

CBSE Class 12 Chemistry Question Paper 2020 with Solution PDF-Set 56-2-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper comprises **four** Sections – **A, B, C** and **D**. There are **37** questions in the question paper. **All** questions are compulsory.
- (ii) **Section A** – Questions no. **1** to **20** are very short answer type questions, carrying **1** mark each. Answer these questions in one word or one sentence.
- (iii) **Section B** – Questions no. **21** to **27** are short answer type questions, carrying **2** marks each.
- (iv) **Section C** – Questions no. **28** to **34** are long answer type-I questions, carrying **3** marks each.
- (v) **Section D** – Questions no. **35** to **37** are long answer type-II questions, carrying **5** marks each.
- (vi) There is no overall choice in the question paper. However, an internal choice has been provided in 2 questions of two marks, 2 questions of three marks and all the 3 questions of five marks. You have to attempt only one of the choices in such questions.
- (vii) In addition to this, separate instructions are given with each section and question, wherever necessary.
- (viii) Use of calculators and log tables is not permitted.

Section A (20 marks)

Read the given passage and answer the questions number 1 to 5 that follow : $1 \times 5 = 5$

Organic compounds containing amine as functional group are present in a vivid variety of compounds, namely amino acids, hormones, neurotransmitters, DNA, alkaloids, dyes, etc. Drugs including nicotine, morphine, codeine and heroin, etc. which have physiological effects on humans also contain amino group in one form or another. Amines are basic because of the presence of lone pair of electrons on nitrogen. Addition of nitrogen into an organic framework leads to the formation of two families of molecules, namely amines and amides. As chemistry students, we must appreciate the versatility of nitrogen.

1. Name the linkage formed when carboxyl end of one amino acid condenses with amino end of other amino acid. [1 mark]

Solution:

Concept:

- A carboxyl group, $-\text{COOH}$, can react with an amino group, $-\text{NH}_2$, in a condensation reaction.
- Condensation eliminates water and joins the two amino-acid residues through an amide group.

Step 1: Identify the reacting ends The carboxyl end of the first amino acid supplies the carbonyl carbon, while the amino end of the second supplies nitrogen. An OH group and a hydrogen are eliminated together as H_2O .

Step 2: Recognise the resulting bond The new connection between the two residues is $-\text{CO} - \text{NH}-$. An amide linkage formed specifically between amino acids is called a peptide linkage; this is the bond that joins amino-acid residues in peptides and proteins.

Step 3: Conclusion The linkage formed is a **peptide linkage**, $-\text{CO} - \text{NH}-$.

Quick Tip to Solve: Look for a carbonyl carbon bonded to nitrogen: between amino acids, this is the peptide linkage.

2. What are essential amino acids? [1 mark]

Solution:

Concept:

- Amino acids are the building units of proteins and are needed for growth and tissue maintenance.
- The term essential describes a nutritional requirement: the human body cannot synthesise these amino acids in sufficient amounts.

Step 1: Identify the limitation of synthesis Some amino acids cannot be produced by the human body in the amounts needed for normal functioning. Their essential status does not mean that other amino acids are unimportant; it identifies the need for an external supply.

Step 2: State how the requirement is met These amino acids must therefore be obtained from dietary proteins. Valine and lysine are examples. The defining feature is dependence on food for their adequate supply, rather than the presence of a particular functional group.

Quick Tip to Solve: Remember essential as essential in the diet; do not define it merely as necessary for protein formation.

Step 3: Conclusion Essential amino acids are amino acids that the body cannot synthesise in sufficient amounts and must obtain through the diet.

Quick Tip to Solve: Remember essential as essential in the diet; do not define it merely as necessary for protein formation.

3. What are amino acids?

[1 mark]

Solution:

Concept:

- Amino acids are organic compounds containing an amino group, $-\text{NH}_2$, and a carboxyl group, $-\text{COOH}$.
- In the common protein-forming α -amino acids, these groups are attached to the same α -carbon.

Step 1: Identify both functional groups The amino group provides the basic functional group and the carboxyl group provides the acidic functional group. Both must be present in the molecule for it to be an amino acid; an amine with no carboxyl group is not an amino acid.

Step 2: Relate the definition to protein building units The general structure of a common α -amino acid is $\text{H}_2\text{N} - \text{CH}(\text{R}) - \text{COOH}$, where R is the side chain. Different side chains distinguish different amino acids. These compounds join through peptide linkages to form proteins.

Step 3: Conclusion Amino acids are organic compounds that contain both an amino group and a carboxyl group.

Quick Tip to Solve: Name both groups in the definition: amino alone describes an amine, whereas amino plus carboxyl describes an amino acid.

4. Why are amino acids amphoteric?

[1 mark]

Solution:

Concept:

- An amphoteric substance can behave as both an acid and a base.
- Amino acids have an acidic carboxyl group, $-\text{COOH}$, and a basic amino group, $-\text{NH}_2$.

Step 1: Explain acidic behaviour The carboxyl group can donate a proton to a base, forming a carboxylate group, $-\text{COO}^-$. Consequently, an amino acid can react with bases and display acidic behaviour.

Step 2: Explain basic behaviour The lone pair on the amino nitrogen can accept a proton from an acid, forming $-\text{NH}_3^+$. Thus, an amino acid also reacts with acids and displays basic behaviour. The two functional groups account for its ability to act in both ways.

Step 3: Conclusion Amino acids are amphoteric because their $-\text{COOH}$ group can donate a proton and their $-\text{NH}_2$ group can accept a proton.

Quick Tip to Solve: For amphoteric behaviour, connect proton donation to the carboxyl group and proton acceptance to the amino group.

5. Give one point of difference between acidic and basic amino acid.

[1 mark]

Solution:

Concept:

- Amino acids contain amino and carboxyl groups; some contain additional groups of one of these types.
- The relative numbers of amino and carboxyl groups distinguish acidic and basic amino acids in the usual CBSE classification.

Step 1: State the acidic case An acidic amino acid contains more carboxyl groups than amino groups. For example, aspartic acid contains two carboxyl groups and one amino group. The extra carboxyl group accounts for the acidic classification.

Step 2: Contrast the basic case A basic amino acid contains more amino groups than carboxyl groups. For example, lysine contains two amino groups and one carboxyl group. The comparison is the number of these functional groups within one molecule, not the overall number of atoms or the length of its carbon chain.

Step 3: Conclusion Acidic amino acids have more carboxyl groups than amino groups, whereas basic amino acids have more amino groups than carboxyl groups.

Quick Tip to Solve: Compare the two group counts: excess carboxyl groups means acidic; excess amino groups means basic.

6. Name the process used for the benefaction of ores which is based on the difference in the gravities of ore and the gangue particles.

[1 mark]

Solution:

Concept:

- Concentration of an ore removes unwanted earthy impurities, called gangue, before extraction of the metal.
- Gravity separation uses the difference in specific gravities, or densities, of the ore and gangue particles in a flowing stream of water.

Step 1: Identify the physical property used The question specifies a difference in the gravities of ore and gangue. Thus the separation depends on density, rather than magnetic properties or preferential wetting of the particles.

Step 2: Relate density to the washing process The powdered ore is washed with a stream of water. The lighter gangue particles are carried away more readily, while the heavier ore particles settle and can be collected. This enriches the ore without chemically changing it.

Step 3: Conclusion The process is **hydraulic washing**, also called gravity separation.

Quick Tip to Solve: Link the phrase “difference in specific gravities” directly to hydraulic washing; water carries away the lighter gangue.

7. What type of isomerism is shown by the complex $[\text{Co}(\text{NH}_3)_5 \text{NO}_2]\text{Cl}_2$?

[1 mark]

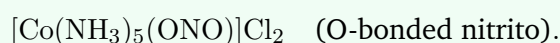
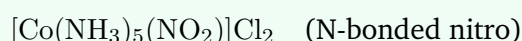
Solution:

Concept:

- Linkage isomerism occurs when an ambidentate ligand coordinates to the same metal through different donor atoms.
- The nitrite ligand, NO_2^- , can coordinate through nitrogen (nitro) or through oxygen (nitrito). Each form uses only one donor atom at a time.

Step 1: Identify the ambidentate ligand In $[\text{Co}(\text{NH}_3)_5 \text{NO}_2]\text{Cl}_2$, the five ammonia ligands coordinate through nitrogen. The nitrite ligand differs because either its nitrogen atom or an oxygen atom can supply the donor pair to cobalt.

Step 2: Compare the possible attachments The two possible forms are



The overall composition is unchanged; only the donor atom of the nitrite ligand changes. In an octahedral complex with five identical ammonia ligands, a cis-trans pair is not possible.

Step 3: Conclusion The complex shows **linkage isomerism**.

Quick Tip to Solve: When a complex contains nitrite, check for N-bonded nitro and O-bonded nitrito forms to identify linkage isomerism.

8. An organic compound is adsorbed on the surface of silica gel. Name the process of removing the organic compound from silica gel.

[1 mark]

Solution:

Concept:

- Adsorption is the accumulation of a substance at the surface of another substance, called the adsorbent.
- Desorption is the reverse process: the adsorbed substance leaves the surface of the adsorbent.

Step 1: Identify the surface and the adsorbed substance Silica gel provides the solid surface and is therefore the adsorbent. The organic compound held on that surface is the adsorbate; it is not described as being distributed throughout the bulk of the silica gel.

Step 2: Identify the direction of the process Removing the organic compound makes the adsorbate leave the surface. This reverses its adsorption on silica gel, so the required term is the name for the reverse of adsorption.

Step 3: Conclusion The process is **desorption**.

Quick Tip to Solve: For a substance leaving an adsorbent's surface, use desorption; accumulation on the surface is adsorption.

9. Give an example of a metal which can be purified by the process of distillation.

[1 mark]

Solution:

Concept:

- Distillation separates substances according to differences in their volatility or boiling points.
- A volatile metal can be purified by vaporising it and then condensing its vapour, leaving less volatile impurities behind.

Step 1: Identify the required property of the metal The metal should be readily converted into vapour on heating compared with the impurities mixed with it. This allows the metal vapour to be collected separately from the non-volatile residue.

Step 2: Apply the principle to zinc Zinc is a comparatively volatile metal and can be refined by distillation. On heating impure zinc, zinc vapour forms while less volatile impurities remain behind. Cooling the vapour gives purified zinc.

Step 3: Conclusion Zinc (Zn) is an example of a metal purified by distillation.

Quick Tip to Solve: Recall zinc and mercury as volatile metals; distillation purifies them by vaporisation followed by condensation.

10. Calculate the overall order of the reaction whose rate law is given by

$$\text{Rate} = k[\text{SO}_2]^{1/4}[\text{O}_2]^{3/4}.$$

[1 mark]

Solution:

Concept:

- The order with respect to a reactant equals its concentration exponent in the experimentally determined rate law.
- For a rate law $r = k[A]^m[B]^n$, the overall reaction order is $m + n$. Here k is the rate constant and square brackets denote concentrations.

Step 1: Read the individual concentration exponents In the given rate law, the exponent of $[\text{SO}_2]$ is $1/4$, and that of $[\text{O}_2]$ is $3/4$. Hence the individual orders are fractional. The rate constant does not contribute an additional order.

Step 2: Add the partial orders Reaction order is obtained by adding these exponents, rather than multiplying them or using coefficients from a chemical equation:

$$n_{\text{overall}} = \frac{1}{4} + \frac{3}{4} = \frac{4}{4} = 1.$$

Step 3: Conclusion The overall order is $\boxed{1}$; the reaction is first order overall.

Quick Tip to Solve: Add only the concentration exponents in the rate law: fractional partial orders can still give an integral overall order.

Questions number 11 to 15 are multiple choice questions:

11. The incorrect statement about interstitial compounds is

[1 mark]

- (A) They are chemically reactive.
- (B) They are very hard.
- (C) They retain metallic conductivity.
- (D) They have high melting point.

Correct Answer: (A) They are chemically reactive.

Solution:

Concept:

- Interstitial compounds form when small atoms such as hydrogen, carbon or nitrogen occupy spaces in a transition-metal lattice.
- They are generally chemically inert, hard and high-melting, while retaining metallic conductivity.

Step 1: Test the chemical-property statement The small atoms are held in the interstices of the metal lattice. These compounds are generally chemically inert; therefore the assertion that they are chemically reactive is inconsistent with their characteristic properties.

Step 2: Check the other three statements Interstitial compounds are very hard and have high melting points, so (B) and (D) state characteristic properties correctly. The metal lattice retains metallic conductivity, making (C) correct as well. The question asks for the incorrect statement, so the three true statements must be excluded.

Step 3: Conclusion The incorrect statement is “They are chemically reactive.” Hence, the correct option is (A).

Quick Tip to Solve: For an incorrect-property question, remember that interstitial compounds are generally inert but retain metallic conductivity.

12. The correct IUPAC name of $\text{CH}_3 - \text{C}(\text{CH}_3)(\text{OH}) - \text{CH}_2\text{CH}_3$ is

[1 mark]

- (A) tert-butyl alcohol
- (B) 2,2-Dimethylpropanol
- (C) 2-Methylbutan-2-ol
- (D) 3-Methylbutan-3-ol

Correct Answer: (C) 2-Methylbutan-2-ol

Solution:

Concept:

- Choose the longest carbon chain containing the carbon bonded to the hydroxyl group; use the suffix “ol” for the alcohol.
- Number the parent chain to give the hydroxyl group the lowest possible locant before locating alkyl substituents.

Quick Tip to Solve: First give the hydroxyl group its lowest locant; then use the same numbering to locate the methyl substituent.

Step 1: Select and number the parent chain In $\text{CH}_3 - \text{C}(\text{CH}_3)(\text{OH}) - \text{CH}_2\text{CH}_3$, the longest chain containing the hydroxyl-bearing carbon has four carbon atoms. Numbering from the nearer end places $-\text{OH}$ on carbon 2 rather than carbon 3. The parent alcohol is therefore butan-2-ol.

Step 2: Locate the substituent and compare options The remaining CH_3 group is a methyl substituent on carbon 2. Option (A) denotes tert-butyl alcohol, which has only four carbon atoms in total; the given molecule has five. Option (B) incorrectly chooses a three-carbon parent chain. Option (D) numbers from the wrong end, giving the hydroxyl group locant 3 instead of 2.

Step 3: Conclusion The correct IUPAC name is 2-methylbutan-2-ol. Hence, the correct option is (C).

Quick Tip to Solve: First give the hydroxyl group its lowest locant; then use the same numbering to locate the methyl substituent.

13. 50 mL of an aqueous solution of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ (Molar mass : 180 g/mol) contains 6.02×10^{22} molecules. The concentration of the solution will be [1 mark]

- (A) 0.1 M
- (B) 0.2 M
- (C) 1.0 M
- (D) 2.0 M

Correct Answer: (D) 2.0 M

Solution:

Concept:

- The number of moles is $n = N/N_A$, where N is the number of solute molecules and $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ is Avogadro's constant.
- Molarity is $M = n/V$, where V is the volume of the solution in litres.

Step 1: Convert molecules into moles The given quantity counts glucose molecules, so divide by Avogadro's constant to obtain the amount of glucose. Its molar mass is unnecessary because the number of molecules is already given.

$$n = \frac{6.02 \times 10^{22}}{6.02 \times 10^{23}} = 0.10 \text{ mol.}$$

Step 2: Calculate the concentration in litres The solution volume is $50 \text{ mL} = 0.050 \text{ L}$. Use the solution volume rather than the solvent volume in the molarity formula.

$$M = \frac{0.10 \text{ mol}}{0.050 \text{ L}} = 2.0 \text{ mol L}^{-1}.$$

Option (A) confuses the amount in moles with the concentration. Options (B) and (C) do not follow from dividing the given amount by 0.050 L.

Step 3: Conclusion The concentration of the glucose solution is 2.0 M. Hence, the correct option is (D).

Quick Tip to Solve: When molecules are given, divide by Avogadro's constant first and convert millilitres to litres before calculating molarity.

14. Total number of unpaired electrons present in Cr^{3+} (Atomic number = 24) is

[1 mark]

- (A) 2
- (B) 7
- (C) 3
- (D) 5

Correct Answer: (C) 3

Solution:

Concept:

- Neutral chromium, atomic number 24, has the exceptional ground-state configuration $[\text{Ar}] 3d^5 4s^1$.
- On ionisation, the electron in $4s$ is removed before electrons in $3d$. Hund's rule places electrons singly in degenerate orbitals before pairing.

Step 1: Obtain the configuration of the ion Formation of Cr^{3+} removes three electrons from neutral chromium: the single $4s$ electron first, followed by two $3d$ electrons. Thus its configuration is $[\text{Ar}] 3d^3$. The argon core contains only paired electrons.

Step 2: Count unpaired electrons and test the options The three $3d$ electrons occupy three different orbitals with parallel spins according to Hund's rule. All three are therefore unpaired. Two would correspond to an incorrect electron count, seven is incompatible with a d^3 ion, and five counts the $3d$ electrons of neutral chromium without removing the two that are lost on ionisation.

Step 3: Conclusion Cr^{3+} contains three unpaired electrons. Hence, the correct option is (C).

Quick Tip to Solve: Write chromium's exceptional neutral configuration, remove its $4s$ electron first, and then apply Hund's rule to the remaining d electrons.

15. If the standard electrode potential of an electrode is greater than zero, then we can infer that its

[1 mark]

- (A) reduced form is more stable compared to hydrogen gas.
- (B) oxidised form is more stable compared to hydrogen gas.
- (C) reduced and oxidised forms are equally stable.
- (D) reduced form is less stable than the hydrogen gas.

Correct Answer: (A) reduced form is more stable compared to hydrogen gas.

Solution:

Concept:

- A standard electrode potential is conventionally a reduction potential, measured relative to the standard hydrogen electrode, whose potential is zero.
- For a spontaneous standard cell reaction, $\Delta G^\circ = -nFE_{\text{cell}}^\circ < 0$; here n is the electron number and F is the Faraday constant.

Step 1: Compare the reduction with hydrogen Couple the electrode to the standard hydrogen electrode. If $E^\circ > 0$, the given electrode is reduced at the cathode while hydrogen is oxidised at the

Quick Tip to Solve: Read electrode potentials as reduction potentials: a value above zero means reduction is favoured relative to the standard hydrogen electrode.

anode. Thus $E_{\text{cell}}^{\circ} = E^{\circ} - 0 > 0$, so this reaction is favourable under standard conditions.

Step 2: Interpret the options The comparison favours formation of the electrode's reduced form relative to hydrogen gas, as stated in (A). Option (B) reverses this tendency. Option (C) incorrectly infers equal stability, and (D) contradicts the positive reduction potential.

Step 3: Conclusion The reduced form is more stable compared to hydrogen gas in the stated electrochemical comparison. The correct option is (A).

Quick Tip to Solve: Read electrode potentials as reduction potentials: a value above zero means reduction is favoured relative to the standard hydrogen electrode.

For questions number 16 to 20, two statements are given – one labelled Assertion (A) and the other labelled Reason (R). Select the correct answer to these questions from the codes (i), (ii), (iii) and (iv) as given below:

- (i) Both assertion (A) and reason (R) are correct statements, and reason (R) is the correct explanation of the assertion (A).
- (ii) Both assertion (A) and reason (R) are correct statements, but reason (R) is not the correct explanation of the assertion (A).
- (iii) Assertion (A) is correct, but reason (R) is incorrect statement.
- (iv) Assertion (A) is incorrect, but reason (R) is correct statement.

16. Assertion (A): o-nitrophenol is a weaker acid than p-nitrophenol.

Reason (R): Intramolecular hydrogen bonding makes ortho isomer weaker than para isomer. [1 mark]

Correct Answer: (i) Both assertion (A) and reason (R) are correct statements, and reason (R) is the correct explanation of the assertion (A).

Solution:

Concept:

- Acid strength depends on the ease of proton release and the relative stability of the acid and its conjugate base in solution.
- In *o*-nitrophenol, the neighbouring nitro and hydroxyl groups form an intramolecular hydrogen bond, stabilising the undissociated molecule.

Step 1: Judge the assertion In aqueous solution, *o*-nitrophenol is slightly less acidic than *p*-nitrophenol. Therefore assertion (A) is correct.

Step 2: Judge the reason The ortho isomer forms an internal $\text{O} - \text{H} \cdots \text{O}$ hydrogen bond with an oxygen of its nitro group. This stabilises the neutral molecule and makes loss of its proton less favourable. Such intramolecular bonding is unavailable to the widely separated groups of the para isomer. Reason (R) is correct.

Step 3: Test the explanatory connection Stabilisation of undissociated *o*-nitrophenol by this intramolecular bond explains its weaker acidity relative to the para isomer. Thus the reason directly explains the assertion; code (ii), which denies that connection, does not apply.

Step 4: Conclusion The correct code is (i): both (A) and (R) are correct, and (R) correctly explains

Quick Tip to Solve: For ortho versus para nitrophenol, identify the internal hydrogen bond in the ortho acid before comparing proton release.

(A).

Quick Tip to Solve: For ortho versus para nitrophenol, identify the internal hydrogen bond in the ortho acid before comparing proton release.

17. Assertion (A): Albumin is a globular protein.

Reason (R): Polypeptide chain coils around to give a straight chain.

[1 mark]

Correct Answer: (iii) Assertion (A) is correct, but reason (R) is incorrect statement.

Solution:

Concept:

- Globular proteins have polypeptide chains folded into compact, approximately spherical shapes and are generally water-soluble.
- Protein shape depends on folding and interactions between different regions of the polypeptide; a globular shape is distinct from an extended chain.

Step 1: Judge the assertion Albumin is a standard example of a globular protein. Its folded, compact structure agrees with this classification, so assertion (A) is correct.

Step 2: Judge the reason In a globular protein, the polypeptide folds and coils into a compact, roughly spherical shape. It does not coil to produce a straight chain. Hence reason (R) gives an incorrect structural description and is false.

Step 3: Select the corresponding code Since the assertion is true and the reason is false, the reason cannot explain albumin's globular nature. Codes (i) and (ii) require a true reason, while code (iv) requires a false assertion; none fits these statements.

Step 4: Conclusion The correct code is (iii): assertion (A) is correct, but reason (R) is incorrect.

Quick Tip to Solve: Associate albumin with a compact spherical fold; a statement that globular folding gives a straight chain must be false.

18. Assertion (A): Bakelite is a thermosetting polymer.

Reason (R): On heating, polymeric chain becomes a long and straight chain.

[1 mark]

Correct Answer: (iii) Assertion (A) is correct, but reason (R) is incorrect statement.

Solution:

Concept:

- Thermosetting polymers form highly cross-linked three-dimensional networks on curing and cannot be softened and remoulded repeatedly by heating.
- Bakelite is a cross-linked phenol-formaldehyde resin; covalent links between its chains account for its rigid structure.

Step 1: Judge the assertion Bakelite is a thermosetting polymer. On curing, cross-linking produces a permanent rigid network, so assertion (A) is correct.

Quick Tip to Solve: For Bakelite, look for cross-links and a permanent three-dimensional network; a straight-chain explanation is the wrong model.

Step 2: Judge the reason Heating during curing promotes cross-linking into a three-dimensional network, rather than converting the polymer into a long straight chain. Once cured, Bakelite does not simply melt on reheating. Thus reason (R) is incorrect.

Step 3: Test the connection and code The stated straight-chain explanation cannot account for thermosetting behaviour because that behaviour depends on extensive cross-links. A true assertion with a false reason matches code (iii); neither code requiring both statements to be true is applicable.

Step 4: Conclusion The correct code is (iii): assertion (A) is correct, but reason (R) is incorrect.

Quick Tip to Solve: For Bakelite, look for cross-links and a permanent three-dimensional network; a straight-chain explanation is the wrong model.

19. Assertion (A): Low spin tetrahedral complexes are rarely observed.

Reason (R): The orbital splitting energies are not sufficiently large to forcing pairing. [1 mark]

Correct Answer: (i) Both assertion (A) and reason (R) are correct statements, and reason (R) is the correct explanation of the assertion (A).

Solution:

Concept:

- The spin state depends on the competition between crystal-field splitting Δ and electron-pairing energy P .
- Tetrahedral splitting Δ_t is small: for comparable metal-ligand combinations, $\Delta_t \approx \frac{4}{9}\Delta_o$, where Δ_o denotes octahedral splitting.

Step 1: Judge the assertion Tetrahedral complexes are generally high spin; low-spin tetrahedral complexes are rarely observed. Assertion (A) is therefore correct.

Step 2: Judge the reason In a tetrahedral field, the splitting is usually smaller than the pairing energy: $\Delta_t < P$. An electron can occupy a higher-energy orbital at a lower energy cost than pairing in an already occupied lower-energy orbital. Hence the splitting is generally insufficient to force pairing, so reason (R) is correct.

Step 3: Establish the explanation Avoiding pairing leaves more electrons unpaired and produces a high-spin arrangement. The small splitting stated in the reason is precisely why low-spin tetrahedral complexes are rare; code (ii), which denies this explanation, is unsuitable.

Step 4: Conclusion The correct code is (i): both (A) and (R) are correct, and (R) correctly explains (A).

Quick Tip to Solve: Compare tetrahedral splitting with pairing energy: $\Delta_t < P$ favours occupying separate orbitals and therefore high spin.

20. Assertion (A): Boiling points of alkyl halides decrease in the order $R-I > R-Br > R-Cl > R-F$.

Reason (R): Van der Waals forces decrease with increase in the size of halogen atom.

[1 mark]

Correct Answer: (iii) Assertion (A) is correct, but reason (R) is incorrect statement.

Solution:

Concept:

- Boiling separates molecules from one another; stronger intermolecular attractions generally lead to a higher boiling point.
- For the same alkyl group R, the halogen's size and polarisability increase from fluorine to iodine, strengthening London dispersion forces.

Step 1: Judge the assertion Keeping the alkyl group unchanged, increasing halogen size and polarisability produces the boiling-point order $R-I > R-Br > R-Cl > R-F$. The assertion gives this order correctly.

Step 2: Judge the reason A larger halogen has a more easily distorted electron cloud and therefore stronger dispersion attractions. These van der Waals forces increase, rather than decrease, with increasing halogen size in this series. Reason (R) states the opposite trend and is incorrect.

Step 3: Check the explanatory relation The false reason cannot explain the true boiling-point sequence. Both codes (i) and (ii) require a correct reason, and code (iv) requires an incorrect assertion. Only the true-assertion, false-reason code fits.

Step 4: Conclusion The correct code is (iii): assertion (A) is correct, but reason (R) is incorrect.

Quick Tip to Solve: Keep the alkyl group fixed, then rank halogen polarisability: iodine gives the strongest dispersion forces and the highest boiling point.

Section B (14 marks)

21. Predict the state of the solute in the following situations:

(a) Experimentally determined molar mass is more than the true value.

(b) 'i' value is 0.4.

[2 marks]

Solution:

Concept:

- Colligative properties depend on the number of solute particles present in solution. Association combines several solute particles into a smaller number of larger particles.
- The van't Hoff factor is $i = M_{\text{true}}/M_{\text{observed}}$, where M_{true} is the normal molar mass and M_{observed} is the molar mass calculated from a colligative property.

Step 1: (a) Compare the observed and true molar masses Given $M_{\text{observed}} > M_{\text{true}}$, their ratio gives $i < 1$. The observed colligative effect is therefore smaller than that expected for an unassociated solute. This happens because individual molecules combine into aggregates, reducing the number of independently moving solute particles.

Step 2: (b) Interpret the value of the van't Hoff factor Here $i = 0.4 < 1$, so the solution contains

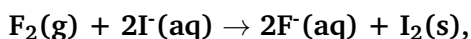
Quick Tip to Solve: Use $i = M_{\text{true}}/M_{\text{observed}}$: an abnormally high observed molar mass or $i < 1$ indicates association.

fewer solute particles than expected without association. Indeed, $M_{\text{observed}} = M_{\text{true}}/0.4 = 2.5M_{\text{true}}$. Dissociation would instead increase the particle count and give $i > 1$. The value alone does not uniquely specify the size of the aggregate or the degree of association.

Step 3: Conclusion In both (a) and (b), the solute undergoes **association** in solution.

Quick Tip to Solve: Use $i = M_{\text{true}}/M_{\text{observed}}$: an abnormally high observed molar mass or $i < 1$ indicates association.

22. For an electrochemical cell



give the cell representation. Also write the Nernst equation for the above cell at 25°C.

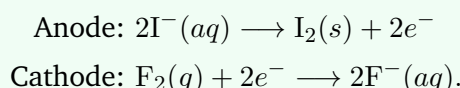
[2 marks]

Solution:

Concept:

- In cell notation, oxidation at the anode is written on the left and reduction at the cathode on the right. Inert platinum provides a conducting surface for these half-cells.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^{\circ} - (0.0591/n) \log Q$, in volts, where n is the number of electrons transferred and Q is the reaction quotient.

Step 1: Identify the half-reactions and write the cell Iodide is oxidised and fluorine is reduced:



Thus $n = 2$. The cell representation is



A single vertical line denotes a phase boundary and the double line denotes the salt bridge.

Step 2: Form the reaction quotient Pure solid iodine has unit activity and is omitted from Q . Using ionic activities a and the fluorine partial pressure p_{F_2} ,

$$Q = \frac{a_{\text{F}^-}^2}{a_{\text{I}^-}^2 (p_{\text{F}_2}/p^{\circ})}.$$

Here p° is the standard pressure. For a dilute solution, each ionic activity is approximated by its concentration divided by the standard concentration; these standard-concentration factors cancel in the ratio.

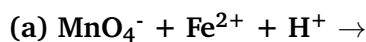
Step 3: Conclusion For the cell represented above, at 25°C,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591 \text{ V}}{2} \log \left(\frac{[\text{F}^-]^2}{[\text{I}^-]^2 (p_{\text{F}_2}/p^{\circ})} \right).$$

When fluorine is at standard pressure, the pressure factor becomes unity.

Quick Tip to Solve: Put iodide oxidation on the left; omit solid iodine from Q , but retain fluorine pressure unless it is specified as standard.

23. Complete and balance the following chemical equations:



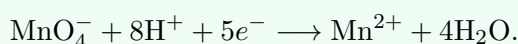
[2 marks]

Solution:

Concept:

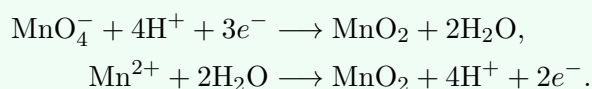
- Balance a redox equation by equating the electrons lost and gained. Use H_2O to balance oxygen and H^+ to balance hydrogen in an acidic ionic equation.
- Permanganate contains manganese in oxidation state +7. It forms Mn^{2+} in the acidic reaction with Fe^{2+} ; with Mn^{2+} in water, both manganese species form MnO_2 , containing manganese in state +4.

Step 1: (a) Balance reduction of permanganate by iron(II) The reduction half-reaction is



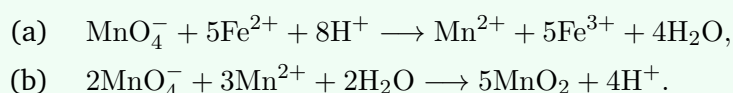
Each Fe^{2+} ion loses one electron to become Fe^{3+} . Multiply this oxidation by five and add. The balanced coefficients give total charge +17 on each side, with one manganese atom and five iron atoms conserved.

Step 2: (b) Balance the reaction between two manganese species Reduction from +7 to +4 gains three electrons, whereas oxidation from +2 to +4 loses two. The half-reactions are



Multiply the first by two and the second by three, then cancel six electrons and common water and hydrogen ions. The net equation conserves five manganese atoms, ten oxygen atoms and four hydrogen atoms, with total charge +4 on each side.

Step 3: Conclusion The completed and balanced equations are:



Quick Tip to Solve: For (a), one permanganate accepts five electrons; for (b), use the electron ratio 2 : 3 for permanganate and manganese(II).

24(a). Give one point of difference between the following:

(a) Tranquilizers and Analgesics

(b) Antiseptics and Disinfectants

[2 marks]

Solution:

Concept:

- Medicinal drugs are classified by their therapeutic effect. Tranquilizers and analgesics differ in their principal action on the body.
- Antiseptics and disinfectants both destroy microorganisms or inhibit their growth. Their distinction is based on the surface on which they are used at suitable concentrations.

Step 1: (a) Distinguish tranquilizers from analgesics by their action **Tranquilizers** act on the central nervous system to reduce anxiety, stress and mental tension, producing a calming effect. **Analgesics** are medicines that relieve or reduce pain without causing loss of consciousness. Thus the required difference is relief of anxiety and tension versus relief of pain; their classification is based on the principal therapeutic effect, not simply on whether a drug acts on the nervous system.

Step 2: (b) Distinguish antiseptics from disinfectants by their use **Antiseptics** are applied to living tissues, such as skin, wounds and cuts, to control microorganisms at concentrations suitable for such use. **Disinfectants** are used on non-living objects and surfaces, such as floors and instruments. Their usual working concentrations are unsuitable for application to living tissues. The same chemical may act as an antiseptic at a lower concentration and as a disinfectant at a higher concentration.

Step 3: Conclusion (a) Tranquilizers relieve anxiety and mental tension; analgesics relieve pain. (b) Antiseptics are used on living tissues; disinfectants are used on non-living surfaces.

Quick Tip to Solve: Compare each pair using one common basis: therapeutic action for (a), and living versus non-living application surface for (b).

OR

24(b). Differentiate on the basis of chemical composition between cationic and anionic detergents.

Also give one example of each category.

[2 marks]

Solution:

Concept:

- Synthetic detergents have a long hydrocarbon chain and an ionic, water-attracting group. Their classification depends on the charge of the organic ion that provides detergent action.
- Cationic detergents have a positively charged organic ion, whereas anionic detergents have a negatively charged organic ion; the accompanying counter-ion balances this charge.

Step 1: Identify the composition of cationic detergents Cationic detergents are quaternary ammonium salts containing a long alkyl chain. Their nitrogen atom carries a positive charge, and the long-chain ammonium cation is the active detergent species. An example is cetyltrimethylammonium bromide, $[\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{CH}_3)_3]^+ \text{Br}^-$. Here bromide is the counter-ion.

Quick Tip to Solve: Look at the charge on the long-chain organic ion: a positive ammonium head means cationic, while a negative sulphate or sulphonate head means anionic.

Step 2: Identify the composition of anionic detergents Anionic detergents are sodium salts of sulphated long-chain alcohols or of alkylbenzenesulphonic acids. Their long-chain organic anion is the active detergent species. An example is sodium lauryl sulphate, $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3^- \text{Na}^+$. Its sulphate-containing head is negatively charged and sodium is the counter-ion.

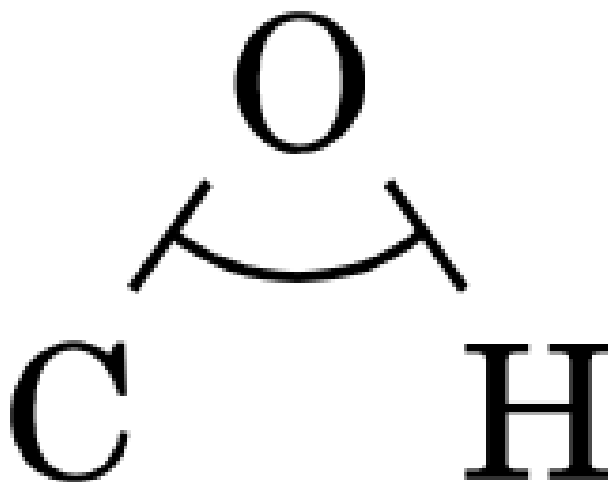
Step 3: Conclusion Cationic detergents are long-chain quaternary ammonium salts, for example cetyltrimethylammonium bromide. Anionic detergents are salts of long-chain alkyl sulphates or alkylbenzenesulphonates, for example sodium lauryl sulphate.

Quick Tip to Solve: Look at the charge on the long-chain organic ion: a positive ammonium head means cationic, while a negative sulphate or sulphonate head means anionic.

25. Give reasons for the following:

- (a) Bond angle C-O-H in alcohol is slightly less than the tetrahedral angle.
(b) C-OH bond length in CH_3OH is slightly more than the C-OH bond length in phenol.

[2 marks]



Solution:

Concept:

- Electron pairs around oxygen repel one another. Lone-pair repulsion is stronger than bond-pair repulsion, so lone pairs can compress the angle between two bonds.
- Resonance increases the bond order of the carbon-oxygen bond in phenol. A bond with partial double-bond character is shorter than the corresponding single bond.

Step 1: Explain the smaller angle in alcohol (a) The oxygen atom of an alcohol has two bond pairs and two lone pairs. Its approximately sp^3 arrangement of electron pairs is based on a tetrahedron, whose ideal angle is 109.5° . The lone pairs occupy more space and repel the bonding pairs more strongly than bonding pairs repel each other. They push the two bonds towards each other, making the carbon-oxygen-hydrogen angle slightly less than the ideal tetrahedral angle.

Quick Tip to Solve: For the angle, count oxygen's two lone pairs; for the bond length, check whether its lone pair can conjugate with an aromatic ring.

Step 2: Compare the carbon-oxygen bonds (b) In methanol, CH_3OH , the carbon-oxygen bond is an ordinary single bond to an sp^3 -hybridised carbon. In phenol, a lone pair on oxygen is delocalised into the benzene ring by resonance. Consequently, the bond between the ring carbon and oxygen acquires partial double-bond character and becomes shorter. The ring carbon is also sp^2 -hybridised, with greater s-character than the methyl carbon, which further favours a shorter bond.

Step 3: Conclusion (a) Stronger repulsion involving the two oxygen lone pairs compresses the bond angle in alcohol. (b) Resonance gives the carbon-oxygen bond of phenol partial double-bond character, so it is shorter than the carbon-oxygen bond of methanol.

Quick Tip to Solve: For the angle, count oxygen's two lone pairs; for the bond length, check whether its lone pair can conjugate with an aromatic ring.

26(a). Define adsorption isotherm. Give the empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. [2 marks]

Solution:

Concept:

- Adsorption is the accumulation of molecules on the surface of a solid adsorbent. Its extent depends on pressure and temperature.
- At a fixed temperature, the Freundlich adsorption isotherm relates the mass of gas adsorbed per unit mass of adsorbent to the equilibrium gas pressure.

Step 1: Define an adsorption isotherm An adsorption isotherm is the relationship, usually shown as a graph, between the amount of gas adsorbed per unit mass of solid adsorbent and the equilibrium pressure of the gas at a constant temperature. If x is the mass of gas adsorbed and m is the mass of adsorbent, the extent of adsorption is expressed as x/m .

Step 2: State the Freundlich relationship The empirical relationship over a limited range of pressures is

$$\frac{x}{m} = kp^{1/n}, \quad 0 < \frac{1}{n} < 1.$$

Here p is equilibrium gas pressure, and k and n are constants for the specified gas-adsorbent pair at the chosen temperature. Thus adsorption increases with pressure, but less rapidly than a directly proportional relation. Taking logarithms gives

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p.$$

The Freundlich expression is empirical and does not describe saturation at arbitrarily high pressure.

Step 3: Conclusion An adsorption isotherm describes the pressure dependence of adsorption at constant temperature. The required empirical law is the Freundlich equation, $x/m = kp^{1/n}$.

Quick Tip to Solve: Remember that an isotherm keeps temperature fixed; a plot of $\log(x/m)$ against $\log p$ has slope $1/n$ and intercept $\log k$.

26(b). Define shape-selective catalysis. Name the process by which alcohols convert directly into gasoline and give a variety of hydrocarbons. [2 marks]

Solution:

Concept:

- A porous catalyst can select molecules according to their size and shape. Only suitable molecules can enter its pores, reach its active sites and form products that can leave the pores.
- Zeolites are porous aluminosilicates with a definite pore structure. Their channels make them useful for shape-selective catalysis.

Step 1: Define shape-selective catalysis Shape-selective catalysis is a catalytic reaction whose selectivity depends on the pore structure of the catalyst and the size and shape of reactant and product molecules. Molecules that fit the channels can reach the catalytic sites, whereas larger or unsuitable molecules are excluded. The restricted space can also favour certain reaction pathways and products.

Step 2: Identify the alcohol-to-gasoline process The process is the methanol-to-gasoline (MTG), or Mobil process. The zeolite ZSM-5 is the shape-selective catalyst used to convert alcohols, especially methanol, into a mixture of hydrocarbons in the gasoline range. The products include alkanes and aromatic hydrocarbons. Its particular pore dimensions help control the sizes and shapes of the hydrocarbons formed, so the product is a hydrocarbon mixture rather than one pure compound.

Step 3: Conclusion Shape-selective catalysis depends on catalyst pore structure and molecular size and shape. The methanol-to-gasoline (MTG or Mobil) process uses ZSM-5 zeolite to convert alcohols into gasoline-range hydrocarbons.

Quick Tip to Solve: Link zeolite pores with molecular shape, and remember the pairing: alcohol to gasoline, MTG process, ZSM-5 catalyst.

27. A reaction is first order w.r.t. reactant A as well as w.r.t. reactant B. Give the rate law. Also give one point of difference between average rate and instantaneous rate. [2 marks]

Solution:

Concept:

- The rate law expresses the reaction rate in terms of reactant concentrations, each raised to its experimentally determined order. Thus, for reactants A and B, $r = k[A]^m[B]^n$, where k is the rate constant.
- Average rate refers to a finite time interval, while instantaneous rate refers to one particular instant. They correspond to the slopes of a secant and a tangent, respectively, on a concentration versus time graph.

Step 1: Substitute the given orders in the rate law First order with respect to A means $m = 1$, and first order with respect to B means $n = 1$. Therefore,

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

Quick Tip to Solve: Put each stated order on its own concentration term; use a finite difference for average rate and a derivative for instantaneous rate.

At fixed concentration of the other reactant, doubling either concentration doubles the rate. The overall order is the sum of the individual powers, $1 + 1 = 2$.

Step 2: Distinguish the two rates by the time interval For a reactant concentration c , its average rate of disappearance between times t_1 and t_2 is

$$-\frac{\Delta c}{\Delta t} = -\frac{c_2 - c_1}{t_2 - t_1}.$$

Its instantaneous rate of disappearance at a specified time is $-dc/dt$, obtained as the time interval tends to zero. Thus the former describes a finite interval, whereas the latter describes a particular instant. The minus sign makes the disappearance rate positive as the reactant concentration decreases.

Step 3: Conclusion The rate law is $r = k[A][B]$. Average rate is measured over a finite time interval; instantaneous rate is measured at a particular instant.

Quick Tip to Solve: Put each stated order on its own concentration term; use a finite difference for average rate and a derivative for instantaneous rate.

Section C (21 marks)

28(a). Give the structures of the monomers of the following polymers:

(a) Natural rubber

(b) Buna-S

(c) Novolac

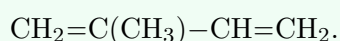
[3 marks]

Solution:

Concept:

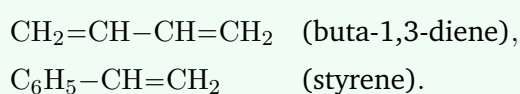
- A monomer is a small molecule from which a polymer is formed. Addition polymerisation joins unsaturated monomers, whereas condensation polymerisation joins molecules with suitable functional groups, usually with elimination of a small molecule.
- Natural rubber is cis-1,4-polyisoprene. Buna-S is a copolymer of a diene and styrene, while novolac is a phenol-formaldehyde condensation polymer.

Step 1: Identify the monomer of natural rubber Natural rubber is formed by 1,4-addition of isoprene. Its monomer is 2-methylbuta-1,3-diene, with condensed structural formula



The methyl group is attached to the second carbon of the four-carbon diene chain. Natural rubber has the cis arrangement of the resulting polyisoprene chain.

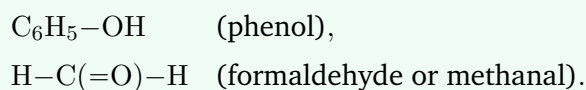
Step 2: Identify both monomers of Buna-S Buna-S is produced by copolymerisation of buta-1,3-diene and styrene. Their structures are



Quick Tip to Solve: Remember the S in Buna-S as styrene, and distinguish the two double bonds of isoprene from the single vinyl group attached to styrene's benzene ring.

In styrene, a vinyl group is directly attached to a benzene ring. The letter S in Buna-S identifies the styrene component; acrylonitrile is the comonomer of Buna-N instead.

Step 3: Identify both monomers of novolac Novolac is obtained by the acid-catalysed condensation of phenol with formaldehyde. The monomer structures are



Phenol bears a hydroxyl group directly on its benzene ring. Condensation introduces methylene bridges between phenolic units, giving the novolac chain.

Step 4: Conclusion (a) Natural rubber: isoprene, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$.

(b) Buna-S: buta-1,3-diene, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, and styrene, $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$.

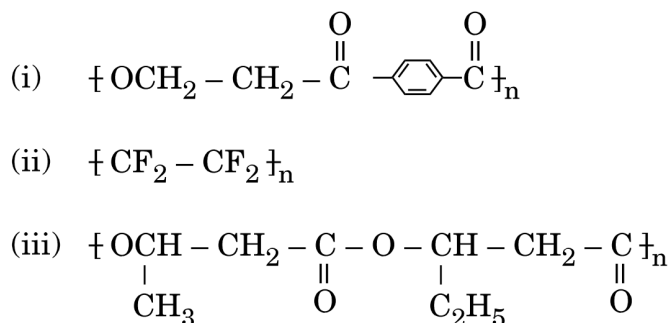
(c) Novolac: phenol, $\text{C}_6\text{H}_5-\text{OH}$, and formaldehyde, $\text{H}-\text{C}(=\text{O})-\text{H}$.

Quick Tip to Solve: Remember the S in Buna-S as styrene, and distinguish the two double bonds of isoprene from the single vinyl group attached to styrene's benzene ring.

OR

28(b). Write the names of monomers in the following polymers:

[3 marks]



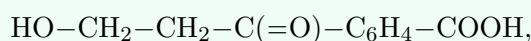
Solution:

Concept:

- Recover condensation monomers by splitting ester linkages $-\text{C}(=\text{O})-\text{O}-$ and restoring $-\text{COOH}$ and $-\text{OH}$ groups. Preserve the remaining bonds.
- Recover an alkene monomer from an addition polymer by restoring its carbon-carbon double bond. A copolyester can contain two hydroxy-acid residues.

Step 1: Trace the first repeat unit In (i), the printed chain contains $-\text{O}-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-$, a para-substituted benzene ring and a terminal $-\text{C}(=\text{O})-$. The first carbonyl is directly bonded to the ring. The ester bond joins the terminal carbonyl of one repeat to the initial oxygen of the next.

Restore the hydroxyl and carboxyl end groups:

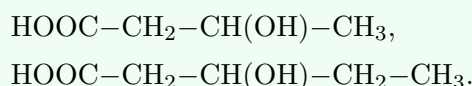


Quick Tip to Solve: Trace every oxygen before naming polyester monomers; split actual ester bonds and count hydroxy-acid positions from the carboxyl carbon.

with para ring substituents: **4-(3-hydroxypropanoyl)benzoic acid**. Self-condensation of its hydroxyl and carboxyl groups regenerates the displayed repeat unit; its ketone remains unchanged.

Step 2: Restore the alkene in the second polymer Restoring a double bond in $-\text{CF}_2-\text{CF}_2-$ gives $\text{CF}_2=\text{CF}_2$. The monomer is **tetrafluoroethene** (tetrafluoroethylene). The polymer is Teflon.

Step 3: Recover the two hydroxy acids in the third polymer Splitting both types of ester links and restoring the functional groups gives



Counting from the carboxyl carbon, each hydroxyl is at carbon 3: **3-hydroxybutanoic acid** and **3-hydroxypentanoic acid** (3-hydroxyvaleric acid).

Step 4: Conclusion (i) For the structure shown: 4-(3-hydroxypropanoyl)benzoic acid.

(ii) Tetrafluoroethene.

(iii) 3-Hydroxybutanoic acid and 3-hydroxypentanoic acid.

Quick Tip to Solve: Trace every oxygen before naming polyester monomers; split actual ester bonds and count hydroxy-acid positions from the carboxyl carbon.

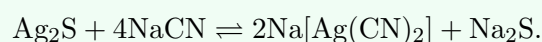
29. Give the chemical reactions involved in the leaching of silver. What is the role of Zn in this process? [3 marks]

Solution:

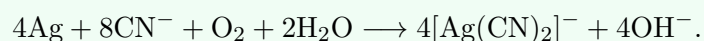
Concept:

- Cyanide leaching selectively dissolves silver by forming the soluble dicyanidoargentate(I) complex, $[\text{Ag}(\text{CN})_2]^-$, while much of the gangue remains undissolved.
- A more reactive metal can reduce a less reactive metal's ions. Zinc supplies electrons to silver(I), precipitating metallic silver from the leach liquor.

Step 1: Leach the silver ore with cyanide Finely powdered silver ore is treated with dilute aqueous sodium cyanide. For silver sulphide (argentite), the complex-formation reaction is



The silver-bearing product is soluble and therefore passes into the leach liquor. Air is supplied during leaching; oxidation of sulphide helps the extraction proceed. Silver itself can also undergo oxidative cyanide leaching, represented by

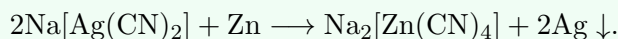


Here oxygen is the oxidising agent, and cyanide stabilises silver(I) as its soluble complex. The undissolved material is separated from the solution.

Step 2: Recover silver using zinc Zinc is added to the clarified leach liquor. The displacement reaction

Quick Tip to Solve: Separate the two stages: cyanide dissolves silver as a complex; zinc then reduces two silver(I) ions for every zinc atom used.

is



Zinc changes from oxidation state zero to +2, whereas each silver ion changes from +1 to zero. Thus one zinc atom supplies the two electrons needed to recover two silver atoms. Zinc acts as the reducing agent, and the silver separates as a solid while the zinc cyanide complex remains in solution.

Step 3: Conclusion Silver is leached as soluble $\text{Na}[\text{Ag}(\text{CN})_2]$. Zinc is the reducing/displacing agent used to precipitate metallic silver from that solution.

Quick Tip to Solve: Separate the two stages: cyanide dissolves silver as a complex; zinc then reduces two silver(I) ions for every zinc atom used.

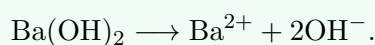
30. State Kohlrausch's law. Calculate the molar conductance of $\text{Ba}(\text{OH})_2$. The molar ionic conductance of Ba^{2+} and OH^- ions are 127 and 199 $\text{S cm}^2 \text{mol}^{-1}$ respectively. [3 marks]

Solution:

Concept:

- Kohlrausch's law states that at infinite dilution each ion contributes independently to the molar conductivity of an electrolyte, irrespective of the nature of the other ion present.
- The limiting molar conductivity is $\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$, where ν_+ and ν_- are the numbers of cations and anions produced per formula unit, and λ_i° is an ion's limiting molar conductivity.

Step 1: Count the ions produced by barium hydroxide The dissociation of barium hydroxide is



Thus one mole of the electrolyte produces one mole of barium ions and two moles of hydroxide ions. Both hydroxide ions contribute to conduction. The ionic coefficient of barium is one; its charge of +2 must not be used as an extra factor because its supplied ionic conductivity already describes the barium ion.

Step 2: Add the independent ionic contributions Applying Kohlrausch's law with the given molar ionic conductances,

$$\begin{aligned}\Lambda_m^\circ[\text{Ba}(\text{OH})_2] &= \lambda_{\text{Ba}^{2+}}^\circ + 2\lambda_{\text{OH}^-}^\circ \\ &= 127 + 2(199) \\ &= 525 \text{ S cm}^2 \text{mol}^{-1}.\end{aligned}$$

The sum is expressed per mole of barium hydroxide, so its unit remains $\text{S cm}^2 \text{mol}^{-1}$. In the context of Kohlrausch's law, this calculated value is the limiting molar conductance, corresponding to infinite dilution.

Step 3: Conclusion The molar conductance of $\text{Ba}(\text{OH})_2$ at infinite dilution is $\boxed{525 \text{ S cm}^2 \text{mol}^{-1}}$.

Quick Tip to Solve: Use dissociation coefficients as multipliers: one barium ion and two hydroxide ions give $127 + 2(199)$, not $2(127) + 199$.

31. An antifreeze solution is prepared by dissolving 31 g of ethylene glycol (Molar mass = 62 g mol⁻¹) in 600 g of water. Calculate the freezing point of the solution. (K_f for water = 1.86 K kg mol⁻¹) [3 marks]

Solution:

Concept:

- A non-volatile solute lowers the freezing point of its solvent. For a dilute solution, the depression is $\Delta T_f = iK_fm$, where K_f is the molal depression constant and m is the number of moles of solute per kilogram of solvent.
- Ethylene glycol is a molecular non-electrolyte, so $i = 1$. The freezing point of the solution is $T_f = T_f^\circ - \Delta T_f$, where T_f° is the freezing point of pure water.

Step 1: Calculate moles of ethylene glycol and molality The mass of ethylene glycol is 31 g, and its molar mass is 62 g mol⁻¹. Therefore,

$$n = \frac{31}{62} = 0.500 \text{ mol.}$$

The mass of water is 600 g = 0.600 kg. Molality uses the mass of solvent, not the total mass of the solution:

$$m = \frac{0.500}{0.600} = \frac{5}{6} \text{ mol kg}^{-1}.$$

No additional particle factor is needed because ethylene glycol does not dissociate into ions in water.

Step 2: Find the freezing point depression and solution temperature Using $K_f = 1.86 \text{ K kg mol}^{-1}$,

$$\Delta T_f = K_fm = 1.86 \times \frac{5}{6} = 1.55 \text{ K.}$$

Pure water freezes at 0 °C under normal pressure. A temperature decrease of 1.55 K has the same magnitude as a decrease of 1.55 °C, so

$$T_f = 0 - 1.55 = -1.55 \text{ °C.}$$

Equivalently, the temperature is 273.15 – 1.55 = 271.60 K. The negative Celsius value is expected because an antifreeze solution remains liquid below the freezing point of pure water.

Step 3: Conclusion The freezing point of the solution is -1.55 °C , or 271.60 K .

Quick Tip to Solve: Convert the 600 g of water to 0.600 kg before finding molality, then subtract the depression from zero on the Celsius scale.

32. Account for the following:

(a) Aniline is a weaker base compared to ethanamine.

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

(c) Only aliphatic primary amines can be prepared by Gabriel Phthalimide synthesis.

[3 marks]

Solution:

Concept:

- An amine acts as a base by donating the nitrogen lone pair to a proton. Greater availability of this lone pair increases basicity.
- Resonance, inductive effects and coordination to a Lewis acid alter electron availability; Gabriel synthesis forms an amine through nucleophilic substitution followed by hydrolysis.

Step 1: (a) Compare the availability of the nitrogen lone pair In aniline, $C_6H_5NH_2$, the nitrogen lone pair is delocalised into the benzene ring by resonance. It is therefore less readily available for bonding to H^+ . In ethanamine, $C_2H_5NH_2$, the lone pair is localised on nitrogen and the ethyl group's positive inductive effect increases electron density on nitrogen. Proton acceptance is consequently easier for ethanamine, explaining the observed order of basicity.

Step 2: (b) Examine the action of the Friedel-Crafts catalyst Friedel-Crafts alkylation and acylation normally require the Lewis acid $AlCl_3$. Aniline donates its nitrogen lone pair to this catalyst and forms a Lewis acid-base adduct (salt). Nitrogen then bears positive character, so the attached group strongly withdraws electron density from the ring. This deactivates the aromatic ring towards electrophilic substitution under Friedel-Crafts conditions; hence the usual alkylation or acylation does not occur.

Step 3: (c) Apply the substitution requirement of Gabriel synthesis The phthalimide anion reacts with an alkyl halide by nucleophilic substitution to form an *N*-alkylphthalimide. Hydrolysis releases the corresponding primary amine, RNH_2 . The nitrogen acquires only one alkyl group before hydrolysis, so secondary and tertiary amines are not formed. Aryl halides do not undergo the required substitution with the phthalimide anion under these conditions: the aryl carbon-halogen bond has partial double-bond character and the carbon is sp^2 -hybridised. Aromatic primary amines therefore cannot be prepared by this method.

Step 4: Conclusion Aniline is weaker than ethanamine because resonance reduces lone-pair availability. Its reaction with $AlCl_3$ deactivates the ring towards Friedel-Crafts reaction. Gabriel synthesis gives aliphatic primary amines because alkyl, but not aryl, halides undergo the required substitution.

Quick Tip to Solve: For these three reasons, track the nitrogen lone pair first, then check whether the halide has an alkyl or aryl carbon bonded to the halogen.

33(a). Give the IUPAC name and electronic configuration of central metal atom in terms of t_{2g} and e_g of $K_4[Mn(CN)_6]$.

(b) What is meant by 'Chelate effect'? Give an example.

[3 marks]

Solution:

Concept:

- The metal oxidation state follows from the complex charge and ligand charges. In an octahedral complex, the five d orbitals split into lower-energy t_{2g} and higher-energy e_g sets.
- A strong-field ligand favours electron pairing in t_{2g} . The chelate effect is the enhanced stability associated with binding through multidentate ligands that form rings with the metal.

Step 1: (a) Determine the oxidation state and name the compound In $K_4[Mn(CN)_6]$, four K^+ ions balance the complex ion $[Mn(CN)_6]^{4-}$. Each cyanido ligand has charge -1 . If manganese has oxidation state x ,

$$x + 6(-1) = -4, \quad x = +2.$$

The six ligands give the prefix hexacyanido; because the coordination entity is an anion, the metal name becomes manganate. The compound is named potassium hexacyanidomanganate(II).

Step 2: (a) Fill the octahedral crystal-field levels Neutral manganese has configuration $[Ar] 3d^5 4s^2$. Loss of the two $4s$ electrons produces Mn^{2+} with configuration $3d^5$. The six cyanido ligands create an octahedral field and are strong-field ligands. Pairing in the lower t_{2g} orbitals is favoured before occupation of e_g . Thus the five d electrons give

$$t_{2g}^5 e_g^0.$$

Two of the three t_{2g} orbitals are doubly occupied and the third is singly occupied.

Step 3: (b) Explain the chelate effect with an example A multidentate ligand binds to the same metal ion through two or more donor atoms, forming one or more chelate rings. The resulting complex has greater stability than comparable complexes with related monodentate ligands; this enhanced stability is called the chelate effect. For example, ethane-1,2-diamine (en), $H_2NCH_2CH_2NH_2$, binds through both nitrogen atoms. In $[Ni(en)_3]^{2+}$, the three bidentate en ligands form three five-membered chelate rings. This illustrates the enhanced stability of chelation relative to the corresponding ammine complex, $[Ni(NH_3)_6]^{2+}$.

Step 4: Conclusion The name is potassium hexacyanidomanganate(II), and the central Mn^{2+} ion has configuration $t_{2g}^5 e_g^0$. The chelate effect is increased complex stability through multidentate ring-forming ligands, as illustrated by $[Ni(en)_3]^{2+}$.

Quick Tip to Solve: Find the complex charge from the four potassium ions before counting manganese's d electrons; strong-field cyanido then gives the low-spin filling.

33(b). Write the hybridisation and magnetic characters of the following complexes:



[Atomic number: Fe = 26, Co = 27, Ni = 28]

[3 marks]

Solution:

Concept:

- Find the metal oxidation state before counting its d electrons. Ligand strength determines whether pairing leaves inner $3d$ orbitals available for hybridisation in an octahedral complex.
- A complex with unpaired electrons is paramagnetic; one with all electrons paired is diamagnetic. Octahedral complexes may use d^2sp^3 or sp^3d^2 hybridisation, while tetrahedral complexes use sp^3 .

Step 1: (i) Analyse the hexacyanidoferrate(II) ion For $[\text{Fe}(\text{CN})_6]^{4-}$, let the iron oxidation state be x . Then $x - 6 = -4$, so iron is Fe^{2+} , with configuration $3d^6$. Cyanido is a strong-field ligand and pairs the six electrons in three $3d$ orbitals, leaving two inner $3d$ orbitals vacant. These combine with one $4s$ and three $4p$ orbitals to form six d^2sp^3 hybrid orbitals. The complex is octahedral and low spin, with $t_{2g}^6e_g^0$. All electrons are paired, so it is diamagnetic.

Step 2: (ii) Analyse the hexafluoridocobaltate(III) ion For $[\text{CoF}_6]^{3-}$, $x - 6 = -3$, giving Co^{3+} and a $3d^6$ configuration. Fluorido is a weak-field ligand, so it does not produce the pairing needed to vacate two inner $3d$ orbitals. The complex uses one $4s$, three $4p$ and two outer $4d$ orbitals, giving sp^3d^2 hybridisation and octahedral geometry. Its high-spin filling is $t_{2g}^4e_g^2$, containing four unpaired electrons. It is therefore paramagnetic.

Step 3: (iii) Analyse tetracarbonylnickel(0) In $[\text{Ni}(\text{CO})_4]$, all four carbonyl ligands are neutral, so nickel has oxidation state zero. Free nickel has configuration $[\text{Ar}] 3d^84s^2$. In the valence-bond description of this complex, the electrons pair to give a filled $3d^{10}$ set, leaving $4s$ and the three $4p$ orbitals available. These four orbitals form sp^3 hybrids, which accept the ligand lone pairs and give tetrahedral geometry. The filled $3d$ set has no unpaired electrons, so the complex is diamagnetic.

Step 4: Conclusion $[\text{Fe}(\text{CN})_6]^{4-}$: d^2sp^3 , diamagnetic. $[\text{CoF}_6]^{3-}$: sp^3d^2 , paramagnetic with four unpaired electrons. $[\text{Ni}(\text{CO})_4]$: sp^3 , diamagnetic.

Quick Tip to Solve: Both metal ions in the first two complexes are d^6 , so use ligand strength to distinguish their pairing; neutral carbonyl leaves nickel in oxidation state zero.

34. Justify and arrange the following compounds namely, ethyl chloride, isopropyl chloride, tertiary butyl chloride in increasing order of reactivity towards the asked displacement namely:

(a) S_N1

(b) S_N2

[3 marks]

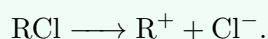
Solution:

Concept:

- In an S_N1 reaction, slow ionisation forms a carbocation. Greater carbocation stability increases the rate, other conditions being comparable.
- An S_N2 reaction occurs by a concerted backside attack of the nucleophile. Alkyl groups near the reacting carbon hinder this approach and decrease the rate.

Step 1: Classify the carbon bearing chlorine Ethyl chloride, $\text{CH}_3\text{CH}_2\text{Cl}$, is primary; isopropyl chloride, $(\text{CH}_3)_2\text{CHCl}$, is secondary; and tertiary butyl chloride, $(\text{CH}_3)_3\text{CCl}$, is tertiary. All three have the same leaving group, chloride, so the different substitution at the reacting carbon controls their relative behaviour under comparable reaction conditions.

Step 2: Compare carbocation formation for part (a) Heterolytic cleavage of the carbon–chlorine bond is the rate-determining step of the S_N1 pathway:



The three compounds would form primary ethyl, secondary isopropyl and tertiary butyl carbocations, respectively. Electron donation by alkyl groups through the positive inductive effect and hyperconjugation stabilises the positive charge. Carbocation stability therefore increases from primary to secondary to tertiary, making ionisation easiest for tertiary butyl chloride. Ethyl chloride is least reactive by this mechanism because its primary carbocation is highly unstable.

Step 3: Compare steric hindrance for part (b) In S_N2 , the nucleophile must approach the carbon from the side opposite the carbon–chlorine bond while chloride leaves. There is no carbocation intermediate. Ethyl chloride presents the least steric obstruction, isopropyl chloride presents more, and tertiary butyl chloride presents the most. The crowded tertiary carbon strongly suppresses backside attack, so the S_N2 trend reverses the S_N1 trend.

Step 4: Conclusion The increasing orders of reactivity are:

(a) S_N1 : ethyl chloride < isopropyl chloride < tertiary butyl chloride.

(b) S_N2 : tertiary butyl chloride < isopropyl chloride < ethyl chloride.

Quick Tip to Solve: First label the reacting carbon primary, secondary or tertiary. For S_N1 , favour carbocation stability; for S_N2 , favour the least crowded carbon.

Section D (15 marks)

35. An amorphous solid 'A' which has a crown shaped structure, burns in air to form a gas 'B' which turns lime water milky. 'B' is also produced by roasting of sulphide ores. 'B' undergoes oxidation in the presence of V_2O_5 to give 'C' and to carry out this oxidation low temperature and high pressure is mandatory to get a good yield of 'C'. 'C' is then absorbed in H_2SO_4 to give 'D'. 'D' is then diluted to give a very important compound 'E'. 'E' is largely responsible for the manufacture of variety of compounds in industry. 'E' in concentrated form, when combined with Cu metal, gives compound 'F'. From this description

[5 marks]

35(a). Elucidate the structure of 'A' to 'F'.

[3 marks]

Solution:

Concept:

- Sulphur burns to form sulphur dioxide, which is oxidised to sulphur trioxide in the contact process. The successive products identify the substances in the passage.
- Sulphur trioxide is absorbed in concentrated sulphuric acid to form oleum, represented by $H_2S_2O_7$. Diluting oleum produces sulphuric acid.

Step 1: Identify the sulphur and its two oxides The crown-shaped molecule identifies A as sulphur, S_8 : eight sulphur atoms form a puckered ring, with each atom bonded to two neighbours. Burning sulphur gives B, sulphur dioxide, SO_2 . Its molecule is bent or V-shaped, with sulphur as the central atom. The gas forms white calcium sulphite with lime water, accounting for the milky appearance:



Oxidation of SO_2 over V_2O_5 gives C, sulphur trioxide, SO_3 . It has a trigonal planar molecular structure: three oxygen atoms surround the central sulphur atom, with bond angles of approximately 120° .

Step 2: Identify oleum and sulphuric acid Absorption of SO_3 in H_2SO_4 gives D, oleum or pyrosulphuric acid, represented by $H_2S_2O_7$. Its structural formula is



The two sulphur atoms are linked through a bridging oxygen atom. Each sulphur is approximately tetrahedrally surrounded by oxygen atoms. Adding water gives E, sulphuric acid, H_2SO_4 , whose structural formula is $HO - S(=O)_2 - OH$. The four oxygen atoms around sulphur have a tetrahedral arrangement.

Step 3: Identify the copper compound Hot concentrated sulphuric acid oxidises copper metal to copper(II) sulphate while some acid is reduced to sulphur dioxide. Thus F is copper(II) sulphate, $CuSO_4$. It is an ionic compound consisting of Cu^{2+} and SO_4^{2-} ions; the sulphate ion has a tetrahedral arrangement of four oxygen atoms around sulphur. No water of crystallisation is specified in this reaction, so the formula required here is $CuSO_4$.

Step 4: Conclusion A = S_8 (puckered crown ring), B = SO_2 (bent), C = SO_3 (trigonal planar), D = $H_2S_2O_7$ (two sulphur centres joined by oxygen), E = H_2SO_4 (tetrahedral oxygen arrangement) and F = $CuSO_4$ (Cu^{2+} and tetrahedral SO_4^{2-} ions).

Quick Tip to Solve: Trace the contact-process chain in order: sulphur, sulphur dioxide, sulphur trioxide, oleum and sulphuric acid; copper then identifies the final salt.

35(b). Give a balanced chemical equation for the conversion of 'E' to 'F'.

[1 mark]

Solution:

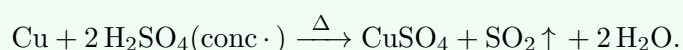
Concept:

- Hot concentrated sulphuric acid acts as an oxidising agent. Copper is oxidised from 0 to +2, while sulphur in some of the acid is reduced from +6 to +4.
- The reaction forms copper(II) sulphate, sulphur dioxide and water; atom balance determines their coefficients.

Step 1: Identify the reactants and products Here E is H_2SO_4 and F is $CuSO_4$. Copper reacts with hot concentrated acid; dilute sulphuric acid does not give this reaction with copper. The gaseous reduction product is SO_2 , rather than hydrogen.

Step 2: Balance the reaction One copper atom forms one formula unit of $CuSO_4$. Two molecules of H_2SO_4 supply two sulphur atoms: one remains in the sulphate salt and one forms SO_2 . Their four hydrogen atoms form two water molecules. The oxygen count is eight on each side, completing the balance.

Step 3: Conclusion The balanced conversion is



Quick Tip to Solve: With copper and hot concentrated sulphuric acid, write sulphur dioxide as the gas, then use two acid molecules to balance both sulphur products.

35(c). Give two important functions of 'E' in the chemical industry.

[1 mark]

Solution:

Concept:

- E is sulphuric acid, H_2SO_4 , an important bulk chemical used in the manufacture of many industrial products.
- An industrial function can be stated by naming the product or process for which the acid is used.

Step 1: State its role in fertiliser manufacture Sulphuric acid is used to manufacture fertilisers such as ammonium sulphate and superphosphate. In the first example it reacts with ammonia to supply the sulphate component of the fertiliser; in the second it is used to process phosphate rock.

Step 2: State its role in petroleum refining Sulphuric acid is used in petroleum refining. Acid treatment helps remove certain impurities from petroleum fractions during processing, improving the quality of the refined products. This is a distinct industrial use from fertiliser manufacture.

Step 3: Conclusion Two important industrial functions of E , sulphuric acid, are **manufacture of fertilisers** and **petroleum refining**.

Quick Tip to Solve: First identify E as sulphuric acid, then name two distinct industries: fertilisers and petroleum refining.

35(a). Give reasons for the following observations:

(i) Halogens are strong oxidising agents.

(ii) Noble gases have very low boiling points.

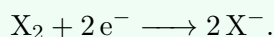
(iii) O and Cl have nearly same electronegativity, yet oxygen forms H bond while Cl doesn't. [3 marks]

Solution:

Concept:

- An oxidising agent accepts electrons and is itself reduced; halogen atoms have the valence-shell configuration ns^2np^5 .
- Boiling separates particles against their intermolecular attractions. Weak attractions require little thermal energy to overcome.
- Strong hydrogen bonding depends on both high electronegativity and small atomic size, which concentrates charge near the bonded hydrogen.

Step 1: Explain the oxidising action of halogens A halogen atom needs only one electron to complete its outer shell. Halogens have high electronegativity and a strong tendency to accept electrons from another substance. They therefore oxidise that substance while being reduced to halide ions:



This electron-accepting tendency accounts for their strong oxidising action; the tendency generally decreases from fluorine to iodine.

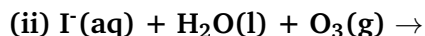
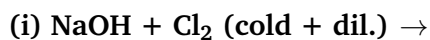
Step 2: Relate noble-gas boiling points to their attractions Noble gases have completely filled valence shells and exist as separate, monatomic particles. They have neither permanent molecular dipoles nor hydrogen bonds. Only weak London dispersion forces act between their atoms. Consequently, little energy is needed to separate the atoms into the gas phase, so their boiling points are very low.

Step 3: Compare the sizes of oxygen and chlorine Oxygen is much smaller than chlorine. Its compact electron cloud and high electronegativity allow a strongly polar O–H bond and a close, strong attraction between hydrogen and a lone pair on a neighbouring oxygen atom. Chlorine's larger, more diffuse electron cloud has lower charge density; comparable electronegativity alone does not produce the strong intermolecular hydrogen bonding seen in oxygen compounds such as water. Thus HCl does not show appreciable hydrogen bonding of this type.

Step 4: Conclusion Halogens readily gain electrons; noble-gas atoms attract one another only weakly; and oxygen's small size, together with high electronegativity, permits strong hydrogen bonding whereas chlorine's larger size does not.

Quick Tip to Solve: For hydrogen-bonding comparisons, check atomic size as well as electronegativity; oxygen and chlorine illustrate why electronegativity alone is insufficient.

35(b). Complete and balance the following chemical equations:



[2 marks]

Solution:

Concept:

- Chlorine disproportionates in cold, dilute alkali: the same element is both reduced and oxidised, giving chloride and hypochlorite.
- Ozone is a strong oxidising agent. In water it oxidises iodide ions to iodine while being reduced to oxygen.

Step 1: Balance chlorine with cold, dilute sodium hydroxide Chlorine changes from oxidation state 0 to -1 in chloride and to $+1$ in hypochlorite. Equal amounts of the two products balance the electron transfer:



The conditions are cold, dilute aqueous NaOH. Both sides contain two sodium atoms, two chlorine atoms, two oxygen atoms and two hydrogen atoms. Hot, concentrated alkali gives a different oxyanion, so the stated conditions must be retained.

Step 2: Balance ozone with aqueous iodide Two iodide ions each lose one electron to form iodine. The corresponding reduction of ozone in water produces oxygen and hydroxide ions. The balanced net ionic equation is



The total charge is -2 on each side. There are two iodine atoms, two hydrogen atoms and four oxygen atoms on both sides, confirming the atom balance as well.

Step 3: Conclusion (i) The products are NaCl, NaClO and H_2O , with coefficients 1, 1, 1 for 1 mole of Cl_2 and 2 moles of NaOH. (ii) Ozone produces I_2 , OH^- and O_2 as shown in the balanced ionic equation.

Quick Tip to Solve: Remember cold, dilute alkali gives hypochlorite; in the ozone equation check both oxygen atoms and the total ionic charge.

36(a). An organic compound 'A' having molecular formula $\text{C}_5\text{H}_{10}\text{O}$ gives negative Tollens' test, forms n-pentane on Clemmensen reduction but doesn't give iodoform test. Identify 'A' and give all the reactions involved.

[2 marks]

Solution:

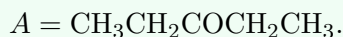
Concept:

- Ordinary ketones do not reduce Tollens' reagent; aldehydes give a silver mirror. Clemmensen reduction converts a carbonyl group into a methylene group using $\text{Zn}(\text{Hg})$ and concentrated HCl.
- A methyl ketone contains the group CH_3CO^- and gives the iodoform test. A ketone lacking this

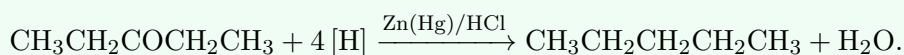
Quick Tip to Solve: First use the reduction product to fix the carbon skeleton; then use the iodoform result to choose between pentan-2-one and pentan-3-one.

group gives a negative result.

Step 1: Identify the carbon skeleton and carbonyl position Formation of *n*-pentane on Clemmensen reduction establishes a straight five-carbon skeleton. The negative Tollens' test excludes pentanal, leaving the straight-chain ketones pentan-2-one and pentan-3-one. Pentan-2-one contains CH_3CO^- and would give iodoform; the negative iodoform test selects the symmetrical ketone with the carbonyl at carbon 3:



Step 2: Write the reduction and the test observations Clemmensen reduction removes the carbonyl oxygen without changing the carbon skeleton:



With Tollens' reagent, $[\text{Ag}(\text{NH}_3)_2]^+$ in alkaline solution, pentan-3-one gives no reaction and no silver mirror. With I_2/NaOH , it gives no iodoform reaction and no yellow precipitate of CHI_3 , because neither side of its carbonyl group is a methyl group. These negative tests agree with the proposed structure.

Step 3: Conclusion Compound *A* is pentan-3-one, $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$. It reduces to *n*-pentane and gives negative Tollens' and iodoform tests.

Quick Tip to Solve: First use the reduction product to fix the carbon skeleton; then use the iodoform result to choose between pentan-2-one and pentan-3-one.

36(b). Carry out the following conversions:

(i) Propanoic acid to 2-Bromopropanoic acid

(ii) Benzoyl chloride to benzaldehyde

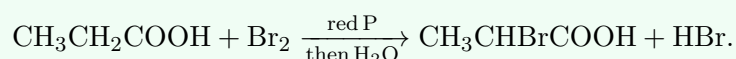
[2 marks]

Solution:

Concept:

- The Hell-Volhard-Zelinsky (HVZ) reaction replaces an alpha hydrogen of a carboxylic acid by halogen using halogen and red phosphorus, followed by hydrolysis.
- Rosenmund reduction converts an acyl chloride into an aldehyde using hydrogen over a poisoned palladium catalyst supported on barium sulphate.

Step 1: Brominate propanoic acid at the alpha carbon Propanoic acid contains alpha hydrogens on the carbon next to COOH . Treat it with Br_2 and red phosphorus, then hydrolyse the intermediate acyl bromide. The net transformation is

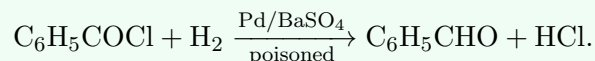


Numbering begins at the carboxyl carbon, so the bromine is attached to carbon 2. This gives the required 2-bromopropanoic acid by the HVZ reaction.

Step 2: Reduce benzoyl chloride selectively Pass hydrogen over benzoyl chloride in the presence

Quick Tip to Solve: Alpha bromination of an acid suggests HVZ; conversion of an acyl chloride to an aldehyde suggests Rosenmund reduction with a poisoned catalyst.

of poisoned Pd/BaSO₄; sulphur or quinoline may be used to poison the catalyst. The Rosenmund reaction is



The controlled catalyst activity allows reduction of the acyl chloride to the aldehyde while suppressing further reduction to benzyl alcohol. The benzene ring and carbon skeleton remain unchanged.

Step 3: Conclusion Use Br₂/red phosphorus followed by hydrolysis for propanoic acid to 2-bromopropanoic acid, and H₂ with poisoned Pd/BaSO₄ for benzoyl chloride to benzaldehyde.

Quick Tip to Solve: Alpha bromination of an acid suggests HVZ; conversion of an acyl chloride to an aldehyde suggests Rosenmund reduction with a poisoned catalyst.

36(c). How will you distinguish between benzaldehyde and acetaldehyde?

[1 mark]

Solution:

Concept:

- The iodoform test detects the CH₃CO– group; acetaldehyde also responds because it contains CH₃CHO.
- A positive test gives a yellow precipitate of iodoform, CHI₃, with iodine and aqueous sodium hydroxide.

Step 1: Test the two samples Warm separate samples with iodine and aqueous NaOH. Acetaldehyde produces a yellow precipitate:

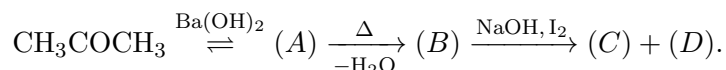


Step 2: Compare the observation Benzaldehyde, C₆H₅CHO, lacks the required methyl group adjoining the carbonyl carbon and gives no yellow iodoform precipitate. Tollens' reagent is unsuitable for distinguishing this pair because both compounds are aldehydes and both give a silver mirror.

Step 3: Conclusion Acetaldehyde gives yellow CHI₃ with I₂/NaOH; benzaldehyde does not.

Quick Tip to Solve: For this aldehyde pair, use iodoform rather than Tollens' reagent: only acetaldehyde gives the yellow precipitate.

36(a)(i). Complete the following sequence of reactions:



Identify (A) to (D).

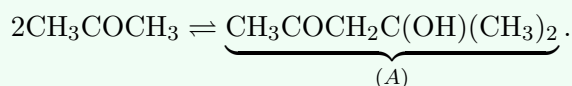
[2 marks]

Solution:

Concept:

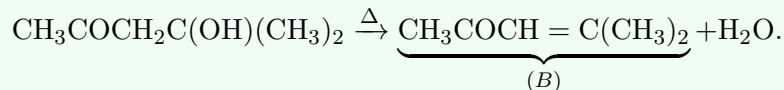
- Acetone has α -hydrogen atoms and undergoes base-catalysed aldol addition: two molecules join to form a β -hydroxy ketone.
- Heating removes water from the aldol product. A methyl ketone then gives CHI_3 and a carboxylate salt with I_2/NaOH .

Step 1: Form the aldol addition product In the presence of $\text{Ba}(\text{OH})_2$, the enolate of one acetone molecule attacks the carbonyl carbon of another. Protonation produces diacetone alcohol:



The product retains one ketone group and has an OH group at the beta carbon relative to it.

Step 2: Dehydrate the addition product Heating eliminates OH from the beta carbon and H from the adjacent alpha carbon, forming the conjugated double bond:



This product is mesityl oxide, an unsaturated methyl ketone.

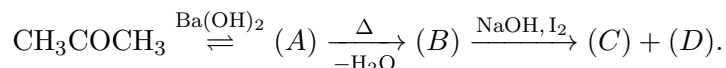
Step 3: Apply the iodoform reaction The $\text{CH}_3\text{CO}-$ group in (B) undergoes the haloform reaction. Its methyl carbon becomes CHI_3 , while the carbonyl carbon remains in the sodium carboxylate. Writing (B) as RCOCH_3 , with $\text{R} = (\text{CH}_3)_2\text{C}=\text{CH}-$, the balanced reaction is



Step 4: Conclusion (A) = $\text{CH}_3\text{COCH}_2\text{C}(\text{OH})(\text{CH}_3)_2$; (B) = $\text{CH}_3\text{COCH}=\text{C}(\text{CH}_3)_2$. The final products are (C) = $(\text{CH}_3)_2\text{C}=\text{CHCOONa}$ and (D) = CHI_3 (their labels may be interchanged).

Quick Tip to Solve: In the last step, replace the methyl group of the methyl ketone by ONa at the carbonyl carbon; that methyl carbon becomes iodoform.

36(a)(ii). Complete the following sequence of reactions:



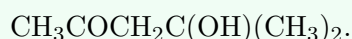
Give the IUPAC name of (A).

[1 mark]

Solution:

Concept:

- Acetone undergoes aldol addition with $\text{Ba}(\text{OH})_2$. The product is a beta-hydroxy ketone:



- In IUPAC naming, the ketone group has priority over the alcohol group: the ketone uses the suffix and OH is named as the hydroxy prefix.

Step 1: Select and number the parent chain Write (A) as $\text{CH}_3\text{COCH}_2\text{C}(\text{OH})(\text{CH}_3)_2$. The longest chain containing the carbonyl group has five carbons. Number it from the end nearer the carbonyl so that the ketone carbon is C-2; the parent is pentan-2-one.

Step 2: Locate the substituents Carbon 4 bears both the hydroxy group and a methyl substituent. Place their prefixes before the parent name in alphabetical order: hydroxy precedes methyl. The common name diacetone alcohol describes the same compound but is not the requested systematic name.

Step 3: Conclusion The IUPAC name of (A) is 4-hydroxy-4-methylpentan-2-one.

Quick Tip to Solve: Give the carbonyl the lower number and the suffix; treat the OH group as hydroxy because ketone has higher naming priority.

36(b). How can you distinguish between:

(i) Ethanol and Propanone, and

(ii) Benzoic acid and Phenol?

[2 marks]

Solution:

Concept:

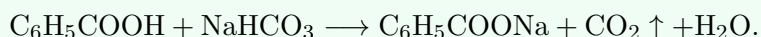
- Aldehydes and ketones react with 2,4-dinitrophenylhydrazine (2,4-DNP) to form coloured hydrazone precipitates; ordinary alcohols do not.
- Carboxylic acids are sufficiently acidic to liberate carbon dioxide from sodium hydrogencarbonate. Phenol is too weak an acid to give this test.

Step 1: Distinguish ethanol and propanone Add 2,4-DNP reagent separately to the two liquids. Propanone contains a ketone carbonyl group and gives a yellow or orange precipitate of its 2,4-dinitrophenylhydrazone. Ethanol contains an alcohol group and gives no precipitate. Hence a positive 2,4-DNP test identifies propanone. The iodoform test is unsuitable here: both propanone and ethanol

Quick Tip to Solve: Avoid iodoform for ethanol versus propanone, as both respond; use 2,4-DNP for this pair and bicarbonate for acid versus phenol.

give it, since ethanol is first oxidised to acetaldehyde under the test conditions.

Step 2: Distinguish benzoic acid and phenol Add aqueous sodium hydrogencarbonate to separate samples. Benzoic acid gives brisk effervescence of carbon dioxide:



The gas turns limewater milky, confirming carbon dioxide. Phenol does not liberate carbon dioxide with this reagent because its acidity is insufficient to displace carbonic acid from its salt.

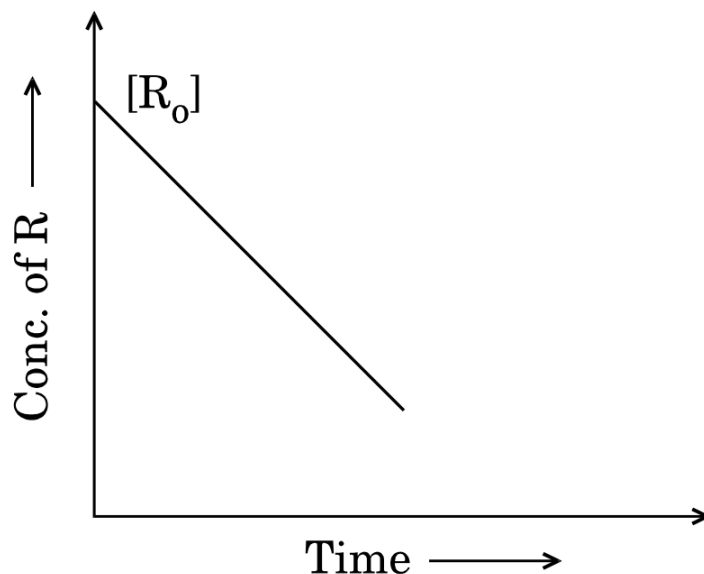
Step 3: Conclusion (i) 2,4-DNP: propanone gives a coloured precipitate; ethanol does not. (ii) NaHCO_3 : benzoic acid gives CO_2 effervescence; phenol does not.

Quick Tip to Solve: Avoid iodoform for ethanol versus propanone, as both respond; use 2,4-DNP for this pair and bicarbonate for acid versus phenol.

37(a). Visha plotted a graph between concentration of R and time for a reaction $\text{R} \rightarrow \text{P}$. On the basis of this graph, answer the following questions:

- (i) Predict the order of reaction.
- (ii) What does the slope of the line indicate?
- (iii) What are the units of rate constant?

[3 marks]



Solution:

Concept:

- For a zero-order reaction, the rate is independent of reactant concentration: $-d[R]/dt = k$, where $[R]$ is the concentration of R and k is the rate constant.
- Integration gives $[R] = [R]_0 - kt$, where $[R]_0$ is the initial concentration. A plot of concentration against time is therefore a straight line of negative slope.

Step 1: Identify the order from the plotted axes The vertical axis represents concentration $[R]$, not its

Quick Tip to Solve: Read the vertical axis before identifying order: a straight decreasing concentration-versus-time line means zero order and slope minus k .

logarithm or reciprocal, and the horizontal axis represents time. The observed straight line decreases from the intercept $[R]_0$. Compare its form with the integrated rate law

$$[R] = [R]_0 - kt.$$

This is the zero-order law. Equal intervals of time correspond to equal decreases in concentration. For a first-order reaction, it is $\ln[R]$, rather than $[R]$, that varies linearly with time.

Step 2: Interpret the slope Comparing with $y = c + mx$, take $y = [R]$, $x = t$, and $c = [R]_0$. Thus the signed slope is

$$m = \frac{\Delta[R]}{\Delta t} = -k.$$

Concentration decreases, so the slope is negative, while the rate constant is positive. The magnitude of the slope gives k , and also the constant rate of disappearance of R during the zero-order interval.

Step 3: Obtain the units of the rate constant From $k = ([R]_0 - [R])/t$, its dimensions are concentration divided by time. With concentration measured in mol L^{-1} and time in seconds,

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

If a different time unit is used on the graph, the corresponding inverse time unit is used in k .

Step 4: Conclusion (i) The reaction is zero order. (ii) The slope equals $-k$; its magnitude gives the rate constant. (iii) The usual units of k are $\boxed{\text{mol L}^{-1} \text{s}^{-1}}$.

Quick Tip to Solve: Read the vertical axis before identifying order: a straight decreasing concentration-versus-time line means zero order and slope minus k .

37(b). A first order reaction takes 25 minutes for 25% decomposition. Calculate $t_{1/2}$.

[Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$]

[2 marks]

Solution:

Concept:

- For a first order reaction, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$, where $[R]_0$ and $[R]_t$ are the initial and remaining reactant concentrations.
- The half-life is $t_{1/2} = \frac{2.303 \log 2}{k}$; it is independent of the initial concentration.

Step 1: Identify the concentration remaining Decomposition of 25% means that 75% of the initial reactant remains after 25 min. Thus $[R]_t = \frac{3}{4}[R]_0$, and the ratio needed in the integrated rate law is $[R]_0/[R]_t = 4/3$, not 4. Using the supplied logarithms,

$$\log(4/3) = \log 4 - \log 3 = 0.6021 - 0.4771 = 0.1250.$$

Step 2: Calculate the rate constant and half-life Substitute the time and remaining concentration

Quick Tip to Solve: Convert percentage decomposed to percentage remaining first: here use 100/75, then calculate $t_{1/2} = t \log 2 / \log(100/75)$.

ratio:

$$k = \frac{2.303}{25}(0.1250) = 0.011515 \text{ min}^{-1}.$$

The half-life corresponds to the concentration falling to one-half of its initial value. Therefore,

$$t_{1/2} = \frac{2.303(0.3010)}{0.011515} = 25 \frac{0.3010}{0.1250} \text{ min}.$$

The units remain minutes because the supplied decomposition time was in minutes.

Step 3: Conclusion The half-life of the reaction is $t_{1/2} = 60.2 \text{ min}$.

Quick Tip to Solve: Convert percentage decomposed to percentage remaining first: here use 100/75, then calculate $t_{1/2} = t \log 2 / \log(100/75)$.

OR

37(a). The rate constant for a first order reaction is 60 s^{-1} . How much time will it take to reduce the initial concentration of the reactant to its $1/16^{\text{th}}$ value? [3 marks]

Solution:

Concept:

- For a first order reaction, the rate is proportional to reactant concentration, and its integrated rate law is $kt = \ln([R]_0/[R]_t)$.
- In common logarithms, $t = \frac{2.303}{k} \log([R]_0/[R]_t)$, where k is the rate constant and $[R]_t$ is the concentration remaining at time t .
- Each half-life reduces the remaining concentration by a factor of two; for first order kinetics, $t_{1/2} = \ln 2/k$.

Step 1: Express the final concentration as a fraction Let the initial concentration be $[R]_0$. The required final concentration is $[R]_t = [R]_0/16$. Consequently,

$$\frac{[R]_0}{[R]_t} = \frac{[R]_0}{[R]_0/16} = 16.$$

The unknown initial concentration cancels, so its numerical value is unnecessary. The fraction $1/16$ describes the reactant remaining, not the fraction that has decomposed.

Step 2: Substitute in the integrated first order law The given rate constant is $k = 60 \text{ s}^{-1}$. Keeping this unit throughout gives time in seconds:

$$\begin{aligned} t &= \frac{2.303}{60} \log 16 \\ &= \frac{2.303}{60} (4 \log 2) \\ &\approx \frac{2.303 \times 4 \times 0.3010}{60} \text{ s}. \end{aligned}$$

Quick Tip to Solve: Recognise $1/16 = (1/2)^4$: a first order reaction reaches this fraction after exactly four half-lives.

The logarithm is dimensionless, and division by s^{-1} supplies the required time unit.

Step 3: Check using successive half-lives The concentration follows the sequence $[R]_0$, $[R]_0/2$, $[R]_0/4$, $[R]_0/8$, $[R]_0/16$, so four half-lives are required. Since $t_{1/2} = 0.693/60$ s, the total time is $4(0.693/60)$ s, consistent with the integrated-law calculation.

Step 4: Conclusion The time required is $t \approx 0.0462 \text{ s} = 4.62 \times 10^{-2} \text{ s}$.

Quick Tip to Solve: Recognise $1/16 = (1/2)^4$: a first order reaction reaches this fraction after exactly four half-lives.

37(b). Write two factors that affect the rate of a chemical reaction.

[1 mark]

Solution:

Concept:

- Reaction rate depends on the frequency of effective collisions between reacting particles.
- Reactant concentration affects how often particles encounter one another; temperature affects their kinetic energies and the fraction able to overcome the activation barrier.

Step 1: State the concentration factor The concentration of the reactants affects reaction rate. For reactions with a positive order in a reactant, increasing its concentration increases the rate because more reacting particles occupy a given volume and encounters become more frequent.

Step 2: State the temperature factor The temperature of the reacting system affects reaction rate. A rise in temperature generally increases the rate by increasing the fraction of collisions having sufficient energy to cross the activation barrier.

Step 3: Conclusion Two factors are $\boxed{\text{reactant concentration and temperature}}$.

Quick Tip to Solve: Name the factors explicitly: concentration controls particle encounters, while temperature strongly affects the fraction of energetic collisions.

37(c). Write two conditions for the collisions to be effective collisions.

[1 mark]

Solution:

Concept:

- Collision theory distinguishes effective collisions, which form products, from collisions that leave reactants unchanged.
- Both sufficient collision energy and suitable molecular orientation are necessary for a collision to be effective.

Step 1: State the energy condition The colliding molecules must possess energy equal to or greater than the threshold energy. They must be able to overcome the activation-energy barrier so that the reacting system can reach the activated complex.

Step 2: State the orientation condition The molecules must collide with proper orientation, bringing

Quick Tip to Solve: Always pair the energy requirement with orientation; sufficient energy alone does not ensure product formation.

the reactive sites into suitable contact for bond rearrangement. Even an energetic collision can be ineffective if the molecules approach in an unsuitable orientation.

Step 3: Conclusion Effective collisions require sufficient energy and proper orientation, with both conditions satisfied together.

Quick Tip to Solve: Always pair the energy requirement with orientation; sufficient energy alone does not ensure product formation.