

CBSE Class 12 Chemistry Question Paper 2004 with Solution PDF-Set 56/3 (Foreign)



Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

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

1. Which point defect lowers the density of a crystal?

[1 mark]

Solution:

Concept:

- Density is mass per unit volume: $\rho = m/V$.
- A Schottky defect consists of vacancies formed by the absence of equal numbers of cations and anions from their normal lattice sites.

Step 1: Identify the vacancy defect In a Schottky defect, ions are missing from the crystal lattice. Equal numbers of oppositely charged ions are absent, so electrical neutrality is maintained.

Step 2: Relate vacancies to density These vacancies reduce the mass associated with a given crystal volume; hence the density falls. In a Frenkel defect an ion merely moves to an interstitial site, so no ion is lost and the density remains unchanged.

Step 3: Conclusion The point defect is the Schottky defect.

Quick Tip to Solve: Missing ions mean less mass per unit volume: associate Schottky vacancies with lower density.

2. Write an expression for mole fraction of a component 'A' present in a solution with another component 'B'.

[1 mark]

Solution:

Concept:

- The mole fraction of a component equals its amount in moles divided by the total amount in moles of all components.
- Mole fraction is dimensionless because both numerator and denominator are amounts in the same unit.

Step 1: Define the amounts Let n_A and n_B denote the numbers of moles of components A and B, respectively. For this binary solution, the total amount is $n_A + n_B$.

Step 2: Form the required ratio Therefore, the mole fraction of A is

$$x_A = \frac{n_A}{n_A + n_B}.$$

Similarly, $x_B = n_B/(n_A + n_B)$, which gives the check $x_A + x_B = 1$.

Step 3: Conclusion The required expression is $x_A = \frac{n_A}{n_A + n_B}$.

Quick Tip to Solve: Use total moles, not the moles of solvent alone, in the denominator.

3. Define activation energy of a reaction.

[1 mark]

Solution:

Concept:

- Reactants must overcome an energy barrier to form the activated complex and undergo reaction.
- Activation energy is the energy difference between the activated complex and the reactants:

$$E_a = E_{\text{activated complex}} - E_{\text{reactants}}$$

Step 1: Identify the threshold A reaction does not occur in every collision. Reacting species must possess sufficient energy to reach the high-energy activated complex along the reaction path.

Step 2: Define activation energy Activation energy is the minimum additional energy that reactant molecules must acquire above their normal energy to reach the activated complex and undergo the reaction. It is generally expressed per mole of reactants.

Step 3: Conclusion Activation energy is the minimum extra energy required by reactants to attain the activated complex and react.

Quick Tip to Solve: Measure the barrier from the reactant energy level to the top of the energy profile.

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

NH₃, EtNH₂, Et₂NH, Et₃N.

[1 mark]

Solution:

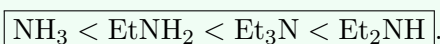
Concept:

- Basicity depends on availability of the nitrogen lone pair for accepting a proton.
- In aqueous solution, the electron-releasing inductive effect of ethyl groups and solvation of the conjugate acid jointly determine basic strength.

Step 1: Compare with ammonia Ethyl groups release electron density towards nitrogen through their positive inductive effect. Consequently, each ethylamine listed is more basic than NH₃ in aqueous solution.

Step 2: Compare the ethylamines For ethyl-substituted amines, the combined effects of electron donation and hydration give secondary greater than tertiary greater than primary basicity. Thus Et₂NH is strongest, followed by Et₃N and then EtNH₂. Using inductive effect alone would ignore the role of the solvent.

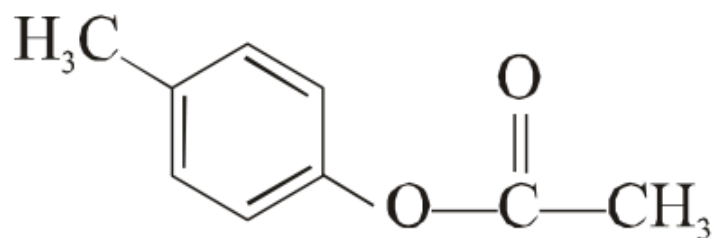
Step 3: Conclusion The increasing order is



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

5. Write the IUPAC name of the following:

[1 mark]



Solution:

Concept:

- An ester has the linkage $R - C(=O) - O - R'$ and is named as an alkyl or aryl alkanoate.
- The group bonded to the single-bonded oxygen is named first; the acid-derived part supplies the alkanoate name.

Step 1: Identify the oxygen-bound aromatic group The single-bonded ester oxygen is attached to a benzene ring. The ring has a methyl group opposite this attachment, at position 4 when the oxygen-bearing carbon is position 1. This group is therefore 4-methylphenyl.

Step 2: Identify the acid-derived part The carbonyl carbon is bonded to CH_3 , so the acid-derived fragment is CH_3COO- , namely ethanoate. Combine the aromatic group name with ethanoate to obtain the ester name.

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

Quick Tip to Solve: Split the structure at the ester oxygen: name the oxygen-bound group first, then the acid-derived ethanoate.

6(a). Write the reactions that occur at the electrodes of lead storage battery (i) when it is in use and (ii) when it is on charging.

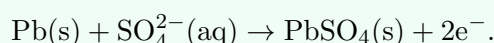
[2 marks]

Solution:

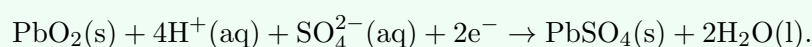
Concept:

- During discharge, a lead storage battery is a galvanic cell: lead is oxidised and lead dioxide is reduced in sulphuric acid.
- Charging supplies electrical energy to reverse the discharge reactions, restoring Pb, PbO_2 and sulphuric acid.

Step 1: Electrode reactions during use At the negative lead electrode (anode), oxidation occurs:

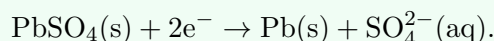


At the positive lead dioxide electrode (cathode), reduction occurs:

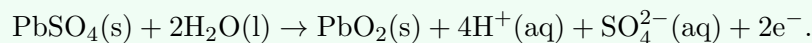


Both plates acquire lead sulphate as the cell discharges.

Step 2: Electrode reactions during charging The external source reverses both reactions. At the negative plate, now the cathode:



At the positive plate, now the anode:



Sulphuric acid is regenerated; the oxidation and reduction roles of the plates are reversed.

Step 3: Conclusion Discharge converts Pb and PbO₂ to PbSO₄; charging reverses the displayed half-reactions.

Quick Tip to Solve: Write the two balanced discharge half-reactions first, then reverse each arrow to obtain the charging reactions.

OR

6(b). Describe the composition of anode and cathode in a mercury cell. Write the electrode reactions for this cell. [2 marks]

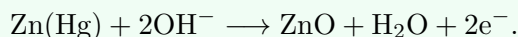
Solution:

Concept:

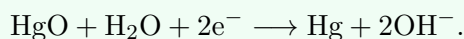
- A mercury cell is a primary alkaline cell: oxidation occurs at its zinc anode, while mercury(II) oxide is reduced at its cathode.
- The electrode equations are balanced in alkaline medium using OH⁻ ions and water; electrons released and consumed must be equal.

Step 1: State the electrode compositions The anode consists of zinc amalgam, that is, zinc associated with mercury. The cathode consists of a paste of mercury(II) oxide, HgO, and carbon. Carbon provides electrical conductivity. The electrolyte is an alkaline paste containing KOH and ZnO.

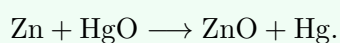
Step 2: Write and combine the electrode reactions At the anode, zinc is oxidised:



At the cathode, mercury(II) oxide is reduced:



Adding cancels the electrons, hydroxide ions and water, giving the overall reaction:



Step 3: Conclusion Thus the zinc-amalgam anode supplies electrons and the mercury(II)-oxide/carbon

cathode accepts them through the electrode reactions written above.

Quick Tip to Solve: Remember Zn is oxidised to ZnO, while HgO is reduced to Hg; balance both half-reactions in alkaline medium.

7(a). Describe mathematically the formation of molecular orbitals in homonuclear diatomic hydrogen molecule by LCAO method. [2 marks]

Solution:

Concept:

- In the linear combination of atomic orbitals (LCAO) method, atomic wave functions of compatible symmetry and similar energy combine to form molecular wave functions.
- Two combining atomic orbitals produce two molecular orbitals: one bonding and one antibonding.

Step 1: Combine the two hydrogen atomic orbitals Let ϕ_A and ϕ_B denote the normalised $1s$ atomic wave functions centred on hydrogen nuclei A and B. Their in-phase sum gives the bonding orbital, while their opposite-phase difference gives the antibonding orbital:

$$\begin{aligned}\psi_{\sigma 1s} &= N_+(\phi_A + \phi_B), \\ \psi_{\sigma^* 1s} &= N_-(\phi_A - \phi_B).\end{aligned}$$

Here N_+ and N_- are normalisation constants.

Step 2: Explain the electron density and occupancy For real wave functions,

$$\psi_{\pm}^2 = N_{\pm}^2 (\phi_A^2 + \phi_B^2 \pm 2\phi_A\phi_B).$$

The positive overlap term increases electron density between the nuclei and lowers energy; the negative term produces a node between the nuclei and raises energy. If $S = \int \phi_A\phi_B d\tau$, then $N_{\pm} = [2(1 \pm S)]^{-1/2}$. The two electrons in ground-state H_2 occupy $\sigma 1s$ with opposite spins.

Step 3: Conclusion The molecular orbitals are the normalised sum $\sigma 1s$ and difference $\sigma^* 1s$ of the two hydrogen $1s$ orbitals. Ground-state hydrogen has configuration $(\sigma 1s)^2$, with bond order 1.

Quick Tip to Solve: Write both the sum and the difference: constructive overlap bonds, while destructive overlap creates the antibonding node.

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

B_2 and O_2^{2-}

[2 marks]

Solution:

Concept:

- Bond order is $\text{BO} = (N_b - N_a)/2$, where N_b and N_a are the numbers of electrons in bonding and antibonding molecular orbitals.
- A species is paramagnetic if it has unpaired electrons and diamagnetic if all its electrons are paired. Equal bond order indicates equal stability on the usual bond-order criterion.

Step 1: Evaluate boron molecule B_2 has ten electrons. For boron, the $\pi 2p$ orbitals lie below $\sigma 2p$, giving

$$\text{B}_2 : (\sigma 1s)^2 (\sigma^* 1s)^2 \\ \times (\sigma 2s)^2 (\sigma^* 2s)^2 (\pi 2p_x)^1 (\pi 2p_y)^1.$$

Thus $N_b = 6$, $N_a = 4$, and $\text{BO} = (6 - 4)/2 = 1$. The two degenerate $\pi 2p$ orbitals each contain one electron by Hund's rule, so B_2 is paramagnetic.

Step 2: Evaluate peroxide ion and compare O_2^{2-} has eighteen electrons. Its molecular-orbital configuration is

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

Hence $N_b = 10$, $N_a = 8$, and $\text{BO} = (10 - 8)/2 = 1$. Both antibonding π^* orbitals are fully occupied, so no electron is unpaired and the ion is diamagnetic.

Step 3: Conclusion Both B_2 and O_2^{2-} have bond order 1, so they have the same relative stability by the bond-order criterion. B_2 is paramagnetic; O_2^{2-} is diamagnetic.

Quick Tip to Solve: Count the extra two electrons in peroxide: they pair the two unpaired electrons of oxygen in the antibonding pi orbitals.

8. Point out the difference between:

(i) chirality and chiral centre, and

(ii) enantiomers and diastereomers.

[2 marks]

Solution:

Concept:

- Chirality is a property of the complete molecular structure, whereas a chiral centre identifies a local stereogenic atom.
- Stereoisomers have the same connectivity but different spatial arrangements. Their mirror-image relationship distinguishes enantiomers from diastereomers.

Step 1: Distinguish chirality and a chiral centre Chirality is the property of a molecule whose mirror image cannot be superimposed on it, even after rotation. A chiral centre is commonly a tetrahedral carbon atom bonded to four different groups, for example the central carbon of $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$. Thus chirality describes the molecule as a whole, whereas a chiral centre describes a particular atom. A molecule with several such centres can be achiral if it has suitable internal symmetry, as in a meso compound.

Step 2: Distinguish enantiomers and diastereomers Enantiomers are stereoisomers that are non-superimposable mirror images of one another. In an achiral environment they have the same physical properties apart from the equal and opposite rotation of plane-polarised light. Diastereomers are stereoisomers that are not mirror images of one another; they generally have different physical and chemical properties. For example, the cis and trans forms of an appropriate disubstituted alkene are diastereomers.

Step 3: Conclusion Chirality is molecular non-superimposability on the mirror image; a chiral centre is a local atom with a stereogenic arrangement. Enantiomers are mirror-image stereoisomers, whereas diastereomers are non-mirror-image stereoisomers.

Quick Tip to Solve: First compare connectivity, then test the mirror-image relationship; the presence of centres alone does not establish whole-molecule chirality.

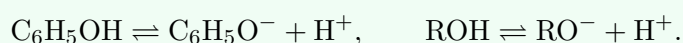
9. Describe the mechanism by which the hydroxyl group attached to an aromatic ring is more acidic than the hydroxyl group attached to an alkyl group. How does the presence of a nitro group in phenol affect its acidic character? [2 marks]

Solution:

Concept:

- Acid strength depends on the stability of the conjugate base formed after loss of H^+ . A more stable conjugate base favours ionisation.
- Resonance delocalises charge; electron-withdrawing groups stabilise a negatively charged conjugate base.

Step 1: Compare phenoxide and alkoxide ions Phenol and an alcohol ionise as follows:



In phenoxide, an oxygen lone pair overlaps with the aromatic pi system, delocalising the negative charge over oxygen and the ortho and para carbon atoms. This resonance stabilisation makes loss of a proton easier. In an alkoxide the negative charge remains localised on oxygen; moreover, the electron-releasing inductive effect of the alkyl group intensifies it. Hence phenol is more acidic than an alcohol.

Step 2: Explain the effect of a nitro group The $-\text{NO}_2$ group withdraws electrons by its negative inductive effect and stabilises the phenoxide ion, increasing acidity. At ortho and para positions it also withdraws through resonance, allowing further delocalisation of the conjugate-base charge. At the meta position mainly the inductive effect operates. Thus nitrophenols are more acidic than phenol.

Step 3: Conclusion Phenol is more acidic because its phenoxide conjugate base is resonance stabilised. A nitro substituent increases the acidic character, especially through additional resonance withdrawal at ortho or para positions.

Quick Tip to Solve: Compare the conjugate bases first: resonance stabilises phenoxide, while a nitro group withdraws still more electron density.

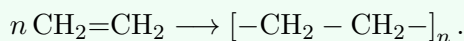
10. Distinguish between homopolymers and copolymers and give one example for each. [2 marks]

Solution:

Concept:

- A monomer is a small molecule from which a polymer is formed by repeated linking.
- Homopolymer and copolymer classification depends on the number of distinct monomer species used, not on the length of the polymer chain.

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



Every segment of this chain originates from ethene molecules. Different molecules of the same monomer do not make it a copolymer.

Step 2: Define and illustrate a copolymer A copolymer is formed by polymerisation of two or more different monomers together. Buna-S is an example: it is made from 1,3-butadiene, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, and styrene, $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$. Its chain therefore contains structural units derived from both monomer species, unlike polyethene. The two types of units need not occur in a strictly alternating sequence.

Step 3: Conclusion Homopolymers use one monomer species, e.g. polyethene from ethene; copolymers use different monomer species, e.g. Buna-S from butadiene and styrene.

Quick Tip to Solve: Count chemically different starting monomers: ethene alone gives a homopolymer; butadiene plus styrene gives a copolymer.

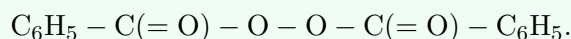
11. Write the structure of a reagent used for initiating a free radical chain reaction. How does it act? [2 marks]

Solution:

Concept:

- Free radical initiators generate species containing an unpaired electron, usually by homolytic cleavage of a weak bond.
- An organic peroxide contains the weak O – O linkage; heating splits it to form radicals that attack an alkene double bond.

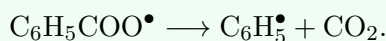
Step 1: Give the reagent and its structure Benzoyl peroxide is a suitable initiator. Its structural formula is



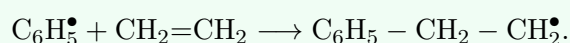
The central oxygen-oxygen bond is relatively weak. On heating, it breaks homolytically: each oxygen retains one electron from the shared pair, producing two benzoyloxy radicals,



Step 2: Explain chain initiation A benzoyloxy radical can lose carbon dioxide to give a phenyl radical:



The radical adds to a monomer double bond, for example



This creates a new carbon-centred radical that adds further monomer molecules, propagating the chain reaction. Thus the peroxide supplies the initial radicals; the growing chain remains reactive at its radical end.

Step 3: Conclusion Benzoyl peroxide initiates the reaction by homolysis of its O-O bond; the radicals produced add to a monomer double bond and start chain growth.

Quick Tip to Solve: Draw both oxygen atoms in the peroxide linkage; its homolysis, followed by radical addition to the double bond, explains initiation.

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

Solution:

Concept:

- The 4s electrons are removed before 3d electrons when first-row transition-metal cations form.
- A half-filled $3d^5$ subshell has extra stability associated with exchange energy and a symmetrical electron distribution.

Step 1: Compare the oxidation states of metal (i) Metal (i), $[\text{Ar}]3d^5 4s^2$, is manganese. Loss of the two 4s electrons gives Mn^{2+} with configuration $[\text{Ar}]3d^5$. Further oxidation gives Mn^{3+} , $[\text{Ar}]3d^4$, and destroys the stable half-filled arrangement. Consequently, the +2 state is relatively more stable than the +3 state for this metal.

Step 2: Compare the oxidation states of metal (ii) Metal (ii), $[\text{Ar}]3d^6 4s^2$, is iron. Its +2 ion is Fe^{2+} , $[\text{Ar}]3d^6$, whereas its +3 ion is Fe^{3+} , $[\text{Ar}]3d^5$. On the electronic-configuration criterion requested, the +3 state is favoured because it has the stable half-filled subshell. Both +2 and +3 are common oxidation states of iron; actual redox stability also depends on the chemical environment.

Step 3: Compare the range of oxidation states Manganese, metal (i), exhibits the larger number of oxidation states. Its five $3d$ and two $4s$ electrons allow a wide range, commonly +2, +3, +4, +5, +6 and +7; iron most commonly shows +2 and +3. The maximum familiar state of manganese is +7, as in permanganate.

Step 4: Conclusion Metal (i) is Mn: +2 is favoured over +3. Metal (ii) is Fe: the half-filled-shell argument favours +3 over +2. Mn exhibits the larger number of oxidation states.

Quick Tip to Solve: Remove $4s$ electrons first, then check which oxidation state gives $3d^5$: Mn(II) and Fe(III).

13. Two elements A and B form compounds having molecular formulae AB_2 and AB_4 . When dissolved in 20 g of benzene, 1 g of AB_2 lowers the freezing point by 2.3 K, whereas 1.0 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 solution of a non-electrolyte, $\Delta T_f = K_f m$, where m is molality and K_f is the molal depression constant.
- If w grams of solute of molar mass M dissolve in W grams of solvent, $M = 1000K_f w / (\Delta T_f W)$. Molecular mass is the sum of the atomic masses in the formula.

Step 1: Find the molar mass of each compound The solvent mass is 20 g = 0.020 kg, and each sample contains 1.0 g of solute. Taking the compounds as non-associating, non-dissociating solutes in benzene, substitute separately for their freezing-point depressions:

$$M_{AB_2} = \frac{5.1 \times 1.0}{2.3 \times 0.020} = 110.87 \text{ g mol}^{-1},$$
$$M_{AB_4} = \frac{5.1 \times 1.0}{1.3 \times 0.020} = 196.15 \text{ g mol}^{-1}.$$

The smaller depression for the same solute mass corresponds to fewer solute molecules and hence the larger molar mass.

Step 2: Separate the atomic masses Let the atomic masses of A and B be a and b , respectively. The two formulae give

$$a + 2b = 110.87, \quad a + 4b = 196.15.$$

Subtract the first relation from the second to eliminate A:

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

Substitute into the first relation:

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

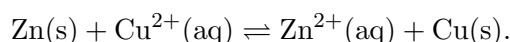
These values also reproduce the molecular mass of AB_4 , providing a check on the simultaneous

equations.

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

Quick Tip to Solve: Subtract the two molecular-mass equations first: the difference equals the mass of two B atoms.

14. Calculate the equilibrium constant for the reaction:



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

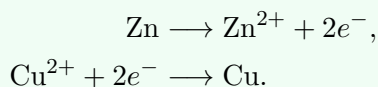
[3 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- Combining $\Delta G^\circ = -nFE^\circ$ and $\Delta G^\circ = -RT \ln K$ gives $\log_{10} K = nE^\circ/0.0591$ at 298 K; n is the number of transferred electrons.

Step 1: Identify the electron transfer and cell potential Zinc is oxidised and copper(II) ions are reduced in the reaction as written:



Thus $n = 2$, zinc is the anode and copper is the cathode. The standard cell potential is

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

Electrode potentials are not multiplied by their stoichiometric coefficients.

Step 2: Calculate the equilibrium constant Use the conventional temperature 298 K for the supplied standard electrode potentials. At equilibrium the cell emf is zero; the Nernst equation therefore gives

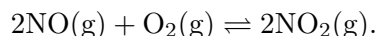
$$\begin{aligned}\log_{10} K &= \frac{nE^\circ_{\text{cell}}}{0.0591} \\ &= \frac{2 \times 1.103}{0.0591} = 37.33, \\ K &= 10^{37.33} \simeq 2.13 \times 10^{37}.\end{aligned}$$

Pure solid zinc and copper have unit activity, so the equilibrium expression is $K = a(\text{Zn}^{2+})/a(\text{Cu}^{2+})$. The very large value is consistent with the positive standard potential and strongly favours products.

Step 3: Conclusion At 298 K, $K \approx 2.1 \times 10^{37}$.

Quick Tip to Solve: Use cathode minus anode with both tabulated values as reduction potentials; here two electrons are transferred.

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



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

Solution:

Concept:

- The order of a reaction is the sum of the powers of the reactant concentrations in its experimentally determined rate law.
- For an elementary one-step reaction, the reactant stoichiometric coefficients give the powers in the forward rate law. Concentration is amount divided by volume, and the rate constant stays fixed at constant temperature.

Step 1: Define order and write the rate law If $r = k[A]^p[B]^q$, the reaction order is $p + q$; it need not generally equal the sum of stoichiometric coefficients. Here the question explicitly says the reaction occurs in one step, so the forward reaction is elementary. Its rate law is therefore

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

It is second order with respect to NO and first order with respect to oxygen, giving an overall order of three. Although the printed reaction is reversible, this law describes its forward rate.

Step 2: Apply the volume reduction Consider the immediate effect of compression at unchanged temperature, before appreciable reaction changes the amounts present. With $V_{\text{new}} = V_{\text{old}}/3$, each reactant concentration becomes three times its original value:

$$[\text{NO}]_{\text{new}} = 3[\text{NO}]_{\text{old}}, \quad [\text{O}_2]_{\text{new}} = 3[\text{O}_2]_{\text{old}}.$$

Hence

$$\frac{r_{\text{new}}}{r_{\text{old}}} = \frac{k(3[\text{NO}])^2(3[\text{O}_2])}{k[\text{NO}]^2[\text{O}_2]} = 3^2 \times 3 = 27.$$

This compares the forward rates; the net rate of a reversible reaction would additionally depend on its reverse rate.

Step 3: Conclusion The order is the sum of concentration exponents in the rate law. For the stated one-step forward reaction it is three, and its rate becomes 27 times the original rate.

Quick Tip to Solve: When every reactant concentration changes by the same factor, raise that factor to the overall reaction order.

16. Explain what happens when

- (i) an electrolyte NaCl is added to ferric hydroxide sol.
- (ii) a direct current is passed through a colloidal sol.
- (iii) an emulsion is subjected to centrifugation.

[3 marks]

Solution:

Concept:

- Colloidal particles usually carry the same sign of electric charge. Their mutual repulsion helps keep them dispersed; removal of this charge promotes coagulation.
- Electrophoresis is the motion of charged colloidal particles towards an oppositely charged electrode. An emulsion consists of droplets of one liquid dispersed in another immiscible liquid.

Step 1: (i) Addition of sodium chloride Ferric hydroxide sol is positively charged. Sodium chloride supplies Na^+ and Cl^- ions. The oppositely charged Cl^- ions are adsorbed on the sol particles and neutralise their positive charge. Consequently, electrostatic repulsion decreases, the particles aggregate and ferric hydroxide coagulates when sufficient electrolyte is added.

Step 2: (ii) Passage of direct current The electric field causes the charged colloidal particles to migrate towards the electrode having the opposite charge: positive particles move to the cathode and negative particles move to the anode. This phenomenon is called electrophoresis. On reaching the electrode, particles can lose their charge and become deposited or coagulated there.

Step 3: (iii) Centrifugation of an emulsion Centrifugation accelerates the separation of the dispersed liquid droplets from the continuous liquid because the two liquids have different densities. The emulsion breaks, or demulsifies, into its constituent liquid layers; the denser liquid collects farther from the axis of rotation.

Step 4: Conclusion (i) Ferric hydroxide sol coagulates through charge neutralisation by chloride ions. (ii) Electrophoresis occurs. (iii) The emulsion separates into its constituent liquids by demulsification.

Quick Tip to Solve: For ferric hydroxide sol, select the negative ion of the electrolyte as the coagulating ion; distinguish electrophoresis from centrifugation.

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

[3 marks]

Solution:

Concept:

- The square of the wave amplitude gives probability per unit volume. For a spherically symmetric s orbital, this density depends only on the distance r from the nucleus.
- A thin spherical shell of radius r and thickness dr has volume $4\pi r^2 dr$. Multiplying the density by this volume gives the probability of finding the electron in that shell.

Step 1: (i) Radial probability density In the notation used in the question, R^2 is the probability density at distance r from the nucleus: the probability per unit volume there. Thus $R^2 dV$ gives the

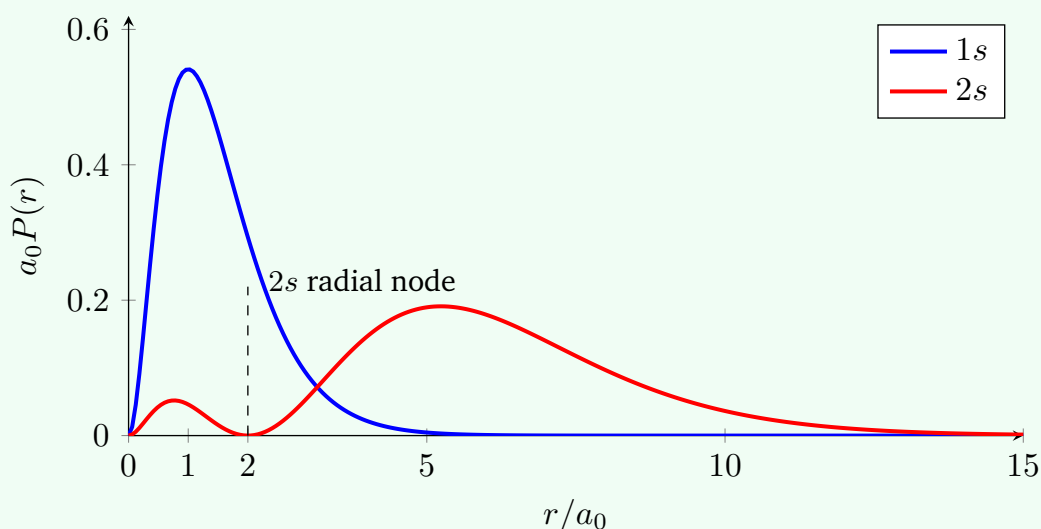
probability in a small volume dV . For the hydrogen 1s orbital the density is greatest at the nucleus and decreases with increasing r . Density at a point must be distinguished from the probability in an entire spherical shell.

Step 2: (ii) Radial probability function The radial probability function is $P(r) = 4\pi r^2 R^2$. Therefore $P(r)dr$ is the probability of finding the electron anywhere in the spherical shell between r and $r + dr$, irrespective of direction. The factor r^2 makes $P(0) = 0$, even when the s-orbital probability density at the nucleus is nonzero. The area under a normalised $P(r)$ curve over a radial interval gives the probability in that interval.

Step 3: Curves for the hydrogen 1s and 2s orbitals Write $x = r/a_0$, where a_0 is the Bohr radius. The normalised radial distributions have the forms

$$a_0 P_{1s} = 4x^2 e^{-2x}, \quad a_0 P_{2s} = \frac{x^2(2-x)^2 e^{-x}}{8}.$$

The 1s curve starts at zero, has one maximum at $r = a_0$, and then approaches zero; it has no radial node. The 2s curve has two maxima separated by a radial node at $r = 2a_0$. Its outer maximum is higher and lies farther from the nucleus. Both curves approach zero as r becomes very large.



Hydrogen radial probability distributions; a_0 is the Bohr radius.

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

Quick Tip to Solve: Multiply the point density by the spherical-shell factor $4\pi r^2$ before sketching; both radial distributions must start at zero.

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

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

[3 marks]

Solution:

Concept:

- A face-centred cubic (FCC) unit cell contains $Z = 4$ atoms: eight corner atoms contribute $8/8 = 1$, and six face-centred atoms contribute $6/2 = 3$.
- In FCC, nearest neighbours touch along a face diagonal. Thus the nearest-neighbour distance $d = a/\sqrt{2}$, where a is the cell edge. The density is $\rho = ZM/(N_A a^3)$, where M is molar mass and N_A is Avogadro's constant.

Step 1: Obtain the unit-cell edge The given 287 pm is the distance between adjacent atoms, not the cell edge. Along a face diagonal, two successive nearest-neighbour distances span the diagonal, so $\sqrt{2}a = 2d$. Hence

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

Since 1 pm = 10⁻¹⁰ cm, the edge is 4.0588 × 10⁻⁸ cm.

Step 2: Calculate cell mass and volume Each silver atom has mass M/N_A , so the mass of one FCC unit cell is

$$m_{\text{cell}} = \frac{4 \times 107.87}{6.02 \times 10^{23}} = 7.1674 \times 10^{-22} \text{ g.}$$

The cubic unit-cell volume is

$$V_{\text{cell}} = a^3 = (4.0588 \times 10^{-8})^3 = 6.6868 \times 10^{-23} \text{ cm}^3.$$

Step 3: Divide cell mass by cell volume Applying the density relation with consistent centimetre and gram units gives

$$\rho = \frac{m_{\text{cell}}}{V_{\text{cell}}} = \frac{7.1674 \times 10^{-22}}{6.6868 \times 10^{-23}} = 10.719 \text{ g cm}^{-3}.$$

The number of atoms per cell is essential: using one atom instead of four would underestimate the density by a factor of four.

Step 4: Conclusion The density of silver is 10.7 g cm⁻³, to three significant figures.

Quick Tip to Solve: For FCC, first multiply the nearest-neighbour distance by $\sqrt{2}$; convert the edge to centimetres before cubing it.

19. (a) Write chemical reactions which occur when

(i) the matte is charged into a converter in the metallurgy of copper.

(ii) acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution reacts with an iron (II) solution.

(b) What is the cause of lanthanoid contraction?

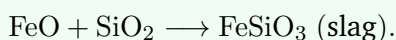
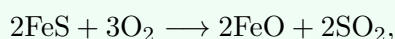
[3 marks]

Solution:

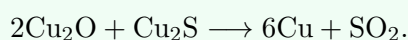
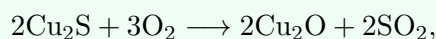
Concept:

- Copper matte contains chiefly Cu_2S and FeS . Air blown through the molten matte oxidises sulphides; silica removes iron oxide as slag, and copper is obtained by self-reduction.
- Acidified dichromate is an oxidising agent: chromium is reduced from +6 to +3, while iron(II) is oxidised to iron(III).
- Lanthanoid contraction is the gradual decrease in atomic and ionic radii with increasing atomic number across the lanthanoid series, owing to the poor shielding by $4f$ electrons.

Step 1: (a)(i) Reactions in the copper converter On blowing air through the matte in a silica-lined converter, iron sulphide is oxidised and the resulting iron(II) oxide forms a fusible silicate slag:

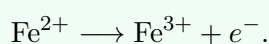
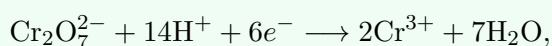


A portion of the copper(I) sulphide is oxidised to copper(I) oxide. This oxide reacts with the remaining sulphide, giving copper by self-reduction:

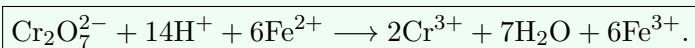


Escaping sulphur dioxide gives the solidified product its blistered appearance; the product is called blister copper.

Step 2: (a)(ii) Oxidation of iron(II) by acidified dichromate The half-reactions are



Multiplying the iron half-reaction by six and adding gives the balanced ionic equation:



Potassium ions are spectators. Both sides have total charge +24, as required.

Step 3: (b) Cause of lanthanoid contraction Across the lanthanoid series, nuclear charge increases and the added electrons enter the inner $4f$ subshell. These $4f$ electrons shield one another and the outer electrons poorly. The increased nuclear charge is therefore not fully screened, so effective nuclear attraction increases and draws the electron cloud progressively closer to the nucleus. Consequently the atomic radii and, particularly, the radii of the corresponding Ln^{3+} ions gradually decrease.

Step 4: Conclusion In the converter, oxidation and slag formation remove iron, followed by self-

reduction to copper. Acidified dichromate oxidises six Fe^{2+} ions per dichromate ion. Poor shielding by $4f$ electrons causes lanthanoid contraction.

Quick Tip to Solve: Balance dichromate reduction first: it takes six electrons, so pair it with six iron(II) ions, each losing one electron.

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

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

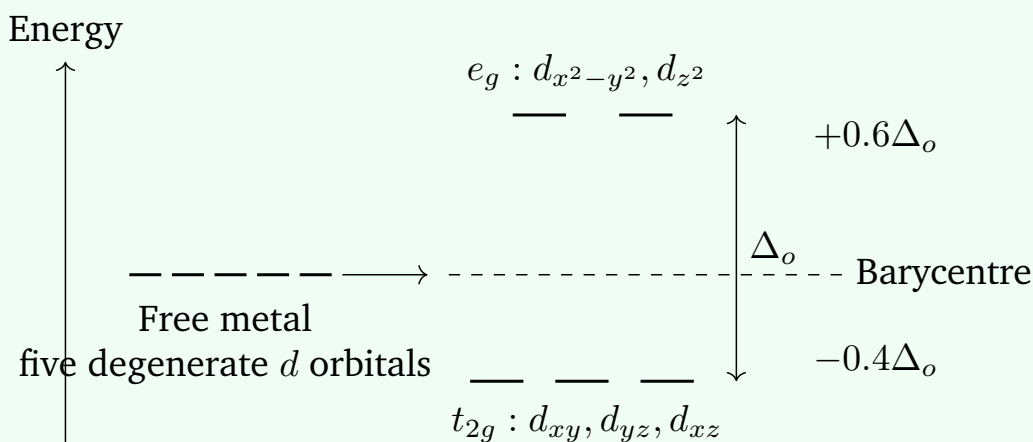
[3 marks]

Solution:

Concept:

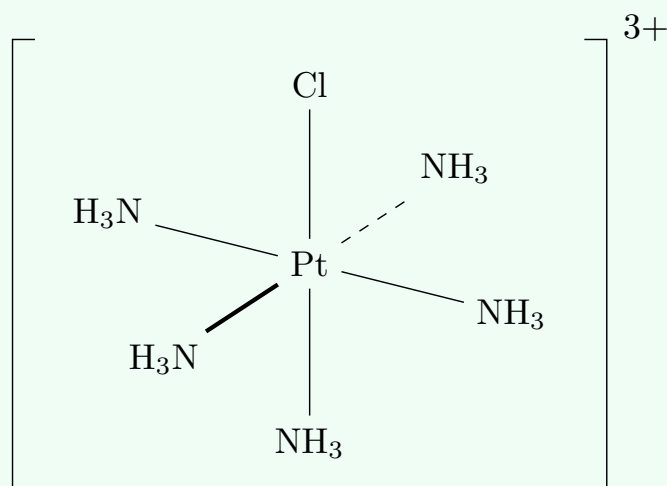
- In an octahedral field, six ligands approach the metal along the Cartesian axes. Orbitals directed along these axes suffer greater repulsion than orbitals directed between them.
- Ammine is a neutral ligand and chlorido has charge -1 . The oxidation state of platinum follows from the charge on the complex ion and determines the Roman numeral in its name.

Step 1: (a) Octahedral splitting of the d orbitals The five initially degenerate d orbitals split into a lower-energy triplet t_{2g} , comprising d_{xy}, d_{yz}, d_{xz} , and a higher-energy doublet e_g , comprising $d_{x^2-y^2}, d_{z^2}$. The latter point directly towards the approaching ligands. The separation is Δ_o ; relative to the barycentre, the triplet lies at $-0.4\Delta_o$ and the doublet at $+0.6\Delta_o$. Their weighted energy changes sum to zero.



Octahedral splitting of the five degenerate d orbitals

Step 2: (b) Name and structure of the coordination entity The three chloride counterions establish that the entity is $[\text{PtCl}(\text{NH}_3)_5]^{3+}$. If the oxidation state of platinum is x , then $x - 1 + 5(0) = +3$, so $x = +4$. Ligand names are arranged alphabetically, ignoring multiplicative prefixes: ammine precedes chlorido. Thus the entity is named pentaamminechloridoplatinum(IV) ion; the complete salt is pentaamminechloridoplatinum(IV) chloride. Its coordination number is six, and its structure is octahedral, with five ammonia ligands and one chlorido ligand bonded directly to platinum. The three counterions are outside the coordination sphere.



Octahedral coordination entity with charge 3+

Step 3: Conclusion The octahedral field gives lower t_{2g} and higher e_g levels. The coordination entity is octahedral $[\text{PtCl}(\text{NH}_3)_5]^{3+}$, pentaamminechloridoplatinum(IV) ion.

Quick Tip to Solve: Count only ligands inside the square brackets for coordination number; use outside chloride ions to obtain the complex charge.

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

(i) Aldol condensation

(ii) Cannizzaro's reaction

(iii) Hell-Volhard-Zelinsky reaction

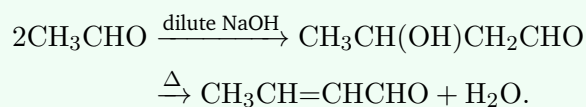
[3 marks]

Solution:

Concept:

- Aldol condensation involves carbonyl compounds with an alpha hydrogen: base-catalysed addition gives a beta-hydroxy carbonyl compound, which dehydrates on heating.
- An aldehyde without an alpha hydrogen undergoes Cannizzaro disproportionation in concentrated alkali, producing an alcohol and a carboxylate salt.
- The Hell-Volhard-Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by halogen using halogen and red phosphorus.

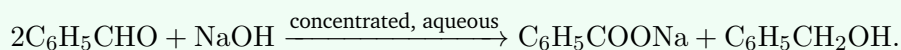
Step 1: (i) Aldol condensation Ethanal has alpha hydrogens and reacts with dilute aqueous sodium hydroxide to give 3-hydroxybutanal (aldol). On heating, this loses water to form but-2-enal:



Showing the dehydration completes the condensation example, rather than stopping at aldol addition.

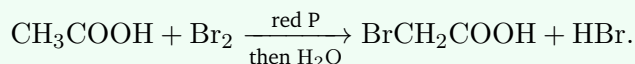
Step 2: (ii) Cannizzaro's reaction Benzaldehyde has no alpha hydrogen. With concentrated sodium

hydroxide, one molecule is oxidised to sodium benzoate while another is reduced to benzyl alcohol:



The salt, rather than free benzoic acid, is obtained because the reaction medium is alkaline.

Step 3: (iii) Hell-Volhard-Zelinsky reaction Ethanoic acid contains alpha hydrogens. Bromine in the presence of red phosphorus, followed by hydrolysis during work-up, gives 2-bromoethanoic acid:



Bromination occurs at the carbon adjacent to the carboxyl group, not by substitution of the acidic hydroxyl hydrogen.

Step 4: Conclusion Suitable examples are ethanal forming but-2-enal, benzaldehyde forming sodium benzoate and benzyl alcohol, and ethanoic acid forming 2-bromoethanoic acid, respectively.

Quick Tip to Solve: Check alpha hydrogens first: their presence permits aldol addition or acid alpha-halogenation, while their absence permits Cannizzaro reaction in an aldehyde.

22(a). In reference to nuclear chemistry describe what you understand by

(i) Nuclear binding energy

(ii) Tracers

(iii) Carbon dating

[3 marks]

Solution:

Concept:

- Nuclear stability is associated with mass defect: the mass of a bound nucleus is smaller than the sum of the masses of its free nucleons.
- Radioisotopes undergo characteristic radioactive decay. Their radiation can be detected, and their decay rate can be used to measure elapsed time.

Step 1: Define nuclear binding energy Nuclear binding energy is the energy required to separate a nucleus completely into its constituent protons and neutrons. Equivalently, it is the energy released when those free nucleons combine to form the nucleus. For a nucleus with atomic number Z , mass number A and nuclear mass M ,

$$E_b = \Delta mc^2, \quad \Delta m = Zm_p + (A - Z)m_n - M.$$

Here m_p and m_n are the proton and neutron masses and c is the speed of light.

Step 2: Explain tracers Tracers are isotopes, usually radioactive isotopes, introduced into a chemical or biological system to follow the movement or fate of an element. They behave chemically like the ordinary isotope, while their emitted radiation makes them detectable. For example, ^{32}P can trace the uptake and distribution of phosphate fertiliser in plants.

Step 3: Explain carbon dating Carbon dating determines the age of once-living material from its remaining radioactive ^{14}C . Living organisms exchange carbon with the environment; after death, this exchange stops and ^{14}C decays with a half-life of about 5730 years. Comparing its present activity a with that of equivalent living material a_0 gives

$$t = \frac{5730}{\ln 2} \ln\left(\frac{a_0}{a}\right) \text{ years.}$$

Thus wood, bones and other organic archaeological remains can be dated.

Step 4: Conclusion Binding energy measures nuclear cohesion; tracers follow an element through a system; carbon dating measures the age of once-living material from residual ^{14}C .

Quick Tip to Solve: For carbon dating, remember that the decay clock starts when carbon exchange stops at death.

OR

22(b). Describe giving suitable example, each of the following:

(i) Activation analysis

(ii) Thermonuclear reactions

(iii) Breeder reactor

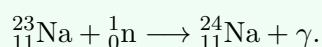
[3 marks]

Solution:

Concept:

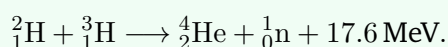
- Neutron capture can convert stable nuclei into identifiable radioactive nuclei; fusion joins light nuclei, whereas breeding converts fertile material into fissile fuel.
- Nuclear equations conserve both mass number and atomic number; beta-minus decay increases atomic number by one without changing mass number.

Step 1: Activation analysis Activation analysis identifies and estimates elements, often present in trace quantities, by irradiating a sample with neutrons and measuring the characteristic radiation of the radioisotopes produced. For example, sodium can be activated as



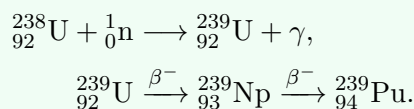
The radioactive ^{24}Na is identified by its characteristic radiation, and the measured activity, compared with a standard under the same conditions, gives the sodium content.

Step 2: Thermonuclear reactions Thermonuclear reactions are nuclear fusion reactions in which light nuclei combine at extremely high temperatures to form heavier nuclei with release of energy. High temperature supplies kinetic energy needed to overcome electrostatic repulsion between the positively charged nuclei. A suitable example is



The energy comes from the decrease in total rest mass.

Step 3: Breeder reactor A breeder reactor produces more fissile fuel than it consumes, by converting fertile nuclei into fissile nuclei using neutrons released during fission. For example, a uranium-plutonium breeder converts fertile ^{238}U into fissile ^{239}Pu :



The plutonium formed can subsequently serve as nuclear fuel.

Step 4: Conclusion Examples are neutron activation of sodium for activation analysis, deuterium-tritium fusion for a thermonuclear reaction, and conversion of ^{238}U into ^{239}Pu in a breeder reactor.

Quick Tip to Solve: Distinguish the three processes by their purpose: detect an element, release fusion energy, or make fissile fuel.

23. What are detergents? Give the scheme of their classification. Why are synthetic detergents preferred over soaps? [3 marks]

Solution:

Concept:

- A detergent has a long hydrophobic hydrocarbon region and a hydrophilic region; this enables it to associate with grease and water and remove dirt.
- Synthetic detergents are classified according to the charge on the cleansing-active species: anionic, cationic or non-ionic.

Step 1: Define detergents Detergents are surface-active cleansing agents that help remove oily dirt by emulsifying it in water. Synthetic detergents commonly contain a long hydrocarbon chain attached to a polar or ionic hydrophilic group. Their molecules gather around grease with the hydrocarbon portions directed towards the grease and the hydrophilic portions towards water, allowing the dirt to be washed away.

Step 2: Give the classification with examples Synthetic detergents are classified as follows. Anionic detergents have a negatively charged active ion; 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 have a positively charged active ion; a suitable example is cetyltrimethylammonium bromide, $[\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]^+ \text{Br}^-$. Non-ionic detergents have uncharged polar groups; examples are polyethylene glycol esters of long-chain fatty acids, whose oxygen-containing groups provide affinity for water.

Step 3: Explain the preference over soaps Soaps are sodium or potassium salts of long-chain fatty acids. In hard water, they form insoluble calcium and magnesium salts, producing scum and wasting soap. Synthetic detergents generally retain their cleansing action because their calcium and magnesium salts do not precipitate as soap scum does. They therefore work in hard water. Suitable synthetic detergents also work in acidic water, where soaps are converted into poorly soluble free fatty acids and lose their cleansing efficiency.

Step 4: Conclusion Synthetic detergents are anionic, cationic or non-ionic cleansing agents. Their effectiveness in hard water, without the scum produced by soaps, is the main reason they are preferred.

Quick Tip to Solve: Classify a detergent by the charge on its active organic species, not by its sodium or bromide counter-ion.

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

(i) Ethyl amine from ethyl bromide

(ii) Sulphanilic acid from aniline

(iii) Phenol from aniline

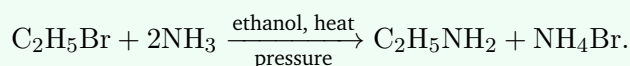
[3 marks]

Solution:

Concept:

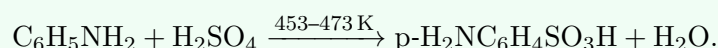
- Ammonolysis replaces the bromine atom of a haloalkane with an amino group. Excess ammonia favours formation of the primary amine over further alkylation.
- Aniline undergoes sulphonation on strong heating with concentrated sulphuric acid. Diazotisation followed by hydrolysis replaces its amino group with a hydroxyl group.

Step 1: (i) Prepare ethylamine by ammonolysis Heat ethyl bromide with excess alcoholic ammonia in a sealed tube (under pressure):



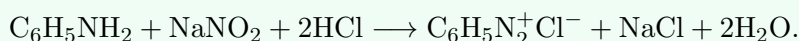
One ammonia molecule supplies the amino group; another accepts the proton released in substitution. A large excess of ammonia limits further reaction of the ethylamine with ethyl bromide, which otherwise gives secondary and tertiary amines.

Step 2: (ii) Prepare sulphanilic acid by sulphonation Treat aniline with concentrated sulphuric acid and heat the resulting anilinium hydrogen sulphate at about 453–473 K:

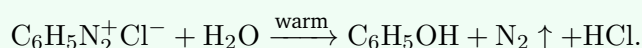


The product is sulphanilic acid, with the sulphonic acid group para to the amino group. It exists predominantly as the internal salt $^+\text{H}_3\text{NC}_6\text{H}_4\text{SO}_3^-$.

Step 3: (iii) Prepare phenol through the diazonium salt First diazotise aniline with sodium nitrite and dilute hydrochloric acid at 273–278 K:



Then warm the aqueous benzenediazonium chloride solution to hydrolyse it:



The low temperature is essential during diazotisation because the diazonium salt decomposes on warming; deliberate warming with water in the next stage produces phenol.

Step 4: Conclusion Ethylamine is obtained using excess alcoholic ammonia and heat; sulphanilic acid using concentrated sulphuric acid at 453–473 K; phenol by cold diazotisation of aniline followed by warm aqueous hydrolysis.

Quick Tip to Solve: For aniline to phenol, always show two stages: cold diazotisation first, then warming with water.

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

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

[5 marks]

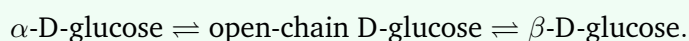
Solution:

Concept:

- Mutarotation is the change in the specific optical rotation of a freshly prepared solution of an optically active substance with time until a constant equilibrium value is reached.
- The two cyclic anomers of D-glucose differ in configuration at the anomeric carbon, C-1. Ring opening and closing in water interconvert these anomers.
- Lipids are water-insoluble biomolecules soluble in nonpolar organic solvents. By chemical composition they are classified as simple, compound (complex), and derived lipids.

Step 1: (a) Observe mutarotation in D-glucose A freshly prepared aqueous solution of pure α -D-glucose has specific rotation approximately $+112^\circ$. Its rotation gradually decreases to about $+52.7^\circ$. A fresh solution of pure β -D-glucose initially has specific rotation approximately $+19^\circ$; its rotation increases to the same final value, $+52.7^\circ$, under the same conditions. This time-dependent change towards a common constant optical rotation is mutarotation.

Step 2: Explain interconversion of the glucose anomers In water, the cyclic hemiacetal ring of either anomer opens to give a very small amount of the open-chain aldehyde form. The planar carbonyl group at C-1 can then form the cyclic hemiacetal with either configuration at that carbon:



Thus, the solution gradually becomes an equilibrium mixture containing roughly 36% of the α anomer and 64% of the β anomer, with only a trace of the open-chain form. Its observed rotation is the combined contribution of the forms present. Once their proportions become constant, the rotation also becomes constant. The D-configuration is retained: mutarotation is anomer interconversion, not conversion of D-glucose to L-glucose.

Step 3: (b) Simple lipids Simple lipids are esters of fatty acids with alcohols and yield fatty acids and alcohols on hydrolysis. Fats and oils are esters of glycerol, whereas waxes contain long-chain monohydric alcohols. For example, tristearin is a simple lipid: it is the triester of glycerol with stearic acid.

Step 4: Compound or complex lipids Compound lipids contain additional groups besides the fatty acid and alcohol components, such as a phosphate-containing group or a carbohydrate group. For example, lecithin (phosphatidylcholine) is a phospholipid containing glycerol, fatty acid residues, phosphate and choline. Glycolipids are another member of this class and contain a carbohydrate

component.

Step 5: Derived lipids Derived lipids include substances obtained by hydrolysis of simple or compound lipids, and related lipid substances that retain lipid characteristics. Examples include fatty acids, glycerol and sterols. Cholesterol is a standard example of a derived lipid; it is a sterol and is an important component of animal cell membranes.

Step 6: Conclusion D-glucose shows mutarotation because its α and β anomers interconvert through the open-chain form, giving an equilibrium rotation of about $+52.7^\circ$. The three lipid classes are simple (tristearin), compound (lecithin), and derived (cholesterol).

Quick Tip to Solve: Connect mutarotation to opening and reclosure at C-1; classify lipids by their composition and attach one named example to each class.

OR

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

Solution:

Concept:

- DNA is a double helix of two complementary polynucleotide strands. Adenine pairs with thymine through two hydrogen bonds, and guanine pairs with cytosine through three hydrogen bonds.
- Replication is semiconservative: each daughter DNA molecule contains one parental strand and one newly synthesised complementary strand. The sequence of bases stores hereditary information.

Step 1: Opening of the parental double helix Before cell division, the DNA double helix unwinds and the hydrogen bonds joining complementary bases break. The two parental strands separate locally, exposing their bases. Each separated strand acts as a template for the formation of a new strand; the covalent sugar-phosphate backbone of the template remains intact.

Step 2: Formation of complementary strands Free deoxyribonucleotides are brought opposite the exposed bases according to the complementary base-pairing rule: an A on the template directs incorporation of T, T directs A, G directs C, and C directs G. DNA polymerase extends the new strand by linking adjacent nucleotides through phosphodiester bonds. New DNA is synthesised in the $5' \rightarrow 3'$ direction, using a short primer to provide the initial free hydroxyl group. Because the two templates run in opposite directions, one new strand is formed continuously while the other is formed in short fragments, which DNA ligase joins into a continuous strand.

Step 3: Production of two daughter molecules As copying proceeds along the parental DNA, each old strand acquires a complete new complementary strand. The strands coil into double helices, producing two daughter DNA molecules. Each has one old strand and one new strand, so this mechanism is called semiconservative replication. For example, a template segment $5'-ATGC-3'$ directs the complementary segment $3'-TACG-5'$; copying its partner similarly restores the same base sequence in the second daughter molecule.

Step 4: Preservation of hereditary information The sequence of bases in DNA specifies genetic

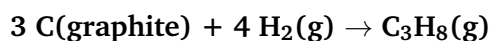
information, which ultimately controls protein formation and inherited characteristics. Specific complementary pairing makes the new strand an accurate copy of the original partner of its template. Consequently, both daughter double helices normally have the same base sequence and genetic information as the parental molecule. When the cell divides, this copied DNA passes to the daughter cells, maintaining genetic continuity. Replication is highly faithful, although occasional copying errors that escape correction can produce mutations.

Step 5: Conclusion DNA replicates by separation of its strands followed by template-directed complementary synthesis. The semiconservative process yields two equivalent DNA molecules, each containing one parental and one new strand, and preserves heredity by transmitting the parental base sequence to daughter cells.

Quick Tip to Solve: Link the answer in order: strand separation, complementary base pairing, one old plus one new strand, and conservation of the base sequence.

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

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



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

Solution:

Concept:

- The second law gives the criterion for spontaneity: $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$ for a spontaneous change; equality holds at equilibrium.
- Standard reaction entropy is $\Delta_r S^\circ = \sum \nu S^\circ_m(\text{products}) - \sum \nu S^\circ_m(\text{reactants})$, where ν denotes the stoichiometric coefficient.
- At temperature T , standard Gibbs energy is $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$. Enthalpy and the entropy term must be expressed in the same energy units.

Step 1: (a) Apply the total entropy criterion A system can exchange energy with its surroundings, so the entropy change of the system alone does not determine spontaneity. For the isolated combination of system and surroundings, the second law requires

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

A positive value indicates a spontaneous change in the stated direction; zero indicates equilibrium, and a negative value means that direction is non-spontaneous.

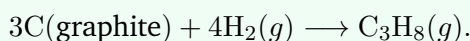
Step 2: (a) Illustrate with heat flow between two bodies Consider a small quantity of heat $q > 0$ passing from a hot body at temperature T_h to a colder body at T_c , with $T_h > T_c$. Take the two bodies together to be isolated and the heat transfer sufficiently small that their temperatures can be treated

as constant. The hot body loses entropy q/T_h , while the cold body gains entropy q/T_c . Hence

$$\Delta S_{\text{total}} = -\frac{q}{T_h} + \frac{q}{T_c} = q \left(\frac{1}{T_c} - \frac{1}{T_h} \right) > 0.$$

Thus heat flows spontaneously from hot to cold even though the entropy of the hot body decreases. The reverse transfer would decrease total entropy and cannot occur spontaneously. This demonstrates why total entropy, rather than one body's entropy, is the criterion.

Step 3: (b) Calculate the standard entropy of formation For the reaction as written, one mole of propane forms from three moles of graphite and four moles of hydrogen:



Using all stoichiometric coefficients,

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

The negative sign is consistent with the reduction from four moles of gaseous reactant to one mole of gaseous product.

Step 4: (b) Substitute into the Gibbs energy equation The given enthalpy is already the standard enthalpy for forming one mole of propane, so $\Delta_f H^\circ = -103.85 \text{ kJ mol}^{-1}$. At 298 K,

$$\begin{aligned}\Delta_f G^\circ &= \Delta_f H^\circ - T\Delta_f S^\circ \\ &= -103.85 - 298(-0.26962) \\ &= -103.85 + 80.34876 \\ &= -23.50124 \text{ kJ mol}^{-1}.\end{aligned}$$

The entropy term opposes formation, but at this temperature the negative enthalpy term has the larger magnitude.

Step 5: Conclusion (a) A spontaneous change has $\Delta S_{\text{total}} > 0$, as shown by spontaneous heat flow from a hotter body to a colder body. (b) The standard Gibbs energy of formation of propane at 298 K is $\Delta_f G^\circ = -23.50 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: Multiply each reactant entropy by its coefficient, then convert J to kJ before subtracting the negative entropy term from the enthalpy.

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

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

(b) Draw the structures of the following species:

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

[5 marks]

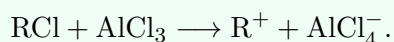
Solution:

Concept:

- Paramagnetism arises from unpaired electrons; high-temperature sulphur vapour contains diatomic S_2 molecules.
- A Lewis acid accepts an electron pair. Electron-deficient AlCl_3 can accept a pair from a reagent and promote electrophile formation.
- Molecular shape depends on bond pairs and lone pairs, while a solid may contain ions rather than discrete molecules.

Step 1: (a)(i) Paramagnetic behaviour of sulphur vapour At high temperature, some of the larger sulphur molecules dissociate to form S_2 . Like O_2 , an S_2 molecule has two unpaired electrons in its antibonding π^* molecular orbitals. These unpaired electrons are attracted by a magnetic field, so the presence of S_2 accounts for the paramagnetic behaviour of sulphur vapour. The explanation concerns the diatomic species in the vapour, rather than the closed-shell cyclic S_8 molecules.

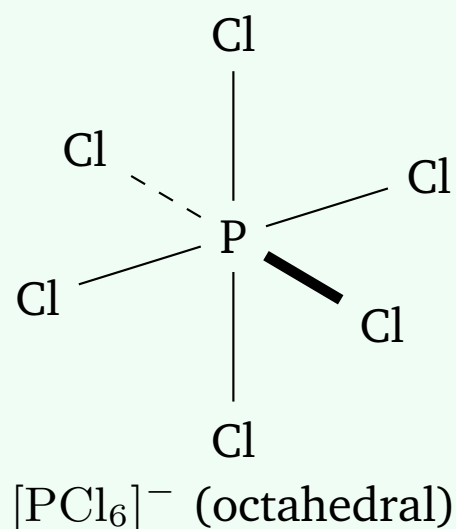
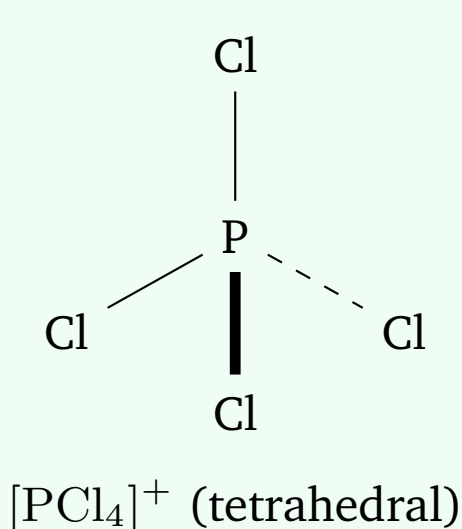
Step 2: (a)(ii) Catalytic action of anhydrous aluminium chloride In monomeric AlCl_3 , aluminium has only six electrons around it and an available orbital for accepting an electron pair. Thus anhydrous aluminium chloride acts as a Lewis acid. By coordinating to a reagent it helps generate a strong electrophile, which then attacks the organic substrate. For example, in Friedel–Crafts alkylation it accepts a chloride ion from an alkyl chloride:



This is a schematic representation of electrophile generation; the catalyst is regenerated during the reaction cycle.

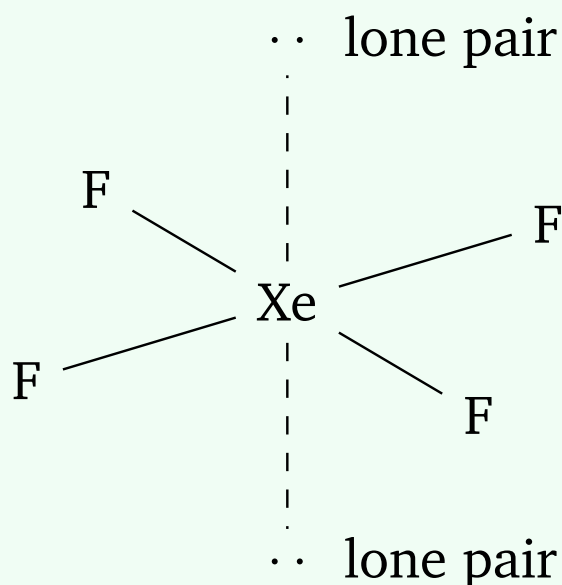
Step 3: (a)(iii) Comparison of fluorine and chlorine bond energies Each atom in F_2 carries three lone pairs. Because fluorine atoms are very small, the nonbonding electron pairs on neighbouring atoms approach closely and repel one another strongly. This lone-pair repulsion weakens the F – F bond. The larger chlorine atoms keep their lone pairs farther apart, reducing this repulsion. Consequently the F – F bond has a lower bond dissociation energy than the Cl – Cl bond, despite its shorter bond length.

Step 4: (b)(i) Structure of solid phosphorus pentachloride In the solid state, PCl_5 is ionic and exists as $[\text{PCl}_4]^+[\text{PCl}_6]^-$. The $[\text{PCl}_4]^+$ cation is tetrahedral, with four P–Cl bonds, whereas the $[\text{PCl}_6]^-$ anion is octahedral, with six P–Cl bonds. Their conventional hybridisations are sp^3 and sp^3d^2 , respectively. A trigonal-bipyramidal molecular drawing would describe gaseous PCl_5 , not the solid requested here.



The tetrahedral cation and octahedral anion present in solid phosphorus pentachloride.

Step 5: (b)(ii) Structure of xenon tetrafluoride Xenon has eight valence electrons. Four Xe–F bonds and two lone pairs give six electron-pair domains around Xe, arranged octahedrally. The two lone pairs occupy opposite positions to minimise repulsion, leaving the four fluorine atoms in one square plane. Therefore XeF_4 is square planar (AX_4E_2), with adjacent F–Xe–F angles of 90° and opposite angles of 180° .



Square-planar xenon tetrafluoride; the two lone pairs lie above and below the fluorine plane.

Step 6: Conclusion Sulphur vapour contains paramagnetic S_2 ; AlCl_3 catalyses reactions by Lewis acidity; strong lone-pair repulsion weakens F – F. Solid PCl_5 contains tetrahedral $[\text{PCl}_4]^+$ and octahedral $[\text{PCl}_6]^-$, while XeF_4 is square planar.

Quick Tip to Solve: Check the state symbol before drawing phosphorus pentachloride: the solid requires two ionic structures. For xenon tetrafluoride, place its two lone pairs opposite each other.