

CBSE Class 12 Chemistry Question Paper 2004 with Solution PDF-Set 56/2 (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. Give an example of a pseudo first order reaction.

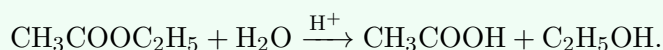
[1 mark]

Solution:

Concept:

- A pseudo first order reaction has a rate proportional to one reactant concentration because another reactant is present in large excess.
- When water is the solvent, its concentration remains practically constant during hydrolysis.

Step 1: Choose an ester hydrolysis Acid-catalysed hydrolysis of ethyl ethanoate in excess water is an example:



The acid catalyst concentration is held fixed.

Step 2: Show the apparent order The water concentration changes negligibly because water is present in large excess. Incorporating its constant contribution into the observed rate constant gives

$$r = k_{\text{obs}}[\text{CH}_3\text{COOC}_2\text{H}_5].$$

Thus, the observed rate depends on the first power of the ester concentration.

Step 3: Conclusion Acid-catalysed hydrolysis of ethyl ethanoate in excess water is a pseudo first order reaction.

Quick Tip to Solve: Always mention excess water: that condition makes the observed hydrolysis first order.

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

[1 mark]

Solution:

Concept:

- The parent chain must include the ketone carbonyl group and the carbon-carbon double bond.
- Number the chain so that the principal functional group, the ketone, receives the lowest possible locant.

Step 1: Choose and number the parent chain Rewrite the structure from the carbonyl end as $\text{CH}_3\text{COCH}=\text{C}(\text{CH}_3)\text{CH}_3$. The longest chain containing both the carbonyl group and the double bond has five carbon atoms. Numbering from the right-hand methyl group of the printed formula puts the carbonyl carbon at position 2.

Step 2: Locate the remaining features The double bond is between carbon atoms 3 and 4, and the extra methyl substituent is attached to carbon atom 4. The parent name is therefore pent-3-en-2-one, with a 4-methyl prefix. Numbering from the opposite end would give the ketone locant 4 and is rejected.

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

Quick Tip to Solve: Give the ketone its lowest locant before assigning the double-bond and substituent locants.

3. Mention two properties of acetonitrile because of which it acts as a good solvent.

[1 mark]

Solution:

Concept:

- Acetonitrile, CH_3CN , is a polar aprotic liquid with a strongly polar nitrile group.
- A high dielectric constant favours separation of opposite charges and helps a solvent dissolve ionic or polar substances.

Step 1: Identify its polarity Acetonitrile has a high dielectric constant and a substantial molecular dipole. It can therefore solvate ions and polar solutes effectively, reducing the electrostatic attraction between oppositely charged ions in a dissolved substance.

Step 2: Identify its solvent compatibility It is miscible with water and with many organic solvents. This compatibility makes it useful for dissolving a wide range of compounds and for preparing homogeneous mixtures in which polar and organic components must be brought together.

Step 3: Conclusion Two useful properties are its high dielectric constant (high polarity) and its miscibility with water and many organic solvents.

Quick Tip to Solve: Link high polarity to ion solvation, and miscibility to the preparation of homogeneous solutions.

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

[1 mark]

Solution:

Concept:

- An impurity ion of higher positive charge can create cation vacancies while maintaining electrical neutrality.
- In AgCl , the normal cation is monovalent Ag^+ .

Step 1: Choose a divalent dopant Cadmium chloride, CdCl_2 , supplies divalent Cd^{2+} ions. When added in a small amount to silver chloride, these ions can enter the crystal at sites normally occupied by Ag^+ ions.

Step 2: Explain vacancy formation One Cd^{2+} ion has the same total positive charge as two Ag^+ ions. It occupies one cation site, while another cation site is left vacant to preserve electrical neutrality. Thus, incorporation of each cadmium ion produces one silver-ion vacancy.

Step 3: Conclusion CdCl_2 (cadmium chloride) causes cation vacancies in AgCl .

Quick Tip to Solve: Compare ionic charges: one divalent ion replaces two monovalent ions but occupies only one site.

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

[1 mark]

Solution:

Concept:

- Reverse osmosis forces solvent through a semipermeable membrane from a concentrated solution by applying pressure greater than its osmotic pressure.
- The membrane allows water to pass while retaining most dissolved salts.

Step 1: State the large scale application Reverse osmosis is used for desalination of seawater or brackish water to obtain fresh water. It is a major water-purification application because dissolved salts must be removed before saline water can serve as a freshwater source.

Step 2: Explain how the separation occurs Pressure exceeding the osmotic pressure is applied on the saline-water side of a semipermeable membrane. Water is driven through the membrane to the freshwater side, while most salt ions remain in the concentrated stream. Continuous removal of the two streams enables large scale operation.

Step 3: Conclusion A large scale use is desalination of seawater to produce fresh water.

Quick Tip to Solve: Remember the direction: applied pressure pushes water out of saline water through the membrane.

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

[2 marks]

Solution:

Concept:

- Total entropy change is $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$.
- A spontaneous process has $\Delta S_{\text{total}} > 0$, whereas at equilibrium the total entropy change is zero.

Step 1: Consider free expansion of an ideal gas Take an insulated rigid vessel divided into two compartments by a partition. One compartment contains an ideal gas and the other is evacuated. On removing the partition the gas expands spontaneously to fill the whole vessel, changing its volume from V_1 to $V_2 > V_1$. No heat crosses the insulated boundary, and no work is done against the vacuum. Thus $q = w = 0$, so the ideal gas has unchanged internal energy and temperature.

Step 2: Evaluate the entropy changes Entropy is a state function. Calculate its change using an imaginary reversible isothermal path joining the same initial and final states:

$$\Delta S_{\text{system}} = nR \ln \frac{V_2}{V_1} > 0.$$

The surroundings exchange no heat with the gas, so $\Delta S_{\text{surroundings}} = 0$. Consequently $\Delta S_{\text{total}} = nR \ln(V_2/V_1) > 0$, in agreement with the observed spontaneous expansion. The gas does not spontaneously return to its initial compartment, since that reverse change would decrease total entropy.

Step 3: Conclusion Free expansion gives $\Delta S_{\text{total}} > 0$, demonstrating that increase in total entropy is the criterion for spontaneity.

Quick Tip to Solve: Use free expansion into vacuum: surroundings entropy is zero, so the positive gas entropy directly gives the total.

7. Draw a diagram showing the formation of bonding and antibonding molecular orbitals by the LCAO in homonuclear hydrogen molecule. [2 marks]

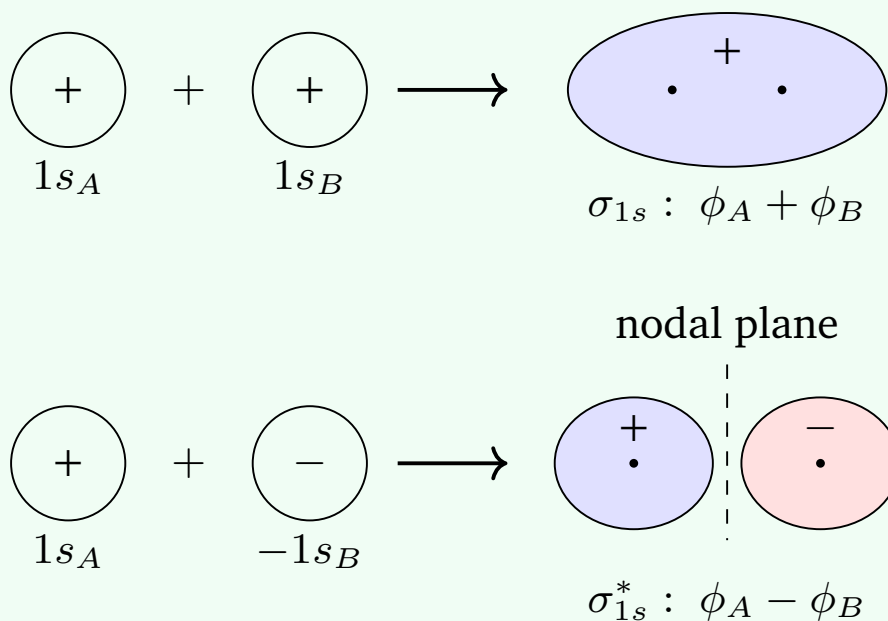
Solution:

Concept:

- In LCAO, atomic wavefunctions ϕ_A and ϕ_B of the two hydrogen $1s$ orbitals combine to produce two molecular orbitals.
- Constructive overlap gives the lower-energy bonding orbital $\psi_b = N_+(\phi_A + \phi_B)$; destructive overlap gives the higher-energy antibonding orbital $\psi_{ab} = N_-(\phi_A - \phi_B)$. Here N_+ and N_- are normalisation constants.

Step 1: Form the bonding orbital by addition Atomic orbitals with the same phase overlap constructively. Electron density increases between the two nuclei, attracting both nuclei and lowering the energy. The resulting orbital is the bonding σ_{1s} molecular orbital. The plus signs in the diagram indicate wavefunction phase, not electric charge.

Step 2: Form the antibonding orbital by subtraction Orbitals of opposite phase overlap destructively, producing a nodal plane midway between the nuclei where the wavefunction and electron density vanish. This orbital, σ_{1s}^* , has energy higher than the parent atomic orbitals. The two electrons of ground-state H_2 occupy σ_{1s} with opposite spins; σ_{1s}^* remains empty.



LCAO of hydrogen $1s$ orbitals; signs denote phases and dots denote nuclei.

Step 3: Conclusion Addition produces bonding σ_{1s} , whereas subtraction produces antibonding σ_{1s}^* ; the configuration of H_2 is $(\sigma_{1s})^2$.

Quick Tip to Solve: Same phase builds density between nuclei; opposite phases create a central node and an antibonding star.

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

(i) phenol to salicylaldehyde

(ii) anisole to p-methoxyacetophenone

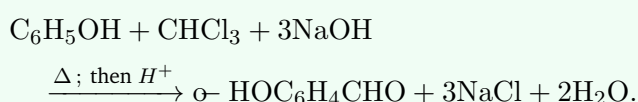
[2 marks]

Solution:

Concept:

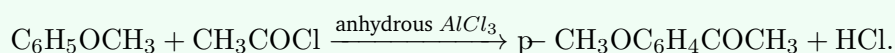
- The Reimer–Tiemann reaction introduces a formyl group mainly ortho to the phenolic hydroxyl group using chloroform and aqueous alkali, followed by acidification.
- Friedel–Crafts acylation introduces COCH_3 into an aromatic ring using acetyl chloride and anhydrous aluminium chloride. The methoxy group directs substitution to ortho and para positions.

Step 1: (i) Convert phenol into salicylaldehyde Heat phenol with chloroform and aqueous sodium hydroxide, then acidify the reaction mixture with dilute hydrochloric acid. This is the Reimer–Tiemann reaction. Its overall equation, showing the product after acidification, is



The main product is salicylaldehyde, or 2-hydroxybenzaldehyde: the CHO group is adjacent to OH.

Step 2: (ii) Convert anisole into p-methoxyacetophenone Treat anisole with acetyl chloride (ethanoyl chloride) in the presence of anhydrous aluminium chloride. After aqueous work-up, Friedel–Crafts acylation gives the para product as the major product:



The para product is favoured over the ortho product by lower steric crowding. The introduced group is COCH_3 , attached to the ring through its carbonyl carbon.

Step 3: Conclusion Phenol gives salicylaldehyde by Reimer–Tiemann formylation. Anisole gives the required para product by Friedel–Crafts acetylation.

Quick Tip to Solve: Phenol to CHO signals Reimer–Tiemann; anisole to COCH_3 signals Friedel–Crafts acylation.

9. Identify and indicate the presence of chirality, if any, in the following molecules. How many stereoisomers are possible for those containing chiral centres?

(i) 3-bromopent-1-ene

(ii) $\text{CH}_3\text{—CH(OH)—CH}_2\text{—CH(OH)—CH}_3$

[2 marks]

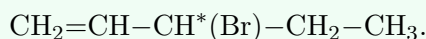
Solution:

Concept:

- A tetrahedral carbon is a stereogenic centre when it is bonded to four different groups; it is indicated by an asterisk.
- For n stereogenic centres, 2^n is the maximum number of configurations; internal symmetry can

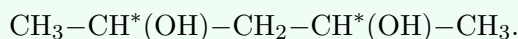
reduce this number through a meso form.

Step 1: (i) Locate the stereogenic carbon in 3-bromopent-1-ene The structure is



Carbon 3 is attached to H, Br, vinyl $\text{CH}_2=\text{CH}-$, and ethyl $-\text{CH}_2\text{CH}_3$. These four groups differ, so C-3 is a chiral centre. One centre gives two non-superimposable mirror-image configurations, *R* and *S*. The terminal double bond has no geometrical isomerism because its first carbon bears two hydrogen atoms.

Step 2: (ii) Account for symmetry in pentane-2,4-diol The indicated centres are at C-2 and C-4:



Each bears four different groups. The nominal four configurations reduce to three because the two ends are identical: $(2R, 4R)$ and $(2S, 4S)$ form an enantiomeric pair, while $(2R, 4S)$ and $(2S, 4R)$ describe the same meso stereoisomer. The meso form is achiral despite having stereogenic centres.

Step 3: Conclusion (i) C-3 is chiral: $\boxed{2}$ stereoisomers. (ii) C-2 and C-4 are stereogenic: $\boxed{3}$ stereoisomers, comprising two enantiomers and one achiral meso form.

Quick Tip to Solve: Before applying 2^n , check whether identical ends permit an internally symmetric meso form.

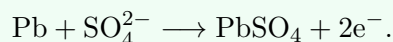
10. Write the cell reactions which occur in lead storage battery (i) when the battery is in use (ii) when the battery is on charging. [2 marks]

Solution:

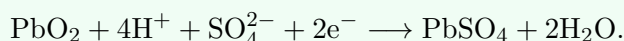
Concept:

- A lead storage battery uses a lead electrode, a lead dioxide electrode and aqueous sulphuric acid. During discharge, chemical energy supplies electrical energy.
- Charging supplies electrical energy to reverse the discharge reactions, regenerating Pb, PbO_2 and sulphuric acid.

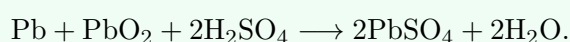
Step 1: (i) Battery in use: discharge At the negative electrode, lead is oxidised:



At the positive electrode, lead dioxide is reduced:

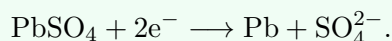


Adding and cancelling electrons gives the cell reaction:

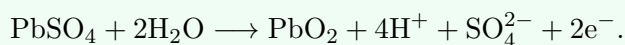


Sulphuric acid is consumed, so its concentration decreases.

Step 2: (ii) Battery on charging An external source drives the reverse changes. At the negative plate:



At the positive plate:



Hence the charging cell reaction is:



The acid concentration increases as the active electrode materials are restored.

Step 3: Conclusion Discharge forms PbSO_4 on both plates and water; charging reverses this reaction and regenerates Pb , PbO_2 and H_2SO_4 .

Quick Tip to Solve: Write discharge first, balance it, and reverse the entire equation for charging.

11. 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 are not equivalent.

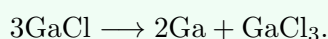
[2 marks]

Solution:

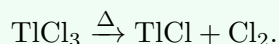
Concept:

- Down Group 13 the inert-pair effect increasingly favours retention of the ns^2 pair, stabilising oxidation state +1 relative to +3.
- Gaseous PCl_5 has a trigonal-bipyramidal structure. Its two axial bonds are longer and weaker than its three equatorial bonds.

Step 1: (i) Reactions supporting the increasing stability of the +1 state Gallium(I) is relatively unstable and can disproportionate into gallium(0) and gallium(III):

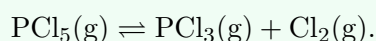


In contrast, thallium(III) readily gives the more stable thallium(I) state; for example, thallium(III) chloride decomposes on heating:



In the first reaction, Ga(I) is lost; in the second, Tl(I) is produced. These contrasting reactions support the increasing preference for +1 from Ga to Tl as the inert-pair effect strengthens.

Step 2: (ii) Reaction supporting inequivalent P-Cl bonds On heating, phosphorus pentachloride dissociates:



The two weaker axial bonds are preferentially broken, leaving the three more strongly bound chlorine atoms in PCl_3 . Axial bond pairs experience three 90° interactions with equatorial bond pairs, whereas

an equatorial bond pair has only two such axial interactions. Thus axial bonds are longer and weaker, and all five P-Cl bonds are not equivalent.

Step 3: Conclusion Instability of GaCl and conversion of TlCl_3 to TlCl support the Group 13 trend. Thermal dissociation of PCl_5 supports its weaker axial and stronger equatorial bonds.

Quick Tip to Solve: For each statement give a balanced reaction, then link it explicitly to oxidation-state stability or bond strength.

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

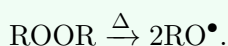
[2 marks]

Solution:

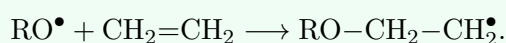
Concept:

- Free radical polymerisation is an addition chain reaction: an initiator produces radicals which open the alkene $\text{C}=\text{C}$ bond and create a growing carbon chain.
- The three stages are chain initiation, chain propagation and chain termination. Ethene provides a simple example, forming polyethene without loss of a small molecule.

Step 1: Chain initiation A peroxide initiator undergoes homolytic cleavage on heating, generating radicals:

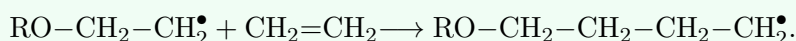


A radical attacks ethene, using one electron of its double bond to form a new bond while leaving a radical at the other carbon:



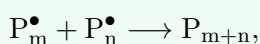
This first chain radical is the active species for growth.

Step 2: Chain propagation The radical repeatedly adds monomer molecules:



Each addition extends the chain by an ethene unit and transfers the radical to the new terminal carbon; repeated additions produce a long-chain radical.

Step 3: Chain termination Two growing chain radicals combine to give a non-radical polymer molecule:



where $\text{P}_m^\bullet$ and $\text{P}_n^\bullet$ denote chains with m and n monomer units. With no terminal unpaired electron remaining, this chain can no longer propagate. The overall ethene reaction is $n\text{CH}_2=\text{CH}_2 \longrightarrow (-\text{CH}_2-\text{CH}_2-)_n$.

Step 4: Conclusion The modes (stages) are initiation, propagation and termination, illustrated above for the radical addition polymerisation of ethene.

Quick Tip to Solve: Keep a radical dot on the growing chain after every propagation step; remove it only at termination.

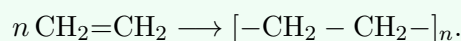
12(b). Differentiate between addition and condensation polymers based on mode of polymerization. Give one example of each type. [2 marks]

Solution:

Concept:

- Polymerization joins small monomer molecules into a macromolecule; its mode determines whether a small molecule is eliminated.
- Addition polymers form by successive addition of unsaturated monomers, whereas condensation polymers form by repeated reactions between functional groups.

Step 1: Addition polymerization Unsaturated monomers add repeatedly through opening of their multiple bonds, without eliminating a small molecule. Thus the polymer contains the same atoms as the monomers that combine. For example, ethene undergoes addition polymerization to form polyethene:



Step 2: Condensation polymerization Bifunctional or polyfunctional monomers react repeatedly through their functional groups, usually eliminating small molecules such as water or hydrogen chloride. For example, hexamethylenediamine and adipic acid form nylon-6,6 with elimination of water. The amine groups of the diamine react with carboxylic acid groups of the diacid, forming amide linkages, $-\text{CO} - \text{NH}-$, in the polymer chain.

Step 3: Conclusion Addition: successive addition without small-molecule elimination, for example polyethene. Condensation: repeated functional-group reactions with small-molecule elimination, for example nylon-6,6.

Quick Tip to Solve: Check for the loss of water or HCl during chain formation: this distinguishes condensation from simple addition of an alkene.

13. 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:

- Depression of freezing point is $\Delta T_f = K_f m$, where K_f is the solvent's molal depression constant and m is solute molality.
- For solute mass w , molar mass M , and solvent mass W in grams, $m = 1000w/(MW)$. Molecular masses are sums of the constituent atomic masses.

Step 1: Obtain the molar mass of each compound Both solutions contain $w = 1 \text{ g}$ solute and

$W = 20 \text{ g} = 0.020 \text{ kg}$ benzene. Using the given depressions for the molecular solutes,

$$M = \frac{K_f \times 1000w}{\Delta T_f W}.$$

Thus,

$$M(\text{AB}_2) = \frac{5.1 \times 1000 \times 1}{2.3 \times 20} = 110.87 \text{ g mol}^{-1},$$
$$M(\text{AB}_4) = \frac{5.1 \times 1000 \times 1}{1.3 \times 20} = 196.15 \text{ g mol}^{-1}.$$

The larger depression corresponds to the smaller molar mass, since equal masses of that solute give more dissolved particles.

Step 2: Solve for the atomic masses Let the numerical atomic masses of A and B be a and b . The formulae give

$$a + 2b = 110.8696, \quad a + 4b = 196.1538.$$

Subtraction removes A and gives $2b = 85.2842$, so $b = 42.6421$. Substituting into the first equation,

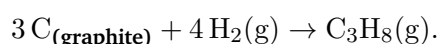
$$a = 110.8696 - 2(42.6421) = 25.5854.$$

As a check, these values give molecular masses 110.87 and 196.15, reproducing both freezing-point depressions with the same mass of benzene.

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

Quick Tip to Solve: Find both molecular masses first, then subtract their equations: the difference between AB₄ and AB₂ is exactly two B atoms.

14. 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:

- At temperature T , the standard reaction Gibbs energy is $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$.
- Standard reaction entropy is the sum of stoichiometric molar entropies of products minus that of reactants: $\Delta_r S^\circ = \sum \nu S_m^\circ(\text{products}) - \sum \nu S_m^\circ(\text{reactants})$.

Step 1: Calculate the entropy change of formation The formation reaction produces one mole of propane from three moles of graphite and four moles of hydrogen gas. Therefore the coefficients must

multiply the corresponding standard molar entropies:

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

The negative sign is consistent with the reduction from four moles of gaseous reactant to one mole of gaseous product; graphite's entropy is also included explicitly.

Step 2: Use the standard Gibbs energy relation The given standard formation enthalpy is $\Delta_f H^\circ = -103.85 \text{ kJ mol}^{-1}$. Using $T = 298 \text{ K}$ and entropy in kilojoules so the units agree,

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

Because the entropy change is negative, the term $-T\Delta_f S^\circ$ is positive. It makes the Gibbs energy less negative than the formation enthalpy, providing a useful sign check.

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 entropy by its reaction coefficient, then convert J to kJ before subtracting the entropy term from the enthalpy.

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

Step 1: Calculate molar conductivity The solution has $c = 0.00241 \text{ mol L}^{-1}$ and $\kappa = 7.896 \times 10^{-5} \text{ S cm}^{-1}$. The factor 1000 converts litres to cubic centimetres. Hence

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

Step 2: Determine the fraction dissociated At infinite dilution the acid is fully dissociated. Consequently the ratio of its measured and limiting molar conductivities gives

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

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

Step 3: Apply the dissociation equilibrium For $\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$, each ion has equilibrium concentration $c\alpha$, and undissociated acid has concentration $c(1 - \alpha)$. Therefore

$$K_a = \frac{(c\alpha)^2}{c(1 - \alpha)} = \frac{0.00241(0.08390)^2}{1 - 0.08390} = 1.852 \times 10^{-5} \text{ mol L}^{-1}.$$

Retaining the denominator avoids the small error from replacing the equilibrium acid concentration by its initial value.

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

Quick Tip to Solve: Calculate conductivity per mole first, then divide by its limiting value; retain $1 - \alpha$ in the equilibrium expression.

16. 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, $Z = 4$: eight corners contribute one atom and six faces contribute three atoms.
- For FCC, the nearest-neighbour distance $d = a/\sqrt{2}$, where a is the edge length. Density is $\rho = ZM/(N_A a^3)$, with molar mass M and Avogadro constant N_A .

Step 1: Relate nearest-neighbour distance to the edge In FCC, atoms touch along a face diagonal. The diagonal contains two nearest-neighbour separations, so $a\sqrt{2} = 2d$. Therefore

$$a = \sqrt{2}(287) = 405.879 \text{ pm}.$$

Since $1 \text{ pm} = 10^{-10} \text{ cm}$, the edge is $a = 4.05879 \times 10^{-8} \text{ cm}$. The given separation is not itself the cube edge.

Step 2: Calculate the mass and volume of one cell The effective number of silver atoms per cell is

$$Z = 8 \left(\frac{1}{8} \right) + 6 \left(\frac{1}{2} \right) = 4.$$

Hence the cell mass is

$$m = \frac{4(107.87)}{6.02 \times 10^{23}} = 7.16744 \times 10^{-22} \text{ g}.$$

Its volume is

$$V = a^3 = (4.05879 \times 10^{-8})^3 = 6.68640 \times 10^{-23} \text{ cm}^3.$$

Step 3: Evaluate density Divide cell mass by cell volume, using centimetres consistently to obtain

density in grams per cubic centimetre:

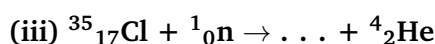
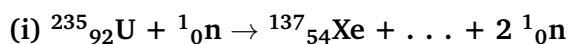
$$\rho = \frac{7.16744 \times 10^{-22}}{6.68640 \times 10^{-23}} = 10.7195 \text{ g cm}^{-3}.$$

The large value is consistent with silver being a closely packed metal.

Step 4: Conclusion The density of silver is 10.7 g cm^{-3} to three significant figures.

Quick Tip to Solve: In FCC use $a = \sqrt{2}d$ for nearest-neighbour distance, and convert picometres before cubing the edge.

17. Complete the following nuclear reactions:



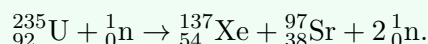
(Note: Put 'X' for the symbol of the element where the name of the element is not known.) [3 marks]

Solution:

Concept:

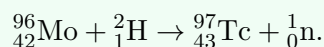
- In a nuclear equation, the total mass number A and total atomic number Z are conserved separately.
- A neutron is ${}^1_0\text{n}$, a deuteron is ${}^2_1\text{H}$, and an alpha particle is ${}^4_2\text{He}$. The atomic number identifies the element.

Step 1: Balance reaction (i) Let the missing fission product be ${}^A_Z\text{X}$. Conservation of mass number gives $235 + 1 = 137 + A + 2(1)$, so $A = 97$. Conservation of atomic number gives $92 = 54 + Z$, so $Z = 38$, which is strontium. The completed reaction is



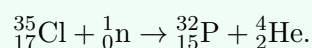
Both sides have mass number 236 and atomic number 92.

Step 2: Balance reaction (ii) For the missing incident particle, $96 + A = 97 + 1$ gives $A = 2$, while $42 + Z = 43$ gives $Z = 1$. It is a deuteron, the nucleus of deuterium:



Each side has total mass number 98 and atomic number 43.

Step 3: Balance reaction (iii) For the missing product, $35 + 1 = A + 4$, so $A = 32$. Atomic-number conservation gives $17 = Z + 2$, so $Z = 15$, identifying phosphorus. Hence



The totals are mass number 36 and atomic number 17 on each side. These balances determine the missing nuclei without requiring their chemical properties.

Step 4: Conclusion The missing species are (i) ${}^{97}_{38}\text{Sr}$, (ii) ${}^2_1\text{H}$ (deuteron), and (iii) ${}^{32}_{15}\text{P}$.

Quick Tip to Solve: Find the missing mass number first and atomic number second; for an incident particle subtract the known reactant from the total products.

18. 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:

- For the spherically symmetric $1s$ state, R^2 denotes the probability density at a point a distance r from the nucleus, using the notation in the question.
- The spherical shell between r and $r + dr$ has volume $4\pi r^2 dr$; hence its electron probability is $4\pi r^2 R^2 dr$.

Step 1: Interpret radial probability density R^2 gives the relative probability per unit volume of finding the electron at a point at distance r from the nucleus. For the hydrogen $1s$ orbital,

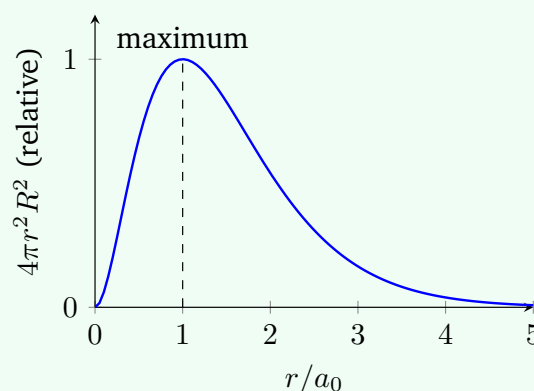
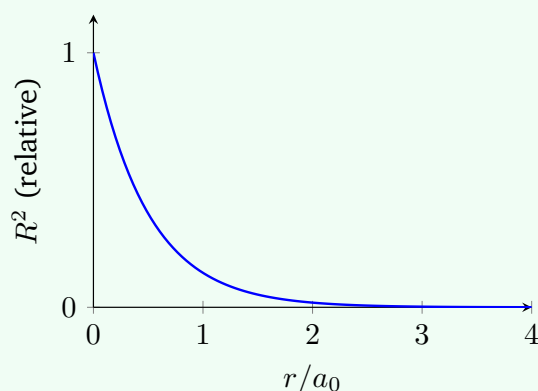
$$R^2 = C e^{-2r/a_0},$$

where C is a positive normalisation constant and a_0 is the Bohr radius. Thus it has its maximum value at $r = 0$, decreases continuously as r increases, and approaches zero at large distance. A finite density at the nucleus does not mean a finite probability at one mathematical point.

Step 2: Interpret the radial probability function $P(r) = 4\pi r^2 R^2$ gives the probability per unit radial distance of finding the electron anywhere in a thin spherical shell of radius r . Thus $P(r)dr$ is the shell probability. For $1s$,

$$P(r) = 4\pi C r^2 e^{-2r/a_0}.$$

At the nucleus, $P(0) = 0$ because the shell volume factor vanishes. It first increases, reaches a maximum at $r = a_0$, and then decreases towards zero. Indeed, for $r > 0$, P is stationary when $2/r - 2/a_0 = 0$. The most probable radius is therefore a_0 , although the pointwise density is largest at the nucleus. The graphs below use independent vertical scales.



Hydrogen 1s: pointwise density and radial shell probability (independent vertical scales).

Step 3: Conclusion For hydrogen 1s, R^2 is maximum at $r = 0$ and decreases exponentially, whereas $4\pi r^2 R^2$ starts at zero, peaks at $r = a_0$, and then tends to zero.

Quick Tip to Solve: Distinguish density at a point from probability in a shell: multiply by $4\pi r^2$ before finding the most probable radius.

19. (a) Give the IUPAC name of $[\text{PtCl}(\text{NH}_2\text{CH}_3)(\text{NH}_3)_2]\text{Cl}$.

(b) Compare the magnetic behaviour of the complex entities $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{FeF}_6]^{3-}$. (Fe = 26)

[3 marks]

Solution:

Concept:

- In a coordination compound, name ligands alphabetically before the metal and give the metal oxidation state in Roman numerals; the counter-ion is named separately.
- For octahedral iron complexes, ligand field strength determines electron pairing. Unpaired electrons cause paramagnetism; a completely paired arrangement is diamagnetic.

Step 1: (a) Name the platinum compound The outer chloride ion has charge -1 , so the complex ion has charge $+1$. Within the complex, chlorido has charge -1 , while methylamine and the two ammine ligands are neutral. Hence

$$x - 1 = +1 \Rightarrow x = +2.$$

The ligand names in alphabetical order are ammine, chlorido and methylamine; the prefix di- for two ammine ligands does not affect this order. The name is **diamminechlorido(methylamine)platinum(II) chloride**. No cis/trans descriptor is assigned because the formula does not specify the geometrical arrangement.

Step 2: (b) Determine the iron electron configurations Iron has atomic number 26 and ground-state configuration $[\text{Ar}]3d^64s^2$. In $[\text{Fe}(\text{CN})_6]^{4-}$, let the oxidation state be x : $x - 6 = -4$, giving Fe(II), a $3d^6$ ion. In $[\text{FeF}_6]^{3-}$, $x - 6 = -3$, giving Fe(III), a $3d^5$ ion. Electrons are removed from $4s$ before $3d$ when forming these ions.

Step 3: (b) Compare pairing and magnetic behaviour Cyanide is a strong-field ligand. In octahedral

$[\text{Fe}(\text{CN})_6]^{4-}$, it gives the low-spin configuration $t_{2g}^6 e_g^0$. All six d electrons are paired, so there are no unpaired electrons and the entity is diamagnetic. Fluoride is a weak-field ligand. In octahedral $[\text{FeF}_6]^{3-}$, the high-spin configuration is $t_{2g}^3 e_g^2$, with five unpaired electrons. It is therefore strongly paramagnetic. Its spin-only magnetic moment is $\sqrt{5(5+2)} = \sqrt{35} \simeq 5.92 \text{ BM}$.

Step 4: Conclusion (a) Diamminechlorido(methylamine)platinum(II) chloride. (b) $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic (zero unpaired electrons); $[\text{FeF}_6]^{3-}$ is paramagnetic (five unpaired electrons).

Quick Tip to Solve: Find the iron oxidation state before counting d electrons: cyanide then pairs the d6 electrons, while fluoride leaves the d5 ion high spin.

20. Describe the following with suitable examples:

(i) Preservatives

(ii) Tranquilizers

(iii) Hybrid propellants

[3 marks]

Solution:

Concept:

- Preservatives protect food against spoilage, while tranquilizers act on the central nervous system to reduce anxiety and tension.
- A rocket propellant contains a fuel and an oxidiser. In a hybrid propellant, these two components are in different physical states.

Step 1: (i) Preservatives Preservatives are substances added to food to retard its deterioration, particularly spoilage caused by the growth of microorganisms. They help maintain the quality of food during storage and increase its shelf life. Sodium benzoate is a suitable example; it is used to preserve acidic foods such as fruit juices and squashes. Common salt and sugar also preserve foods when used in sufficiently high concentrations, as in pickles and jams respectively.

Step 2: (ii) Tranquilizers Tranquilizers are drugs used to reduce mental stress, anxiety and tension by acting on the central nervous system. They produce a calming effect and are used in the treatment of certain mental disorders under medical supervision. Diazepam and equanil (meprobamate) are suitable examples. Their defining role here is the relief of anxiety and tension, rather than the prevention of infection or food spoilage.

Step 3: (iii) Hybrid propellants Hybrid propellants are rocket propellants in which the fuel and oxidiser are in different physical states, usually a solid fuel and a liquid oxidiser. A suitable example is solid polybutadiene fuel with liquid oxygen as the oxidiser. The liquid oxidiser is supplied to the solid fuel surface, where combustion generates hot gases that provide thrust. It is the combination of physical states that makes this system hybrid.

Step 4: Conclusion Preservatives prevent food spoilage (sodium benzoate); tranquilizers relieve anxiety and tension (diazepam); hybrid propellants combine fuel and oxidiser in different states (solid polybutadiene and liquid oxygen).

Quick Tip to Solve: For each term, state its function or defining feature first, then give one matching example; for hybrid propellants explicitly name the two physical states.

21. 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 rate law. Thus first order in A and second order in B give $r = k[A][B]^2$.
- At fixed temperature, the rate constant k is independent of reactant concentrations. Rate changes are found by taking the ratio of the new rate to the original rate.

Step 1: (i) Write the differential rate equation Let r denote the reaction rate and let $[A]$ and $[B]$ be the molar concentrations of the reactants. The specified orders give

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

The overall order is $1 + 2 = 3$. Reaction orders specify the powers in this equation; they do not by themselves specify the stoichiometric coefficients needed to relate individual disappearance rates.

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

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

The rate therefore becomes nine times its original value. The factor is squared because the reaction is second order with respect to B.

Step 3: (iii) Double both concentrations At the same temperature, substitute $2[A]$ and $2[B]$ in the rate law:

$$r'' = k(2[A])(2[B])^2 = 2 \times 4k[A][B]^2 = 8r.$$

Thus doubling both concentrations increases the rate by a factor of eight.

Step 4: Explain the significance of the rate constant The rate constant is the proportionality constant relating the rate to the product of reactant concentrations raised to their respective orders. Numerically, it equals the reaction rate when each reactant has unit concentration, expressed in the chosen concentration units. It characterises the reaction at a specified temperature and changes with temperature or a change in catalyst. For this third-order reaction, if rate is in $\text{mol L}^{-1} \text{s}^{-1}$, the units of k are $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$.

Step 5: Conclusion The rate law is $r = k[A][B]^2$. Tripling only B makes the rate $9r$; doubling both A and B makes it $8r$. The constant k is the rate at unit reactant concentrations and a measure of the reaction rate under specified conditions.

Quick Tip to Solve: Raise each concentration multiplier to its own reaction order: the required rate factors are $3^2 = 9$ and $2^1 \times 2^2 = 8$.

22(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 colloidal sol contains a dispersed phase distributed in a dispersion medium. Classification as lyophilic or lyophobic depends on the affinity between these two components.
- Strong solvation of dispersed particles increases their stability. Weak affinity makes particles more liable to aggregate, so protection may be needed to preserve the sol.

Step 1: Identify the two classes On the basis of the interaction between the dispersed phase and the dispersion medium, colloids are classified into lyophilic sols and lyophobic sols. The words mean solvent-loving and solvent-hating respectively. When water is the medium, these are also called hydrophilic and hydrophobic sols.

Step 2: Describe lyophilic sols Lyophilic sols have a strong affinity between the dispersed phase and the dispersion medium. The colloidal particles become well solvated, which makes these sols comparatively stable. An important characteristic is their reversibility: after the medium is removed, the sol can generally be formed again by adding the dispersion medium. Starch or gelatin dispersed in water provides a suitable example. These sols do not normally require an added protective agent for preservation.

Step 3: Describe lyophobic sols and their preservation Lyophobic sols have little affinity between the dispersed particles and the dispersion medium. They are comparatively less stable and are generally irreversible: adding the medium back to coagulated material does not readily regenerate the original sol. Gold sol and arsenic sulphide sol in water are examples. Their stability often depends on the electrical charge on the particles, and adding a suitable electrolyte can cause coagulation. These are the sols that need stabilising agents for preservation. A small amount of a protective lyophilic colloid, such as gelatin, can form a solvated protective layer around lyophobic particles and inhibit aggregation.

Step 4: Conclusion The two classes are lyophilic (strong affinity, generally reversible and stable) and lyophobic (weak affinity, generally irreversible and less stable). Lyophobic sols need stabilising or protective agents for preservation.

Quick Tip to Solve: Link strong affinity with solvation, reversibility and stability; identify the weak-affinity lyophobic sol as the one needing a protective colloid.

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

Solution:

Concept:

- A detergent is a synthetic cleansing agent whose molecules contain a water-attracting (hydrophilic) part and an oil-attracting (hydrophobic) hydrocarbon part.
- Synthetic detergents are classified by the charge on the cleansing-active part into anionic, cationic and non-ionic detergents.

Step 1: Define detergents and their cleansing action Detergents are synthetic surface-active cleansing agents that can remove oily dirt in water. Their hydrocarbon tails enter grease, while their hydrophilic heads remain in water. Aggregation into micelles disperses the grease in water so that it can be washed away.

Step 2: Give the scheme of classification (i) Anionic detergents have a negatively charged active part. Examples include sodium alkyl sulphates, $R-OSO_3^- Na^+$, and sodium alkylbenzenesulphonates.

(ii) Cationic detergents have a positively charged active part. They are commonly quaternary ammonium salts, such as cetyltrimethylammonium bromide, $[C_{16}H_{33}N(CH_3)_3]^+ Br^-$.

(iii) Non-ionic detergents have no ionic charge in their hydrophilic part. Examples are polyethylene glycol derivatives containing a long hydrocarbon chain and several ether oxygen atoms.

Step 3: Explain their advantage over soaps Soaps are sodium or potassium salts of higher fatty acids. In hard water, their carboxylate ions form insoluble calcium and magnesium salts (scum), wasting soap and reducing lather. Detergents remain effective because their calcium and magnesium salts do not form this insoluble scum. Thus, detergents clean efficiently even in hard water. Sulphonate detergents also retain cleansing action in acidic water, where soaps are converted into insoluble fatty acids.

Step 4: Conclusion Detergents are synthetic cleansing agents classified as anionic, cationic and non-ionic. Their main advantage over soaps is effective cleaning in hard water without the formation of insoluble scum.

Quick Tip to Solve: Classify a detergent by the charge on its active head, then explain hard-water cleaning using calcium and magnesium ions.

23. 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]

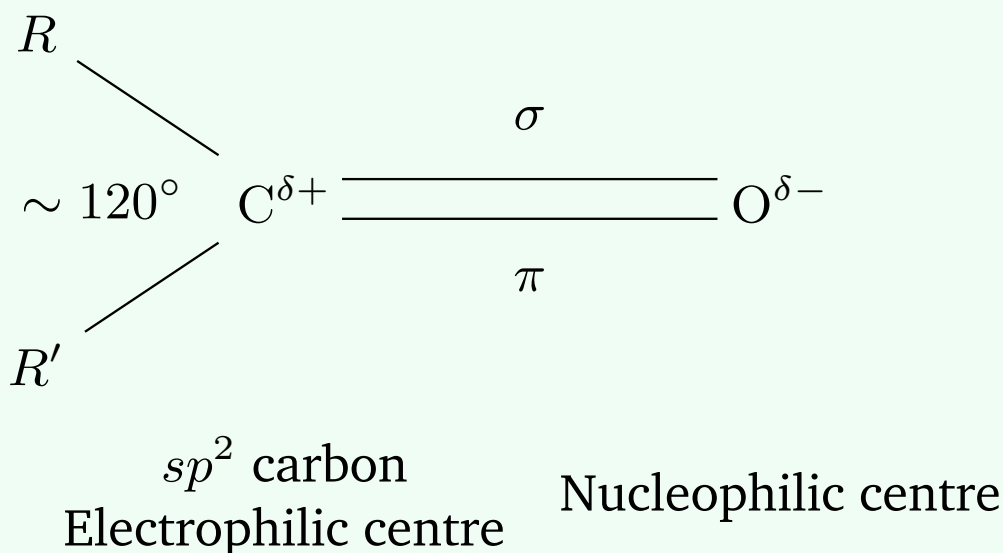
Solution:

Concept:

- The carbonyl group, $>C=O$, contains a carbon atom double-bonded to oxygen. Its carbon atom is sp^2 -hybridized and has trigonal planar geometry.

- A double bond comprises one σ bond from head-on overlap and one π bond from sideways overlap of parallel unhybridized p orbitals.
- Oxygen is more electronegative than carbon, so the carbonyl bond is polar: $C^{\delta+} = O^{\delta-}$.

Step 1: Draw and identify the hybridization The labelled structure below represents the carbonyl group; R and R' denote the two substituents attached to carbon (one or both may be hydrogen). The three sp^2 hybrid orbitals of carbon form three coplanar σ bonds, two to the substituents and one to oxygen. The bond angles around carbon are approximately 120° , giving trigonal planar geometry.



Carbonyl structure with bond types, hybridization and reactive centres

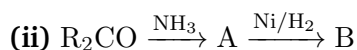
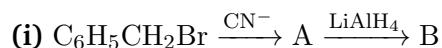
Step 2: Identify the sigma and pi bonds In the $C = O$ bond, one σ bond is formed by head-on overlap of an sp^2 orbital of carbon with an sp^2 orbital of oxygen. Each atom also has an unhybridized p orbital perpendicular to the molecular plane. Sideways overlap of these parallel orbitals produces the one π bond of the carbonyl double bond. Thus, $C = O$ contains exactly one σ and one π bond.

Step 3: Mark the reactive centres Oxygen attracts the shared electrons more strongly and acquires a partial negative charge, while carbon acquires a partial positive charge. Therefore, carbon is the electrophilic (electron-pair-accepting) centre, attacked by nucleophiles. Oxygen, with its partial negative charge and lone pairs, is the nucleophilic (electron-pair-donating) centre and can interact with electrophiles such as H^+ .

Step 4: Conclusion Carbonyl carbon is sp^2 -hybridized. The $C = O$ double bond has one σ and one π bond; $C^{\delta+}$ is the electrophilic centre and $O^{\delta-}$ is the nucleophilic centre.

Quick Tip to Solve: Put the positive partial charge on carbon: oxygen pulls electron density toward itself, so nucleophiles attack carbon.

24. (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:

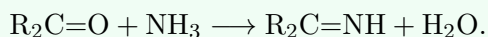
- Cyanide ion forms a carbon-carbon bond on replacing halide; reduction of a nitrile converts $-\text{C} \equiv \text{N}$ into $-\text{CH}_2\text{NH}_2$.
- A ketone reacts with ammonia to form an imine, which gives a primary amine on catalytic hydrogenation.
- Basicity depends on the availability of the nitrogen lone pair for accepting a proton.

Step 1: (a)(i) Identify the nitrile and its reduction product Cyanide ion attacks benzyl bromide through carbon and replaces bromide. Thus A is benzyl cyanide (phenylacetonitrile), $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$. Lithium aluminium hydride reduces its nitrile group to a primary amino group:

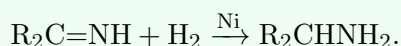


Therefore B is 2-phenylethan-1-amine. The carbon atom introduced by cyanide remains in the product, so the side chain contains two carbon atoms.

Step 2: (a)(ii) Identify the imine and the amine Ammonia condenses with the carbonyl group of the ketone, eliminating water:



Hence A is the imine $\text{R}_2\text{C}=\text{NH}$. Hydrogenation across its carbon-nitrogen double bond gives



Thus B is the primary amine R_2CHNH_2 ; nitrogen bears only one carbon substituent.

Step 3: (b) Compare the availability of the nitrogen lone pair In an aromatic amine such as aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance. It is therefore less available to bind H^+ . Protonation removes this lone pair from conjugation, so the resonance stabilisation of the free amine also makes proton acceptance less favourable. In ammonia the lone pair is localised on nitrogen. In aliphatic amines, alkyl groups exert a positive inductive effect and increase electron density on nitrogen. Consequently aromatic amines are less basic than ammonia and 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: R_2CHNH_2 . (b) Resonance delocalisation makes the nitrogen lone pair of aromatic amines less available for protonation.

Quick Tip to Solve: Count the extra carbon supplied by cyanide; hydrogenation changes the nitrile group, not the carbon skeleton.

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

(i) Cobalt(II) is stable in aqueous solution but in the presence of strong ligands it is easily oxidised. (Co = 27)

(ii) The transition metals form interstitial compounds.

(iii) Silver halides find use in photography.

(b) What is lanthanoid contraction? Mention its main consequence.

[5 marks]

Solution:

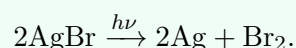
Concept:

- Ligands can stabilise particular oxidation states through crystal-field splitting; strong-field ligands especially stabilise low-spin d^6 cobalt(III).
- Small atoms can occupy interstitial holes in a metallic lattice. Silver halides undergo photochemical reduction.
- Poor shielding by $4f$ electrons causes the effective nuclear charge and the contraction of lanthanoid ions to increase across the series.

Step 1: (a)(i) Explain cobalt(II) stability and oxidation with strong ligands Cobalt has atomic number 27 and configuration $[\text{Ar}]3d^74s^2$. Thus Co^{2+} is $3d^7$, while Co^{3+} is $3d^6$. In ordinary aqueous solution, further oxidation of cobalt(II) requires considerable energy; hydrated cobalt(III) is a strong oxidising agent and tends to return to cobalt(II). The +2 state is therefore stable in water. Strong-field ligands, such as CN^- , give a large octahedral splitting and strongly stabilise low-spin cobalt(III), with the configuration $t_{2g}^6e_g^0$. This additional stabilisation of the +3 complex makes oxidation of cobalt(II) much easier in their presence.

Step 2: (a)(ii) Explain interstitial compound formation The crystal lattices of transition metals contain interstitial voids. Small atoms such as hydrogen, carbon and nitrogen can enter these spaces without destroying the basic metal lattice. Compounds such as titanium carbide, TiC , are therefore formed. The metal atoms retain their extended lattice while the smaller atoms occupy its holes; this accounts for the formation of interstitial compounds.

Step 3: (a)(iii) Explain the photographic use of silver halides Silver halides, especially silver bromide, are photosensitive. Light causes their decomposition, producing finely divided metallic silver. The overall reaction can be represented as



The extent of change depends on exposure to light. In photographic film this creates a latent image, which is made visible during development as a pattern of metallic silver; unexposed silver halide is subsequently removed during fixing.

Step 4: (b) Define lanthanoid contraction and state its main consequence Lanthanoid contraction is the gradual decrease in atomic radii and, especially, the ionic radii of Ln^{3+} ions as atomic number increases from lanthanum to lutetium. Across the series the nuclear charge increases while the added electrons enter the $4f$ subshell. Since $4f$ electrons shield one another poorly, the effective nuclear attraction increases and draws the electron cloud inward. A major consequence is that corresponding elements of the second and third transition series have almost equal radii. For example, zirconium

and hafnium have nearly identical sizes and very similar chemical properties, which makes their separation difficult. The contraction accumulated before hafnium offsets the increase in size expected from adding an electron shell.

Step 5: Conclusion Strong ligands stabilise cobalt(III); small atoms in lattice holes produce interstitial compounds; photosensitive silver halides generate metallic silver. Lanthanoid contraction is the progressive decrease in lanthanoid size and leads particularly to the close size and chemical similarity of pairs such as Zr and Hf.

Quick Tip to Solve: Link each observation to its cause: ligand stabilisation, lattice holes, light sensitivity, and poor shielding by 4f electrons.

26. (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]

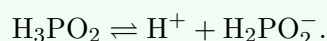
Solution:

Concept:

- A Lewis acid accepts an electron pair. Electron-deficient aluminium chloride can therefore activate reagents in catalytic reactions.
- The basicity of an oxyacid is the number of ionisable O – H hydrogens, rather than its total number of hydrogen atoms.
- Hydrolysis depends on bond strength and the accessibility of the central atom; effective sideways orbital overlap is needed for stable extended π -bonding.
- VSEPR theory places five bond pairs and lone pairs in a trigonal-bipyramidal electron-pair arrangement; lone pairs prefer equatorial sites.

Step 1: (a)(i) Catalytic action of anhydrous aluminium chloride In AlCl_3 , aluminium is electron deficient and can accept an electron pair from a donor. Thus anhydrous aluminium chloride acts as a Lewis acid. For example, it accepts a lone pair from the chlorine atom of an alkyl chloride and polarises the C – Cl bond, facilitating formation of the electrophile used in a Friedel–Crafts reaction. Its electron-pair-accepting ability explains its catalytic use. The anhydrous condition is necessary because water reacts with it and destroys this catalytic activity.

Step 2: (a)(ii) Monoprotic nature of phosphinic acid Phosphinic acid, H_3PO_2 , has the structure $\text{H}_2\text{P}(=\text{O})(\text{OH})$. Of its three hydrogen atoms, only one is bonded to oxygen; the other two are bonded directly to phosphorus. Only the hydrogen of the O – H group is released as a proton in aqueous ionisation:



The two P – H hydrogens are not ionisable in this acid-base process. Hence one molecule supplies

only one proton and the acid is monoprotic.

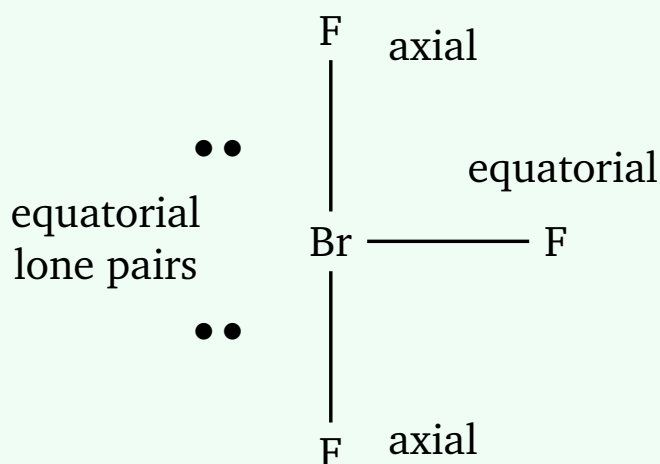
Step 3: (a)(iii) Difference in hydrolysis of the sulphur fluorides In octahedral SF_6 , six fluorine atoms surround and shield the sulphur atom effectively, hindering attack by water. Its strong S – F bonds and compact, saturated arrangement make it kinetically resistant to hydrolysis. In SF_4 , the sulphur atom is less effectively shielded and is accessible to attack by water; consequently it hydrolyses readily. Complete hydrolysis is represented by



Thus the contrast is explained by the greater protection of the central sulphur atom in SF_6 .

Step 4: (a)(iv) Absence of a graphite-like form of silicon Graphite contains planar sheets of sp^2 -hybridised carbon atoms. The remaining $2p$ orbitals overlap sideways, producing an extended delocalised π -electron system. Silicon atoms are larger and their more diffuse $3p$ orbitals overlap sideways much less effectively. Silicon therefore does not readily form the strong extended $p\pi - p\pi$ bonding needed for an analogous graphite structure. Instead elemental silicon favours a three-dimensional tetrahedral covalent network with predominantly σ bonds.

Step 5: (b) Structure of bromine trifluoride Choosing BrF_3 , the central bromine has seven valence electrons. Formation of three Br – F bonds leaves two lone pairs, giving five electron domains in total: AX_3E_2 . Their electron-pair arrangement is trigonal bipyramidal. Both lone pairs occupy equatorial sites, where each has fewer 90° interactions than at an axial site. The three fluorine atoms occupy two axial sites and one equatorial site, producing a T-shaped molecule. Lone-pair repulsion slightly compresses the axial–equatorial bond angles below 90° .



T-shaped BrF_3 : two axial fluorines, one equatorial fluorine and two equatorial lone pairs.

Step 6: Conclusion AlCl_3 acts as a Lewis acid; H_3PO_2 has only one ionisable O – H hydrogen; shielding of sulphur makes SF_6 resistant to hydrolysis; weak sideways $3p$ -orbital overlap prevents graphite-like bonding in silicon. The chosen molecule, BrF_3 , is T-shaped with two equatorial lone pairs.

Quick Tip to Solve: Count O-H bonds to find oxyacid basicity, and count both bond pairs and lone pairs before assigning the molecular shape of BrF_3 .

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

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

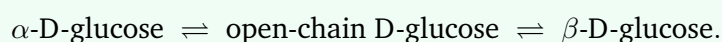
[5 marks]

Solution:

Concept:

- Mutarotation is the change in the specific optical rotation of a freshly prepared sugar solution with time until a constant equilibrium value is reached.
- The two anomers of D-glucose differ at C-1, the anomeric carbon, and interconvert through the open-chain aldehyde form in water.
- Lipids are classified by composition and hydrolysis products into simple, compound (complex), and derived lipids.

Step 1: (a) Explain the interconversion of glucose anomers Crystalline α -D-glucose and β -D-glucose are cyclic hemiacetals. In their usual Haworth representations, the anomeric OH group at C-1 is down in the α form and up in the β form. When either form dissolves in water, its hemiacetal ring can open to give the open-chain aldehyde. Ring closure can then produce either anomer:



Thus, the composition and optical rotation change until the same equilibrium mixture is established, irrespective of which pure anomer was dissolved initially.

Step 2: (a) State the observed optical rotations Freshly prepared α -D-glucose solution has specific rotation about $+112^\circ$, which gradually decreases. Freshly prepared β -D-glucose solution has specific rotation about $+19^\circ$, which gradually increases. Both attain the equilibrium specific rotation of approximately $+52.5^\circ$. The equilibrium solution contains roughly 36% α and 64% β anomer, with only a trace of the open-chain form. This time-dependent change is mutarotation; it results from anomer interconversion, rather than conversion of D-glucose into L-glucose.

Step 3: (b) Classify lipids and give examples The principal classes are:

1. **Simple lipids:** Esters of fatty acids with alcohols. On hydrolysis they yield fatty acids and alcohol only. Example: tristearin, a fat formed from glycerol and stearic acid. Waxes also belong to this class.
2. **Compound or complex lipids:** Lipids containing an additional group besides fatty acid and alcohol components, such as a phosphate or carbohydrate group. Example: lecithin (phosphatidylcholine), a phospholipid containing phosphate and choline.
3. **Derived lipids:** Substances obtained from hydrolysis of simple or compound lipids, and related lipid substances. Example: stearic acid, a fatty acid released on hydrolysis of fats. Sterols such as cholesterol are also included among derived lipids.

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

Quick Tip to Solve: Link mutarotation to a free hemiacetal group at C-1; for lipid classes, recall fat, phospholipid, and fatty acid as one example of each.

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

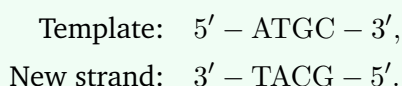
Solution:

Concept:

- DNA replication is the formation of two daughter DNA molecules from one parental DNA molecule before cell division. The base sequence stores hereditary information.
- Complementary base pairing is specific: adenine pairs with thymine, A – T, and guanine pairs with cytosine, G – C. Thus either parental strand can act as a template for a new complementary strand.
- Replication is semiconservative: each daughter double helix contains one original parental strand and one newly synthesised strand.

Step 1: Separate the parental strands The DNA double helix unwinds and the hydrogen bonds between complementary bases break. The two polynucleotide strands separate locally, exposing their bases. Each separated strand acts as a template. The covalent sugar-phosphate backbone of each parental strand remains intact; replication does not require breaking the parental molecule into individual nucleotides.

Step 2: Build a complementary strand on each template Free deoxyribonucleotides arrange opposite the exposed template bases according to complementary pairing. A template A directs the addition of T, T directs A, G directs C and C directs G. DNA polymerase catalyses formation of phosphodiester bonds between adjacent nucleotides, extending the new sugar-phosphate chain. Each new strand is complementary and antiparallel to its template. For example,



In the cell, synthesis proceeds in the $5' \rightarrow 3'$ direction: one new strand is made continuously, while the other is made as fragments that are joined by DNA ligase.

Step 3: Form two daughter double helices On completion, the newly formed complementary strand associates with its parental template to form a double helix. The other parental strand similarly produces its own complementary strand. Consequently, one parental DNA molecule gives two daughter DNA molecules, each containing one old strand and one new strand. This explains the term semiconservative replication.

Step 4: Explain preservation of heredity Hereditary information resides in the sequence of bases in DNA. Specific complementary pairing makes the sequence of each new strand determined by its template, so the two daughter DNA molecules normally reproduce the same genetic information as the parent. During cell division these copies pass to daughter cells, maintaining the characteristic genetic instructions through successive generations of cells. Through reproduction, DNA also transmits hereditary information from parents to offspring. Accurate replication preserves this information; occasional errors or mutations can introduce variation, so preservation does not imply that errors are impossible.

Step 5: Conclusion DNA replicates by the semiconservative mechanism: its strands separate, each directs synthesis of a complementary strand, and two daughter double helices result. Specific base pairing copies the base sequence accurately, thereby preserving and transmitting hereditary information.

Quick Tip to Solve: Link heredity to the base sequence: first state A pairs with T and G with C, then explain why each daughter DNA carries the parental information.