylaldehyde (2-hydroxybenzaldehyde), with the CHO group adjacent to OH.

Step 2: Convert anisole into p-methoxyacetophenone Use acetyl chloride (ethanoyl chloride), CH_3COCl , in the presence of anhydrous aluminium chloride, AlCl_3 :



This Friedel–Crafts acylation gives the para product as the major product because it is less sterically hindered than the ortho product.

Step 3: Conclusion Phenol gives salicylaldehyde with $\text{CHCl}_3/\text{NaOH}$, heat and acid work-up; anisole gives p-methoxyacetophenone with CH_3COCl and anhydrous AlCl_3 .

Quick Tip to Solve: Use formylation for phenol to make CHO, and acetylation for anisole to make COCH₃; retain the original oxygen substituent.

12(a). Write the modes of free radical polymerization of an alkene.

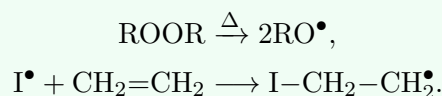
[2 marks]

Solution:

Concept:

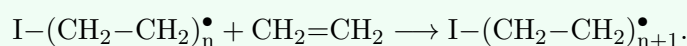
- Free-radical polymerisation converts alkene double bonds into single bonds that link successive monomers; it proceeds by initiation, propagation and termination.
- A dot denotes an unpaired electron. Let $\text{I}^\bullet$ represent an initiator radical and $\text{P}_n^\bullet$ a growing chain radical containing n monomer units.

Step 1: Initiation: produce radicals and start a chain For ethene as the alkene, heat a peroxide initiator to cleave its weak O–O bond homolytically. The radical then adds across the alkene double bond:



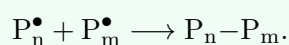
One electron of the double bond forms the new bond; the other remains at the chain end.

Step 2: Propagation: extend the chain The terminal radical successively adds more ethene molecules:



Repeated additions form a long polyethylene chain, while retaining an active radical at its end.

Step 3: Termination: remove the radical centres Two chain radicals can combine to form a stable covalent bond:



Quick Tip to Solve: In each propagation equation leave a radical on the new chain end; remove radicals only in the termination step.

Growth then stops because no unpaired electron remains. Termination may also occur by disproportionation: hydrogen transfer between two chain radicals gives one saturated chain end and one unsaturated chain end.

Step 4: Conclusion The three stages are chain initiation, chain propagation and chain termination; termination occurs by combination or disproportionation.

Quick Tip to Solve: In each propagation equation leave a radical on the new chain end; remove radicals only in the termination step.

OR

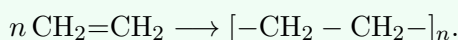
12(b). Differentiate between addition and condensation polymers based on mode of polymerization. Give one example of each type. [2 marks]

Solution:

Concept:

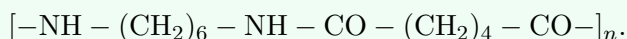
- Polymerization joins many monomer molecules into a macromolecule. The mode of joining distinguishes addition and condensation polymers.
- Addition uses unsaturated monomers without eliminating small molecules; condensation involves repeated reactions of functional groups with elimination of small molecules such as water.

Step 1: Addition polymerization and its example In addition polymerization, monomers containing a carbon-carbon double bond add successively. The double bond opens to provide bonds connecting neighbouring monomer units, and no small molecule is lost. For example, ethene forms polythene:



The repeating unit therefore contains the same atoms as the ethene monomer.

Step 2: Condensation polymerization and its example In condensation polymerization, bifunctional or polyfunctional monomers react through their functional groups, with repeated elimination of small molecules. For example, hexamethylenediamine and adipic acid form nylon-6,6 by condensation of amino and carboxyl groups. The polymer contains the repeating unit



Formation of an amide linkage joins the monomers with elimination of water. Thus the polymer backbone is built by functional-group reactions, unlike the opening of double bonds in the addition example.

Step 3: Conclusion Addition polymers form by successive addition of unsaturated monomers without loss of small molecules, for example polythene. Condensation polymers form by repeated functional-group reactions with elimination of small molecules, for example nylon-6,6.

Quick Tip to Solve: Compare the joining reaction: opening a carbon-carbon double bond gives polythene, while forming amide links with loss of water gives nylon-6,6.

13. What information is given by (i) Radial probability density, R^2 and (ii) Radial probability function, $4\pi r^2 R^2$ in hydrogen atom? How do they vary with r for $1s$ orbital of hydrogen atom? Show diagrammatically. [3 marks]

Solution:

Concept:

- Probability density describes probability per unit volume. For a spherically symmetric s orbital it is the same in all directions at a given distance r from the nucleus.
- A spherical shell of radius r and thickness dr has volume $4\pi r^2 dr$; multiplying density by this volume gives the probability of finding the electron in that shell.

Step 1: Interpret radial probability density In the notation of the question, R^2 measures the electron probability density at distance r from the nucleus. Thus $R^2 dV$ is the probability of finding the electron in a small volume dV there. It compares equal small volume elements at different distances; it is not itself the probability for an entire spherical shell. For the hydrogen $1s$ orbital,

$$R^2 \propto e^{-2r/a_0},$$

where a_0 is the Bohr radius. Hence the density is finite and maximum at $r = 0$, decreases continuously as r increases, and approaches zero as $r \rightarrow \infty$.

Step 2: Interpret the radial probability function The function $P(r) = 4\pi r^2 R^2$ gives the radial probability per unit radial distance: $P(r)dr$ is the probability of finding the electron anywhere in the spherical shell between r and $r + dr$, irrespective of direction. For the $1s$ orbital,

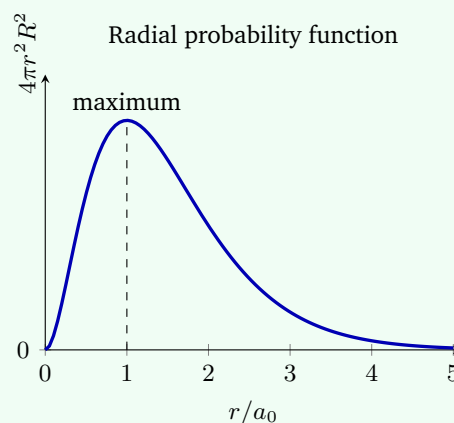
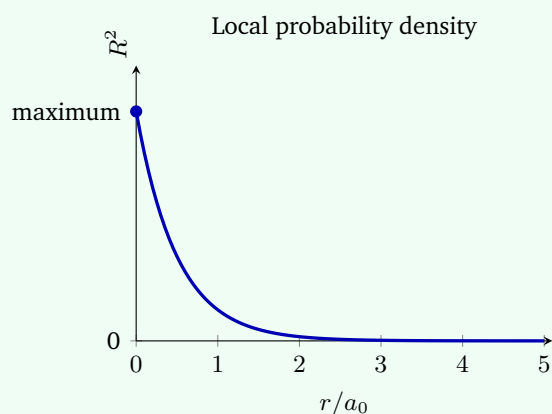
$$P(r) \propto r^2 e^{-2r/a_0}.$$

It is zero at the nucleus because the shell-volume factor r^2 vanishes there, even though the local density is maximum. It first increases, reaches its maximum at $r = a_0$, and then decreases towards zero. Indeed,

$$\frac{d}{dr} \left(r^2 e^{-2r/a_0} \right) = 2r e^{-2r/a_0} \left(1 - \frac{r}{a_0} \right),$$

so the nonzero maximum occurs at a_0 , the most probable distance. Neither curve has a radial node for positive finite r .

Quick Tip to Solve: Multiply the local density by the spherical-shell factor $4\pi r^2$: this moves the maximum from the nucleus to a_0 for hydrogen $1s$.



Hydrogen 1s: local density and shell probability function. Vertical scales are arbitrary; a_0 is the Bohr radius.

Step 3: Conclusion R^2 describes local probability density and is greatest at the nucleus for 1s. The shell probability function $4\pi r^2 R^2$ is zero at the nucleus and greatest at $r = a_0$, approximately 52.9 pm. Both approach zero at large r .

Quick Tip to Solve: Multiply the local density by the spherical-shell factor $4\pi r^2$: this moves the maximum from the nucleus to a_0 for hydrogen 1s.

14. Calculate the density of silver which crystallizes in the face-centred cubic structure. The distance between the nearest silver atoms in this structure is 287 pm.

(Molar mass of Ag = $107.87 \text{ g mol}^{-1}$, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)

[3 marks]

Solution:

Concept:

- In a face-centred cubic (fcc) unit cell the effective number of atoms is $Z = 8(1/8) + 6(1/2) = 4$.
- Nearest neighbours touch along a face diagonal: $d = a/\sqrt{2}$, where d is the nearest-neighbour distance and a is the edge length.
- Density is mass per unit-cell volume: $\rho = ZM/(N_A a^3)$, where M is the molar mass and N_A is Avogadro's constant.

Step 1: Relate the given distance to the edge length A face diagonal contains the centres of a corner atom, a face-centred atom and the next corner atom. Thus its length is twice the nearest-neighbour distance. Since the diagonal also equals $\sqrt{2}a$,

$$a = \sqrt{2}d = \sqrt{2}(287) = 405.88 \text{ pm.}$$

The quoted 287 pm is therefore not the unit-cell edge. Using $1 \text{ pm} = 10^{-10} \text{ cm}$, we obtain $a = 4.0588 \times 10^{-8} \text{ cm}$.

Step 2: Calculate the mass and volume of one unit cell Each fcc cell contains four silver atoms, so its

Quick Tip to Solve: For fcc silver first multiply the nearest-neighbour distance by $\sqrt{2}$; cube the resulting edge only after converting pm to cm.

mass and volume are

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

Hence $\rho = m_{\text{cell}}/V_{\text{cell}} = 10.7195 \text{ g cm}^{-3}$. The use of centimetres for the edge makes the density unit consistent with the molar mass in grams.

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

Quick Tip to Solve: For fcc silver first multiply the nearest-neighbour distance by $\sqrt{2}$; cube the resulting edge only after converting pm to cm.

15. Two elements A and B form compounds having molecular formulae AB_2 and AB_4 . Dissolved in 20 g of benzene, 1 g of AB_2 lowers the freezing point by 2.3 K, whereas 1 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is $5.1 \text{ K kg mol}^{-1}$. Calculate the atomic masses of A and B. [3 marks]

Solution:

Concept:

- For a dilute molecular solution, depression of freezing point is $\Delta T_f = K_f m$, where m is solute molality and K_f is the solvent's molal depression constant.
- For solute mass w , molar mass M , and solvent mass W in grams, $m = (w/M)/(W/1000)$; hence $M = 1000K_f w/(\Delta T_f W)$.
- If the atomic masses are x for A and y for B, the molecular masses of AB_2 and AB_4 are $x + 2y$ and $x + 4y$, respectively.

Step 1: Determine the molar mass of each compound In each experiment the mass of solute is 1 g and the mass of benzene is $20 \text{ g} = 0.020 \text{ kg}$. Applying the freezing-point relation separately,

$$M(\text{AB}_2) = \frac{5.1 \times 1}{2.3 \times 0.020} = 110.8696 \text{ g mol}^{-1},$$
$$M(\text{AB}_4) = \frac{5.1 \times 1}{1.3 \times 0.020} = 196.1538 \text{ g mol}^{-1}.$$

The smaller depression for the same mass of AB_4 indicates fewer dissolved molecules and therefore a larger molar mass, consistent with these results.

Step 2: Solve the two atomic-mass equations Writing the numerical molecular masses in terms of the atomic masses gives

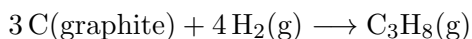
$$x + 2y = 110.8696, \quad x + 4y = 196.1538.$$

Subtracting eliminates A: $2y = 85.2842$, so $y = 42.6421$. Substituting in the first equation gives $x = 110.8696 - 2(42.6421) = 25.5854$. Retaining extra digits during subtraction prevents avoidable rounding error; these values reproduce both observed freezing-point depressions.

Step 3: Conclusion The atomic masses are $A \approx 25.6 \text{ u}$, $B \approx 42.6 \text{ u}$, corresponding to atomic molar masses of approximately 25.6 and 42.6 g mol^{-1} , respectively.

Quick Tip to Solve: The two molecular masses differ by exactly two B atoms; subtract their equations before calculating the mass of A.

16. Calculate the standard Gibbs energy change for the formation of propane at 298 K.



$\Delta_f H^\circ$ for propane, $\text{C}_3\text{H}_8(\text{g})$, is $-103.85 \text{ kJ mol}^{-1}$. Given: $S_m^\circ[\text{C}_3\text{H}_8(\text{g})] = 270.2 \text{ J K}^{-1} \text{ mol}^{-1}$, $S_m^\circ[\text{C}(\text{graphite})] = 5.70 \text{ J K}^{-1} \text{ mol}^{-1}$, and $S_m^\circ[\text{H}_2(\text{g})] = 130.68 \text{ J K}^{-1} \text{ mol}^{-1}$. [3 marks]

Solution:

Concept:

- The standard Gibbs energy change is $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, with temperature T in kelvin and consistent energy units.
- Reaction entropy is the stoichiometric sum of product standard molar entropies minus that of reactants: $\Delta_r S^\circ = \sum \nu S_m^\circ(\text{products}) - \sum \nu S_m^\circ(\text{reactants})$.
- The stated reaction forms one mole of propane from carbon in its graphite standard state and hydrogen gas, so its reaction Gibbs energy is the standard Gibbs energy of formation of propane.

Step 1: Calculate the standard entropy of formation For $3 \text{C}(\text{graphite}) + 4 \text{H}_2(\text{g}) \longrightarrow \text{C}_3\text{H}_8(\text{g})$, include the coefficients 3 and 4 in the reactant entropy sum:

$$\begin{aligned}\Delta_f S^\circ &= 270.2 - [3(5.70) + 4(130.68)] \\ &= 270.2 - (17.10 + 522.72) \\ &= -269.62 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -0.26962 \text{ kJ K}^{-1} \text{ mol}^{-1}.\end{aligned}$$

The entropy decreases substantially, as expected when four moles of gaseous hydrogen are consumed to form one mole of gaseous propane. The entropy of graphite must still be included: an element's standard molar entropy is not generally zero.

Step 2: Apply the Gibbs energy equation at 298 K The given formation enthalpy is $\Delta_f H^\circ = -103.85 \text{ kJ mol}^{-1}$. Using entropy in kJ to match this enthalpy,

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

Because $\Delta_f S^\circ$ is negative, the term $-T\Delta_f S^\circ$ is positive and makes the Gibbs energy less negative than the enthalpy. This sign check supports the numerical substitution.

Step 3: Conclusion The standard Gibbs energy change for formation of propane at 298 K is

$$\Delta_f G^\circ = -23.50 \text{ kJ mol}^{-1}.$$

Quick Tip to Solve: Multiply each reactant entropy by its equation coefficient, then divide the entropy change by 1000 before combining it with enthalpy in kJ.

17. Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity. If Λ_m° for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what is its dissociation constant? [3 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when conductivity κ is in S cm^{-1} and concentration c is in mol L^{-1} .
- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$. For a monoprotic weak acid, $K_a = c\alpha^2/(1 - \alpha)$.

Step 1: Calculate the molar conductivity Here $c = 0.00241 \text{ mol L}^{-1}$ and $\kappa = 7.896 \times 10^{-5} \text{ S cm}^{-1}$. Converting the concentration from moles per litre to moles per cubic centimetre introduces the factor 1000:

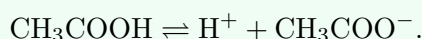
$$\Lambda_m = \frac{1000 \times 7.896 \times 10^{-5}}{0.00241} = 32.7635 \text{ S cm}^2 \text{ mol}^{-1}.$$

Step 2: Find the fraction of acid dissociated At infinite dilution, the weak acid is completely dissociated. Comparing the conductivity at the given concentration with its limiting value gives

$$\alpha = \frac{32.7635}{390.5} = 0.08390.$$

Thus approximately 8.39% of the acetic acid is dissociated at this concentration.

Step 3: Apply the dissociation equilibrium expression The equilibrium is



Therefore the equilibrium concentrations of hydrogen ions and acetate ions are each $c\alpha$, while that of undissociated acid is $c(1 - \alpha)$. Hence

$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \\ &= \frac{0.00241(0.08390)^2}{1 - 0.08390} = 1.852 \times 10^{-5} \text{ mol L}^{-1}. \end{aligned}$$

Retaining $1 - \alpha$ avoids the error from treating the undissociated concentration as exactly the initial concentration.

Step 4: Conclusion The molar conductivity is $32.76 \text{ S cm}^2 \text{ mol}^{-1}$, and the dissociation constant is $K_a = 1.85 \times 10^{-5} \text{ mol L}^{-1}$.

Quick Tip to Solve: First convert conductivity to molar conductivity with the factor 1000; use its ratio to the limiting value as alpha, retaining the denominator 1-alpha.

18. A reaction is first order in A and second order in B.

(i) Write differential rate equation.

(ii) How is the rate affected if the concentration of B is tripled?

(iii) How is the rate affected when the concentrations of both A and B are doubled?

What is the significance of rate constant in the rate expression?

[3 marks]

Solution:

Concept:

- The order with respect to a reactant is its concentration exponent in the experimentally determined rate law. First order in A and second order in B imply $r = k[A][B]^2$.
- At fixed temperature and otherwise identical conditions, the rate constant k is independent of reactant concentrations. Its units follow from the overall order, which here is $1 + 2 = 3$.

Step 1: (i) Write the differential rate law The instantaneous reaction rate is

$$r = k[A]^1[B]^2.$$

If the stoichiometric coefficient of A is a , the differential form is $-\frac{1}{a} \frac{d[A]}{dt} = k[A][B]^2$. In particular, for unit stoichiometric coefficient this is $-d[A]/dt = k[A][B]^2$. The reaction orders alone do not specify the stoichiometric coefficients.

Step 2: (ii) Triple the concentration of B Keeping $[A]$ and temperature constant, substitute $[B]' = 3[B]$:

$$\frac{r'}{r} = \frac{k[A](3[B])^2}{k[A][B]^2} = 3^2 = 9.$$

The rate becomes nine times its initial value because the concentration of B occurs squared.

Step 3: (iii) Double both concentrations With $[A]' = 2[A]$ and $[B]' = 2[B]$,

$$\frac{r'}{r} = \frac{k(2[A])(2[B])^2}{k[A][B]^2} = 2 \times 2^2 = 8.$$

The rate therefore becomes eight times its original value.

Step 4: Explain the significance of the rate constant The rate constant is the proportionality constant relating the reaction rate to the specified product of reactant concentrations. It is numerically equal to the reaction rate when each reactant concentration is unity in the chosen concentration units. For this third-order rate law, using rate in $\text{mol L}^{-1} \text{s}^{-1}$, its units are $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$. It characterises the reaction at a given temperature and may change with temperature or a catalyst, although changing concentrations alone does not change it.

Step 5: Conclusion $r = k[A][B]^2$; tripling B gives $9r$, and doubling both A and B gives $8r$. The rate constant is the rate-law proportionality constant, numerically equal to the rate at unit concentrations.

Quick Tip to Solve: To compare rates, multiply each concentration-change factor raised to its own order: here the factors are x for A and y squared for B.

19(a). How are the colloids classified on the basis of the nature of interaction between dispersed phase and dispersion medium? Describe an important characteristic of each class. Which of these sols need stabilising agents for preservation?

[3 marks]

Solution:

Concept:

- A colloid contains a dispersed phase distributed through a dispersion medium. On the basis of affinity between these two phases, sols are classified as lyophilic and lyophobic.
- Strong solvation stabilises lyophilic particles; lyophobic particles have little affinity for the medium and depend mainly on surface charge for stability.

Step 1: Describe lyophilic sols Lyophilic means solvent-loving. In these colloids, the dispersed phase has a strong attraction for the dispersion medium. The particles become solvated, forming a protective solvent layer around them. Consequently, these sols are relatively stable and are readily formed by mixing the dispersed substance with a suitable medium. An important characteristic is their reversibility: after removing the medium, the sol can generally be formed again by adding the medium. Starch or gelatin in water are examples; when water is the medium, the term hydrophilic is used.

Step 2: Describe lyophobic sols Lyophobic means solvent-hating. The dispersed phase has little or no affinity for the dispersion medium. These sols usually require special preparation methods because merely mixing the two phases does not readily form the sol. An important characteristic is their irreversibility: once coagulated, the precipitated dispersed phase cannot ordinarily be converted back into the sol simply by adding the medium. Gold sol and arsenic sulphide sol in water are examples. They are less stable than lyophilic sols and are readily coagulated by small quantities of suitable electrolytes.

Step 3: Identify the sols requiring protection Lyophobic sols need stabilising agents for preservation. A suitable lyophilic protective colloid, such as gelatin, adsorbs on their particle surfaces and supplies a solvated protective layer. This helps prevent particles from coming together and coagulating. Lyophilic sols already have strong solvation and generally do not need an added protective colloid for this purpose.

Step 4: Conclusion The two classes are lyophilic and lyophobic sols. Lyophilic sols are strongly solvated, stable and reversible; lyophobic sols have weak solvent affinity, are less stable and are irreversible. Lyophobic sols require stabilising agents for preservation.

Quick Tip to Solve: Link solvent affinity to stability: a solvent-loving particle carries a protective solvent layer, while a lyophobic sol needs extra protection against coagulation.

19(b). What are detergents? Give their scheme of classification. Why are the detergents preferred over soaps? [3 marks]

Solution:

Concept:

- Synthetic detergents are cleansing agents containing a long hydrophobic hydrocarbon chain and a hydrophilic group. They remove oily dirt by forming micelles in water.
- Detergents are classified by the charge on their cleansing-active part: anionic, cationic and non-ionic.

Step 1: Define detergents Detergents are synthetic surface-active cleansing agents. Their hydrocarbon tails enter grease while their water-attracting heads remain in water. On agitation, they surround and disperse greasy dirt in micelles, allowing it to be washed away.

Step 2: Classify them by the active group **Anionic detergents:** The active cleansing species is an anion. Examples include sodium alkyl sulphates, such as sodium lauryl sulphate, $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^-\text{Na}^+$, and sodium alkylbenzene sulphonates.

Cationic detergents: The active cleansing species is a cation. They are generally quaternary ammonium salts containing a long alkyl chain, for example cetyltrimethylammonium bromide, $[\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]^+\text{Br}^-$.

Non-ionic detergents: Their hydrophilic groups carry no ionic charge. Examples are condensation products of long-chain alcohols with ethylene oxide; ether oxygen atoms help the molecules interact with water.

Step 3: Explain the advantage over soap In hard water, soap forms insoluble calcium and magnesium salts, producing scum and wasting soap. Detergents do not form such insoluble precipitates with these ions, so they retain their cleansing action in hard water. Sulphate- and sulphonate-based detergents can also clean in acidic water, where soap is converted into poorly soluble free fatty acids.

Step 4: Conclusion Detergents are synthetic cleansing agents classified as anionic, cationic and non-ionic. Their chief advantage over soaps is effective cleansing in hard water without insoluble scum; suitable detergents also work in acidic water.

Quick Tip to Solve: Classify a detergent by the charge on its long-chain cleansing species, and compare hard-water behaviour with soap scum.

20. Draw a figure to show splitting of degenerate d orbitals in an octahedral crystal field. How does the magnitude of Δ_o decide the actual configuration of d orbitals in a complex entity? [3 marks]

Solution:

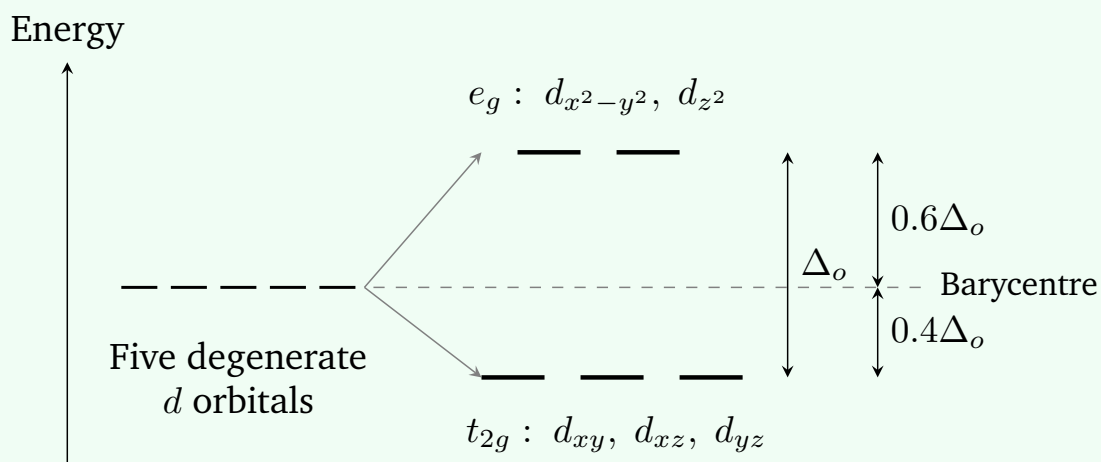
Concept:

- In an octahedral complex, six ligands approach the central metal ion along the coordinate axes. Electrostatic repulsion removes the degeneracy of the five metal d orbitals.

Quick Tip to Solve: Draw three lower and two upper orbital lines, then compare the cost of promotion, Δ_o , with pairing, P .

- The octahedral splitting energy is $\Delta_o = E(e_g) - E(t_{2g})$. The pairing energy P is the energy required to pair electrons within an orbital.

Step 1: Show octahedral crystal-field splitting The $d_{x^2-y^2}$ and d_{z^2} orbitals point towards the ligands and experience greater repulsion; together they form the higher-energy e_g set. The d_{xy} , d_{xz} and d_{yz} orbitals lie between the axes, experience less repulsion and form the lower-energy t_{2g} set. Relative to the barycentre, each t_{2g} orbital is lowered by $0.4\Delta_o$, and each e_g orbital is raised by $0.6\Delta_o$.



Octahedral splitting of five degenerate d orbitals; dashed line marks the barycentre.

Step 2: Compare splitting with pairing energy Electrons first occupy the lower t_{2g} orbitals singly, according to Hund's rule. For configurations where pairing competes with occupation of the upper set, compare Δ_o with P .

If $\Delta_o < P$, promoting an electron to e_g costs less energy than pairing it in t_{2g} . Electrons therefore occupy the upper orbitals before extra pairing occurs, giving a weak-field, high-spin complex.

If $\Delta_o > P$, pairing in t_{2g} costs less energy than promotion. Electrons pair in the lower set before entering e_g , giving a strong-field, low-spin complex. For example, a d^4 ion has $t_{2g}^3 e_g^1$ in a weak field and $t_{2g}^4 e_g^0$ in a strong field. The high-spin/low-spin distinction applies to octahedral d^4 through d^7 configurations.

Step 3: Conclusion Octahedral splitting produces lower t_{2g} and higher e_g levels separated by Δ_o . A splitting smaller than P favours high spin; a splitting larger than P favours low spin.

Quick Tip to Solve: Draw three lower and two upper orbital lines, then compare the cost of promotion, Δ_o , with pairing, P .

21. Complete the following nuclear reactions:

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

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

(iii) ${}_{82}^{210}\text{Pb}$ undergoes β -decay

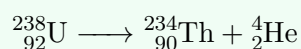
[3 marks]

Solution:

Concept:

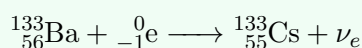
- A nuclear equation conserves the total mass number A (number of nucleons) and the total atomic number Z (electric charge in proton-charge units).
- An alpha particle is ${}^4_2\text{He}$. K-capture absorbs an inner-shell electron, whereas beta-minus decay emits an electron when a neutron changes into a proton.

Step 1: Complete the alpha-decay equation (i) Emission of an alpha particle lowers the parent's mass number by 4 and atomic number by 2. Thus $A = 238 - 4 = 234$ and $Z = 92 - 2 = 90$; the element of atomic number 90 is thorium.



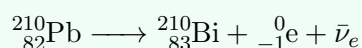
The balances are $238 = 234 + 4$ and $92 = 90 + 2$.

Step 2: Complete the K-capture equation (ii) A proton in the nucleus captures a K-shell electron and becomes a neutron, emitting an electron neutrino ν_e . No nucleon leaves the nucleus, so $A = 133$, while $Z = 56 - 1 = 55$, corresponding to caesium.



The total atomic number on the left is $56 + (-1) = 55$, equal to that of the daughter nucleus.

Step 3: Complete the beta-decay equation (iii) In beta-minus decay a neutron becomes a proton and emits an electron together with an electron antineutrino $\bar{\nu}_e$. Hence the mass number remains 210, while the atomic number increases to $82 + 1 = 83$, giving bismuth.



Charge balances because $82 = 83 + (-1)$, and the nucleon count remains 210. The neutrinos have zero charge and zero nucleon number.

Step 4: Conclusion The daughter nuclei are respectively ${}_{90}^{234}\text{Th}$, ${}_{55}^{133}\text{Cs}$ and ${}_{83}^{210}\text{Bi}$, with the complete balanced nuclear equations shown above.

Quick Tip to Solve: For alpha decay subtract (4, 2) from (A, Z); for K-capture change only Z by -1 , and for beta-minus decay change only Z by $+1$.

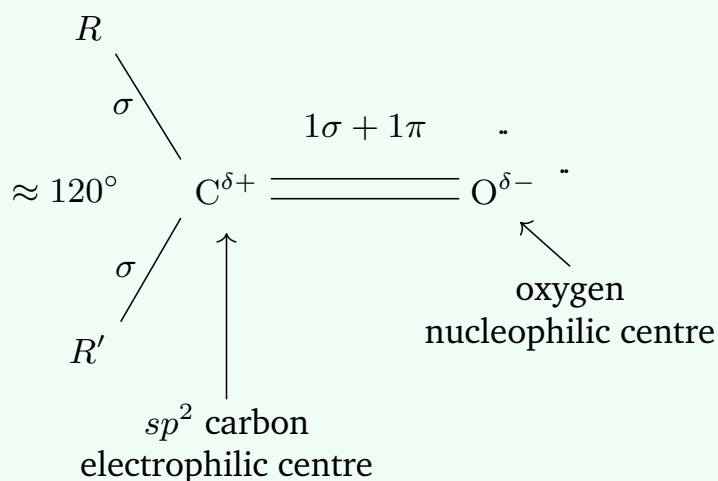
22. Draw the structure of a carbonyl group and indicate clearly (i) the hybridized state of carbon, (ii) the σ and π bonds present and (iii) the electrophilic and nucleophilic centres in it. [3 marks]

Solution:

Concept:

- The carbonyl group, $\text{C}=\text{O}$, contains a carbon-oxygen double bond. Its carbon atom is sp^2 -hybridised and has trigonal planar geometry with bond angles approximately 120° .
- A double bond consists of one σ bond from head-on orbital overlap and one π bond from sideways overlap of parallel unhybridised p orbitals.
- Oxygen is more electronegative than carbon, so the carbonyl bond is polar: $\text{C}^{\delta+}=\text{O}^{\delta-}$. Electron-deficient centres are electrophilic and electron-rich centres are nucleophilic.

Step 1: Draw the group and show carbon hybridisation Draw a carbon atom double-bonded to oxygen and single-bonded to two substituents R and R' . The three sp^2 orbitals of carbon lie in one plane: two form bonds to the substituents, while the third forms the carbon-oxygen σ bond. One unhybridised p orbital remains perpendicular to the plane.



Planar carbonyl group showing bond types, hybridisation and reactive centres

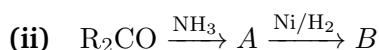
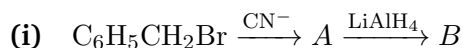
Step 2: Identify the sigma and pi bonds The carbon-oxygen σ bond is formed by head-on overlap of an sp^2 orbital on carbon with an sp^2 orbital on oxygen. Parallel unhybridised p orbitals on carbon and oxygen overlap sideways to give the π bond. Thus the $\text{C}=\text{O}$ linkage contains exactly one σ and one π bond; each bond from carbon to a substituent is a σ bond.

Step 3: Locate the reactive centres Oxygen attracts the shared electron density more strongly, so carbon carries a partial positive charge $\delta+$ and oxygen a partial negative charge $\delta-$. Carbon is therefore the electrophilic centre and accepts an electron pair from an attacking nucleophile. Oxygen, with its lone pairs and increased electron density, is the nucleophilic centre and can donate an electron pair to an electrophile such as a proton.

Step 4: Conclusion Carbonyl carbon is sp^2 -hybridised; the $\text{C}=\text{O}$ bond has one σ and one π bond. Carbon ($\delta+$) is the electrophilic centre and oxygen ($\delta-$) is the nucleophilic centre, as labelled in the drawing.

Quick Tip to Solve: Label carbon sp^2 and $\delta+$ first, then oxygen $\delta-$; place one σ and one π label on the double bond, with 120° planar geometry at carbon.

23. (a) Identify A and B in the following:



(b) Explain why the aromatic amines are less basic than ammonia and aliphatic amines.

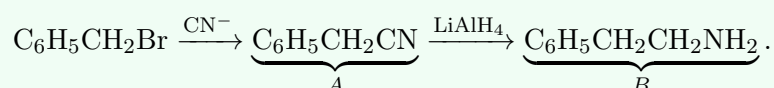
[3 marks]

Solution:

Concept:

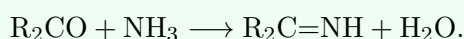
- Cyanide ion substitutes a halide to form a nitrile, adding one carbon to the chain. Reduction of $-\text{C} \equiv \text{N}$ with LiAlH_4 gives $-\text{CH}_2\text{NH}_2$.
- A ketone condenses with ammonia to give an imine, $\text{R}_2\text{C}=\text{NH}$. Catalytic hydrogenation converts its carbon-nitrogen double bond into a single bond.
- Basicity depends on the availability of the nitrogen lone pair for accepting a proton; resonance delocalisation decreases this availability.

Step 1: (a)(i) Identify the nitrile and its reduction product Cyanide replaces bromide in benzyl bromide through its carbon end. Thus the first product is benzyl cyanide (phenylacetone nitrile). Reduction changes the nitrile carbon into a methylene group without removing it:

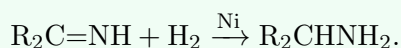


The amine B is 2-phenylethan-1-amine.

Step 2: (a)(ii) Identify the imine and the primary amine Ammonia first condenses with the ketone, with elimination of water:



Therefore A is the imine $\text{R}_2\text{C}=\text{NH}$. Hydrogenation over nickel adds hydrogen across the double bond:



Hence B is the primary amine R_2CHNH_2 .

Step 3: (b) Compare the availability of the nitrogen lone pair In an aromatic amine such as aniline, the nitrogen lone pair is conjugated with the benzene ring and is delocalised into it by resonance. It is consequently less available to bind a proton.

In ammonia the lone pair is localised on nitrogen. In aliphatic amines, alkyl groups donate electron density by their positive inductive effect, increasing the tendency of nitrogen to accept a proton. Aromatic amines are therefore less basic than ammonia and the usual aliphatic amines.

Step 4: Conclusion (a)(i) $A = \text{C}_6\text{H}_5\text{CH}_2\text{CN}$, $B = \text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{NH}_2$. (a)(ii) $A = \text{R}_2\text{C}=\text{NH}$, $B = \text{R}_2\text{CHNH}_2$. (b) Resonance delocalisation makes the nitrogen lone pair in aromatic amines less available for protonation.

Quick Tip to Solve: Count the carbon of CN when reducing a nitrile: the sequence adds one carbon before forming the primary amine.

24. On the basis of application, how are dyes classified? Describe essential features of any two of them. [3 marks]

Solution:

Concept:

- Classification by application depends on how a dye is applied and fixed to a fibre. It differs from classification by chemical structure, such as azo or anthraquinone dyes.
- A useful dye must have affinity for the material being dyed and remain fixed during normal washing and use. Different classes achieve fixation by ionic attraction, direct adsorption, chemical bonding or formation of an insoluble coloured substance.

Step 1: State the application classes On the basis of their application, dyes are classified as acid dyes, basic dyes, direct dyes, disperse dyes, fibre-reactive dyes, vat dyes, mordant dyes and ingrain dyes. Ingrain dyes include insoluble azo dyes formed within the fibre. The names indicate the method of application or fixation rather than merely the colour of the dye.

Step 2: Essential features of acid dyes Acid dyes are generally sodium salts of sulphonic acids or, in some cases, carboxylic acids. They are water-soluble and yield coloured anions in solution. They are applied from an acidic bath, chiefly to wool, silk and nylon. In the acidic bath, amino groups of these fibres become protonated; attraction between these positively charged sites and the dye anions helps fix the colour. Orange II is an example of an acid dye. Untreated cotton has little affinity for such dyes.

Step 3: Essential features of basic dyes Basic dyes are salts of coloured organic bases, generally with acids such as hydrochloric acid. They are usually water-soluble and yield coloured cations. These cations bind to suitable negatively charged sites in the fibre, and the dyes commonly give bright, intense shades. They are used especially for acrylic fibres and can also dye silk and wool. Cotton generally requires a suitable mordant or pretreatment for their fixation. Malachite green is a familiar example. Thus acid and basic dyes differ in the charge on the coloured ion as well as in their application conditions.

Step 4: Conclusion The application classes are acid, basic, direct, disperse, fibre-reactive, vat, mordant and ingrain dyes. Acid dyes give coloured anions and are applied from an acidic bath; basic dyes give coloured cations and are salts of coloured organic bases.

Quick Tip to Solve: For application classification, name how the dye fixes to a fibre; distinguish acid and basic dyes by their coloured anion and cation, respectively.

25. (a) Assign appropriate reason for each of the following observations:

- (i) Anhydrous AlCl_3 is used as a catalyst.
- (ii) Phosphinic acid behaves as a monoprotic acid.
- (iii) SF_6 is not easily hydrolysed whereas SF_4 is readily hydrolysed.
- (iv) No form of elemental silicon is comparable to graphite.

(b) Draw the structure of XeOF_4 or BrF_3 .

[5 marks]

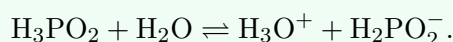
Solution:

Concept:

- A Lewis acid accepts an electron pair. The acidic hydrogens in phosphorus oxyacids are those bonded to oxygen.
- Hydrolysis depends on bond strength and access to the central atom. VSEPR places lone pairs at sites of least repulsion.

Step 1: (a)(i) Catalytic action of anhydrous aluminium chloride Anhydrous AlCl_3 is electron deficient: aluminium can accept an electron pair, so it acts as a Lewis acid. By coordinating to a reactant, it helps generate an electrophile, as in Friedel–Crafts reactions. Water would coordinate to and hydrolyse the catalyst, so anhydrous conditions are required.

Step 2: (a)(ii) Monoprotic nature of phosphinic acid Phosphinic acid, H_3PO_2 , has structure $\text{H}_2\text{P}(=\text{O})\text{OH}$. Only one hydrogen is bonded to oxygen and can ionise; the two $\text{P}-\text{H}$ hydrogens do not ionise in water. Hence its basicity is one:



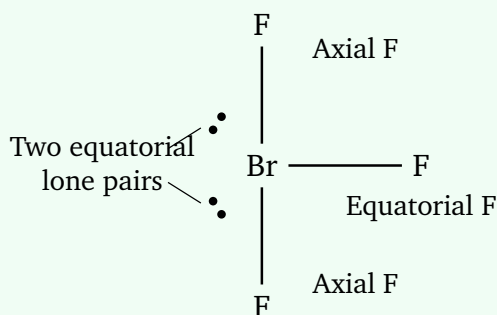
Step 3: (a)(iii) Different behaviour towards hydrolysis In octahedral SF_6 , six fluorine atoms shield sulphur from attack by water. This shielding and strong $\text{S}-\text{F}$ bonds make it kinetically resistant to hydrolysis. The four fluorines in seesaw-shaped SF_4 leave sulphur more accessible, so it readily hydrolyses:



Step 4: (a)(iv) Absence of a graphite-like form of silicon Graphite has planar sp^2 -bonded carbon sheets stabilised by delocalised $p\pi-p\pi$ bonding. Small carbon atoms give effective sideways overlap of $2p$ orbitals. Larger silicon atoms have more diffuse $3p$ orbitals and much poorer sideways overlap, so comparable graphite-like sheets are unfavourable. Silicon normally forms a three-dimensional tetrahedral network of single bonds.

Step 5: (b) Structure of bromine trifluoride Choosing BrF_3 : seven valence electrons on bromine give three bond pairs and two lone pairs. Its five electron domains have a trigonal-bipyramidal arrangement (sp^3d description). The two lone pairs occupy equatorial sites to minimise repulsion. Two F atoms are axial and one is equatorial, giving a T-shaped molecule. Actual axial–equatorial angles are slightly below 90° ; the drawing is idealised.

Quick Tip to Solve: Write phosphinic acid as $\text{H}_2\text{P}(=\text{O})\text{OH}$ before counting acidic hydrogens; for BrF_3 , count five electron domains and place both lone pairs equatorially.



Idealised T-shaped BrF_3 ; both lone pairs occupy equatorial positions.

Step 6: Conclusion The reasons are Lewis acidity of AlCl_3 , one ionisable O – H hydrogen in H_3PO_2 , shielding of sulphur in SF_6 , and poor sideways orbital overlap in silicon. BrF_3 is T-shaped with two equatorial lone pairs.

Quick Tip to Solve: Write phosphinic acid as $\text{H}_2\text{P}(=\text{O})\text{OH}$ before counting acidic hydrogens; for BrF_3 , count five electron domains and place both lone pairs equatorially.

26. (a) How would you account for the following:

- (i) The transition elements exhibit high enthalpies of atomization.
 - (ii) The 4d and 5d series of the transition metals have more frequent metal-metal bonding in their compounds than do the 3d metals.
 - (iii) There is a greater range of oxidation states among the actinoids than that in the lanthanoids.
- (b) Write the complete chemical equation for each of the following:**
- (i) An alkaline solution of KMnO_4 reacts with an iodide.
 - (ii) An excess of SnCl_2 solution is added to a solution of mercury(II) chloride.

[5 marks]

Solution:

Concept:

- Enthalpy of atomization is the enthalpy required to produce one mole of separated gaseous atoms from an element in its standard state; stronger metallic bonding requires more energy.
- Metal-metal bonding depends on effective orbital overlap. More radially extended orbitals can overlap more effectively between neighbouring metal centres.
- Orbitals of comparable energy can participate in bonding, permitting different oxidation states. In redox equations, both atoms and total electric charge must balance.

Step 1: (a)(i) High enthalpies of atomization Transition metals have strong metallic bonds because both the outer ns electrons and the $(n-1)d$ electrons can participate in bonding. Their relatively large numbers of unpaired d electrons permit strong interatomic interactions. Consequently, considerable energy is needed to separate the metal atoms completely into gaseous atoms, giving high enthalpies of atomization. The magnitude varies across a series as the number of available bonding electrons changes.

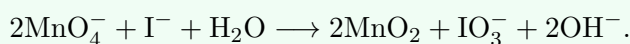
Step 2: (a)(ii) More frequent metal-metal bonding in the 4d and 5d series The 4d and 5d orbitals

Quick Tip to Solve: For the mercury reaction, the word excess requires the second reduction to Hg; stopping at white Hg_2Cl_2 misses the final product.

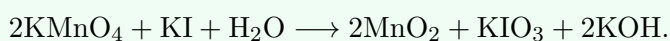
are spatially more extended than the $3d$ orbitals. They therefore give more effective overlap between orbitals on adjacent metal atoms. The resulting metal-metal bonds are stronger and occur more frequently in compounds of the $4d$ and $5d$ metals than in those of the $3d$ metals.

Step 3: (a)(iii) Wider range of oxidation states of actinoids In actinoids the $5f$, $6d$ and $7s$ subshells have comparable energies, so different numbers of electrons from these subshells can participate in bonding. This produces a wide range of oxidation states. In lanthanoids the $4f$ electrons are more deeply buried and less readily involved in bonding; removal of two $6s$ electrons and one further electron commonly gives the dominant $+3$ state. Thus the oxidation states of lanthanoids are less varied.

Step 4: (b)(i) Alkaline permanganate and iodide Iodide is oxidised to iodate while permanganate is reduced to manganese dioxide. The balanced ionic equation is

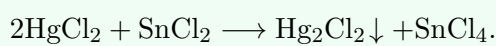


Using potassium iodide as the iodide, the complete molecular equation is

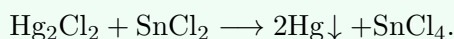


Iodine changes from -1 to $+5$, losing six electrons; the two manganese atoms each gain three electrons on changing from $+7$ to $+4$. Both atoms and charge are balanced.

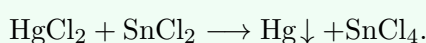
Step 5: (b)(ii) Excess tin(II) chloride and mercury(II) chloride Tin(II) chloride first reduces mercury(II) chloride to white mercury(I) chloride:



Since tin(II) chloride is in excess, the precipitate is reduced further to grey metallic mercury:



Hence the overall reaction with excess reducing agent is



Tin is oxidised from $+2$ to $+4$, while mercury is reduced from $+2$ to zero in the overall change.

Step 6: Conclusion (a) Strong metallic bonding explains high atomization enthalpies; extended $4d/5d$ orbitals favour metal-metal bonding; comparable $5f/6d/7s$ energies give actinoids more oxidation states. (b) Alkaline permanganate converts iodide to iodate with MnO_2 formation, and excess SnCl_2 reduces HgCl_2 completely to metallic mercury.

Quick Tip to Solve: For the mercury reaction, the word excess requires the second reduction to Hg ; stopping at white Hg_2Cl_2 misses the final product.

27(a). Name the products obtained on complete hydrolysis of DNA. Enumerate the structural differences between DNA and RNA. In what way is a nucleotide different from a nucleoside? Illustrate with examples. [5 marks]

Solution:

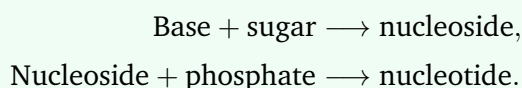
Concept:

- Nucleic acids are polynucleotides. Each nucleotide contains a pentose sugar, a nitrogenous base and a phosphate group; complete hydrolysis separates these components.
- DNA contains 2-deoxy-D-ribose, whereas RNA contains D-ribose. The sugars differ at carbon 2': DNA has H and RNA has OH at this position.
- A nucleoside is a base joined to a sugar; phosphorylation of a nucleoside gives a nucleotide. Adjacent nucleotides in a nucleic-acid chain are connected by 3'-5' phosphodiester linkages.

Step 1: Products of complete hydrolysis of DNA Complete hydrolysis breaks the sugar-phosphate backbone as well as the bonds between the sugar and the bases. The products are 2-deoxy-D-ribose, phosphoric acid and the four nitrogenous bases adenine (A), guanine (G), cytosine (C) and thymine (T). Adenine and guanine are purines; cytosine and thymine are pyrimidines. Thus the complete products are the free sugar, phosphate and bases, rather than merely the nucleotide units formed by partial hydrolysis.

Step 2: Structural differences between DNA and RNA The principal structural differences are as follows. First, DNA has 2-deoxy-D-ribose as its pentose sugar, while RNA has D-ribose. Consequently, at carbon 2' the DNA sugar has H in place of the OH group present in RNA. Second, DNA contains adenine, guanine, cytosine and thymine, whereas RNA contains adenine, guanine, cytosine and uracil: uracil replaces thymine in RNA. Third, DNA usually consists of two antiparallel polynucleotide strands coiled into a double helix, whereas RNA is generally a single polynucleotide strand, although it can fold into regions with base pairing. In the DNA double helix, complementary bases on opposite strands pair through hydrogen bonds: A with T and G with C. Both DNA and RNA possess a sugar-phosphate backbone, so the presence of phosphate itself is not a structural distinction between them.

Step 3: Distinguish a nucleoside from a nucleotide with examples In a nucleoside, a nitrogenous base is linked to the 1' carbon of a pentose sugar through an N-glycosidic bond; no phosphate group is present. For example, adenine joined to ribose forms adenosine, while adenine joined to deoxyribose forms deoxyadenosine. A nucleotide contains the corresponding base-sugar unit together with a phosphate group, commonly esterified at the sugar's 5'-OH group. Thus adenosine 5'-monophosphate (AMP) is a nucleotide derived from adenosine, and deoxyadenosine 5'-monophosphate (dAMP) is derived from deoxyadenosine. The relationship is



Step 4: Conclusion DNA yields deoxyribose, phosphoric acid and A, G, C and T on complete hydrolysis. DNA and RNA differ in their sugar, thymine versus uracil, and usual double-stranded versus single-stranded structure. A nucleotide is a phosphorylated nucleoside, as illustrated by AMP and adenosine, respectively.

Quick Tip to Solve: Check three structural features separately: the sugar at carbon 2', T versus U, and the usual strand number. For nucleoside versus nucleotide, look specifically for phosphate.

27(b). Define and classify vitamins. Name the diseases caused due to lack of any three of them.

[5 marks]

Solution:

Concept:

- Vitamins are organic compounds required in small amounts in the diet for normal growth, maintenance of health and regulation of metabolic processes. Most cannot be synthesised by the human body in adequate quantities and must therefore be supplied through food.
- Vitamins are classified on the basis of their solubility into fat-soluble and water-soluble vitamins. A prolonged inadequate intake of a particular vitamin produces characteristic deficiency symptoms or diseases.

Step 1: Define vitamins and state their role Vitamins are essential organic micronutrients: the body needs only small quantities, but those quantities are necessary for normal physiological functions. Many vitamins or their derivatives assist enzymes in metabolic reactions. They are not a major source of energy; their importance lies in helping the body carry out and regulate essential processes. Since the body generally cannot make enough of them, a balanced diet must provide them.

Step 2: Classify vitamins according to solubility **Fat-soluble vitamins:** Vitamins A, D, E and K dissolve in fats and oils. They are absorbed along with dietary fats and can be stored in the liver and fatty tissues. Consequently, their supply need not be replenished as frequently as that of most water-soluble vitamins.

Water-soluble vitamins: The B-complex vitamins and vitamin C dissolve in water. Examples of the B-complex group are thiamine (B_1), riboflavin (B_2), niacin and cobalamin (B_{12}). Most water-soluble vitamins are not stored appreciably, and excess quantities are generally excreted in urine, so a regular dietary supply is required. Vitamin B_{12} is an exception because significant stores can be maintained in the liver.

Step 3: Name three vitamin-deficiency diseases Three suitable examples, with each disease matched to its deficient vitamin, are:

Vitamin	Deficiency disease	Main effect
A	Night blindness	Poor vision in dim light
D	Rickets in children	Soft, deformed bones
C	Scurvy	Bleeding gums, poor wound healing

Vitamin A supports normal vision. Vitamin D helps maintain calcium and phosphate availability for bone mineralisation. Vitamin C is needed for normal collagen formation, which explains the weak connective tissues and bleeding gums associated with scurvy.

Step 4: Conclusion Vitamins are organic nutrients needed in small amounts for normal growth and health. They are classified as fat-soluble (A, D, E and K) and water-soluble (B-complex and C). Three deficiency diseases are night blindness due to vitamin A deficiency, rickets in children due to vitamin D deficiency, and scurvy due to vitamin C deficiency.

Quick Tip to Solve: Recall ADEK for the fat-soluble group, then pair A with night blindness, D with rickets and C with scurvy to answer the disease part precisely.