

CBSE Class 12 Chemistry Question Paper 2008 with Solution PDF-Set 56/1 (Delhi)



Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) All questions are compulsory.
- (ii) Question nos. 1 to 8 are very short answer questions and carry 1 mark each.
- (iii) Question nos. 9 to 18 are short answer questions and carry 2 marks each.
- (iv) Question nos. 19 to 27 are also short answer questions and carry 3 marks each.
- (v) Question nos. 28 to 30 are long answer questions and carry 5 marks each.
- (vi) Use log tables if necessary, use of calculators is not allowed.

1. What is the coordination number of each type of ions in a rock-salt type crystal structure? [1 mark]

Solution:

Concept:

- Coordination number is the number of nearest neighbouring ions of opposite charge surrounding a given ion.
- In the rock-salt structure, the cations occupy octahedral sites in the anion lattice.

Step 1: Consider a cation In rock salt, each Na^+ ion is surrounded by six nearest Cl^- ions. These neighbours are arranged octahedrally, with one along each positive and negative direction of the three perpendicular axes.

Step 2: Consider an anion The arrangement is reciprocal: every Cl^- ion also has six nearest Na^+ neighbours. Count only nearest opposite ions, rather than all ions in the unit cell.

Step 3: Conclusion The coordination number of each type of ion is $\boxed{6}$; the coordination is 6 : 6.

Quick Tip to Solve: Recall rock salt as octahedral coordination: six opposite ions surround either ion.

2. Define the term 'order of reaction' for chemical reactions. [1 mark]

Solution:

Concept:

- The rate law expresses reaction rate in terms of reactant concentrations at a fixed temperature.
- Orders are the experimentally determined exponents in this rate law.

Step 1: Write a general rate law For reactants A and B , suppose the measured rate law is $r = k[A]^m[B]^n$, where k is the rate constant and m, n are the individual orders with respect to the two reactants.

Step 2: Add the exponents The overall order is obtained by adding these powers, giving $m + n$. These exponents must come from the rate law; they are not generally the coefficients of the balanced chemical equation. An order can be zero, integral or fractional.

Step 3: Conclusion The order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate-law expression.

Quick Tip to Solve: Write the rate law first, then add its concentration exponents; do not add equation coefficients.

3. What causes Brownian movement in a colloidal solution? [1 mark]

Solution:

Concept:

- Brownian movement is the continuous, random zigzag motion of colloidal particles.
- Molecules of the dispersion medium undergo ceaseless thermal motion.

Step 1: Identify the collisions The moving molecules of the dispersion medium continuously strike the dispersed colloidal particles from all sides. The colloidal particles receive momentum in these collisions.

Step 2: Explain the random displacement At any instant, the impacts on different sides are unequal, so the resultant force does not cancel exactly. The resulting impulses change unpredictably in magnitude and direction, producing the observed irregular zigzag movement. The motion is not caused by gravity or a chemical reaction.

Step 3: Conclusion Brownian movement is caused by continuous, unequal bombardment of colloidal particles by the molecules of the dispersion medium.

Quick Tip to Solve: Link the random motion to unequal molecular impacts, and explicitly name the dispersion medium.

4. In which one of the two structures, NO_2^+ and NO_2^- , the bond angle has a higher value? [1 mark]

Solution:

Concept:

- According to VSEPR theory, electron pairs around a central atom arrange themselves to minimise repulsion.
- A multiple bond counts as one bonding domain when predicting the molecular geometry.

Step 1: Examine the nitronium ion In NO_2^+ , nitrogen has two bonding domains and no lone pair. The two domains lie opposite one another, so the ion is linear and the $\text{O} - \text{N} - \text{O}$ angle is 180° .

Step 2: Compare the nitrite ion In NO_2^- , nitrogen has two bonding domains and one lone pair. Lone-pair repulsion produces a bent shape; its bond angle is about 115° , much smaller than the linear angle. Thus comparing the electron-pair arrangements directly determines which angle is larger.

Step 3: Conclusion NO_2^+ has the higher bond angle: 180° , compared with about 115° in NO_2^- .

Quick Tip to Solve: Count lone pairs on nitrogen: no lone pair gives linear nitronium, while one gives bent nitrite.

5. Write the IUPAC name of the following compound:



[1 mark]

Solution:

Concept:

- Choose the longest carbon chain containing both hydroxyl groups, then number it to give the hydroxyl groups the lowest locants.
- Two hydroxyl groups are indicated by the suffix diol, with their positions stated.

Step 1: Choose and number the parent chain The longest chain containing both $-\text{OH}$ groups has

six carbon atoms. Number from the terminal CH_2OH end: the hydroxyl groups then occur at carbon atoms 1 and 3. Numbering from the other end would give 4 and 6, so it is rejected.

Step 2: Locate the substituents and construct the name With this numbering, the two methyl substituents are on carbon atoms 2 and 5. The parent name is hexane-1,3-diol, and the methyl substituents are specified together as 2,5-dimethyl. The suffix e in hexane is retained before diol.

Step 3: Conclusion The IUPAC name is 2,5-dimethylhexane-1,3-diol.

Quick Tip to Solve: Number from the terminal alcohol end so that the two hydroxyl locants are 1,3 rather than 4,6.

6. Arrange the following compounds in an increasing order of their acid strengths:

$(\text{CH}_3)_2\text{CHCOOH}$, $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$

[1 mark]

Solution:

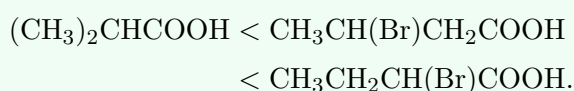
Concept:

- Acid strength increases when the conjugate carboxylate ion is stabilised.
- Bromine withdraws electron density by the negative inductive effect, which decreases with distance; alkyl groups have an electron-releasing inductive effect.

Step 1: Compare the unhalogenated acid In $(\text{CH}_3)_2\text{CHCOOH}$, the alkyl groups release electron density and do not provide the electron-withdrawing stabilisation supplied by bromine. It is therefore the weakest acid among the three.

Step 2: Compare the positions of bromine In $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$, bromine is on the beta carbon, whereas in $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, it is on the alpha carbon. The closer alpha bromine exerts a stronger negative inductive effect and stabilises the carboxylate ion more effectively. Hence the alpha-bromo acid is stronger than the beta-bromo acid.

Step 3: Conclusion The increasing acid-strength order is



Quick Tip to Solve: Count distance from COOH : alpha bromine strengthens the acid more than beta bromine.

7. Write a chemical reaction in which the iodide ion replaces the diazonium group in a diazonium salt.

[1 mark]

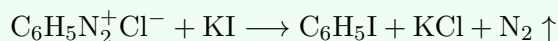
Solution:

Concept:

- Arenediazonium salts release molecular nitrogen when their diazonium group is replaced by a suitable nucleophile.
- Potassium iodide supplies the iodide ion, I^- , needed to prepare an aryl iodide.

Step 1: Choose the diazonium salt Take benzenediazonium chloride, $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$, and add aqueous potassium iodide. The iodide replaces the diazonium group attached to the benzene ring.

Step 2: Write the balanced substitution



The gaseous nitrogen escapes; no copper salt is required for this replacement.

Step 3: Conclusion Benzenediazonium chloride reacts with potassium iodide to form iodobenzene, with evolution of nitrogen.

Quick Tip to Solve: For iodination of a diazonium salt, use KI directly; a copper catalyst is unnecessary.

8. Name a substance that can be used as an antiseptic as well as a disinfectant.

[1 mark]

Solution:

Concept:

- Antiseptics act against microorganisms on living tissues; disinfectants are used on non-living surfaces.
- The concentration of some substances determines which of these applications is suitable.

Step 1: Identify a suitable substance Phenol can act as both an antiseptic and a disinfectant. Its application depends on the concentration of its solution, because stronger solutions are harmful to living tissue.

Step 2: Specify the concentration-dependent uses A 0.2% solution of phenol is used as an antiseptic, whereas a 1% solution is used as a disinfectant. Thus the same compound serves both purposes at different concentrations.

Step 3: Conclusion Phenol is an example: 0.2% solution is antiseptic and 1% solution is disinfectant.

Quick Tip to Solve: Remember phenol with its concentrations: 0.2 percent for antiseptic use and 1 percent for disinfection.

9(a). Explain as to why haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions.

[2 marks]

Solution:

Concept:

- In haloarenes, a lone pair of the halogen overlaps with the aromatic π system, giving the carbon-halogen bond partial double-bond character.
- Nucleophilic substitution requires carbon-halogen bond cleavage and either ionisation or backside attack.

Step 1: Explain the stronger bond Resonance delocalisation gives the aryl C – X bond partial double-

bond character. Also, the bonded carbon is sp^2 -hybridised, with greater s-character than the sp^3 carbon of a haloalkane. Consequently the aryl bond is shorter and stronger, and its cleavage is more difficult.

Step 2: Explain the difficulty of the substitution pathways An S_N1 reaction would require an extremely unstable phenyl cation. In an S_N2 reaction, backside approach to the halogen-bearing aromatic carbon is hindered by the ring and its electron cloud. Hence the ordinary substitution pathways available to haloalkanes are unfavourable for haloarenes.

Step 3: Conclusion Haloarenes undergo nucleophilic substitution much less readily because their aryl carbon-halogen bond is stronger and the usual S_N1 and S_N2 pathways are unfavourable.

Quick Tip to Solve: Link low aryl-halide reactivity to resonance, the stronger sp^2 carbon bond, and difficult substitution pathways.

OR

9(b). Which compound in each of the following pairs will react faster in S_N2 reaction with $-OH$? Why?

(i) CH_3Br or CH_3I

(ii) $(CH_3)_3CCl$ or CH_3Cl

[2 marks]

Solution:

Concept:

- An S_N2 reaction is a single-step substitution in which OH^- attacks the carbon from the side opposite the leaving group.
- With similar steric environments, a better leaving group increases the rate; with the same leaving group, less crowding favours backside attack.

Step 1: Compare methyl bromide and methyl iodide CH_3I reacts faster than CH_3Br . Both compounds have the same methyl group, so steric hindrance is comparable. The $C-I$ bond is weaker than the $C-Br$ bond, and I^- is a better leaving group than Br^- .

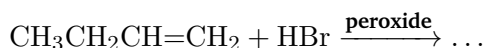
Step 2: Compare tert-butyl chloride and methyl chloride CH_3Cl reacts faster than $(CH_3)_3CCl$. The methyl carbon permits easy backside attack by OH^- . In tert-butyl chloride, the three bulky methyl groups shield the reaction centre and severely hinder the S_N2 transition state. Its possible reactions by other mechanisms do not make it fast in S_N2 .

Step 3: Conclusion (i) CH_3I , because iodide is the better leaving group. (ii) CH_3Cl , because it has much less steric hindrance.

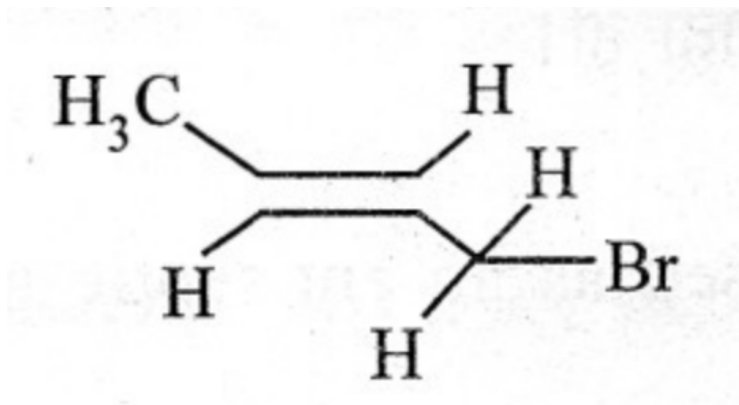
Quick Tip to Solve: Compare the leaving group when the carbon skeleton is unchanged; compare crowding when the leaving group is unchanged.

10. (a) State the IUPAC name of the following compound (shown below).

(b) Complete the following chemical equation:



[2 marks]



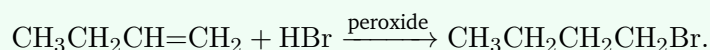
Solution:

Concept:

- IUPAC naming gives the double bond the lowest possible locant and then resolves a numbering tie using substituent locants.
- In peroxide, HBr adds to an unsymmetrical alkene through a radical chain mechanism, giving anti-Markovnikov addition.

Step 1: Name the structure in part (a) The four-carbon chain is $\text{BrCH}_2\text{CH}=\text{CHCH}_3$. The double bond has locant 2 from either end; numbering from the bromine end gives bromo locant 1 instead of 4. The name is therefore 1-bromobut-2-ene. In the printed structure, the higher-priority groups CH_3 and CH_2Br lie on opposite sides of the double bond, so the stereochemical name is (*E*)-1-bromobut-2-ene.

Step 2: Complete the peroxide addition in part (b) Bromine adds to the terminal carbon, forming the more stable secondary carbon radical; this radical then abstracts hydrogen from HBr. Thus the final product is 1-bromobutane:



Step 3: Conclusion (a) (*E*)-1-bromobut-2-ene (trans-1-bromobut-2-ene). (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, 1-bromobutane.

Quick Tip to Solve: When the double-bond locant ties, minimise the bromo locant; peroxide reverses the usual orientation of HBr addition.

11. State Henry's law correlating the pressure of a gas and its solubility in a solvent and mention two applications for the law. [2 marks]

Solution:

Concept:

- At constant temperature, the solubility of a gas in a liquid is directly proportional to its partial pressure above the liquid.
- In mole-fraction form, Henry's law is $p = K_H x$, where p is the partial pressure of the gas, x is its mole fraction in solution and K_H is Henry's law constant for the gas-solvent pair at that temperature.

Step 1: State the law For a given gas and solvent at a fixed temperature,

$$x = \frac{p}{K_H}.$$

Thus, raising the partial pressure increases the amount of gas dissolved. The temperature condition is essential because K_H changes with temperature.

Step 2: Apply the law in two situations (i) Soft drinks and soda water are bottled under high carbon dioxide pressure. The greater pressure increases the solubility of CO_2 , so more of it remains dissolved in the sealed bottle.

(ii) Scuba divers use breathing mixtures containing helium in place of much of the nitrogen. At high underwater pressure, appreciable nitrogen would dissolve in blood; on rapid ascent it can form bubbles and cause the bends. Helium is much less soluble and reduces this risk.

Step 3: Conclusion Henry's law is $p = K_H x$ at constant temperature. Two applications are carbonation of soft drinks under pressure and helium-containing breathing mixtures for deep-sea divers.

Quick Tip to Solve: Always state constant temperature and use the gas partial pressure, rather than total pressure of a gas mixture.

12. A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value. [2 marks]

Solution:

Concept:

- For a first-order reaction, $k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t}$, where $[A]_0$ and $[A]_t$ are initial and remaining reactant concentrations.
- The half-life is $t_{1/2} = \ln 2/k$, independent of the initial concentration.

Step 1: Find the fraction of reactant remaining After 40 min, 30% of the reactant has decomposed. Therefore 70% remains and

$$\frac{[A]_t}{[A]_0} = 0.70.$$

The integrated rate law uses the concentration remaining, not the fraction decomposed.

Step 2: Calculate the rate constant and half-life Using minutes consistently,

$$\begin{aligned}k &= \frac{1}{40} \ln \frac{100}{70} \\&= \frac{0.356675}{40} \\&= 8.9169 \times 10^{-3} \text{ min}^{-1}.\end{aligned}$$

Hence

$$t_{1/2} = \frac{0.693147}{8.9169 \times 10^{-3}} = 77.7 \text{ min}.$$

This is greater than 40 min, as expected: half decomposition takes longer than the observed thirty-percent decomposition.

Step 3: Conclusion The half-life is $t_{1/2} \approx 77.7 \text{ min}$ (approximately 78 min).

Quick Tip to Solve: For a stated percentage decomposition, subtract it from 100 before substituting into the first-order logarithm.

13. What is meant by the ‘rate constant, k ’ of a reaction? If the concentration be expressed in mol L^{-1} units and time in seconds, what would be the units for k (i) for a zero order reaction and (ii) for a first order reaction? [2 marks]

Solution:

Concept:

- The rate constant is the proportionality constant in the rate law. For $r = k[A]^n$, r is reaction rate, $[A]$ is reactant concentration and n is the reaction order.
- With concentration in mol L^{-1} and time in seconds, rate has units $\text{mol L}^{-1} \text{ s}^{-1}$.

Step 1: Define the rate constant At a fixed temperature, k is the constant that relates reaction rate to the product of reactant concentrations raised to their respective orders. Numerically, it equals the rate when each reactant concentration appearing in the rate law has unit value in the chosen concentration units. Its units depend on the overall order of the reaction.

Step 2: Derive the units for the two orders (i) For a zero-order reaction, $r = k[A]^0 = k$. Therefore,

$$[k] = \text{mol L}^{-1} \text{ s}^{-1}.$$

(ii) For a first-order reaction, $r = k[A]$, so

$$[k] = \frac{\text{mol L}^{-1} \text{ s}^{-1}}{\text{mol L}^{-1}} = \text{s}^{-1}.$$

The concentration units cancel only in the first-order case.

Step 3: Conclusion k is the proportionality constant in the rate law. Its units are (i) zero order: $\text{mol L}^{-1} \text{ s}^{-1}$; (ii) first order: s^{-1} .

Quick Tip to Solve: Divide rate units by concentration raised to the reaction order; never assign first-order units to every rate constant.

14. Define the following terms in relation to proteins:

(i) Peptide linkage

(ii) Denaturation

[2 marks]

Solution:

Concept:

- Proteins are polypeptides: amino-acid residues are connected by covalent amide bonds called peptide linkages.
- A protein's biological activity depends on its characteristic folded conformation, maintained by interactions between different parts of its chain.

Step 1: Define peptide linkage A peptide linkage is the amide bond $-\text{CO}-\text{NH}-$ formed when the carboxyl group of one amino acid reacts with the amino group of another amino acid, eliminating a molecule of water. This condensation connects the two amino-acid residues and repeated peptide linkages form the backbone of a polypeptide.

Step 2: Define denaturation Denaturation is the loss of the native conformation and biological activity of a protein through disruption of its secondary and tertiary structures, for example on heating or changing pH. The interactions responsible for folding are disturbed, so the protein can no longer perform its normal function. Its primary structure, including the peptide bonds linking the amino-acid sequence, remains intact during denaturation. Coagulation of egg white on heating is a familiar example.

Step 3: Conclusion (i) Peptide linkage: the $-\text{CO}-\text{NH}-$ bond joining amino-acid residues. (ii) Denaturation: loss of native protein conformation and biological activity without cleavage of its primary peptide chain.

Quick Tip to Solve: Distinguish denaturation from hydrolysis: denaturation changes folding, whereas hydrolysis breaks peptide bonds.

15. List the reactions of glucose which cannot be explained by its open chain structure.

[2 marks]

Solution:

Concept:

- The open-chain structure of glucose contains an aldehyde group, $-\text{CHO}$, and five hydroxyl groups. A free aldehyde group should show the usual carbonyl addition reactions.
- Reactions indicating the absence of a freely available aldehyde group require the cyclic hemiacetal structure.

Step 1: List the missing aldehyde reactions Despite the aldehyde group in its proposed open-chain formula, glucose does not give Schiff's test and does not form a hydrogen sulphite addition product with NaHSO_3 . These observations cannot be explained by a molecule having a permanently free $-\text{CHO}$ group.

Step 2: Examine the acetylated derivative Glucose pentaacetate does not react with hydroxylamine, NH_2OH , to form an oxime. If acetylation merely replaced the hydrogen atoms of the five hydroxyl

groups in an open-chain molecule, its aldehyde group would remain available and should form an oxime. The absence of this reaction contradicts that picture. The existence of two crystalline forms, α - and β -glucose, is also unexplained by a single open-chain formula.

Step 3: Conclusion The unexplained reactions are the failure to give Schiff's test, to form a NaHSO_3 addition product, and the failure of glucose pentaacetate to form an oxime with hydroxylamine.

Quick Tip to Solve: Remember the three negative tests: Schiff's reagent, bisulphite addition, and hydroxylamine with glucose pentaacetate.

16. Assign a reason for each of the following statements:

(i) Ammonia is a stronger base than phosphine.

(ii) Sulphur in vapour state exhibits a paramagnetic behaviour.

[2 marks]

Solution:

Concept:

- A Lewis base donates a lone pair of electrons. Greater availability of the lone pair favours proton acceptance and hence basicity.
- A substance is paramagnetic if its molecules contain unpaired electrons; paired electrons alone do not produce this behaviour.

Step 1: Compare ammonia with phosphine In NH_3 , the lone pair on the small nitrogen atom is concentrated in a relatively small region and is more readily donated to a proton. In PH_3 , the lone pair on the larger phosphorus atom is more diffuse and less available for bond formation. Thus ammonia accepts a proton more readily and is a stronger base than phosphine.

Step 2: Account for sulphur vapour At high temperature, sulphur vapour contains diatomic S_2 molecules. Like O_2 , an S_2 molecule has two unpaired electrons in its degenerate antibonding π^* molecular orbitals. These unpaired electrons cause attraction towards an applied magnetic field and hence paramagnetic behaviour. The explanation concerns the diatomic species in the vapour, rather than the usual cyclic S_8 molecules of solid sulphur.

Step 3: Conclusion (i) The nitrogen lone pair is more readily donated, so NH_3 is more basic than PH_3 . (ii) S_2 in sulphur vapour has two unpaired electrons and is paramagnetic.

Quick Tip to Solve: For basicity compare lone-pair availability; for sulphur vapour first identify S_2 , then count its unpaired electrons.

17. Draw the structures of the following molecules:

(i) SF_4

(ii) XeF_4

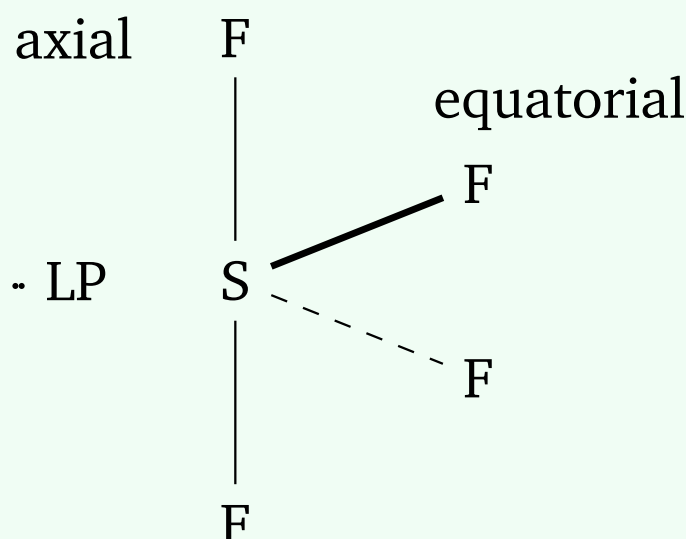
[2 marks]

Solution:

Concept:

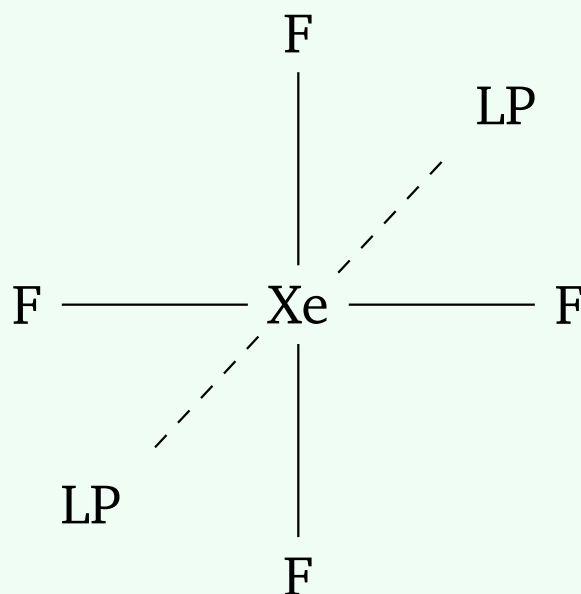
- VSEPR theory determines shape from the number of bonding pairs and lone pairs around the central atom. Lone pairs occupy more space and repel bonding pairs more strongly.
- SF_4 has five electron domains (four bonds and one lone pair); XeF_4 has six (four bonds and two lone pairs).

Step 1: Draw the see-saw structure of sulphur tetrafluoride Sulphur has six valence electrons. Four S–F bonds leave one lone pair on sulphur, giving AX_4E . The five electron pairs have a trigonal-bipyramidal arrangement. The lone pair takes an equatorial position, where it experiences fewer close interactions than at an axial position. Two fluorine atoms are axial and two are equatorial, giving a see-saw molecular shape; the textbook hybridisation is sp^3d .



See-saw structure of SF_4 ; LP denotes the equatorial lone pair.

Step 2: Draw the square-planar structure of xenon tetrafluoride Xenon has eight valence electrons. Four Xe–F bonds leave two lone pairs, giving AX_4E_2 . The six electron pairs have an octahedral arrangement, with the two lone pairs occupying opposite positions to minimise repulsion. The four fluorine atoms therefore lie at the corners of a square with xenon at its centre. Adjacent F–Xe–F angles are 90° , and opposite bonds make 180° ; the textbook hybridisation is sp^3d^2 .



Square-planar XeF_4 ; the opposite lone pairs lie above and below the molecular plane.

Step 3: Conclusion SF_4 is see-saw shaped with one equatorial lone pair; XeF_4 is square planar with two mutually opposite lone pairs.

Quick Tip to Solve: Count lone pairs before naming the shape: five domains with one lone pair gives see-saw; six with two opposite lone pairs gives square planar.

18. What are biodegradable and non-biodegradable detergents? Give one example of each class.

[2 marks]

Solution:

Concept:

- Biodegradation is the breakdown of a substance by microorganisms into simpler products. The structure of the hydrocarbon chain influences whether a detergent is readily degraded.
- Detergents with straight hydrocarbon chains are generally biodegradable; extensive branching hinders microbial attack and makes a detergent non-biodegradable.

Step 1: Biodegradable detergents Biodegradable detergents are detergents that can be decomposed by bacteria and other microorganisms. Their straight hydrocarbon chains can be attacked and broken down by microbial enzymes, so they do not persist for long in the environment. An example is sodium lauryl sulphate (sodium dodecyl sulphate), $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$.

Step 2: Non-biodegradable detergents Non-biodegradable detergents resist decomposition by microorganisms. Highly branched hydrocarbon chains hinder the action of microbial enzymes, so these detergents can remain in water and cause persistent foaming and pollution. An example is sodium branched-chain dodecylbenzene sulphonate, an alkylbenzene sulphonate with a highly branched alkyl group.

Step 3: Conclusion Thus sodium lauryl sulphate is biodegradable, whereas branched-chain dodecylbenzene sulphonate is non-biodegradable.

Quick Tip to Solve: Check the alkyl chain: straight chains are readily degraded, whereas extensive branching obstructs microbial breakdown.

19. What is a semiconductor? Describe the two main types of semiconductors and explain mechanisms for their conduction. [3 marks]

Solution:

Concept:

- A semiconductor has electrical conductivity intermediate between that of a conductor and an insulator. Its small energy gap permits some electrons to reach the conduction band, and its conductivity increases with temperature.
- Doping silicon or germanium with a small amount of a suitable impurity gives an extrinsic semiconductor. The two main doped types are n-type and p-type, distinguished by their majority charge carriers.

Step 1: Define a semiconductor A semiconductor is a solid whose electrical conductivity lies between that of conductors and insulators; silicon and germanium are examples. In the pure (intrinsic) crystal, each atom forms four covalent bonds. Thermal excitation can free a valence electron, leaving an electron vacancy or hole. Both the mobile electron and the hole contribute to intrinsic conduction.

Step 2: n-type semiconductor: electron conduction When silicon or germanium is doped with a pentavalent impurity such as phosphorus or arsenic, four of the five valence electrons of the impurity form covalent bonds with neighbouring atoms. The fifth electron is only weakly bound and becomes mobile readily. Under an applied electric field these electrons drift towards the positive terminal and carry current. Electrons are the majority carriers and holes are minority carriers; hence the name n-type. The doped crystal as a whole remains electrically neutral.

Step 3: p-type semiconductor: hole conduction Doping silicon or germanium with a trivalent impurity such as boron, aluminium or gallium leaves one of the four neighbouring covalent bonds deficient in an electron. This vacancy is called a hole. An electron from a neighbouring bond can fill the hole, leaving a new hole behind; successive electron transfers make the hole move through the crystal. In an electric field holes move towards the negative terminal. Holes are the majority carriers and electrons are minority carriers, so this is p-type conduction. The crystal remains electrically neutral.

Step 4: Conclusion The two main extrinsic semiconductors are n-type (pentavalent doping; conduction mainly by electrons) and p-type (trivalent doping; conduction mainly by holes).

Quick Tip to Solve: Compare the dopant valency with four: five supplies an extra electron, while three leaves an electron-deficient bond or hole.

20. Calculate the temperature at which a solution containing 54 g of glucose, ($C_6H_{12}O_6$), in 250 g of water will freeze.

(K_f for water = $1.86\text{ K mol}^{-1}\text{ kg}$)

[3 marks]

Solution:

Concept:

- For a dilute solution, the depression in freezing point is $\Delta T_f = iK_fm$, where i is the van t Hoff factor, K_f is the cryoscopic constant and m is molality in moles of solute per kilogram of solvent.
- Glucose is a non-electrolyte and does not dissociate in water, so $i = 1$. Dissolved glucose lowers the freezing point below that of pure water.

Step 1: Calculate the amount of glucose The molar mass of glucose is

$$M(C_6H_{12}O_6) = 6(12) + 12(1) + 6(16) = 180\text{ g mol}^{-1}.$$

Therefore the amount of glucose dissolved is

$$n = \frac{54\text{ g}}{180\text{ g mol}^{-1}} = 0.300\text{ mol}.$$

Glucose remains molecular in this solution; no extra solute particles arise from dissociation.

Step 2: Find the molality and freezing point depression The mass of the solvent, water, is $250\text{ g} = 0.250\text{ kg}$. Molality uses the mass of solvent, not the mass of the complete solution:

$$m = \frac{0.300\text{ mol}}{0.250\text{ kg}} = 1.20\text{ mol kg}^{-1}.$$

Substituting the given cryoscopic constant,

$$\Delta T_f = (1)(1.86\text{ K kg mol}^{-1})(1.20\text{ mol kg}^{-1}) = 2.232\text{ K}.$$

The units of molality cancel those in K_f , leaving a temperature difference in kelvin.

Step 3: Obtain the temperature at which freezing begins Pure water freezes at 0°C , or 273.15 K . A depression of 2.232 K is also a temperature difference of 2.232°C . Therefore

$$T_f = 0 - 2.232 = -2.232^\circ\text{C}.$$

Equivalently, the freezing temperature is $273.15 - 2.232 = 270.918\text{ K}$. The negative Celsius value is consistent with the lowering of freezing point caused by a dissolved nonvolatile solute.

Step 4: Conclusion The solution will freeze at approximately -2.23°C (270.92 K).

Quick Tip to Solve: Convert the water mass to kilograms before calculating molality, then subtract the depression from the freezing point of pure water.

21. What are lyophilic and lyophobic sols? Give one example of each type. Which one of these two types of sols is easily coagulated and why? [3 marks]

Solution:

Concept:

- A sol is a colloidal dispersion of a solid in a liquid. Its stability depends on the affinity between the dispersed particles and the dispersion medium.
- Coagulation is the aggregation of colloidal particles into larger particles that separate out; removing their stabilising charge promotes this process.

Step 1: Define lyophilic sols and give an example Lyophilic means solvent-loving. In these sols the dispersed substance has a strong affinity for the dispersion medium, and its particles are extensively solvated. They are readily formed by mixing the substance with a suitable solvent and are generally reversible. Starch dispersed in water is an example of a lyophilic sol; gelatin in water is another.

Step 2: Define lyophobic sols and give an example Lyophobic means solvent-hating. In these sols the dispersed substance has little affinity for the dispersion medium, so the particles are not appreciably solvated. Special methods are needed to prepare them, and they are generally irreversible. A gold sol in water is an example; an arsenic sulphide sol is another.

Step 3: Compare ease of coagulation A lyophobic sol is easily coagulated by adding a small amount of a suitable electrolyte. Its particles are stabilised mainly by their electric charge. Oppositely charged ions from the electrolyte neutralise that charge, reduce interparticle repulsion and allow the particles to aggregate. Lyophilic particles possess a protective solvation layer in addition to charge and hence resist coagulation much more strongly.

Step 4: Conclusion Lyophilic sols have strong solvent affinity (for example, starch in water); lyophobic sols have little solvent affinity (for example, gold in water). Lyophobic sols coagulate more readily because their stabilisation is chiefly electrostatic.

Quick Tip to Solve: For the coagulation comparison, identify both protections: charge and a solvent layer in lyophilic sols, chiefly charge in lyophobic sols.

22. State briefly the principles which serve as basis for the following operations in metallurgy:

(i) Froth floatation process

(ii) Zone refining

(iii) Refining by liquation

[3 marks]

Solution:

Concept:

- Metallurgical separation exploits differences in physical or chemical properties of the metal, its ore and accompanying impurities.
- Froth floatation uses selective wetting, zone refining uses unequal impurity solubility, and liquation uses a difference in melting points.

Step 1: (i) Froth floatation: selective wetting The principle is the difference in the wetting properties

of sulphide ore and gangue. Sulphide ore particles are preferentially wetted by oil, whereas gangue is wetted by water. When air is blown through the agitated mixture, the oil-wetted ore particles attach to air bubbles and rise as froth; the water-wetted gangue remains in the water and settles. Skimming the froth therefore concentrates the sulphide ore.

Step 2: (ii) Zone refining: unequal solubility of impurities The principle is that impurities are more soluble in the molten metal than in the solid metal. A narrow molten zone is produced in a metal rod and moved slowly along it. As the metal behind the moving heater solidifies, it rejects impurities into the liquid zone. Repeated passes carry the impurities towards one end, which is then removed. The remaining portion is highly pure metal, as required for semiconductor materials such as silicon.

Step 3: (iii) Liquefaction: different melting points The principle is that a low-melting metal can be separated from higher-melting impurities by controlled heating. The impure metal is heated on a sloping hearth just above its own melting point but below that of the impurities. The metal melts and flows down the slope into a receiver, while the unmelted impurities remain behind. This method is suitable, for example, for refining tin when the impurities have substantially higher melting points.

Step 4: Conclusion The respective principles are selective wetting of ore and gangue, greater solubility of impurities in molten metal, and separation of a low-melting metal from high-melting impurities.

Quick Tip to Solve: Link each operation to its separating property first: wetting for froth, solubility for a moving molten zone, and melting point for liquefaction.

23(a). Write chemical equations for the following processes:

(i) Chlorine reacts with a hot concentrated solution of sodium hydroxide

(ii) Orthophosphorous acid is heated

(iii) PtF_6 and xenon are mixed together

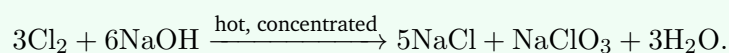
[3 marks]

Solution:

Concept:

- Disproportionation occurs when the same element is oxidised and reduced in a single reaction; oxidation numbers help identify the correct products.
- Equations must conserve every atom and, for ionic species, the total electric charge. Reaction conditions distinguish chlorate formation from hypochlorite formation.

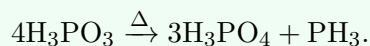
Step 1: (i) Chlorine with hot concentrated sodium hydroxide Hot concentrated alkali converts chlorine into chloride and chlorate. The balanced equation is



Chlorine disproportionates from oxidation state zero to -1 in chloride and $+5$ in chlorate. Five chlorine atoms are reduced for each one oxidised, giving the displayed coefficient ratio. Cold dilute alkali would instead produce hypochlorite.

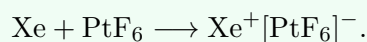
Step 2: (ii) Heating orthophosphorous acid Orthophosphorous acid, H_3PO_3 , disproportionates on

heating:



Phosphorus changes from +3 to +5 in phosphoric acid and to -3 in phosphine. Three phosphorus atoms each lose two electrons, balancing the six electrons gained by the phosphorus atom forming phosphine. Hydrogen and oxygen are also balanced.

Step 3: (iii) Mixing xenon and platinum hexafluoride Xenon reacts with the powerful oxidising agent platinum hexafluoride to form xenon hexafluoroplatinate, conventionally represented in the school-level equation as



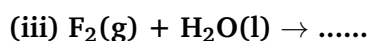
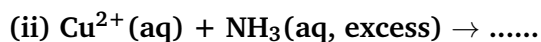
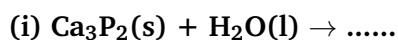
This expresses oxidation of xenon and reduction of the platinum fluoride reagent. There is one xenon atom, one platinum atom and six fluorine atoms on each side, and the product is electrically neutral overall.

Step 4: Conclusion The products are NaCl, NaClO₃ and water in (i); H₃PO₄ and PH₃ in (ii); and xenon hexafluoroplatinate, Xe⁺[PtF₆]⁻, in (iii), with coefficients as balanced above.

Quick Tip to Solve: For the first two equations, balance oxidation and reduction within the same element before checking hydrogen and oxygen atoms.

OR

23(b). Complete the following chemical equations:



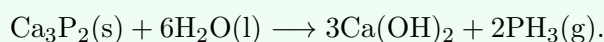
[3 marks]

Solution:

Concept:

- Calcium phosphide undergoes hydrolysis: water supplies hydrogen to phosphide, producing phosphine, and hydroxide to calcium.
- Ammonia is a Lewis base and coordinates to copper(II) through its nitrogen lone pair. Excess ammonia favours the soluble deep-blue ammine complex.
- Fluorine is a powerful oxidising agent: it is reduced to fluoride while water is oxidised to oxygen.

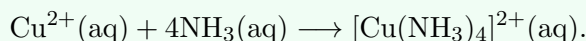
Step 1: (i) Hydrolysis of calcium phosphide The products are calcium hydroxide and phosphine. Balance calcium and phosphorus first, then supply six water molecules to balance hydrogen and oxygen:



There are three calcium atoms, two phosphorus atoms, twelve hydrogen atoms and six oxygen atoms on each side.

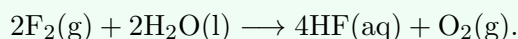
Step 2: (ii) Reaction with excess ammonia Four ammonia molecules coordinate to each copper(II)

ion. Since ammonia is neutral, the charge of the complex remains +2:



This conventional equation represents the deep-blue tetraamminecopper(II) complex in aqueous solution; water ligands are omitted. The word excess matters because a small amount of ammonia can first produce a hydroxide precipitate, which dissolves in excess ammonia.

Step 3: (iii) Oxidation of water by fluorine Fluorine forms hydrogen fluoride and oxygen is liberated:



Four fluorine atoms each gain one electron, while the two oxygen atoms together lose four electrons. Both atom balance and electron balance therefore agree.

Step 4: Conclusion The missing products are (i) $3\text{Ca}(\text{OH})_2 + 2\text{PH}_3$, (ii) $[\text{Cu}(\text{NH}_3)_4]^{2+}$, and (iii) $4\text{HF} + \text{O}_2$, with the balanced coefficients shown above.

Quick Tip to Solve: For the excess-ammonia reaction, retain the copper charge: neutral ammonia ligands cannot change it.

24. (a) What is a ligand? Give an example of a bidentate ligand.

(b) Explain as to how the two complexes of nickel, $[\text{Ni}(\text{CN})_4]^{2-}$ and $\text{Ni}(\text{CO})_4$, have different structures but do not differ in their magnetic behaviour. (Ni = 28) [3 marks]

Solution:

Concept:

- A ligand is an ion or molecule that donates one or more lone pairs to a central metal atom or ion to form coordinate bonds.
- Denticity is the number of donor atoms of a ligand that bind to the same metal centre. Geometry depends on the orbitals used, while magnetism depends on unpaired electrons.

Step 1: (a) Ligand and bidentate example A ligand acts as a Lewis base towards the central metal atom or ion. Ethane-1,2-diamine (ethylenediamine), $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, is a bidentate ligand: both nitrogen atoms donate lone pairs to the same metal centre, forming two coordinate bonds.

Step 2: (b) Analyse the cyanide complex Nickel has atomic number 28 and ground-state configuration $[\text{Ar}]3d^84s^2$. In $[\text{Ni}(\text{CN})_4]^{2-}$, the oxidation state of nickel is +2, because $x + 4(-1) = -2$. Thus Ni^{2+} is $3d^8$. Cyanide is a strong-field ligand and pairs the eight $3d$ electrons in four orbitals, leaving one $3d$ orbital vacant. One $3d$, one $4s$ and two $4p$ orbitals undergo dsp^2 hybridisation. The complex is square planar, and all its electrons are paired.

Step 3: (b) Analyse the carbonyl complex and compare Carbon monoxide is neutral, so nickel is in oxidation state zero in $\text{Ni}(\text{CO})_4$. In forming the complex, its valence electrons become paired in a filled $3d^{10}$ subshell. The empty $4s$ and three $4p$ orbitals undergo sp^3 hybridisation, producing a tetrahedral complex. There are no unpaired electrons here either. Consequently both complexes are diamagnetic even though their geometries and hybridisations differ.

Step 4: Conclusion An example of a bidentate ligand is ethane-1,2-diamine. $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar (dsp^2); $\text{Ni}(\text{CO})_4$ is tetrahedral (sp^3). Both are diamagnetic because all electrons are paired.

Quick Tip to Solve: Find the nickel oxidation state before its d-electron count: cyanide is anionic, whereas CO is neutral.

25. Name the reagents which are used in the following conversions:

(i) A primary alcohol to an aldehyde

(ii) Butan-2-one to butan-2-ol

(iii) Phenol to 2, 4, 6-tribromophenol

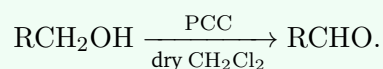
[3 marks]

Solution:

Concept:

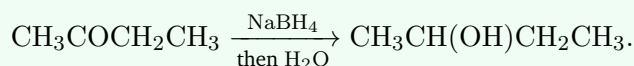
- A primary alcohol gives an aldehyde by controlled oxidation. The reagent and conditions must prevent further oxidation of the aldehyde to a carboxylic acid.
- A ketone is reduced to a secondary alcohol by a hydride reducing agent. The hydroxyl group of phenol strongly activates the ring towards electrophilic substitution at the ortho and para positions.

Step 1: (i) Primary alcohol to aldehyde Use pyridinium chlorochromate (PCC) in dry dichloromethane, CH_2Cl_2 :



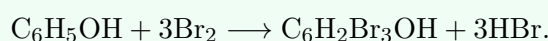
PCC is a mild oxidising reagent. Under these anhydrous conditions it stops the oxidation at the aldehyde stage. Strong aqueous oxidants under prolonged heating would tend to carry oxidation further to the carboxylic acid.

Step 2: (ii) Butan-2-one to butan-2-ol Use sodium borohydride, NaBH_4 , followed by aqueous work-up:



Hydride adds to the carbonyl carbon; protonation of the oxygen then gives the secondary alcohol. The carbon skeleton remains unchanged. Lithium aluminium hydride followed by hydrolysis is another suitable reducing reagent.

Step 3: (iii) Phenol to 2,4,6-tribromophenol Use bromine water, $\text{Br}_2(\text{aq})$, at room temperature:



The hydroxyl group activates both ortho positions and the para position, so bromination occurs at positions 2, 4 and 6 without a Lewis-acid catalyst. A white precipitate of 2,4,6-tribromophenol forms. The aqueous medium is specified because bromination under other conditions can be controlled to give monobromination.

Step 4: Conclusion The required reagents are (i) PCC in dry CH_2Cl_2 , (ii) NaBH_4 followed by aqueous work-up, and (iii) bromine water at room temperature.

Quick Tip to Solve: Choose a mild anhydrous oxidant for the aldehyde; use aqueous bromine for all three substitutions on phenol.

26. Account for the following observations:

(i) pK_b for aniline is more than that for methylamine.

(ii) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.

(iii) Aniline does not undergo Friedel-Crafts reaction.

[3 marks]

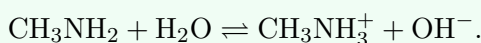
Solution:

Concept:

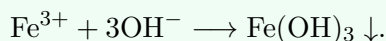
- Basicity depends on the availability of the nitrogen lone pair for protonation. Since $pK_b = -\log K_b$, a weaker base has a larger pK_b .
- Aqueous amines establish a base equilibrium with water, producing hydroxide ions. Lewis acids such as $AlCl_3$ accept the nitrogen lone pair.

Step 1: (i) Compare aniline and methylamine In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance. It is therefore less available to accept a proton. In methylamine, the methyl group exerts a positive inductive effect and increases the electron density on nitrogen; its lone pair is not delocalised into an aromatic ring. Consequently methylamine is the stronger base: $K_b(\text{aniline}) < K_b(\text{methylamine})$. Taking the negative logarithm reverses this order, giving a larger pK_b for aniline.

Step 2: (ii) Explain ferric hydroxide precipitation Methylamine accepts a proton from water and supplies hydroxide ions:



Ferric chloride supplies Fe^{3+} ions. Their reaction with the hydroxide ions produces insoluble, reddish-brown ferric hydroxide:



Thus precipitation results from the basic nature of aqueous methylamine.

Step 3: (iii) Explain failure of the Friedel-Crafts reaction Aniline coordinates through its nitrogen lone pair to the Lewis-acid catalyst $AlCl_3$, forming a salt-like complex, represented as $C_6H_5NH_2 \rightarrow AlCl_3$. This ties up the lone pair and strongly deactivates the benzene ring towards electrophilic substitution. The catalyst is also bound by the amino group, so the usual Friedel-Crafts alkylation or acylation does not proceed.

Step 4: Conclusion Aniline has the larger pK_b because resonance reduces its basicity; methylamine supplies OH^- to precipitate $Fe(OH)_3$; and aniline binds the Friedel-Crafts catalyst, deactivating its ring.

Quick Tip to Solve: First ask whether the nitrogen lone pair is free, delocalised, or bound to a Lewis acid; this explains all three observations.

27. Write the names and structures of the monomers of the following polymers:

(i) Buna-S

(ii) Neoprene

(iii) Nylon-6

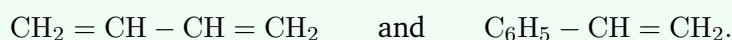
[3 marks]

Solution:

Concept:

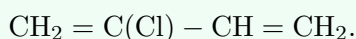
- Monomers are the small molecules from which a polymer is prepared. A copolymer requires two different monomer species; a homopolymer requires one.
- Addition polymerisation uses carbon-carbon double bonds, whereas ring-opening polymerisation of a lactam forms the amide-linked chain of nylon-6.

Step 1: (i) Monomers of Buna-S Buna-S is a copolymer of buta-1,3-diene and styrene (phenylethene). Their condensed structural formulae are, respectively,



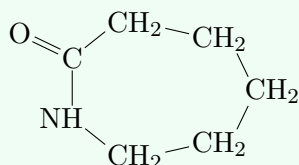
Both monomers contain carbon-carbon double bonds that participate in addition polymerisation. The S in Buna-S identifies styrene, distinguishing this rubber from Buna-N, which contains acrylonitrile instead.

Step 2: (ii) Monomer of neoprene Neoprene is made from chloroprene, whose systematic name is 2-chlorobuta-1,3-diene. Its structure is



The chlorine is attached to carbon 2 of the conjugated diene, not substituted for a carbon atom in the chain. Addition polymerisation of this monomer gives polychloroprene, commonly called neoprene.

Step 3: (iii) Monomer of nylon-6 The monomer is ϵ -caprolactam, a seven-membered cyclic amide. Its closed-ring structural formula is



The ring contains five methylene groups, one carbonyl carbon and one nitrogen atom. Ring opening produces the polyamide repeating unit $[-\text{NH} - (\text{CH}_2)_5 - \text{CO}-]_n$. Thus the numeral 6 counts the six carbon atoms supplied by each caprolactam molecule; nylon-6 is distinct from nylon-6,6, which uses a diamine and a dicarboxylic acid.

Step 4: Conclusion Buna-S: buta-1,3-diene and styrene; neoprene: chloroprene; nylon-6: ϵ -caprolactam. Their structures are given in the respective steps above.

Quick Tip to Solve: Remember S for styrene, chlorine for neoprene, and the six-carbon cyclic lactam for nylon-6.

28(a). Conductivity of 0.00241 M acetic acid solution is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity in this solution. If Λ_m^0 for acetic acid be $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, what would be its dissociation constant? [5 marks]

Solution:

Concept:

- Molar conductivity is the conductance associated with one mole of electrolyte. When conductivity κ is in S cm^{-1} and concentration c in mol L^{-1} , $\Lambda_m = 1000\kappa/c$, in $\text{S cm}^2 \text{ mol}^{-1}$.
- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^0$. At infinite dilution, dissociation is effectively complete, so Λ_m^0 provides the reference conductivity.
- For a monobasic weak acid HA, the equilibrium concentrations give $K_a = c\alpha^2/(1 - \alpha)$. Both ions have concentration $c\alpha$, while undissociated acid has concentration $c(1 - \alpha)$.

Step 1: Calculate molar conductivity The given concentration is $c = 0.00241 \text{ mol L}^{-1}$, and the conductivity is $\kappa = 7.896 \times 10^{-5} \text{ S cm}^{-1}$. Thus

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

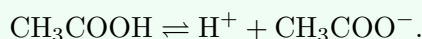
The factor 1000 converts the litre-based molar concentration to the cubic-centimetre volume convention used with conductivity. It must be included before comparing with the limiting molar conductivity.

Step 2: Find the degree of dissociation Using $\Lambda_m^0 = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{32.7635}{390.5} = 0.0839014.$$

Therefore approximately 8.39% of the acetic acid is dissociated in this solution. The small value is consistent with acetic acid being a weak electrolyte; nevertheless, we retain $1 - \alpha$ in the equilibrium expression for accuracy.

Step 3: Apply the acid dissociation equilibrium The equilibrium is



Starting with concentration c , the equilibrium concentrations of hydrogen ions and acetate ions are each $c\alpha$, and that of acetic acid is $c(1 - \alpha)$. Hence

$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \\ &= \frac{c\alpha^2}{1 - \alpha} \\ &= \frac{0.00241(0.0839014)^2}{1 - 0.0839014} \\ &= 1.85188 \times 10^{-5} \text{ mol L}^{-1}. \end{aligned}$$

This concentration-form equilibrium constant uses the usual dilute-solution approximation relating activities to concentrations.

Step 4: Conclusion The molar conductivity is $32.8 \text{ S cm}^2 \text{ mol}^{-1}$, and the dissociation constant is $K_a = 1.85 \times 10^{-5} \text{ mol L}^{-1}$.

Quick Tip to Solve: First use the factor 1000 in molar conductivity, then divide by limiting conductivity; keep the denominator $1 - \alpha$ when calculating K_a .

OR

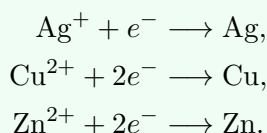
28(b). Three electrolytic cells A, B and C containing solutions of zinc sulphate, silver nitrate and copper sulphate, respectively are connected in series. A steady current of 1.5 ampere was passed through them until 1.45 g of silver were deposited at the cathode of cell B. How long did the current flow? What mass of copper and what mass of zinc were deposited in the concerned cells? (Atomic masses of Ag = 108, Zn = 65.4, Cu = 63.5) [5 marks]

Solution:

Concept:

- Faraday's first law gives $m = MQ/(nF)$, where m is deposited mass, M is molar mass, $Q = It$ is charge, n is the number of electrons needed per metal ion, and $F = 96500 \text{ C mol}^{-1}$.
- Cells connected in series carry the same current for the same time. Therefore the same quantity of electricity passes through every cell, and deposited masses are proportional to their equivalent masses M/n .

Step 1: Identify the cathode reactions The metal ions are reduced at the cathodes according to



Thus silver requires one mole of electrons per mole deposited, whereas both copper and zinc require two. Their equivalent masses are consequently 108, $63.5/2 = 31.75$, and $65.4/2 = 32.7$, respectively.

Step 2: Calculate the charge and the duration Since 1.45 g of silver is deposited, the amount of silver, and hence the amount of electrons passed, is $1.45/108 \text{ mol}$. The charge through cell B is

$$Q = \frac{mnF}{M} = \frac{1.45 \times 1 \times 96500}{108} = 1295.60 \text{ C}.$$

With steady current $I = 1.5 \text{ A} = 1.5 \text{ C s}^{-1}$, the duration is

$$t = \frac{Q}{I} = \frac{1295.60}{1.5} = 863.73 \text{ s} = 14.40 \text{ min}.$$

Step 3: Calculate the copper deposited in cell C The charge in cell C equals that in cell B because the

cells are in series. Applying Faraday's second law to copper and silver gives

$$\frac{m_{\text{Cu}}}{m_{\text{Ag}}} = \frac{M_{\text{Cu}}/2}{M_{\text{Ag}}/1}.$$

Substituting the given atomic masses,

$$m_{\text{Cu}} = 1.45 \times \frac{63.5}{2 \times 108} = 0.42627 \text{ g}.$$

The factor two in the denominator accounts for the two electrons required by each copper ion.

Step 4: Calculate the zinc deposited in cell A For zinc, the same charge reduces $Q/(2F)$ moles of ions. Thus

$$m_{\text{Zn}} = 1.45 \times \frac{65.4}{2 \times 108} = 0.43903 \text{ g}.$$

Both divalent metals receive equal amounts in moles. Zinc has a slightly higher molar mass than copper, so its deposited mass is correspondingly slightly greater, consistent with these calculations.

Step 5: Conclusion The current flows for approximately 864 s (14.4 min) . The masses deposited are $0.426 \text{ g of copper}$ in cell C and 0.439 g of zinc in cell A.

Quick Tip to Solve: In a series combination, first use the silver deposit to find the common charge; compare equivalent masses M/n to obtain the other deposits directly.

29. Assign reasons for the following:

- (i) The enthalpies of atomisation of transition elements are high.
- (ii) The transition metals and many of their compounds act as good catalyst.
- (iii) From element to element the actinoid contraction is greater than the lanthanoid contraction.
- (iv) The E° value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$.
- (v) Scandium ($Z = 21$) does not exhibit variable oxidation states and yet it is regarded as a transition element.

[5 marks]

Solution:

Concept:

- Transition-metal properties depend on the availability of valence d and s electrons for bonding and on the relative stability of different d-electron configurations.
- Reduction potentials measure the tendency to gain electrons. Half-filled subshells and crystal-field stabilisation influence the relative stability of ions.
- Across an f-block series, incomplete shielding of the increasing nuclear charge causes a progressive decrease in atomic and ionic radii.

Step 1: (i) High enthalpies of atomisation Transition metals form strong metallic bonds because both the outer s electrons and the available d electrons participate in bonding. Their numerous valence electrons, especially unpaired d electrons, strengthen the attraction between metal centres and the delocalised electrons. Consequently considerable energy is needed to separate the solid into individual

gaseous atoms, so their enthalpies of atomisation are generally high.

Step 2: (ii) Catalytic activity Their variable oxidation states allow transition metals and their compounds to form intermediate compounds and transfer electrons during a reaction, returning to their original state at the end of the catalytic cycle. Metal surfaces also adsorb reactants through available orbitals, bringing them together and weakening their bonds. These effects provide an alternative reaction pathway with lower activation energy; the catalyst changes the rate without being consumed overall.

Step 3: (iii) Greater actinoid contraction From one actinoid to the next, added electrons enter the 5f subshell while nuclear charge increases. The 5f electrons shield one another less effectively than the 4f electrons in the lanthanoid series. Hence the increase in effective nuclear attraction is greater across the actinoids, producing a greater progressive contraction of their radii.

Step 4: (iv) Compare the reduction potentials The relevant reductions are $\text{Mn}^{3+} + \text{e}^- \rightarrow \text{Mn}^{2+}$ and $\text{Cr}^{3+} + \text{e}^- \rightarrow \text{Cr}^{2+}$. The first converts $3d^4$ into the especially stable half-filled $3d^5$ configuration of Mn^{2+} , so it is strongly favoured. The second converts the stable $3d^3$ ion Cr^{3+} into $3d^4$ Cr^{2+} . In an octahedral aqueous complex, the d^3 configuration has three singly occupied lower-energy t_{2g} orbitals and appreciable stabilisation. Reduction of chromium(III) is therefore much less favourable, explaining the more positive manganese reduction potential.

Step 5: (v) Scandium as a transition element A transition element has an incompletely filled d subshell in its atom or in at least one of its ions. Scandium has ground-state configuration $[\text{Ar}]3d^1 4s^2$; its atom therefore satisfies this definition. Its usual oxidation state is +3, producing the stable $[\text{Ar}]$ configuration. Lack of common variable oxidation states does not remove scandium from the transition elements, because its neutral atom already has a partially filled d subshell.

Step 6: Conclusion Strong metallic bonding, variable oxidation states and adsorption, poor 5f shielding, the relative stability of Mn^{2+} and Cr^{3+} , and scandium's $3d^1$ atomic configuration respectively explain the five observations.

Quick Tip to Solve: For a reduction-potential comparison, write both d-electron configurations before deciding which direction gains stability.

OR

29(a). What may be the possible oxidation states of the transition metals with the following d electronic configurations in the ground state of their atoms:

$3d^3 4s^2$, $3d^5 4s^2$ and $3d^6 4s^2$. Indicate relative stability of oxidation states in each case.

[3 marks]

Solution:

Concept:

- Transition metals can use both the outer 4s and inner 3d electrons in bonding because their energies are comparable. The 4s electrons are removed first when forming cations.
- Empty d^0 , half-filled d^5 , and, in suitable environments, d^3 configurations confer additional stability. Relative stability also depends on the ligand and the medium.

Step 1: Examine $3d^34s^2$: vanadium Vanadium commonly exhibits +2, +3, +4 and +5 oxidation states, corresponding formally to d^3 , d^2 , d^1 and d^0 , respectively. All five valence electrons can participate in bonding, accounting for the maximum state +5. The +5 state is particularly stable in oxides and oxoanions because of strong metal-oxygen bonds and the d^0 configuration. The lower states are accessible; for example, aqueous V^{2+} is a reducing agent and is readily oxidised.

Step 2: Examine $3d^54s^2$: manganese Manganese exhibits +2, +3, +4, +5, +6 and +7, although +5 is uncommon. Removal of the two 4s electrons gives Mn^{2+} , with the especially stable half-filled $3d^5$ configuration. Thus +2 is particularly stable for the simple aqueous ion, whereas Mn^{3+} , a d^4 ion, tends to gain an electron to form Mn^{2+} . Higher states are stabilised by oxygen: +4 occurs in MnO_2 , +6 in manganate and +7 in permanganate. The maximum +7 state uses all seven valence electrons, but permanganate is a strong oxidising agent, so a high oxidation state must not be confused with resistance to reduction.

Step 3: Examine $3d^64s^2$: iron The common oxidation states of iron are +2 and +3. Loss of the two 4s electrons gives Fe^{2+} , with configuration $3d^6$; loss of one further electron gives Fe^{3+} , with the stable half-filled $3d^5$ configuration. The +3 state is consequently especially favoured under oxidising conditions, while +2 is stable under reducing conditions. Iron also attains +6 in ferrate, FeO_4^{2-} , but this is an uncommon, strongly oxidising state rather than a common simple-ion state.

Step 4: Conclusion The principal states are V: +2, +3, +4, +5, with +5 stabilised in oxo compounds; Mn: +2 to +7, with half-filled d^5 making +2 especially stable; and Fe: mainly +2, +3, with half-filled d^5 favouring +3. The chemical environment determines the detailed relative stability.

Quick Tip to Solve: Remove the two 4s electrons first, then count the remaining d electrons; look especially for d-zero and half-filled d-five configurations.

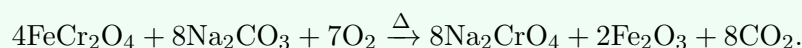
29(b). Write steps involved in the preparation of (i) Na_2CrO_4 from chromite ore and (ii) K_2MnO_4 from pyrolusite ore. [2 marks]

Solution:

Concept:

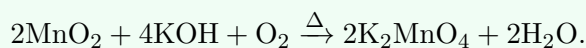
- Oxidative roasting in an alkaline medium converts chromium(III) in chromite into soluble chromate, containing chromium(VI).
- Fusion of manganese(IV) oxide with potassium hydroxide in air oxidises manganese to the +6 state in potassium manganate.

Step 1: (i) Sodium chromate from chromite ore Finely powdered chromite ore, $FeCr_2O_4$, is roasted with sodium carbonate in an excess of air. The balanced reaction is



The roasted mass is extracted with water. Sodium chromate dissolves, giving a yellow solution, whereas insoluble iron(III) oxide is removed by filtration. The filtrate is concentrated to obtain sodium chromate.

Step 2: (ii) Potassium manganate from pyrolusite ore Pyrolusite, MnO_2 , is fused with potassium hydroxide in the presence of air or another suitable oxidising agent. With oxygen the reaction is

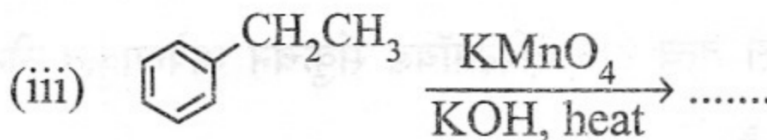
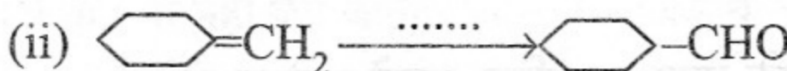
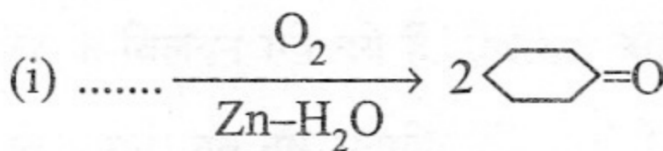


The green fused product contains potassium manganate. Extraction with water gives its green solution; the alkaline conditions help preserve manganate rather than converting it into permanganate.

Step 3: Conclusion Chromite gives yellow Na_2CrO_4 by roasting with Na_2CO_3 in air; pyrolusite gives green K_2MnO_4 by fusion with KOH in air.

Quick Tip to Solve: Check the final colours: chromate is yellow and manganate is green; both preparations require oxidation in alkali.

30(a). Complete the following reaction statements by giving the missing starting material, reagent or product as required: [3 marks]



Solution:

Concept:

- Reductive ozonolysis cleaves an alkene double bond and converts each alkene carbon into a carbonyl carbon. Rejoining the carbonyl carbons reconstructs the starting alkene.
- Hydroboration-oxidation of an alkene gives the anti-Markovnikov alcohol; controlled oxidation of a primary alcohol then gives an aldehyde.
- Hot alkaline permanganate oxidises an alkylbenzene with a benzylic hydrogen to the benzoate salt. Acidification is needed to obtain free benzoic acid.

Step 1: (i) Reconstruct the missing alkene Each product is cyclohexanone. Remove the oxygen from each carbonyl carbon and join these two ring carbons by a double bond. The starting material is therefore cyclohexylidenecyclohexane: two cyclohexane rings linked directly by an exocyclic

C = C bond between their ring carbons. Reductive ozonolysis of this alkene gives two molecules of cyclohexanone. The printed arrow shows O_2 ; the carbonyl-cleavage reaction with a subsequent Zn/H_2O work-up requires ozone, O_3 , rather than ordinary oxygen. Thus the specified products identify the missing alkene through reductive ozonolysis.

Step 2: (ii) Convert methylenecyclohexane into the aldehyde Use the sequence (1) $BH_3 \cdot THF$, (2) H_2O_2/OH^- , and (3) PCC in dry CH_2Cl_2 . Hydroboration-oxidation places the hydroxyl group on the less substituted, terminal carbon of the exocyclic double bond, giving cyclohexylmethanol, $C_6H_{11}CH_2OH$. PCC then oxidises this primary alcohol to cyclohexanecarbaldehyde, $C_6H_{11}CHO$, without further oxidation to an acid. Direct ozonolysis would break the carbon skeleton and would not give this aldehyde.

Step 3: (iii) Oxidise the ethyl side chain Ethylbenzene has benzylic hydrogen atoms, so hot alkaline $KMnO_4$ oxidises its side chain to a carboxylate group attached directly to the benzene ring. The organic product under the stated KOH conditions is potassium benzoate, C_6H_5COOK . The carbon directly attached to the ring becomes the carboxylate carbon; the remaining side-chain carbon is oxidised further. On subsequent acidification, potassium benzoate gives benzoic acid, C_6H_5COOH , but acidification is not shown in the printed reaction.

Step 4: Conclusion (i) Cyclohexylidenecyclohexane; (ii) $BH_3 \cdot THF$, then H_2O_2/OH^- , then PCC; (iii) potassium benzoate, C_6H_5COOK (benzoic acid after acidification).

Quick Tip to Solve: Rejoin carbonyl carbons to reverse ozonolysis; check whether an oxidation medium gives the acid or its salt.

30(b). Describe the following reactions:

(i) Cannizzaro reaction

(ii) Cross aldol condensation

[2 marks]

Solution:

Concept:

- Cannizzaro reaction is the base-induced disproportionation of an aldehyde having no α hydrogen into an alcohol and a carboxylate salt.
- Cross aldol condensation involves two different carbonyl compounds; at least one must have an α hydrogen to form the enolate.

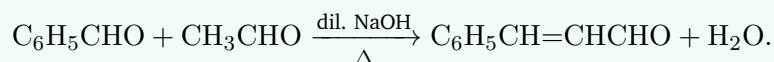
Step 1: (i) Cannizzaro reaction On treatment with concentrated alkali, an aldehyde without an α hydrogen undergoes self oxidation and reduction. One molecule forms a carboxylate salt and another forms an alcohol. For example, benzaldehyde reacts as follows:



Benzaldehyde has no α hydrogen, so it does not undergo ordinary self aldol condensation.

Step 2: (ii) Cross aldol condensation When two different aldehydes or ketones undergo aldol condensation together in dilute alkali, the process is called cross aldol condensation. The carbonyl

compound with an alpha hydrogen supplies the enolate; addition gives a beta-hydroxy carbonyl compound, which loses water on heating to form an alpha,beta-unsaturated carbonyl compound. For example, benzaldehyde and ethanal give cinnamaldehyde:



Here ethanal supplies the alpha hydrogen, while benzaldehyde acts as the other carbonyl reactant. If both reactants have alpha hydrogens, several self and cross condensation products can form.

Step 3: Conclusion Cannizzaro reaction gives an alcohol and a carboxylate salt from an aldehyde without alpha hydrogen; cross aldol condensation combines two different carbonyl compounds to form an unsaturated carbonyl compound after dehydration.

Quick Tip to Solve: Before choosing the named reaction, check for alpha hydrogens: Cannizzaro requires none, whereas aldol needs an enolate donor.

OR

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

- (i) Aldehydes are more reactive than ketones towards nucleophiles.
- (ii) The boiling points of aldehydes and ketones are lower than of the corresponding acids.
- (iii) The aldehydes and ketones undergo a number of addition reactions.

[3 marks]

Solution:

Concept:

- The carbonyl bond is polar: $\text{C}^{\delta+} = \text{O}^{\delta-}$. A nucleophile donates an electron pair to the electrophilic carbon atom.
- Alkyl groups reduce carbonyl electrophilicity by their electron-releasing inductive effect, while bulky groups hinder a nucleophile's approach. Intermolecular hydrogen bonding raises boiling points.

Step 1: (i) Compare aldehydes and ketones towards nucleophiles An aldehyde, RCHO , has one alkyl group and one small hydrogen atom attached to its carbonyl carbon; a ketone, RCOR' , has two alkyl groups. The two electron-releasing alkyl groups in the ketone reduce the positive character of the carbonyl carbon more than the single alkyl group in an aldehyde. Consequently, the ketone carbon is less susceptible to nucleophilic attack. Moreover, its two alkyl groups cause greater steric hindrance to the approaching nucleophile. Both the electronic and steric effects therefore make aldehydes more reactive. Methanal, which has no alkyl group, is especially reactive.

Step 2: (ii) Compare boiling points with carboxylic acids Carboxylic acid molecules contain both a hydrogen-bond donor, the $\text{O}-\text{H}$ group, and an acceptor, the carbonyl oxygen. They associate strongly through intermolecular hydrogen bonds, commonly forming cyclic dimers. More energy is needed to separate these associated molecules during boiling. Aldehydes and ketones lack an $\text{O}-\text{H}$ bond and cannot form such hydrogen bonds with one another; their intermolecular attractions are mainly dipole-dipole and dispersion forces. Thus their boiling points are lower than those of corresponding

carboxylic acids of comparable molecular mass. Their ability to accept hydrogen bonds from water does not imply self-association of this kind.

Step 3: (iii) Explain the tendency to undergo addition The polar carbonyl group provides an electrophilic carbon that attracts nucleophiles. Its relatively weak π bond can open as the nucleophile forms a new bond to carbon, transferring the π -electron pair to oxygen. Protonation of the resulting alkoxide gives an addition product:



Carbon changes from trigonal planar to tetrahedral coordination. Hence reagents such as hydrogen cyanide add across the carbonyl bond, without requiring loss of a substituent from the carbonyl carbon.

Step 4: Conclusion Aldehydes are more reactive because they have less electron donation and steric hindrance; carboxylic acids boil higher because of strong hydrogen-bonded association; the polar, readily opened carbonyl π bond enables addition reactions.

Quick Tip to Solve: For carbonyl reactivity compare both electronic and steric effects; for boiling points compare the intermolecular forces between molecules of the pure substance.

30(b). Give chemical tests to distinguish between:

(i) Acetaldehyde and benzaldehyde

(ii) Propanone and propanol

[2 marks]

Solution:

Concept:

- The iodoform test detects the CH_3CO- unit and ethanal. A positive test gives a yellow precipitate of iodoform, CHI_3 , with iodine and aqueous alkali.
- 2,4-Dinitrophenylhydrazine (2,4-DNP) gives a yellow or orange hydrazone precipitate with aldehydes and ketones; ordinary alcohols do not give this carbonyl test.

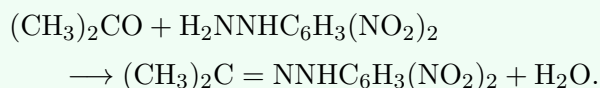
Step 1: (i) Acetaldehyde and benzaldehyde: iodoform test Warm separate samples with iodine and aqueous sodium hydroxide. Acetaldehyde (ethanal), CH_3CHO , gives a yellow precipitate of iodoform:



Benzaldehyde, C_6H_5CHO , does not give this yellow precipitate because it has no methyl group directly attached to its carbonyl carbon. Thus the yellow solid identifies acetaldehyde. Tollens' reagent would not distinguish this pair because both are aldehydes and reduce it.

Step 2: (ii) Propanone and propanol: 2,4-DNP test Add acidified 2,4-dinitrophenylhydrazine reagent to separate samples. Propanone gives a yellow to orange precipitate of its 2,4-dinitrophenylhydrazone,

formed by condensation at the carbonyl group:



Propanol gives no such precipitate because it has an alcohol group and no carbonyl group. This test distinguishes propanone from either propan-1-ol or propan-2-ol, so it does not depend on which propanol isomer is meant.

Step 3: Conclusion Acetaldehyde gives a yellow iodoform precipitate whereas benzaldehyde does not. Propanone gives a yellow or orange precipitate with 2,4-DNP whereas propanol does not.

Quick Tip to Solve: Use 2,4-DNP for the ketone-alcohol pair: iodoform is unsuitable if the unspecified propanol is propan-2-ol, which also gives that test.