

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

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

[1 mark]

Solution:

Concept:

- An amino acid contains both amino and carboxyl functional groups.
- Its acidic or basic character depends on the relative number of carboxyl groups, $-\text{COOH}$, and amino groups, $-\text{NH}_2$.

Step 1: Count the acidic groups An acidic amino acid has more carboxyl groups than amino groups. For example, glutamic acid contains two $-\text{COOH}$ groups and one $-\text{NH}_2$ group.

Step 2: Compare with a basic amino acid A basic amino acid has more amino groups than carboxyl groups. For example, lysine contains two $-\text{NH}_2$ groups and one $-\text{COOH}$ group. Thus the difference is the relative number of the two functional groups.

Step 3: Conclusion Acidic amino acids have more $-\text{COOH}$ groups than $-\text{NH}_2$ groups; basic amino acids have more $-\text{NH}_2$ groups than $-\text{COOH}$ groups.

Quick Tip to Solve: Compare the numbers of carboxyl and amino groups; an extra carboxyl group indicates an acidic amino acid.

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 repair.
- Essential amino acids are classified by whether the human body can synthesise enough of them to meet its needs.

Step 1: Identify the limitation of synthesis The human body cannot synthesise essential amino acids in amounts sufficient for its requirements. Consequently, protein synthesis depends on obtaining these amino acids from outside the body.

Step 2: State how they are supplied They must be supplied through the diet, for example from suitable dietary proteins. Lysine and valine are examples. Here essential refers to their required dietary supply, rather than to any special functional group.

Quick Tip to Solve: Use the phrase must be obtained from the diet to distinguish essential amino acids from non-essential ones.

Step 3: Conclusion Essential amino acids are amino acids that the body cannot synthesise adequately and must therefore obtain through the diet.

Quick Tip to Solve: Use the phrase must be obtained from the diet to distinguish essential amino acids from non-essential ones.

3. Why are amino acids amphoteric?

[1 mark]

Solution:

Concept:

- Amphoteric substances can react with both acids and bases.
- An amino acid contains an acidic carboxyl group, $-\text{COOH}$, and a basic amino group, $-\text{NH}_2$.

Step 1: Explain the acidic behaviour The carboxyl group can donate a proton and hence reacts with a base. It is converted into the carboxylate group, $-\text{COO}^-$, when the proton is removed.

Step 2: Explain the basic behaviour The amino group has a lone pair on nitrogen and can accept a proton from an acid, forming $-\text{NH}_3^+$. In aqueous solution, proton transfer can give the zwitterion $\text{H}_3\text{N}^+ - \text{CHR} - \text{COO}^-$, containing both positive and negative centres.

Step 3: Conclusion Amino acids are amphoteric because their $-\text{COOH}$ group is acidic while their $-\text{NH}_2$ group is basic, so they react with both bases and acids.

Quick Tip to Solve: Link each behaviour to its own group: carboxyl donates a proton, while amino accepts a proton.

4. Name the linkage formed when carboxyl end of one amino acid condenses with amino end of other amino acid.

[1 mark]

Solution:

Concept:

- Condensation joins two molecules with elimination of a small molecule such as water.
- A carboxyl group of one amino acid reacts with an amino group of another to produce an amide bond.

Step 1: Identify the groups that react The carboxyl end supplies the carbonyl carbon, and the amino end supplies the nitrogen. During the condensation, an $-\text{OH}$ from the carboxyl group and an H from the amino group are eliminated as water.

Step 2: Recognise the resulting linkage The new bond joins the carbonyl carbon to nitrogen and gives the unit $-\text{CO} - \text{NH}-$. This amide linkage between amino acid residues is given the special name peptide linkage; repeated formation of this linkage produces polypeptides.

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

Quick Tip to Solve: Look for the carbonyl-carbon to nitrogen bond in the product; this is the peptide linkage.

5. What are amino acids?

[1 mark]

Solution:

Concept:

- A functional group determines characteristic chemical behaviour of an organic compound.
- Amino acids contain an amino group, $-\text{NH}_2$, and a carboxyl group, $-\text{COOH}$, in the same molecule.

Step 1: Identify both functional groups The term amino identifies the amino group, while acid identifies the carboxyl group. An organic molecule containing only an amino group is an amine; the presence of both groups is required for it to be an amino acid.

Step 2: Relate the definition to protein building units In the common α -amino acids that form proteins, the amino group is attached to the carbon adjacent to the carboxyl group. Their general formula is $\text{H}_2\text{N} - \text{CH}(\text{R}) - \text{COOH}$, where R is the side chain.

Step 3: Conclusion Amino acids are organic compounds containing both an amino group and a carboxyl group in the same molecule.

Quick Tip to Solve: Include both functional groups in the definition; mentioning only the amino group describes an amine.

6. Name the process where the metal is converted into a volatile compound and is collected elsewhere.

[1 mark]

Solution:

Concept:

- Refining removes impurities from a metal to obtain a purer sample.
- In vapour phase refining, the metal forms a volatile compound which can later be decomposed to regenerate the metal.

Step 1: Match the formation of a volatile compound The stated process first converts the metal into a compound that can enter the vapour phase. The compound must form readily under suitable conditions so that the desired metal can be separated from the remaining impurities.

Step 2: Explain collection elsewhere The vapour is carried to another region and decomposed there to deposit pure metal. The compound must therefore also decompose readily. Mond refining of nickel and the van Arkel method for zirconium are examples of this general refining method.

Step 3: Conclusion Vapour phase refining.

Quick Tip to Solve: Use the general process name vapour phase refining when no particular metal or reagent is specified.

7. 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 on the surface of another material.
- The material retained is the adsorbate; the surface that retains it is the adsorbent.

Step 1: Identify the two roles The organic compound is the adsorbate because it is held on the surface. Silica gel is the adsorbent because its surface provides the sites on which the compound is accumulated.

Step 2: Name the reverse surface process Removing the adsorbed organic compound from the silica-gel surface is the reverse of adsorption and is called desorption. The description concerns release from a surface; it does not describe absorption into the bulk of the silica gel.

Step 3: Conclusion Desorption.

Quick Tip to Solve: Pair adsorption with its reverse, desorption; focus on removal from the surface rather than from the bulk.

8. Give an example of a metal which can be purified by the process of distillation. [1 mark]

Solution:

Concept:

- Distillation separates a volatile metal from impurities that are much less volatile.
- On heating, the metal vaporises; cooling its vapour gives the purified metal.

Step 1: Choose a suitable volatile metal Zinc has a sufficiently low boiling point to be vaporised during refining. It can therefore be separated from non-volatile impurities present in the crude metal.

Step 2: Explain the separation Crude zinc is heated so that zinc passes into the vapour phase while less volatile impurities remain behind. The zinc vapour is collected and condensed in a cooler receiver. The separation depends on the difference in volatility, rather than on dissolving the impurities.

Step 3: Conclusion Zinc is an example of a metal that can be purified by distillation.

Quick Tip to Solve: For distillation, recall zinc: vaporise the metal and then condense its vapour.

9. 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:

- An ambidentate ligand can coordinate through either of two different donor atoms.
- Linkage isomers have the same composition but differ in the donor atom through which such a ligand is attached to the central metal.

Quick Tip to Solve: Look for nitrite: binding through N or O immediately indicates linkage isomerism.

Step 1: Identify the ambidentate ligand In $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$, the nitrite ligand NO_2^- can bind through nitrogen or through oxygen. Ammonia has only its nitrogen donor atom and does not cause this isomerism.

Step 2: Compare the two linkages Nitrogen coordination gives the nitro form, $\text{Co}-\text{NO}_2$; oxygen coordination gives the nitrito form, $\text{Co}-\text{ONO}$. The ligand composition remains unchanged while its point of attachment changes. The chloride ions outside the coordination sphere are counter-ions.

Step 3: Conclusion The complex shows linkage isomerism, due to the ambidentate nitrite ligand.

Quick Tip to Solve: Look for nitrite: binding through N or O immediately indicates linkage isomerism.

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

$$\text{Rate} = k[\text{NH}_3]^{5/2}[\text{O}_2]^{1/2}.$$

[1 mark]

Solution:

Concept:

- For $r = k[A]^m[B]^n$, the overall order is $m + n$, the sum of the concentration exponents.
- Reaction order is obtained from the experimental rate law, not from coefficients in a balanced reaction.

Step 1: Read the individual orders The printed rate law is $r = k[\text{NH}_3]^{5/2}[\text{O}_2]^{1/2}$. Hence the partial order with respect to ammonia is $5/2$, and that with respect to oxygen is $1/2$. The rate constant k is not included in the sum.

Step 2: Add the concentration powers

$$n = \frac{5}{2} + \frac{1}{2} = \frac{6}{2} = 3.$$

Fractional partial orders are allowed; they can add to an integer overall order. Since order is a sum of exponents, it is dimensionless.

Step 3: Conclusion The overall order is 3; this is a third-order reaction.

Quick Tip to Solve: Add the printed powers directly: $5/2 + 1/2 = 3$, without using reaction coefficients.

11. 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.
- Number this chain to give the principal functional group, -OH , the lowest possible locant.

Step 1: Choose and number the parent chain The longest chain through the hydroxyl-bearing carbon contains four carbons, so the parent is butane. Numbering from the nearer end places -OH at carbon 2, giving butan-2-ol.

Step 2: Locate the substituent and compare options The remaining CH_3 group is also attached to carbon 2. Option (A) names tert-butyl alcohol, which has only four carbons in total. Option (B) chooses an unsuitable three-carbon parent. Option (D) numbers from the wrong end and assigns locant 3 instead of the lower locant 2.

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

Quick Tip to Solve: Choose the four-carbon chain, then give the hydroxyl group locant 2 before naming the methyl group.

12. 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:

- Moles of solute are $n = N/N_A$, where N is the number of molecules and $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$.
- Molarity is $M = n/V$, with solution volume V expressed in litres.

Step 1: Convert molecules to moles

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

The given molar mass is unnecessary because the number of molecules already determines the amount

Quick Tip to Solve: First obtain 0.10 mol from the molecules, then divide by 0.050 L rather than 50 mL.

of glucose.

Step 2: Convert the volume and calculate concentration The solution volume is $50 \text{ mL} = 0.050 \text{ L}$. Thus

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

Option (A) confuses the numerical amount in moles with molarity; options (B) and (C) also fail to divide the amount by the actual volume in litres.

Step 3: Conclusion The solution concentration is 2.0 M , option (D).

Quick Tip to Solve: First obtain 0.10 mol from the molecules, then divide by 0.050 L rather than 50 mL .

13. 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:

- Standard electrode potentials are reduction potentials measured relative to the standard hydrogen electrode, whose potential is zero.
- A positive reduction potential indicates a greater tendency for reduction than that of hydrogen ions under standard conditions.

Step 1: Interpret the sign of the potential For the electrode reduction $\text{Ox} + ne^- \rightarrow \text{Red}$, $E^\circ > 0$ means that reduction is favoured relative to the hydrogen reference. Paired with the standard hydrogen electrode, this electrode acts as the cathode while hydrogen is oxidised at the anode.

Step 2: Compare the printed statements The favourable reduction produces the reduced form; in the comparison intended by the question, this form is more stable than hydrogen gas. Option (B) assigns the preference to the oxidised form, and option (D) reverses it. Option (C) would imply no preference, inconsistent with the positive potential.

Step 3: Conclusion The reduced form is more stable compared to hydrogen gas, option (A).

Quick Tip to Solve: A positive standard reduction potential favours the reduced form relative to the hydrogen reference.

14. Total number of unpaired electrons present in Mn^{2+} (Atomic number = 25) is

[1 mark]

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

Correct Answer: (D) 5

Solution:

Concept:

- Manganese has atomic number 25 and the ground-state configuration $[\text{Ar}] 3d^5 4s^2$.
- For transition-metal cations, the $4s$ electrons are removed before the $3d$ electrons; Hund's rule gives maximum single occupancy in degenerate orbitals.

Step 1: Form the divalent ion The Mn^{2+} ion is obtained by removing the two $4s$ electrons from neutral manganese. Its configuration is therefore $[\text{Ar}] 3d^5$. The argon core contains only paired electrons.

Step 2: Count singly occupied orbitals The five $3d$ electrons occupy the five d orbitals singly with parallel spins before any pairing occurs. Hence each d orbital contributes one unpaired electron. Options (A) and (C) incorrectly pair some d electrons; option (B) exceeds the five unpaired electrons allowed for the $3d^5$ configuration.

Step 3: Conclusion Mn^{2+} has 5 unpaired electrons, option (D).

Quick Tip to Solve: Remove the two $4s$ electrons first; the remaining half-filled $3d^5$ shell has five unpaired electrons.

15. 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 carbon, nitrogen or hydrogen occupy interstitial sites in a metal lattice.
- They generally retain metallic conductivity, have high melting points and are very hard; they are also chemically inert.

Step 1: Identify the incorrect property The small atoms fit into the spaces between metal atoms and strengthen the lattice. The characteristic chemical property of these compounds is inertness, so describing them as chemically reactive reverses their usual behaviour.

Quick Tip to Solve: For interstitial compounds, remember hard, high melting, conducting and chemically inert; look for a reversal of one property.

Step 2: Check the other statements The strong, rigid lattice accounts for their hardness and high melting point, so (B) and (D) are correct properties. The metallic framework is retained, allowing metallic conductivity; therefore (C) is also correct. These statements must not be selected when the question asks for the incorrect statement.

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

Quick Tip to Solve: For interstitial compounds, remember hard, high melting, conducting and chemically inert; look for a reversal of one property.

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:
 $1 \times 5 = 5$.

(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]

Solution:

Concept:

- Acid strength depends on the ease of loss of a proton and the stability of the conjugate base.
- In ortho-nitrophenol, the phenolic hydrogen can form an intramolecular hydrogen bond with an oxygen of the adjacent nitro group.

Step 1: Judge the assertion Ortho-nitrophenol is slightly less acidic than para-nitrophenol in aqueous solution. The ortho isomer forms a stabilising hydrogen bond within the molecule, whereas the para isomer cannot form this corresponding intramolecular bond. Thus the assertion is correct.

Step 2: Judge the reason The intramolecular hydrogen bond stabilises the undissociated ortho isomer and makes its proton less readily available for ionisation. It also reduces its interaction with water. The ortho conjugate base is less effectively solvated than the para conjugate base. The stated reason is correct.

Step 3: Connect the reason to the assertion The stabilisation of the un-ionised ortho form through intramolecular hydrogen bonding helps explain why it loses a proton less readily than the para form. Thus the reason explains the assertion, rather than merely stating an unrelated property.

Step 4: Conclusion Both (A) and (R) are correct, and (R) is the correct explanation of (A). Hence, the correct code is (i).

Quick Tip to Solve: When comparing ortho- and para-nitrophenol acidity, check whether hydrogen bonding stabilises the neutral molecule before comparing ionisation.

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

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

[1 mark]

Solution:

Concept:

- Globular proteins have folded, compact, approximately spherical structures; albumin is an example.
- Fibrous proteins are generally elongated, with polypeptide chains arranged in extended structures.

Step 1: Judge the assertion Albumin is a globular protein. Its polypeptide chain folds into a compact three-dimensional form, and albumin is generally soluble in water. Hence the assertion is correct.

Step 2: Judge the reason A polypeptide chain that coils and folds in a globular protein gives a compact, roughly spherical structure, not a straight chain. The words "straight chain" make the stated reason incorrect.

Step 3: Assess the explanatory link Since the reason itself is false, it cannot explain the correct assertion about albumin. The code for two correct statements is ruled out, as is the code in which the assertion is incorrect. Select the code for a correct assertion and an incorrect reason.

Step 4: Conclusion (A) is correct, but (R) is incorrect. Hence, the correct code is (iii).

Quick Tip to Solve: Associate albumin with a compact globular fold; a statement calling that fold a straight chain is false.

18. 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]

Solution:

Concept:

- For alkyl halides with the same alkyl group, boiling points depend strongly on intermolecular dispersion forces.
- The size and polarisability of the halogen increase from fluorine to iodine, strengthening van der Waals attractions.

Step 1: Judge the assertion Keeping the alkyl group R the same, the boiling points decrease as $R-I > R-Br > R-Cl > R-F$. The heavier, larger halogen atoms give more polarisable molecules. Hence the assertion is correct.

Step 2: Judge the reason Van der Waals forces increase, rather than decrease, as the size and polarisability of the halogen atom increase. The larger electron cloud is more easily distorted, producing stronger instantaneous dipole-induced dipole attractions. Thus the reason is incorrect.

Step 3: Assess the explanatory link Stronger attractions require more energy to separate molecules into the vapour phase and hence raise the boiling point. This explains the assertion using the reverse of the printed reason. A false reason cannot be the correct explanation; the applicable code is the one for a correct assertion and an incorrect reason.

Step 4: Conclusion (A) is correct, but (R) is incorrect. Hence, the correct code is (iii).

Quick Tip to Solve: For the same alkyl group, follow halogen size: iodine gives the strongest dispersion forces and the highest boiling point.

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]

Solution:

Concept:

- In a tetrahedral ligand field, the five d orbitals split into lower-energy e and higher-energy t_2 sets.
- Electrons pair in the lower set only when the splitting energy Δ_t is sufficiently large relative to the pairing energy P .

Step 1: Judge the assertion Low spin tetrahedral complexes are rarely observed. In the usual tetrahedral ligand field, the energy separation between the two sets of d orbitals is small, so electrons generally occupy the higher set before pairing. Thus the assertion is correct.

Step 2: Judge the reason Tetrahedral splitting is typically too small to compensate for the energy needed to pair electrons. Usually $\Delta_t < P$, so occupying another orbital costs less energy than pairing in a lower orbital. This is precisely the meaning of the printed reason, so the reason is correct.

Step 3: Connect the reason to the assertion Because tetrahedral splitting is insufficient to force pairing, tetrahedral complexes generally adopt high spin arrangements whenever alternative spin arrangements are possible. This small splitting directly explains why low spin tetrahedral complexes are rare.

Step 4: Conclusion Both (A) and (R) are correct, and (R) is the correct explanation of (A). Hence, the correct code is (i).

Quick Tip to Solve: Compare tetrahedral splitting with pairing energy: the usual small splitting favours unpaired electrons and high spin.

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

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

[1 mark]

Solution:

Concept:

- Thermosetting polymers form extensively cross-linked, three-dimensional networks during curing and cannot be remoulded by heating.
- Bakelite is the thermosetting phenol-formaldehyde polymer; cross-links restrict the movement of its chains.

Step 1: Judge the assertion Bakelite is a thermosetting polymer. On curing, the phenol-formaldehyde material forms a hard, rigid network that does not soften into a mouldable melt on reheating. Thus the assertion is correct.

Step 2: Judge the reason During formation of Bakelite, heating promotes cross-linking between polymer chains, producing a three-dimensional network. The chains do not become a single long, straight chain. Hence the stated reason is incorrect.

Step 3: Assess the explanatory link The thermosetting behaviour follows from irreversible network

Quick Tip to Solve: For Bakelite, connect thermosetting behaviour with a rigid cross-linked network; a straight-chain explanation is incorrect.

formation, which prevents the chains from sliding freely past one another. Since the printed reason describes a straight chain instead of the cross-linked network, it cannot explain the true assertion. The code for a true assertion with a false reason is required.

Step 4: Conclusion (A) is correct, but (R) is incorrect. Hence, the correct code is (iii).

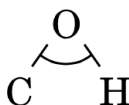
Quick Tip to Solve: For Bakelite, connect thermosetting behaviour with a rigid cross-linked network; a straight-chain explanation is incorrect.

Section B (14 marks)

21. 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:

- The oxygen atom in an alcohol has two bond pairs and two lone pairs. Its approximately tetrahedral electron-pair arrangement is described by sp^3 hybridisation.
- Lone-pair-bond-pair repulsion is stronger than bond-pair-bond-pair repulsion. Resonance can give a formally single bond partial double-bond character and shorten it.

Step 1: (a) Explain the smaller C-O-H angle In an alcohol, oxygen forms one bond with carbon and one with hydrogen and retains two lone pairs. The lone pairs occupy more space around oxygen than the bonding pairs. Their stronger repulsion pushes the two bond pairs closer together, compressing the C – O – H angle below the ideal tetrahedral angle of 109.5° .

Step 2: (b) Compare the carbon-oxygen bonds In phenol, a lone pair on oxygen is conjugated with the benzene ring. Delocalisation through resonance gives the bond between the ring carbon and oxygen partial double-bond character. This makes that bond shorter than an ordinary carbon-oxygen single bond. In CH_3OH , there is no aromatic π -system for such conjugation, so its C – O bond retains single-bond character. The attachment to an sp^2 carbon in phenol also favours a shorter bond than attachment to the sp^3 carbon in methanol.

Step 3: Conclusion (a) Strong lone-pair repulsions compress the C – O – H angle. (b) Resonance gives the C – O bond in phenol partial double-bond character, so it is shorter than the C – O bond in methanol.

Quick Tip to Solve: For a bond-angle question count lone pairs first; for a bond-length comparison check whether resonance gives either bond partial double-bond character.

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

(a) Tranquilizers and Analgesics

(b) Antiseptics and Disinfectants

[2 marks]

Solution:

Concept:

- Drugs are classified by their therapeutic action: tranquilizers act to relieve mental stress, whereas analgesics relieve pain.
- Antiseptics and disinfectants both control microorganisms; their main distinction is whether they are suitable for living tissue or used on non-living objects.

Step 1: (a) Distinguish tranquilizers from analgesics Tranquilizers are used to relieve anxiety, tension and mental stress by producing a calming effect. Analgesics are used to reduce or relieve physical pain. Thus their principal purposes differ: a tranquilizer calms the patient, whereas an analgesic provides pain relief. For example, diazepam is a tranquilizer and aspirin is an analgesic.

Step 2: (b) Distinguish antiseptics from disinfectants Antiseptics are applied to living tissues, such as skin, cuts and wounds, to kill microorganisms or inhibit their growth without damaging the tissue at the concentration used. Disinfectants are applied to non-living objects and surfaces, such as floors and drains, and are generally unsuitable for application to living tissue. The difference is the intended site of use and the safe concentration, rather than whether either substance acts against microbes.

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

Quick Tip to Solve: Compare each pair on the same basis: therapeutic purpose for the drugs, and site of application for the antimicrobial agents.

OR

22(b). Differentiate on the basis of chemical composition between cationic and anionic detergents. Also give one example of each category.

[2 marks]

Solution:

Concept:

- A detergent contains a long hydrophobic hydrocarbon chain and a hydrophilic ionic head. Its category depends on the charge of the surface-active ion.
- Cationic detergents commonly contain quaternary ammonium ions; anionic detergents commonly contain alkyl sulfate or alkylbenzenesulfonate ions.

Step 1: Describe cationic detergents and give an example Cationic detergents are generally quaternary ammonium salts in which at least one alkyl group is a long hydrocarbon chain. Their detergent-active part is the positively charged organic ion, while the anion is a counterion. An example is cetyltrimethylammonium bromide, $[C_{16}H_{33}N(CH_3)_3]^+Br^-$. Here the long cetyl group and the positively charged nitrogen belong to the same surface-active cation.

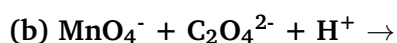
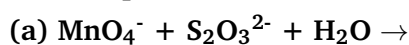
Quick Tip to Solve: Identify the charge on the ion carrying the long hydrocarbon chain, rather than the charge on its small counterion.

Step 2: Describe anionic detergents and give an example Anionic detergents are usually sodium salts of long-chain alkyl hydrogen sulfates or alkylbenzenesulfonic acids. Their detergent-active part is the negatively charged organic ion, with sodium as the counterion. An example is sodium lauryl sulfate (sodium dodecyl sulfate), $\text{C}_{12}\text{H}_{25}\text{OSO}_3^-\text{Na}^+$. Its hydrocarbon chain is attached to a negatively charged sulfate head group.

Step 3: Conclusion Cationic detergents have a positively charged surface-active ion, for example cetyltrimethylammonium bromide. Anionic detergents have a negatively charged surface-active ion, for example sodium lauryl sulfate.

Quick Tip to Solve: Identify the charge on the ion carrying the long hydrocarbon chain, rather than the charge on its small counterion.

23. Complete and balance the following chemical equations:



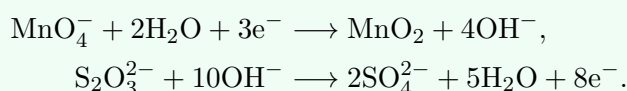
[2 marks]

Solution:

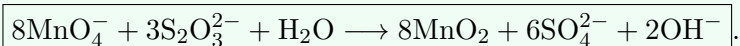
Concept:

- Redox equations must conserve atoms and total charge. The product of permanganate reduction depends on the medium: MnO_2 in neutral or weakly alkaline medium, and Mn^{2+} in acidic medium.
- Thiosulfate is oxidised to sulfate, losing eight electrons per thiosulfate ion. Oxalate is oxidised to carbon dioxide, losing two electrons per oxalate ion.

Step 1: (a) Balance the reaction with thiosulfate and water With water and no added acid, manganese changes from +7 in permanganate to +4 in MnO_2 . Thiosulfate forms sulfate; its two sulfur atoms have a combined oxidation number of +4, which rises to +12 in two sulfate ions, so eight electrons are lost per thiosulfate ion. The half-reactions in basic form are

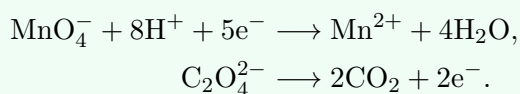


Multiply the reduction half-reaction by 8 and the oxidation half-reaction by 3. Add them and cancel the 24 electrons, then cancel water and hydroxide ions common to both sides. This gives



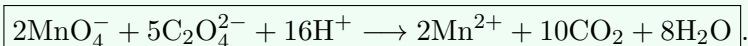
The charge on each side is -14 . Both sides also contain 8 manganese atoms, 6 sulfur atoms, 42 oxygen atoms and 2 hydrogen atoms.

Step 2: (b) Balance the reaction with oxalate in acid The presence of H^+ specifies acidic medium, so permanganate is reduced to Mn^{2+} . The half-reactions are



Quick Tip to Solve: Choose the manganese reduction product from the stated medium before balancing, then check total charge as well as every element.

Multiply these half-reactions by 2 and 5 respectively to cancel ten electrons. The balanced equation is



Both sides have charge +4; carbon, oxygen, hydrogen and manganese are conserved.

Step 3: Conclusion (a) $8\text{MnO}_4^- + 3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \longrightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^-$.

(b) $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$.

Quick Tip to Solve: Choose the manganese reduction product from the stated medium before balancing, then check total charge as well as every element.

24. 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 dependence of reaction rate on reactant concentrations. The exponent of a concentration is the order with respect to that reactant.
- For a reactant concentration $[A]$, the average disappearance rate is $-\Delta[A]/\Delta t$, while the instantaneous disappearance rate is $-d[A]/dt$.

Step 1: Write the rate law First order with respect to A means that its concentration enters to the power one; first order with respect to B means the same for B. Therefore,

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

where r is the reaction rate and k is the rate constant at the given temperature. The overall order is $1 + 1 = 2$; being first order in each reactant does not make the overall reaction first order.

Step 2: Distinguish the two rates Average rate measures the concentration change over a finite time interval t_1 to t_2 :

$$r_{\text{avg}} = -\frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1}.$$

Instantaneous rate measures the rate at one particular instant:

$$r_{\text{inst}} = -\frac{d[A]}{dt}.$$

On a concentration–time graph, these correspond respectively to the negative slope of a secant and the negative slope of the tangent at the selected instant. The minus signs make a reactant disappearance rate positive.

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

Quick Tip to Solve: Add the concentration exponents to obtain overall order; use a finite interval for average rate and a derivative for instantaneous rate.

25(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 accumulation of a substance on the surface of an adsorbent. An adsorption isotherm describes adsorption while temperature remains constant.
- In the Freundlich relation, x is the mass of gas adsorbed, m is the mass of solid adsorbent, and p is the equilibrium gas pressure.

Step 1: Define adsorption isotherm An adsorption isotherm is the relationship between the quantity of gas adsorbed per unit mass of a solid adsorbent and the pressure of the gas at a constant temperature. It can be represented by a graph of x/m against pressure p , keeping the temperature fixed throughout. Fixing temperature is essential because the extent of adsorption also depends on temperature.

Step 2: State the empirical relationship The Freundlich adsorption isotherm gives

$$\frac{x}{m} = kp^{1/n},$$

where k and n are constants for a particular gas-adsorbent pair at the selected temperature, with $0 < 1/n < 1$. Thus adsorption per unit mass increases with pressure in the applicable pressure range. Taking logarithms gives the equivalent straight-line form

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

Its slope is $1/n$ and its intercept is $\log k$. This empirical relation describes adsorption over a limited pressure range.

Step 3: Conclusion An adsorption isotherm relates x/m to gas pressure at constant temperature. The empirical Freundlich relationship is $x/m = kp^{1/n}$.

Quick Tip to Solve: Keep temperature fixed in the definition and distinguish x , the adsorbed gas mass, from m , the solid adsorbent mass.

OR

25(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:

- Shape-selective catalysis depends on the pore structure of a catalyst and the sizes and shapes of reactant and product molecules.
- Zeolites are microporous aluminosilicates. Their molecular-sized channels can admit some molecules and exclude others.

Quick Tip to Solve: Associate molecular-sized zeolite pores with shape selectivity, and remember ZSM-5 as the catalyst for alcohol-to-gasoline conversion.

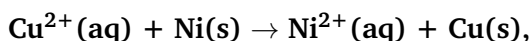
Step 1: Define shape-selective catalysis Shape-selective catalysis is catalysis in which the activity and selectivity depend on the pore size and pore structure of the catalyst, as well as the size and shape of the reactant and product molecules. Molecules that fit the pores can enter and react at the active sites; molecules that cannot fit are excluded. The dimensions of the channels can also favour formation or escape of particular products. Zeolites are standard examples of such catalysts.

Step 2: Name the alcohol-to-gasoline process The conversion is the methanol-to-gasoline (MTG) process, using the shape-selective zeolite catalyst ZSM-5. ZSM-5 converts alcohols into a mixture of hydrocarbons in the gasoline range. In this conversion, the alcohol feed undergoes reactions leading to carbon-carbon bond formation and a range of hydrocarbon products; the zeolite channels control which molecular shapes are favoured. Thus the requested example is zeolite-catalysed alcohol-to-gasoline conversion using ZSM-5.

Step 3: Conclusion Shape-selective catalysis depends on catalyst pore geometry and molecular size and shape. The MTG process using zeolite ZSM-5 converts alcohols into gasoline hydrocarbons.

Quick Tip to Solve: Associate molecular-sized zeolite pores with shape selectivity, and remember ZSM-5 as the catalyst for alcohol-to-gasoline conversion.

26. For an electrochemical cell



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

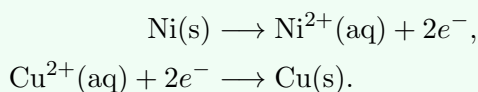
[2 marks]

Solution:

Concept:

- Oxidation occurs at the anode and reduction at the cathode. A cell is written with the anode on the left and the cathode on the right.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^{\circ} - (0.0591/n) \log Q$, where n is the number of electrons transferred and Q is the reaction quotient.

Step 1: Identify electrodes and represent the cell In the given reaction, nickel is oxidised and copper(II) ions are reduced:



Nickel is therefore the anode and copper is the cathode. The cell representation is



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

Step 2: Write the Nernst equation Two electrons are transferred, so $n = 2$. Pure nickel and copper solids have unit activity and are omitted from the reaction quotient. Using the concentration form for

Quick Tip to Solve: Place the oxidised metal on the left; omit pure solids from Q and use $n=2$ for these divalent metal ions.

the aqueous ions,

$$Q = \frac{[\text{Ni}^{2+}]}{[\text{Cu}^{2+}]}$$

Hence, at 25°C,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log \frac{[\text{Ni}^{2+}]}{[\text{Cu}^{2+}]} \quad (\text{in V}).$$

Here log is the base-ten logarithm, and $E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Ni}^{2+}/\text{Ni}}^{\circ}$. Concentrations are understood relative to their standard concentration.

Step 3: Conclusion The cell is $\text{Ni}|\text{Ni}^{2+}||\text{Cu}^{2+}|\text{Cu}$, and its Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^{\circ} - (0.0591/2) \log([\text{Ni}^{2+}]/[\text{Cu}^{2+}])$ at 25°C.

Quick Tip to Solve: Place the oxidised metal on the left; omit pure solids from Q and use $n=2$ for these divalent metal ions.

27. Predict the state of the solute in the solution in the following situations:

(a) When 'i' is found to be 0.3.

(b) When 'i' is found to be 4.

[2 marks]

Solution:

Concept:

- The van't Hoff factor i is the ratio of the actual number of solute particles in solution to the number expected if the solute neither associates nor dissociates.
- Association decreases the particle count, giving $i < 1$; dissociation increases it, giving $i > 1$. An unchanged particle count gives $i = 1$.

Step 1: Interpret the value 0.3 In (a), $i = 0.3 < 1$, so the solution has only 0.3 times the number of independently moving solute particles expected for an unassociated solute. Solute molecules therefore combine to form larger aggregates: the solute is associated. The value alone does not uniquely establish the size of the aggregate or the degree of association.

Step 2: Interpret the value 4 In (b), $i = 4 > 1$, so the particle count is four times the expected count. The solute therefore undergoes dissociation into smaller particles, ordinarily ions. Complete dissociation into four ions per formula unit would give this value, although the factor by itself specifies the net particle increase rather than a unique chemical identity.

Step 3: Conclusion (a) The solute undergoes association. (b) The solute undergoes dissociation.

Quick Tip to Solve: Compare each value of i with 1 first: below 1 means association; above 1 means dissociation.

Section C (21 marks)

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

(a) Neoprene

(b) Nylon-6,6

(c) Dacron

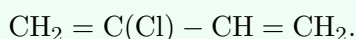
[3 marks]

Solution:

Concept:

- Monomers are the small molecules whose repeated linking forms a polymer. Addition polymers retain the atoms of their monomers as a carbon-carbon double bond opens.
- Condensation polymers are formed by reactions between functional groups, with elimination of small molecules such as water. Polyamides require amine and carboxylic-acid groups; polyesters require alcohol and carboxylic-acid groups.

Step 1: Identify the monomer of neoprene Neoprene is formed by addition polymerisation of chloroprene, also called 2-chlorobuta-1,3-diene. Its structural formula is



The chlorine substituent is on carbon 2 of the conjugated diene; it must not be omitted when identifying this monomer.

Step 2: Identify both monomers of nylon-6,6 Nylon-6,6 is a condensation polyamide made from hexamethylenediamine and adipic acid. Their structures are respectively



The diamine contains six carbon atoms, while adipic acid also contains six, including its two carboxyl carbon atoms. Their amino and carboxyl groups react to form amide linkages with elimination of water.

Step 3: Identify both monomers of Dacron Dacron is the polyester formed from ethylene glycol and terephthalic acid. Their structures are

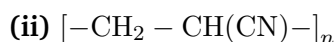


In terephthalic acid, the two carboxyl groups occupy the 1,4 positions of the benzene ring. The hydroxyl and carboxyl groups form ester linkages during condensation.

Step 4: Conclusion (a) Neoprene: chloroprene. (b) Nylon-6,6: hexamethylenediamine and adipic acid. (c) Dacron: ethylene glycol and terephthalic acid, with the structures shown above.

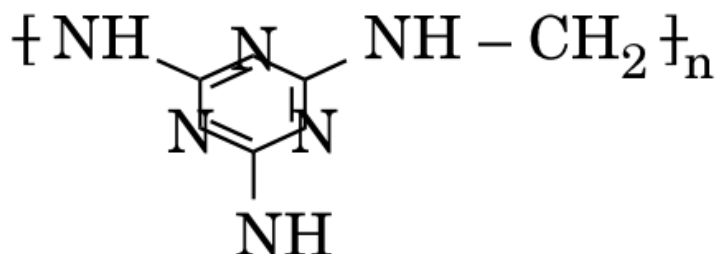
Quick Tip to Solve: For nylon-6,6 count both carboxyl carbons in adipic acid; for Dacron keep the acid groups para on the benzene ring.

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



(iii)

[3 marks]



Solution:

Concept:

- A polymer repeat unit reveals the functional groups and carbon skeleton inherited from its monomer. The linkage must be examined before naming the starting material.
- Nylon-6 is obtained by ring-opening polymerisation of caprolactam; polyacrylonitrile forms by addition polymerisation of acrylonitrile. Melamine-formaldehyde resin is formed by condensation of melamine with formaldehyde.

Step 1: Name the monomer for structure (i) The repeat unit $[-\text{NH} - (\text{CH}_2)_5 - \text{CO}-]_n$ contains an amide linkage and a sequence of five methylene groups. It is nylon-6. Its standard monomer is **caprolactam**, also called ϵ -caprolactam, a cyclic amide. Opening the lactam ring links successive units while preserving the six-carbon skeleton, including the carbonyl carbon.

Step 2: Name the monomer for structure (ii) The repeat unit $[-\text{CH}_2 - \text{CH}(\text{CN})-]_n$ has a carbon-carbon backbone with a nitrile group on every alternate carbon. Restoring the double bond gives the monomer



This is **acrylonitrile** (vinyl cyanide). Addition across its carbon-carbon double bond produces polyacrylonitrile; the nitrile group remains as a side group.

Step 3: Name the monomers for structure (iii) The printed structure contains a six-membered triazine ring with three ring nitrogen atoms and amino-derived groups participating in methylene cross-links. This identifies melamine-formaldehyde resin. Its monomers are **melamine**, or 2,4,6-triamino-1,3,5-triazine, and **formaldehyde**, also called methanal, HCHO . Melamine provides several reactive amino groups, and formaldehyde supplies the methylene bridges, producing a cross-linked condensation polymer.

Step 4: Conclusion (i) Caprolactam. (ii) Acrylonitrile (vinyl cyanide). (iii) Melamine and formaldehyde (methanal).

Quick Tip to Solve: An amide repeat suggests nylon, a pendant CN group identifies acrylonitrile, and a triazine ring identifies melamine.

29(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 oxidation state of a metal is obtained by balancing ligand charges against the charge on the coordination entity. Each cyanido ligand, CN^- , has charge -1 .
- In an octahedral complex the five d orbitals split into lower-energy t_{2g} and higher-energy e_g orbitals. Cyanide is a strong-field ligand and favours electron pairing.
- A multidentate ligand coordinates through two or more donor atoms and forms a ring with the metal. Chelation generally increases complex stability compared with analogous monodentate ligands.

Step 1: (a) Determine the oxidation state and name The four potassium ions give the coordination entity a charge of -4 . If the oxidation state of manganese is x , then

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

Name the cation first. The six cyanido ligands give the prefix hexacyanido, and an anionic manganese complex uses manganate followed by the oxidation state in Roman numerals. This constructs the systematic name directly from the formula.

Step 2: (a) Fill the octahedral orbitals Manganese has atomic number 25 and ground-state configuration $[Ar] 3d^5 4s^2$. Removing the two $4s$ electrons gives $Mn^{2+} : [Ar] 3d^5$. Because CN^- is strong field, the five d electrons occupy the three lower t_{2g} orbitals with pairing before any enters e_g . Their occupancies are 2, 2, 1, leaving one unpaired electron; both e_g orbitals are empty.

Step 3: (b) Explain the chelate effect with an example The chelate effect is the enhanced stability of a complex containing a chelating multidentate ligand relative to a comparable complex with monodentate ligands. For example, ethane-1,2-diamine (en) binds through its two nitrogen atoms and forms rings with nickel. Thus $[Ni(en)_3]^{2+}$ is more stable than the comparable ammine complex $[Ni(NH_3)_6]^{2+}$. Ring formation and the favourable entropy change when several monodentate ligands are replaced help explain this greater stability.

Step 4: Conclusion (a) The IUPAC name is potassium hexacyanomanganate(II), and the central Mn^{2+} ion has octahedral configuration $t_{2g}^5 e_g^0$. (b) The chelate effect is the enhanced stability due to chelating ligands, as illustrated by $[Ni(en)_3]^{2+}$ compared with $[Ni(NH_3)_6]^{2+}$.

Quick Tip to Solve: First use the four potassium ions to find Mn(II); then place all five d electrons in the lower t_{2g} set because cyanide is strong field.

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



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

[3 marks]

Solution:

Concept:

- Determine the metal oxidation state and d -electron count before assigning hybridisation. Cyanide and carbon monoxide are strong-field ligands; fluoride is a weak-field ligand.
- Octahedral inner-orbital complexes use d^2sp^3 hybridisation, whereas outer-orbital octahedral complexes use sp^3d^2 . Tetrahedral complexes use sp^3 hybridisation in valence bond theory.
- A complex with unpaired electrons is paramagnetic; a complex with all electrons paired is diamagnetic.

Step 1: (i) Analyse the hexacyanidoferrate(II) ion For $[\text{Fe}(\text{CN})_6]^{4-}$, charge balance gives $x - 6 = -4$, so iron is Fe^{2+} . Neutral Fe is $[\text{Ar}] 3d^6 4s^2$; the ion is $3d^6$. Strong-field cyanide causes pairing, giving octahedral occupancy $t_{2g}^6 e_g^0$. Two inner $3d$ orbitals become vacant and combine with one $4s$ and three $4p$ orbitals to accommodate the six ligand pairs. All six metal d electrons are paired.

Step 2: (ii) Analyse the hexafluoridocobaltate(III) ion For $[\text{CoF}_6]^{3-}$, $x - 6 = -3$, hence cobalt is Co^{3+} . Neutral Co is $[\text{Ar}] 3d^7 4s^2$, so Co^{3+} is $3d^6$. Weak-field fluoride does not cause the additional pairing needed for an inner-orbital complex. The high-spin octahedral distribution is $t_{2g}^4 e_g^2$, with four unpaired electrons. One $4s$, three $4p$, and two outer $4d$ orbitals provide the six hybrid orbitals.

Step 3: (iii) Analyse tetracarbonylnickel(0) Carbon monoxide is neutral, so the nickel oxidation state in $[\text{Ni}(\text{CO})_4]$ is zero. Neutral nickel begins as $[\text{Ar}] 3d^8 4s^2$. In the presence of strong-field CO, the two $4s$ electrons pair into the $3d$ set, giving a completely filled $3d^{10}$ configuration. The vacant $4s$ and three $4p$ orbitals form four equivalent hybrids directed tetrahedrally towards the ligands. No electron remains unpaired.

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

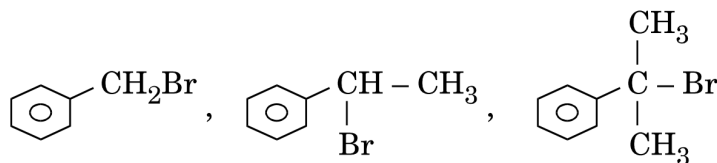
Quick Tip to Solve: Fe(II) and Co(III) are both d^6 , but cyanide pairs electrons while fluoride leaves four unpaired; neutral Ni with CO forms tetrahedral sp^3 hybrids.

30. Justify and arrange the following compounds namely $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$, $\text{C}_6\text{H}_5\text{CH}(\text{Br})\text{CH}_3$, and $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{Br}$ in increasing order of reactivity towards the asked displacement namely:

(a) $\text{S}_{\text{N}}1$

(b) $\text{S}_{\text{N}}2$

[3 marks]



Solution:

Concept:

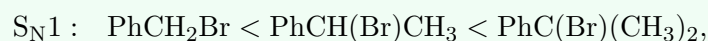
- In $\text{S}_{\text{N}}1$ substitution, carbon-halogen bond cleavage forms a carbocation in the slow step. A more stable carbocation forms more readily and gives faster reaction.
- In $\text{S}_{\text{N}}2$ substitution, nucleophilic attack from the back side and departure of the leaving group occur in one step. Greater crowding at the carbon bearing the leaving group slows the reaction.
- A benzylic carbocation is resonance-stabilised by the phenyl ring. Alkyl groups further stabilise it by hyperconjugation and their electron-releasing inductive effect.

Step 1: Identify the substitution at the benzylic carbon Let $\text{Ph} = \text{C}_6\text{H}_5$. The three substrates are PhCH_2Br , $\text{PhCH}(\text{Br})\text{CH}_3$, and $\text{PhC}(\text{Br})(\text{CH}_3)_2$. The carbon bearing Br is benzylic in all three. Their benzylic centres have, respectively, no methyl group, one methyl group and two methyl groups. Thus they are primary, secondary and tertiary benzylic bromides. The leaving group is identical, so the main comparison is the stability or crowding of the reacting carbon centre.

Step 2: (a) Compare the carbocations formed in an $\text{S}_{\text{N}}1$ reaction Loss of Br^- produces PhCH_2^+ , PhCH^+CH_3 , and $\text{PhC}^+(\text{CH}_3)_2$, respectively. Each carbocation is stabilised by delocalisation of positive charge into the phenyl ring. The methyl groups provide additional stabilisation through hyperconjugation and the $+I$ effect. Therefore the tertiary benzylic carbocation is most stable, followed by the secondary and then the primary one. Carbocation formation is consequently easiest for the substrate with two methyl groups and hardest for benzyl bromide.

Step 3: (b) Compare access for an $\text{S}_{\text{N}}2$ reaction In this mechanism the nucleophile must approach the carbon bearing Br from the side opposite the C–Br bond. Benzyl bromide has two small hydrogen atoms at this centre, so the attack is least hindered. Replacing one hydrogen by methyl increases crowding and slows attack. Replacing both hydrogens by methyl gives a tertiary centre where the required back-side approach is severely hindered; its $\text{S}_{\text{N}}2$ reaction is essentially blocked under ordinary conditions. Hence the order is reversed from the $\text{S}_{\text{N}}1$ order.

Step 4: Conclusion The increasing orders of reactivity are



The first follows increasing carbocation stability; the second follows decreasing steric hindrance.

Quick Tip to Solve: Count methyl groups on the carbon bearing Br: more methyl groups favour $\text{S}_{\text{N}}1$, but obstruct the back-side attack required for $\text{S}_{\text{N}}2$.

31. 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 lone pair on its nitrogen atom to a proton. Greater availability of this lone pair generally increases basicity.
- Resonance delocalises the nitrogen lone pair in aniline, whereas the electron-releasing ethyl group in ethanamine increases electron density on nitrogen.
- Friedel-Crafts reactions require a Lewis-acid catalyst, and Gabriel synthesis requires nucleophilic substitution of an alkyl halide by the phthalimide anion.

Step 1: (a) Compare the availability of the nitrogen lone pair In aniline, $\text{C}_6\text{H}_5\text{NH}_2$, the lone pair on nitrogen is delocalised into the benzene ring by resonance. It is therefore less readily available for accepting H^+ . In ethanamine, $\text{C}_2\text{H}_5\text{NH}_2$, the lone pair is localised on nitrogen; the ethyl group also exerts a positive inductive effect, increasing electron density on nitrogen. Consequently, ethanamine accepts a proton more readily and is the stronger base.

Step 2: (b) Explain the effect of the Friedel-Crafts catalyst The nitrogen lone pair of aniline coordinates with the Lewis acid AlCl_3 , the usual Friedel-Crafts catalyst, to form a salt-like complex. This interaction ties up the lone pair and makes nitrogen positively charged in the adduct. The resulting strong electron-withdrawing effect deactivates the benzene ring towards electrophilic substitution. Hence, aniline does not undergo the usual Friedel-Crafts alkylation or acylation reaction.

Step 3: (c) Explain the limitation of Gabriel synthesis Potassium phthalimide supplies a nitrogen nucleophile that reacts with an alkyl halide by nucleophilic substitution. Hydrolysis of the resulting N-alkylphthalimide releases RNH_2 , a primary aliphatic amine. Aryl halides do not undergo this substitution readily: the aryl carbon-halogen bond has partial double-bond character through resonance, and substitution at the sp^2 aryl carbon by the usual $\text{S}_{\text{N}}2$ pathway is not feasible. Thus, N-arylphthalimide, needed for an aromatic primary amine, is not formed by this route.

Step 4: Conclusion Aniline is less basic because its lone pair is delocalised; its complex with AlCl_3 deactivates the ring in Friedel-Crafts conditions; and Gabriel synthesis gives primary aliphatic amines because alkyl halides, unlike aryl halides, undergo the required nucleophilic substitution.

Quick Tip to Solve: Track the nitrogen lone pair in each explanation: resonance reduces basicity, catalyst binding deactivates the ring, and nucleophilic substitution limits Gabriel synthesis.

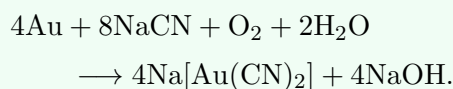
32. Give the chemical reactions involved in the leaching of gold. What is the role of Zn in this process? [3 marks]

Solution:

Concept:

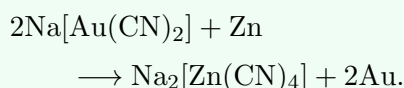
- Cyanide leaching converts gold into the water-soluble dicyanidoaurate(I) complex, $[\text{Au}(\text{CN})_2]^-$, in the presence of oxygen from air.
- A more electropositive metal, zinc, displaces gold from its dissolved complex. Zinc is oxidised while gold(I) is reduced to metallic gold.

Step 1: Dissolve gold by cyanide leaching The crushed gold-bearing material is treated with a dilute solution of sodium cyanide in the presence of air. Cyanide ions stabilise dissolved gold as a complex, while oxygen acts as the oxidising agent. The balanced leaching reaction is



Gold changes from oxidation state zero to +1 in $[\text{Au}(\text{CN})_2]^-$. The soluble complex passes into the leach solution, which is separated from the insoluble residue.

Step 2: Recover gold by adding zinc Zinc is added to the solution containing the gold complex. Being more electropositive than gold, zinc displaces it according to



Zinc supplies the electrons needed to reduce the two gold(I) ions to gold metal: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$. The oxidised zinc is stabilised as the soluble tetracyanidozincate(II) complex, $[\text{Zn}(\text{CN})_4]^{2-}$, whereas metallic gold is precipitated and can be collected.

Step 3: Conclusion Gold is leached as soluble $\text{Na}[\text{Au}(\text{CN})_2]$ using sodium cyanide and oxygen. Zinc acts as the reducing agent and displacing metal, precipitating gold while forming $\text{Na}_2[\text{Zn}(\text{CN})_4]$.

Quick Tip to Solve: Balance four gold atoms in the oxygen-assisted leaching equation, then use one zinc atom to reduce two gold(I) ions in the recovery equation.

33. State Kohlrausch's law. Calculate the molar conductance of $\text{Sr}(\text{NO}_3)_2$. The molar ionic conductance of Sr^{2+} and NO_3^- ions are $119 \text{ S cm}^2 \text{ mol}^{-1}$ and $72 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. [3 marks]

Solution:

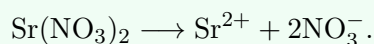
Concept:

- Kohlrausch's law of independent migration of ions states that at infinite dilution each ion makes a definite contribution 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

Quick Tip to Solve: Write the dissociation equation first and multiply each ionic conductivity by its stoichiometric coefficient, not by the magnitude of its charge.

cations and anions per formula unit and λ_i° is the limiting molar ionic conductivity.

Step 1: State the law and identify the ion numbers At infinite dilution, interactions between ions become negligible, so the cation and anion contributions can be added independently. Strontium nitrate dissociates as



Thus, one mole of strontium nitrate gives one mole of strontium ions and two moles of nitrate ions. The nitrate contribution must therefore be counted twice. The ionic charge +2 on strontium does not introduce an additional factor of two: the given ionic molar conductivity already refers to Sr^{2+} .

Step 2: Add the ionic contributions Using the supplied ionic molar conductivities in Kohlrausch's law gives

$$\begin{aligned}\Lambda_m^\circ(\text{Sr}(\text{NO}_3)_2) &= \lambda^\circ(\text{Sr}^{2+}) + 2\lambda^\circ(\text{NO}_3^-) \\ &= 119 + 2(72) \\ &= 263 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

Each term has the same conductivity unit, so the sum retains that unit. The result is the limiting molar conductivity, as the calculation uses independent ionic contributions at infinite dilution.

Step 3: Conclusion By Kohlrausch's law, the molar conductivity of $\text{Sr}(\text{NO}_3)_2$ at infinite dilution is $263 \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: Write the dissociation equation first and multiply each ionic conductivity by its stoichiometric coefficient, not by the magnitude of its charge.

34. 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:

- Freezing-point depression is a colligative property: $\Delta T_f = iK_f m$, where K_f is the molal depression constant, m is the molality and i is the van't Hoff factor.
- Ethylene glycol is a non-electrolyte in water, so $i = 1$. Molality is moles of solute per kilogram of solvent, not per kilogram of solution.
- The solution freezes below pure water: $T_f = T_f^\circ - \Delta T_f$, with $T_f^\circ = 0^\circ\text{C}$.

Step 1: Calculate the amount of ethylene glycol The solute mass is 31 g and its molar mass is 62 g mol⁻¹. Thus the number of moles dissolved is

$$n = \frac{31 \text{ g}}{62 \text{ g mol}^{-1}} = 0.50 \text{ mol}.$$

Ethylene glycol does not dissociate into ions, so these moles directly determine the number of solute particles.

Quick Tip to Solve: Convert the water mass to kilograms before finding molality, and subtract the positive depression from 0 °C.

Step 2: Calculate the molality Convert the given mass of water into kilograms: $600\text{ g} = 0.600\text{ kg}$. Use only the water mass in the denominator because water is the solvent:

$$m = \frac{0.50\text{ mol}}{0.600\text{ kg}} = 0.8333\text{ mol kg}^{-1}.$$

The total solution mass would not give the required molality.

Step 3: Find the depression and the new freezing point Substitute the molality into the freezing-point depression expression:

$$\Delta T_f = (1)(1.86\text{ K kg mol}^{-1})(0.8333\text{ mol kg}^{-1}) = 1.55\text{ K}.$$

A temperature difference of 1.55 K equals a difference of 1.55°C . Subtract this depression from the freezing point of pure water:

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

Step 4: Conclusion The freezing point of the antifreeze solution is -1.55°C (approximately 271.60 K).

Quick Tip to Solve: Convert the water mass to kilograms before finding molality, and subtract the positive depression from 0°C .

Section D (15 marks)

35(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]

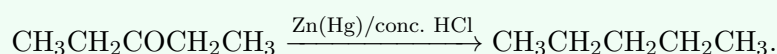
Solution:

Concept:

- Ordinary aldehydes reduce Tollens' reagent; ketones do not. A negative Tollens' test points to a ketone here.
- Clemmensen reduction, using Zn(Hg)/conc. HCl , replaces a carbonyl group by CH_2 without changing the carbon skeleton.
- A methyl ketone containing $\text{CH}_3\text{CO}-$ gives the iodoform test. A ketone without this group gives no yellow CHI_3 precipitate.

Step 1: Use the formula and reduction product The formula $\text{C}_5\text{H}_{10}\text{O}$ is consistent with a saturated acyclic carbonyl compound. The negative Tollens' test excludes an ordinary aldehyde. Since Clemmensen reduction gives *n*-pentane, the ketone must have an unbranched five-carbon chain. The possible positions are pentan-2-one and pentan-3-one.

Step 2: Apply the iodoform test and write the reactions Pentan-2-one has the $\text{CH}_3\text{CO}-$ group and would give a positive iodoform test. Therefore A has the carbonyl group at carbon 3. Its reactions are



Quick Tip to Solve: Use the reduction product to fix the carbon skeleton, then rule out the methyl ketone with the negative iodoform test.

$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 \xrightarrow{\text{Tollens' reagent}}$ No reaction (no silver mirror),

$\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3 \xrightarrow{\text{I}_2/\text{NaOH}}$ No iodoform precipitate.

These negative tests agree with a non-methyl ketone.

Step 3: Conclusion $A = \text{pentan-3-one, CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$. It reduces to *n*-pentane and gives neither a silver mirror nor an iodoform precipitate.

Quick Tip to Solve: Use the reduction product to fix the carbon skeleton, then rule out the methyl ketone with the negative iodoform test.

35(b). Carry out the following conversions:

(i) Propanoic acid to 2-Bromopropanoic acid

(ii) Benzoyl chloride to benzaldehyde

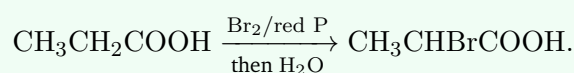
[2 marks]

Solution:

Concept:

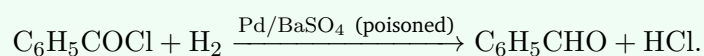
- The Hell–Volhard–Zelinsky (HVZ) reaction brominates the alpha carbon of a carboxylic acid possessing an alpha hydrogen, using Br_2 and red phosphorus followed by hydrolysis.
- Rosenmund reduction converts an acyl chloride into an aldehyde using hydrogen over poisoned Pd/BaSO_4 ; the poisoned catalyst prevents further reduction.

Step 1: Convert propanoic acid into 2-bromopropanoic acid Propanoic acid has alpha hydrogens on the carbon next to COOH . Treat it with bromine in the presence of red phosphorus, then hydrolyse the intermediate acyl bromide:



One alpha hydrogen is replaced by bromine. Numbering from the carboxyl carbon places bromine at carbon 2; this is the HVZ reaction.

Step 2: Convert benzoyl chloride into benzaldehyde Use Rosenmund reduction with hydrogen gas and palladium supported on barium sulphate:



The controlled activity of the catalyst allows reduction of the acyl chloride to the aldehyde while avoiding further reduction to benzyl alcohol.

Step 3: Conclusion The conversions use $\text{Br}_2/\text{red P, then H}_2\text{O}$ for alpha bromination and $\text{H}_2/\text{Pd}-\text{BaSO}_4$ for Rosenmund reduction.

Quick Tip to Solve: For bromination next to COOH , choose HVZ; for an acyl chloride to an aldehyde, choose poisoned Pd/BaSO_4 .

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

[1 mark]

Solution:**Concept:**

- Acetaldehyde, CH_3CHO , gives the iodoform test, whereas benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, does not.
- Yellow iodoform, CHI_3 , is the distinguishing precipitate when iodine and aqueous sodium hydroxide are used.

Step 1: Perform the iodoform test Add iodine and aqueous sodium hydroxide to separate samples and warm gently. Acetaldehyde produces a yellow precipitate of iodoform:



Step 2: Compare the observations Benzaldehyde does not produce the yellow iodoform precipitate under the same test conditions. Both compounds are aldehydes and both give Tollens' test, so a silver mirror would not distinguish them. The contrasting iodoform observations identify the two samples.

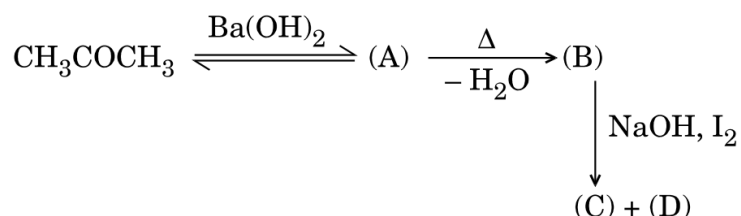
Step 3: Conclusion Acetaldehyde: yellow iodoform precipitate; benzaldehyde: no precipitate.

Quick Tip to Solve: Choose iodoform to distinguish these aldehydes: acetaldehyde responds positively, but benzaldehyde does not.

OR

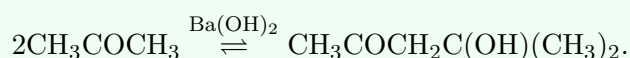
35(a)(i). Complete the following sequence of reactions. Identify (A) to (D).

[2 marks]

**Solution:****Concept:**

- Acetone has alpha hydrogen atoms, so two molecules undergo base-catalysed aldol addition to give a beta-hydroxy ketone.
- Heating a beta-hydroxy ketone removes water to form an alpha,beta-unsaturated ketone. A methyl ketone, RCOCH_3 , gives RCOONa and iodoform, CHI_3 , with iodine and sodium hydroxide.

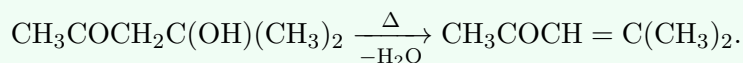
Step 1: Identify the aldol addition product (A) The enolate formed from one acetone molecule adds to the carbonyl group of a second acetone molecule. Protonation gives diacetone alcohol:



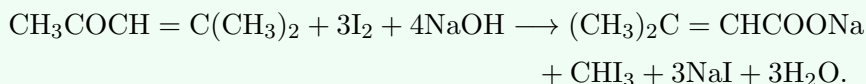
Thus (A) retains one ketone group and contains a hydroxyl group on its beta carbon.

Quick Tip to Solve: For the iodoform step, cut the bond beside the methyl carbonyl: the methyl group gives CHI_3 and the acyl part gives the sodium carboxylate.

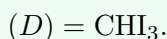
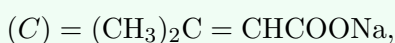
Step 2: Dehydrate (A) and apply the iodoform reaction to (B) On heating, loss of the hydroxyl group and a hydrogen from the adjacent carbon produces mesityl oxide:



This product still contains the $\text{CH}_3\text{CO}-$ group. In alkaline iodine, that methyl group is converted into yellow iodoform and the remaining acyl fragment becomes a sodium carboxylate. The overall final reaction is



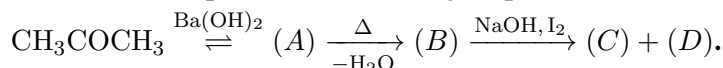
Step 3: Conclusion The required compounds are



The order of the two final products may be interchanged.

Quick Tip to Solve: For the iodoform step, cut the bond beside the methyl carbonyl: the methyl group gives CHI_3 and the acyl part gives the sodium carboxylate.

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



Give the IUPAC name of (A).

[1 mark]

Solution:

Concept:

- The aldol product of acetone is $\text{CH}_3\text{COCH}_2\text{C}(\text{OH})(\text{CH}_3)_2$. The parent chain must include the ketone carbonyl.
- The ketone has priority over the alcohol in the suffix. Number the chain to give the carbonyl group its lowest locant; use hydroxy as the prefix for the hydroxyl group.

Step 1: Select and number the parent chain The longest chain containing the carbonyl group has five carbon atoms. Starting from the end nearest the carbonyl gives a pentan-2-one parent. Numbering from the opposite end would put the carbonyl at carbon 4 and is therefore rejected.

Step 2: Locate the substituents At carbon 4, the parent chain carries both a hydroxyl group and a methyl group. The hydroxyl group becomes the prefix 4-hydroxy because the ketone supplies the suffix. The other prefix is 4-methyl; these are placed in alphabetical order before pentan-2-one.

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

Quick Tip to Solve: Give the ketone the lowest number first; treat the OH group as a hydroxy prefix, not an alcohol suffix.

35(b). How can you distinguish between:

(i) Ethanol and Propanone, and

(ii) Benzoic acid and Phenol?

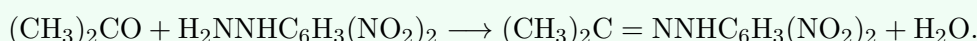
[2 marks]

Solution:

Concept:

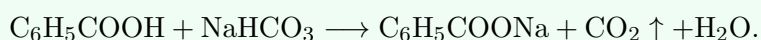
- 2,4-Dinitrophenylhydrazine (2,4-DNP) gives a yellow or orange precipitate with aldehydes and ketones, but not with alcohols.
- Carboxylic acids release carbon dioxide from aqueous sodium hydrogencarbonate. Phenol is too weak an acid to give this reaction.

Step 1: Distinguish ethanol and propanone Add 2,4-DNP reagent separately to small samples of the two compounds. Propanone gives a yellow or orange precipitate of its 2,4-dinitrophenylhydrazone, whereas ethanol gives no precipitate. The ketone carbonyl of propanone undergoes condensation with the reagent:



The iodoform test should not be used to distinguish this pair, since both ethanol and propanone give a positive result.

Step 2: Distinguish benzoic acid and phenol Add aqueous sodium hydrogencarbonate separately to each sample. Benzoic acid produces brisk effervescence of carbon dioxide, whereas phenol produces no effervescence. For benzoic acid,



The evolved gas turns limewater milky, confirming carbon dioxide. Phenol does not liberate carbon dioxide from the hydrogencarbonate solution.

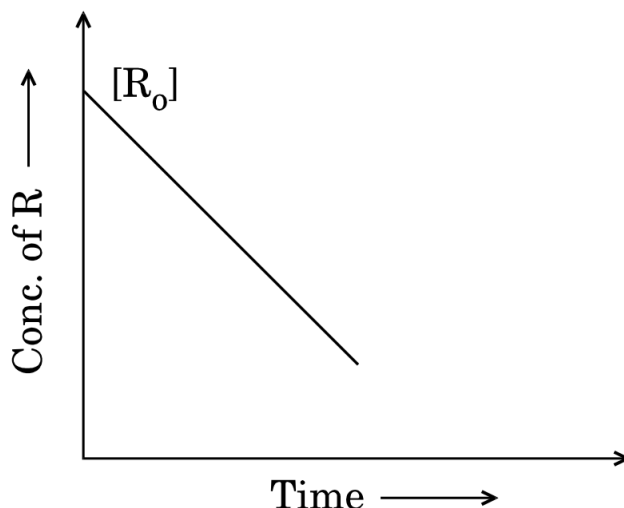
Step 3: Conclusion Use 2,4-DNP: propanone gives a yellow/orange precipitate; ethanol does not. Use aqueous NaHCO_3 : benzoic acid gives CO_2 effervescence; phenol does not.

Quick Tip to Solve: Choose a test that gives different observations: iodoform is positive for both ethanol and propanone.

36(a). Visha plotted a graph between concentration of R and time for a reaction $R \rightarrow P$. 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 reactant concentration and k is the rate constant.
- The integrated zero-order rate equation is $[R] = [R]_0 - kt$. It matches a straight line $y = c + mx$ with concentration on the vertical axis and time on the horizontal axis.
- The units of a zero-order rate constant are concentration divided by time. The signed gradient must be distinguished from its positive magnitude.

Step 1: Predict the order from the plotted axes The graph shows the concentration $[R]$, rather than its logarithm or its reciprocal, decreasing along a straight line as time increases. Comparing it with

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

shows that it is the integrated rate plot for a zero-order reaction. The vertical intercept gives the initial concentration $[R]_0$. A first-order reaction would instead produce a straight line for $\ln[R]$ against time; a second-order reaction would give a straight line for $1/[R]$ against time.

Step 2: Interpret the negative slope For any two points on the straight line,

$$\text{slope} = \frac{[R]_2 - [R]_1}{t_2 - t_1} = -k.$$

The negative sign records the decrease in reactant concentration as the reaction proceeds. Thus the slope indicates the negative of the rate constant, while the magnitude of the slope equals k . Since

Quick Tip to Solve: Read the vertical axis before choosing the order: a straight line for concentration itself means zero order, with slope $-k$.

the reaction is zero order, this also equals the constant rate of disappearance of R during the range represented by the line.

Step 3: Obtain the units of the rate constant Rearranging the integrated equation gives

$$k = \frac{[R]_0 - [R]}{t}.$$

Consequently k has units of concentration per unit time. With concentration expressed in mol L^{-1} and time in seconds, the units are $\text{mol L}^{-1} \text{s}^{-1}$, also written M s^{-1} . If time were measured in minutes, the corresponding time unit would be min^{-1} .

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

Quick Tip to Solve: Read the vertical axis before choosing the order: a straight line for concentration itself means zero order, with slope $-k$.

36(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.
- Its half-life is $t_{1/2} = \frac{2.303 \log 2}{k}$; it does not depend on the initial concentration.

Step 1: Use the concentration remaining after 25 minutes If the initial concentration is a , decomposition of 25% leaves $0.75a$. Thus the concentration ratio in the integrated rate law is $a/(0.75a) = 4/3$, not 4. Using the given common logarithms,

$$\begin{aligned} k &= \frac{2.303}{25} \log \frac{4}{3} \\ &= \frac{2.303}{25} (0.6021 - 0.4771) \\ &= 0.011515 \text{ min}^{-1}. \end{aligned}$$

Step 2: Calculate the time for half the reactant to remain At half-life, $[R]_t = [R]_0/2$, so the concentration ratio is 2. Substituting the rate constant,

$$t_{1/2} = \frac{2.303(0.3010)}{0.011515} = 60.2 \text{ min}.$$

Equivalently, the ratio of the two times is $t_{1/2}/25 = \log 2 / \log(4/3)$. This is greater than two because first order decomposition slows as the concentration falls; successive equal fractions of the initial amount do not take equal times.

Quick Tip to Solve: Convert percentage decomposed to percentage remaining before forming the logarithmic concentration ratio.

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 before forming the logarithmic concentration ratio.

OR

36(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:

- The integrated first order rate law is $kt = \ln([R]_0/[R]_t)$, where k is the rate constant and $[R]_t$ is the concentration remaining at time t .
- A first order reaction has a constant half-life $t_{1/2} = \ln 2/k$, independent of the initial reactant concentration.

Step 1: Identify the required concentration ratio The initial concentration is $[R]_0$, and the final concentration is $[R]_0/16$. Hence

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

This means $15/16$ of the original reactant has decomposed. The rate law uses the concentration remaining, so the ratio must be 16, rather than $16/15$. Since $k = 60 \text{ s}^{-1}$, the time obtained from the integrated law will be in seconds.

Step 2: Apply the integrated rate equation Rearranging the first order equation and substituting the concentration ratio gives

$$\begin{aligned} t &= \frac{\ln 16}{k} = \frac{4 \ln 2}{60} \\ &= \frac{4(0.6931)}{60} \\ &= 0.04621 \text{ s.} \end{aligned}$$

The same result follows using common logarithms: $t = (2.303/60) \log 16$, with $\log 16 = 4 \log 2$. The inverse of the rate constant supplies the time unit, while the logarithmic ratio is dimensionless.

Step 3: Check by counting half-lives Successive halvings reduce the concentration as

$$[R]_0 \longrightarrow \frac{[R]_0}{2} \longrightarrow \frac{[R]_0}{4} \longrightarrow \frac{[R]_0}{8} \longrightarrow \frac{[R]_0}{16}.$$

Thus four half-lives are needed. Each lasts $0.6931/60 = 0.01155 \text{ s}$, so their total agrees with the integrated-law calculation.

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

Quick Tip to Solve: Recognise a remaining fraction of $1/16 = 1/2^4$ as four half-lives for a first order reaction.

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

[1 mark]

Solution:

Concept:

- Reaction rate depends on how often reacting particles undergo effective collisions.
- Reactant concentration and temperature can change the frequency or effectiveness of these collisions.

Step 1: Effect of reactant concentration Reactant concentration is one factor. For a reaction whose rate depends on that reactant, increasing its concentration increases the number of reacting particles per unit volume and generally increases the frequency of collisions. Its quantitative effect is specified by the reaction's rate law.

Step 2: Effect of temperature Temperature is another factor. Raising temperature generally increases the rate constant because a larger fraction of molecules have sufficient energy to overcome the activation-energy barrier. Therefore more collisions can lead to products.

Step 3: Conclusion Two factors affecting reaction rate are reactant concentration and temperature.

Quick Tip to Solve: Name concentration and temperature, then link them to collision frequency and sufficient collision energy respectively.

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

[1 mark]

Solution:

Concept:

- Collision theory states that products form through effective collisions of reacting particles.
- An effective collision requires both sufficient collision energy and a suitable relative orientation of the particles.

Step 1: Sufficient collision energy The colliding molecules must possess energy equal to or greater than the threshold energy needed for reaction. They can then overcome the activation-energy barrier and form the activated complex. Collisions with insufficient energy do not produce the required chemical change.

Step 2: Proper molecular orientation Molecules must collide with their reacting sites oriented suitably toward one another. This allows the necessary bonds to break and new bonds to form. Even a sufficiently energetic collision may be ineffective if the molecules approach with an unsuitable orientation.

Step 3: Conclusion The two conditions are sufficient collision energy and proper orientation of the reacting molecules.

Quick Tip to Solve: Remember both energy and orientation: a collision with enough energy alone need not form products.

37(a). 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

Elucidate the structure of 'A' to 'F'.

[3 marks]

Solution:

Concept:

- Sulphur consists of puckered S_8 rings; burning it gives sulphur dioxide, which is oxidised to sulphur trioxide in the contact process.
- Sulphur trioxide is absorbed in concentrated sulphuric acid to form oleum, $H_2S_2O_7$. Dilution of oleum produces sulphuric acid.
- Hot concentrated sulphuric acid acts as an oxidising agent towards copper and produces copper(II) sulphate.

Step 1: Identify A, B and C and describe their structures The crown-shaped unit identifies A as sulphur, S_8 . Its eight sulphur atoms form a non-planar, puckered ring, with each atom bonded to its two neighbours. Burning sulphur produces B is sulphur dioxide, SO_2 , a bent or V-shaped molecule: sulphur has two oxygen neighbours and one lone pair. Lime-water milkiness is due to insoluble calcium sulphite. Catalytic oxidation of B gives C, sulphur trioxide. The SO_3 molecule is trigonal planar, with three S–O bonds arranged at approximately 120° .

Step 2: Identify D, E and F and describe their structures Absorption of C in sulphuric acid gives D, oleum or disulphuric acid, $H_2S_2O_7$. Its connectivity is $HO - S(=O)_2 - O - S(=O)_2 - OH$: the two sulphur centres are joined by a bridging oxygen, and each sulphur has an approximately tetrahedral oxygen environment. Dilution of oleum gives E, sulphuric acid, H_2SO_4 . Its conventional structural formula is $HO - S(=O)_2 - OH$, with four oxygen atoms arranged approximately tetrahedrally around sulphur. Copper reacts with hot concentrated E to form F, copper(II) sulphate, $CuSO_4$. F is an ionic compound containing Cu^{2+} and SO_4^{2-} ; the sulphate ion is tetrahedral, with sulphur at the centre and four oxygen atoms around it.

Step 3: Conclusion A = S_8 (puckered crown ring), B = SO_2 (bent), C = SO_3 (trigonal planar), D = $H_2S_2O_7$ (two oxygen-bridged sulphur centres), E = H_2SO_4 (tetrahedral oxygen environment) and F = $CuSO_4$ (ionic, with tetrahedral sulphate).

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

37(b). 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

Give a balanced chemical equation for the conversion of 'E' to 'F'.

[1 mark]

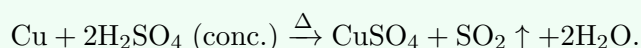
Solution:

Concept:

- Hot concentrated H_2SO_4 acts as an oxidising agent: copper is oxidised to Cu^{2+} , while sulphur in the acid is reduced from +6 to +4.
- A balanced chemical equation must conserve the number of atoms of every element.

Step 1: Identify the acid and the copper product E is sulphuric acid, H_2SO_4 , obtained by diluting oleum. Its reaction with copper produces F, copper(II) sulphate, $CuSO_4$, along with sulphur dioxide and water. Concentrated acid and heating are needed for this reaction.

Step 2: Balance the reaction One acid molecule supplies the sulphate group in copper(II) sulphate, and another is reduced to sulphur dioxide. The balanced equation is



Both sides contain one Cu atom, two S atoms, four H atoms and eight O atoms, confirming the balance. Hydrogen gas is not the product because concentrated sulphuric acid acts as an oxidising acid here.

Step 3: Conclusion $Cu + 2H_2SO_4 \text{ (conc.)} \xrightarrow{\Delta} CuSO_4 + SO_2 \uparrow + 2H_2O$, where $E = H_2SO_4$ and $F = CuSO_4$.

Quick Tip to Solve: For copper with hot concentrated sulphuric acid, write sulphur dioxide rather than hydrogen, then use two acid molecules to balance sulphur.

37(c). 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

Give two important functions of 'E' in the chemical industry.

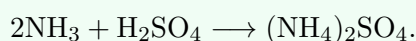
[1 mark]

Solution:

Concept:

- E is sulphuric acid, H_2SO_4 , an important industrial chemical obtained by diluting oleum.
- Its acidic nature and ability to form sulphate salts make it useful in manufacturing fertilizers and many other chemicals.

Step 1: Manufacture of fertilizers Sulphuric acid is used to manufacture fertilizers such as ammonium sulphate and superphosphate of lime. For example, it neutralises ammonia to produce ammonium sulphate:



This fertilizer supplies nitrogen to plants.

Step 2: Manufacture of other industrial chemicals Sulphuric acid is also used in the manufacture of dyes and explosives. For example, concentrated sulphuric acid is used with nitric acid in industrial nitration reactions, where it helps generate the nitrating species and removes water. Thus its role extends beyond the manufacture of sulphate fertilizers.

Step 3: Conclusion Two important industrial uses of E, sulphuric acid, are the manufacture of fertilizers and the manufacture of dyes and explosives.

Quick Tip to Solve: Identify E as sulphuric acid first, then name two industrial manufacturing uses, such as fertilizers and dyes or explosives.

OR

37(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:

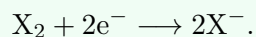
- An oxidising agent accepts electrons and is itself reduced. Halogen atoms need one electron to complete their valence shell.
- London dispersion forces depend on the polarizability of the electron cloud; weak intermolecular

Quick Tip to Solve: Match each observation to its controlling factor: electron acceptance for halogens, dispersion forces for noble gases, and small atomic size for hydrogen bonding.

forces give low boiling points.

- Strong hydrogen bonding requires a highly electronegative, small atom bonded to hydrogen and an available lone pair on a neighbouring atom.

Step 1: Explain the oxidising nature of halogens Halogens have the valence-shell configuration ns^2np^5 . They readily gain one electron to attain the stable noble-gas configuration ns^2np^6 . Their high electronegativity and strong tendency to accept electrons make them strong oxidising agents. In a reaction they oxidise another substance by taking electrons from it, while the halogen is reduced to halide ions:



Thus the essential reason is the ease with which a halogen gains electrons, rather than loses them.

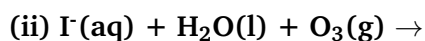
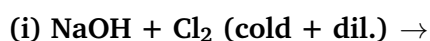
Step 2: Explain the low boiling points of noble gases Noble gases exist as individual, non-polar atoms with complete valence shells. The attractions between their atoms are only weak London dispersion forces; there is no permanent dipole attraction or hydrogen bonding. Very little energy is required to separate these atoms into the gaseous state, so their boiling points are very low. Boiling points increase down the group as larger electron clouds become more polarizable, but the interatomic forces remain comparatively weak.

Step 3: Compare hydrogen bonding by oxygen and chlorine Oxygen is much smaller than chlorine. Its lone pairs are concentrated in compact orbitals, so an O–H bond and a neighbouring oxygen lone pair can form a strong hydrogen bond. Although chlorine has comparable electronegativity, its larger size spreads its lone-pair electron density over a much larger volume. The resulting attraction is too weak to give the strong, characteristic hydrogen bonding found in oxygen compounds such as water. Thus electronegativity alone is insufficient; small atomic size is also essential in the usual CBSE explanation.

Step 4: Conclusion Halogens are strong oxidising agents because they readily gain electrons; noble gases have low boiling points because their atoms experience only weak dispersion forces; oxygen forms strong hydrogen bonds because it is small and highly electronegative, whereas chlorine is much larger.

Quick Tip to Solve: Match each observation to its controlling factor: electron acceptance for halogens, dispersion forces for noble gases, and small atomic size for hydrogen bonding.

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



[2 marks]

Solution:

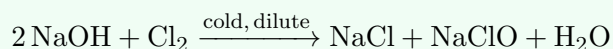
Concept:

- Chlorine undergoes disproportionation in cold, dilute alkali: chlorine in Cl_2 has oxidation state zero and forms chloride, Cl^- , and hypochlorite, ClO^- , with oxidation states -1 and $+1$, respectively.
- Ozone is an oxidising agent. In aqueous medium it oxidises iodide, I^- , to iodine, I_2 , while forming

Quick Tip to Solve: For chlorine with alkali, identify the conditions first: cold and dilute gives hypochlorite. For an ionic equation, check total charge as well as atoms.

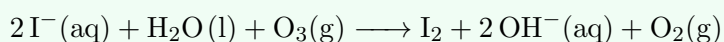
oxygen, O_2 . A balanced ionic equation must conserve both atoms and total charge.

Step 1: Complete the chlorine reaction with cold, dilute alkali Under the stated conditions the products are sodium chloride, sodium hypochlorite and water. Balance sodium and chlorine by using two molecules of sodium hydroxide for one molecule of chlorine:



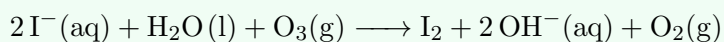
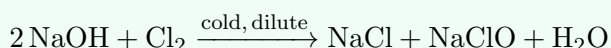
The equation has two atoms each of sodium, chlorine, oxygen and hydrogen on either side. Hypochlorite is the product for cold, dilute alkali; the chlorate product belongs to hot, concentrated alkali and is therefore inappropriate here.

Step 2: Balance the oxidation of iodide by ozone Two iodide ions supply the two iodine atoms in I_2 . Water supplies hydrogen, and hydroxide ions account for both the hydrogen balance and the negative charge:



Check the balance: both sides contain two iodine atoms, two hydrogen atoms and four oxygen atoms. The total charge is -2 on both sides. Iodine changes from oxidation state -1 to zero, confirming that iodide is oxidised by ozone.

Step 3: Conclusion The completed balanced equations are:



Quick Tip to Solve: For chlorine with alkali, identify the conditions first: cold and dilute gives hypochlorite. For an ionic equation, check total charge as well as atoms.